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# Volume 3

**Book of abstracts  
in 6 volumes**

**Saint Petersburg  
9 –13 September**

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Energy efficiency, environmental safety and risk management of chemical industry.

Chemical aspects of modern energetics and alternative energy resources.

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Correspondence reports of the "Physical chemistry of metallurgical processes",  
"Energy efficiency, environmental safety and risk management of chemical industry",  
"Chemical aspects of modern energetics and alternative energy resources",  
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# **PLENARY LECTURES**

## THE STORY OF SINGLE MOLECULES, FROM EARLY HIGH-RESOLUTION SPECTROSCOPY IN SOLIDS, TO SUPER-RESOLUTION NANOSCOPY IN CELLS AND BEYOND

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In the late 1970s and 1980s, many researchers around the world were exploring a novel optical storage concept, frequency domain optical storage, which was based on spectral hole-burning in the zero-phonon lines of impurities in solids at low temperatures. In 1989, experiments aimed at establishing the ultimate limits this optical storage idea led to the first optical detection and spectroscopy of a single molecule in the condensed phase using laser FM spectroscopy. This represented optical exploration of the ultimate limit of one individual molecule at a time, an amount of material equal to  $(1/\text{Avogadro's Number})$  of mol. As one might expect from an unexplored new regime, many surprises occurred where single molecules showed both spontaneous changes (blinking due to spectral diffusion) and also light-driven control of emission. These properties were subsequently also observed in 1997 at room temperature with single green fluorescent protein variants, and blinking, or reversible entry into dark states, was found to occur in many situations. In 2006, PALM and related approaches showed that Abbe's optical diffraction limit of  $\sim 200$  nm can be circumvented to achieve super-resolution fluorescence microscopy, or nanoscopy, with relatively nonperturbative visible light. Essential to imaging with single molecules beyond the diffraction limit are several requirements: single-molecule fluorescence imaging, active control of the emitting concentration, and sequential localization of single fluorophores decorating a structure. Super-resolution microscopy has opened up a new frontier in which biological structures and behavior can be observed in live cells or other materials with resolutions down to 20-40 nm and below. Examples range from protein superstructures in bacteria to bands in axons to details of the shapes of cytoskeletal structures, amyloid fibrils and much more. Current methods development research addresses ways to extract more information from each single molecule such as 3D position and orientation, and to assure not only precision, but also accuracy. Still, it is worth noting that in spite of all the current interest in super-resolution microscopy of extended structures, even in the "conventional" single-molecule tracking regime where the motions of individual biomolecules are recorded in solution or in materials, much can be learned about the dynamics of nanoscale processes when ensemble averaging is removed.

## FROM CATENANES AND ROTAXANES TO MOLECULAR MACHINES

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The simplest catenane, a [2] catenane, consists of two interlocking rings. Rotaxanes consist of rings threaded by acyclic fragments (axes). Interlocking ring compounds have attracted much interest in the molecular sciences, first as pure synthetic challenges and, more recently, as components of functional materials. In particular, these compounds appear as perfect precursors to dynamic systems for which motions can be triggered and controlled in a precise manner. This property led to the use of catenanes and rotaxanes as *molecular machine prototypes*.

Subsequently, the research field of artificial molecular machines has experienced a spectacular development, in relation to molecular devices at the nanometric level or mimics of biological motors. In biology, motor proteins are of the utmost importance in a large variety of processes essential to life (ATPase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). A few recent systems are based on simple or more complex rotaxanes or catenanes acting as switchable systems or molecular machines. Particularly significant examples include a "swinging catenane", "molecular shuttles" as well as multi-rotaxanes reminiscent of muscles or able to act as molecular compressors or switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Examples will be given which cover the various approaches used for triggering the molecular motions implied in various synthetic molecular machine prototypes. The work of various groups using non interlocking compounds will also be briefly discussed. Potential applications of rotaxanes and molecular machines will also be mentioned.

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J.-P. SAUVAGE, "From Chemical Topology to Molecular Machines", *Angew. Chem. Int. Ed.*, 2017, 56, 11080.

## CATALYSIS AND THE PERIODIC TABLE OF ELEMENTS

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Catalytic technologies are currently used in the production of the vast majority of chemicals and materials and about 90% of all contemporary industrial technologies involve catalytic processes. As we have mentioned before, interdisciplinary projects, which interconnect the fields of catalysis, organic synthesis and organometallic chemistry, have quickly and drastically changed the image of the chemical industry [1]. It is important to note that numerous developments made by organic chemists in the field of catalytic technologies find rapid implementation in the industry and facilitate appearance of innovative products.

In this lecture we will touch upon the phenomenon of catalysis in terms of the diversity of catalytic processes, with the emphasis on the unique features of the application of different elements of the Periodic Table in catalytic reactions.

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## MATERIALS FOR DEVELOPMENT OF ARCTIC AND COLD TERRITORIES

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The success of the development of cold areas, including the Arctic, largely depends on the availability of materials that can work effectively in hard climatic conditions. The development of cold zones has a long history, but the Arctic materials science (AMS) was formed a few decades in modern form. Now there is an intensive search, synthesis and experimental studies of the arctic materials, but there is virtually no generalizing analysis of the current state of AMS and not formulated trends in its development<sup>1</sup>. Domestic AMS significantly behind the indicators of industrial development of the Arctic in the Russian Federation, although to succeed, the trend should be reversed.

The number and variety of materials used in cold climate zones is great: construction, functional, fuel and lubricants and other auxiliary materials of natural and anthropogenic origin and different chemical composition (metal, ceramic, low and high molecular weight, etc.). The specific features and requirements for these materials give reason to allocate AMS in a special section of material sciences. The evolution of AMS has features characteristic of modern materials science: the transition from natural materials to anthropogenic, the chemical and morphological composition and structure, versatility and giving the materials smart elements, etc. The report discusses the climatic factors of the Arctic and the mechanisms of their impact on the properties of materials, formulated requirements for arctic materials necessary for their operation. The classification of arctic materials, taking into account their properties, structure and application in technical devices and constructions is offered. Obtaining Arctic materials are adaptation of existing materials for the Arctic conditions and development of new specifically for Arctic. The report will give examples of the creation of some Arctic materials obtained in domestic scientific organizations. The methods of studying the structure of Arctic materials, their laboratory and nature tests, including the influence of climatic factors, were also discussed. Analysis of the survey of experts and international bibliometric databases revealed research organizations with the greatest competence in certain areas of AMS. The features of interaction between researchers and between scientific structures are evaluated, and proposals to improve the cooperative climate are made.

*This work was supported by RSF (grants 14-13-032 and 18-13-0392)*

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## SYNCHROTRON RADIATION AND INVESTIGATION OF CATALYTIC SYSTEMS

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Over recent years the progress in development of material science and adjacent fields such as energetics, catalysis, membrane and sensor technologies, elemental base of micro- and nanoelectronics is largely defined by the level of a country's research infrastructure including the sources of synchrotrone radiation and neutrons, in other words, by the presence of "mega-science" plants. We can rely on the international cooperation in conducting such studies assuming the use of the international centers of competence in this field, HZB (known before as BESSY-II) and DESY in Germany, ESRF in France, Daresbury in Great Britain, centers of synchrotron radiation within the National Laboratories in the USA. Indeed, these options are available and should be used, albeit on a competitive basis; however, the existence of the domestic "mega-science" plants, their regular use and upgrading would not only increase the time for such studies and widen the circle of objects over the technological tasks, but also keep up the research and methodological level of the scholars participating in this international differentiation of labor as well as the technological level of production of non-standard equipment for various purposes.

In my lecture I intend to argue for the importance of using the potential of synchrotron radiation for catalytic studies; I will present not only the forming tendencies but also the latest research results obtained lately while studying the structure of active centers of heterogeneous catalysts in various centers of synchrotron radiation. I will also show the latest results of our experiments on studying the bimetallic Pd-Au catalysts of low-temperature oxidation with CO (the XPS experiments were carried out on the RGBL and ISSS stations of the Berlin source of synchrotron radiation, HCB), the Pt/Al<sub>2</sub>O<sub>3</sub> nanocatalysts of the total methane oxidation (studied at the station of the Kurchatov center of synchrotron radiation upgraded for the in-situ XRD and XAFS measurements with our participation), reactions of methane oxidation in the self-oscillation regime on Ni catalyst (studied at the XRD station of the Siberian center of synchrotron radiation in Budker Institute of Nuclear Physics SB RAS).

In conclusion I would analyze the possible directions of development of this approach to the basic research in the field of catalysis, already employed in some countries (Germany, USA, Great Britain, Scandinavian countries), for example by creation of national catalytic hubs with the purpose of coordination of means for conducting the oriented studies including those in the interest of industrial partners as well as the Russian national network of "mega-science" plants planned to be built.



## CHEMISTRY OF 2D MATERIALS: FROM 2D MOLECULAR MAGNETS TO HYBRID MOLECULAR/2D HETEROSTRUCTURES

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Graphene and other 2D materials are a hot focus of interest in physics, chemistry and materials science. These materials are almost exclusively based on inorganic lattices and cover a wide range of electronic and magnetic properties: from insulators to superconductors, from diamagnetic to ferromagnetic (FM) and from metallic to non-metallic compositions. Except for the chemical functionalization of the surface of the 2D material, molecules have been scarcely considered in this field. In this talk I will emphasize the role of chemistry in this area paying particular attention to the magnetic properties. In the first part I will show how coordination chemistry can provide examples of molecular 2D magnets that, in contrast to what happens with the inorganic 2D magnets, are chemically stable in open air, keeping their magnetic properties preserved upon functionalizing their surface with different organic molecules.<sup>1</sup> In the second part I propose to create hybrid heterostructures by interfacing a layer of a functional molecular material with a 2D material. The aim is that of tuning the properties of the “all surface” 2D material via an active control of the hybrid interface.<sup>2</sup> To reach this goal the molecular system of choice will be based on spin-crossover complexes able to switch between the two spin states upon the application of an external stimulus (temperature, light or pressure). This concept will provide an entire new class of stimuli-responsive molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics and molecular sensing.

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## ORIGIN OF ELEMENTS AND CHEMISTRY IN SPACE

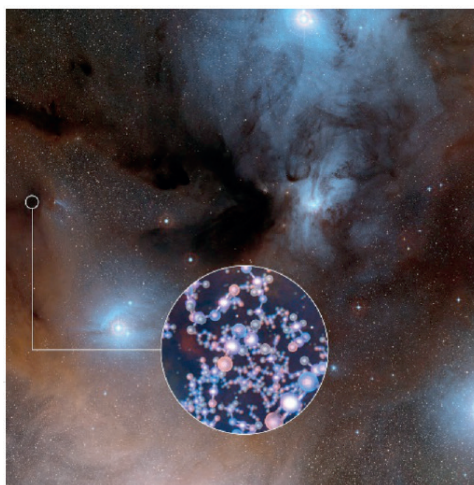
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'We are all stardust'. Most of the elements in the periodic table were formed in space. The simplest species - H, D, He, and Li - were made shortly after the Big Bang in the early Universe, whereas the rest of the elements that make 'us' were produced by nuclear fusion in the interior of stars, gradually enriching the Universe with heavier elements. A brief overview of the production of the main elements that are important for interstellar chemistry will be given.<sup>1</sup>

Chemistry starts in the cold and tenuous clouds between the stars. In spite of extremely low temperatures and densities, these clouds contain a surprisingly rich and interesting chemistry, as evidenced by the detection of more than 200 different molecules, from simple to complex<sup>1</sup>. Chemistry takes place both in the gas and on the surfaces of interstellar dust grains.<sup>1,2</sup> New facilities such as ALMA allow us to zoom in on the formation sites of new stars and planets with unprecedented sharpness and sensitivity. Spectral scans of young protoplanetary disks contain tens of thousands of rotational lines<sup>3</sup>, revealing water and a surprisingly rich variety of organic materials, including simple sugars<sup>3</sup>, molecules with peptide bonds<sup>4</sup> and high abundances of deuterated species<sup>3</sup>. What are the dominant chemical processes at work? How common are they? What material is available to build new exo-cometary and planetary systems?



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# NON-CRYSTALLINE NANOSTRUCTURED MATERIALS: THE WAY TO NEW SOLIDS WITH NEW STRUCTURES AND PROPERTIES

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Today's technologies are based primarily on utilizing crystalline materials (e.g. metals, semiconductors or crystalline ceramics). The way to new technologies may be opened by nanostructured materials that are totally or partially on non-crystalline. One group of them are nano-glasses. They consist of nanometer-sized glassy regions connected by (nanometer-wide) interfacial regions with atomic and electronic structures that do not exist in melt-cooled glasses. Due to their new atomic/electronic structures, the properties of nano-glass differ from the corresponding properties of melt-cooled glasses. For example, their ductility, their biocompatibility, their catalytic and ferromagnetic properties are changed by up to several orders of magnitude. Moreover, they permit the alloying of components e.g. ionic materials (e.g. SiO) and metallic materials (e.g. PdSi glasses) that are immiscible in the crystalline state. The properties of nano-glasses may be controlled by varying the sizes and/or chemical compositions of the glassy clusters which opens the perspective of a new age of technologies - a "glass age". A second group of nanostructured partially non-crystalline materials with tunable properties are nano-porous metals with electrolyte filled pores. By applying an external voltage between the electrolyte and the nano-porous metal their properties e.g. their superconductivity, magnetic moment, electric resistivity may be varied. Single or multi-atom switchable contacts represent a third group of these materials. They open the way to spontaneously formed single-atom or multi-atom transistors which allow quasi solid state bi-stable switching between quantized conduction levels of  $2e^2/h$  or multiples of  $2e^2/h$ .

## THE FUNCTION OF FUNDAMENTAL STUDIES IN DEVELOPMENT OF THE NEW GENERATION MATERIALS

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New generation materials are the basis for development of the competitive civil and special equipment on the world market. The "Strategic directions for the development of materials and technologies of their treatment for the period up to 2030" developed upon the VIAM initiative and approved by the Science & Technology Council of the Military-Industrial Commission of the Russian Federation determine the approaches and implementation phases of fundamental and applied studies in the field of materials science.

The main principles of creation of the new generation materials are materialized on the basis of unity paradigm "material – technology – design". During the development of the new generation materials the multilevel approach is used: material modeling on nano-, micro, meso- and macro-levels, study of mechanisms of elemental samples behavior with results validation for structural elements and goods. Today the development of the new generation materials is impossible without computer modeling of materials and mathematic models of their manufacturing. They allow optimizing the parts and structures production technology by conditions of strain-stress state; evaluate the influence of the initial stock on physical and mechanical properties of the materials; reduce the value of the development of the new materials.

The development of the new generation polymer composite materials (PCM) is the most important direction of growth of the Russian economy. This calls for the new high-strength, high-modulus fillers, foremost – the carbon fiber. It should be noted that nowadays Russia does not possess both the production of intermediate modulus carbon fibers similar to T700 and T800 in their properties and the capacity of the end-to-end cycle of PAN-fiber production, the quality of which predefines the properties of carbon fiber. At the same time the development of PCM branch is in direct dependence on the achievements of the chemical industry. The main task is to develop the components of polymer matrices – oligomers, catalyst systems meeting the high requirements not only to properties, but also to ecological compatibility of production. Under present conditions the technological breakthrough is closely connected with the intense development and wide application of principles of "green chemistry" and molecular design, development of atomic-molecular engineering during the new compounds production. It is necessary to generate the program of manufacturing process management for the highly purified materials for microelectronics, photonics, optoelectronics and biomedicine, as well as to determine the competence center – an industry organization in charge of technologies and production development for chemical compounds of highly purified materials.

The digital and additive technologies play the key part in improvement of the manufacturing process of complex technical systems parts. They allow manufacturing of high-quality parts by means of direct material synthesis ("addition"); it is impossible to create these parts by means of traditional "extracting" technologies, such as welding, mechanical treatment, etc. Additive technologies are rightfully the technologies of 21st century and they have great potential in the realm of energy cost reduction during the various products manufacturing. Thus, it is evident that the intensity index of using of the additive technologies is one of the indicators of industrial and innovative national development.

In general the joint achievements of the Russian Academy of Sciences, state scientific centers and the leading institutes of chemistry and materials science allow creating the basis for the development of the new generation materials. At present it is necessary to expand the scope of application of the scientific knowledge and discoveries and to intensify the innovative activity of scientific facilities and business by means of formation of consortia for implementation of large-scale projects of end-to-end innovative cycle (idea – material – technology – production of innovative products).

## SYSTEMS THINKING TO EDUCATE ABOUT THE MOLECULAR BASIS OF SUSTAINABILITY

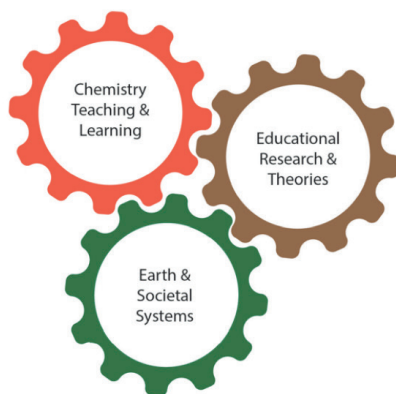
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A Systems Thinking in Chemistry Education (STICE) framework has been developed by a global IUPAC project team with the goal of moving learners from fragmented knowledge of chemical reactions and processes toward a more holistic understanding of the field. Systems thinking shows promise in guiding students to see the relevance of their chemistry education for addressing multiple emerging global challenges such as sustainability, alternative energy, planetary boundaries, and the UN Sustainable Development Goals. We will explore progress to date in implementing the IUPAC STICE project and suggest approaches that can be used by chemistry educators to help students develop a deeper understanding of the molecular basis of sustainability.<sup>ii</sup> To give chemists and educators a concrete example of how systems thinking can be used, we will consider the Haber-Bosch process for the synthesis of ammonia, and the way systems thinking visualization tools can help students move beyond a narrow view of this process to consider chemical and energy inputs, reaction conditions, outputs such as the Ostwald Process leading to ammonium nitrate, and the intended uses of nitrogenous compounds derived from ammonia in agriculture and munitions, as well as unintended consequences resulting from the overuse of reactive nitrogen. Next steps for the IUPAC STICE project will be discussed, including suggestions arising from contributions to a special issue of the Journal of Chemical Education on "Reimagining Chemistry Education: Systems Thinking and Green & Sustainable Chemistry," to be published in late 2019.<sup>iii</sup>

Abstract graphic (if one can be used):



**Systems Thinking in Chemistry Education  
An IUPAC Project**

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## THE CHEMICAL ELEMENT: HOW CHEMISTRY IS KEY TO SOLVING OUR GLOBAL CHALLENGES

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Chemistry is a global endeavor that has greatly contributed to improving our quality of life by protecting us against illness and by putting food and clean water on our table.<sup>1</sup> But now, our global challenges are so big that only if we focus all our efforts in solving our most pressing problems we can create a sustainable and better future for all.<sup>2</sup> From climate change to our dependence on finite natural resources, many of our most global challenges require a technical solution that only better science and technology in general and chemistry in particular can provide.<sup>3</sup> During its almost 100 years of existence, IUPAC has created universally accepted chemistry nomenclature and terminology as well as a global platform to discuss and advance some of the most relevant topics on pure and applied chemistry.

Chemistry education is of particular importance. We must train, engage, and inspire the new generation of young chemists able and committed to building a more sustainable future.<sup>4,5</sup> In order to get there, science education, from primary school to college, needs to be reinvented to put the student at the center of the learning process and provide him or her with the skills needed to become a more complete and creative scientist.

There is still a significant gap between academia and industry that needs to be bridged by bold entrepreneurs able to connect these two worlds and successfully commercialize the new and exciting research carried out in universities. Entrepreneurship is another important part of the equation, taking the discoveries made in the lab to the market place is essential to implementing the solutions we need, and scientists have a key role to play here.<sup>6</sup>

During the presentation some examples and various ideas will be shared to accelerate the discovery and application of chemistry breakthroughs that, hopefully, will ignite a thriving and constructive discussion.

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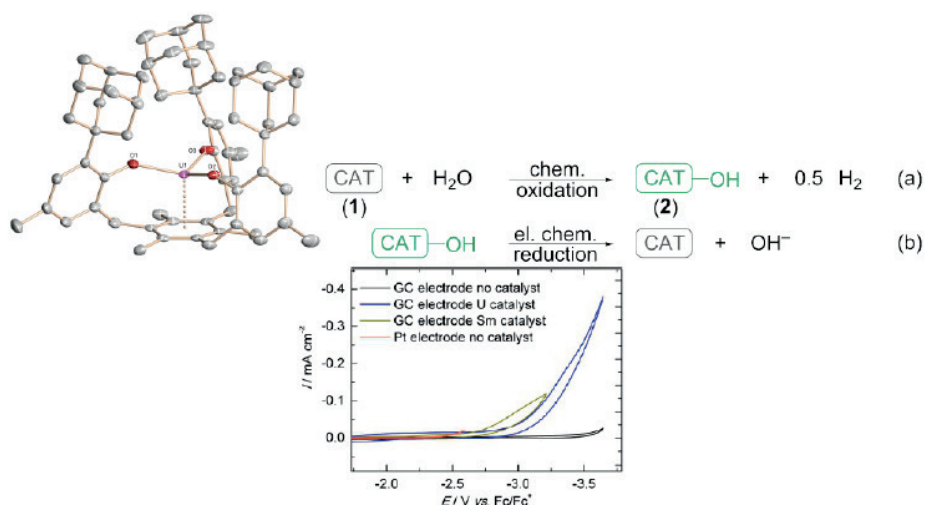
ELECTROCATALYTIC PRODUCTION OF H<sub>2</sub> FROM WATER  
WITH F-ELEMENT-BASED MOLECULAR CATALYSTSMeyer K.

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Research on renewable energies and energy storage, such as H<sub>2</sub> production from H<sub>2</sub>O, has become a key challenge for our society. The low efficiency of conventional H<sub>2</sub>O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium, uranium complexes are widely discussed as effective and economic catalysts for stable substrates.

In our previous studies of the arene-anchored tris-aryloxy uranium complex [U<sup>(Ad,Me)</sup>ArO<sub>3</sub>mes] (1), unique electrochemical and well-defined synthetic behavior were found, rendering 1 a perfect candidate for electrocatalysis.

Indeed, trivalent uranium coordination complex 1 was found to be the first molecular uranium catalyst for electrocatalytic H<sub>2</sub> production. Utilization of 1 during H<sub>2</sub>O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance by 3 orders of magnitude. Isolation of key intermediates and *in situ* EPR experiments allowed to determine the reaction mechanism of H<sub>2</sub>O reduction with low valent U(III). This reactivity is now studied in a series of lanthanide complexes [Ln<sup>(Ad,Me)</sup>ArO<sub>3</sub>mes] (2–Ln), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the 4f ion.



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## PERIODIC TABLE AFTER 150 YEARS

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One of the fundamental consequences of the modern theory of atomic nuclei (1969) is the prediction of an ‘Islands of Stability’ in the region of hypothetical super heavy elements (SHEs). In a heavy nucleus, going through the large-scale deformation on the way to fission, the motion of single nucleons is coupled with the collective degrees of freedom of the whole system. The most striking effect of this coupling is obtained for the case of fission of the heaviest nuclei, whose existence is defined entirely by the nuclear structure, i.e. by the shell effect.

From this point of view, the synthesis and study of properties of super heavy nuclei (SHN) is a direct way for checking the basic statements of the microscopic nuclear theory. On the nuclide map, SHN outline the border of the heaviest nuclear masses. SHN set the limits of the periodic system of chemical elements. The study of possible existence of SHN in nature offers a way for testing different scenarios of astrophysical nucleosynthesis.

The talk presents results concerning the synthesis and decay properties of the super heavy nuclei from this ‘Stability Islands’ of SHEs obtained in cold and hot fusion reactions. The region of heavy nuclei have expanded and advanced up to mass of 294. New elements filled the 7th row of the Periodic Table of Elements. The results of the first chemical experiments and theoretical predictions about the influence of the "relativistic effect" on the electronic structure of the SH atom are presented.

Super heavy atoms are synthesized today in unit quantities. Theoretical expectations of the chemical properties of the new elements with respect to their light homologues is discussed in connection with the synthesis of elements heavier than 118. A significant increase in the sensitivity of experiments is expected with accelerator complexes of the new generation. At one of them, the “SHE Factory” in JINR (Dubna) the first beam was obtained in the end 2018.

The talk used results of the experiments conducted in 2000-2015 at FLNR (JINR, Dubna) at the U400 heavy ion accelerator in collaboration with researchers from national laboratories and universities: LLNL (Livermore, USA), ORNL (Oak-Ridge, USA), IAR (Dimitrovgrad, Russia), Vanderbilt, Knoxville and Texas A & M Universities (all in USA), as well as data obtained at national nuclear centers: GSI (Darmstadt, Germany), GANIL (Caen, France) and RIKEN (Wako-shi, Japan).



## THE PERIODIC TABLE AT 150: METALS, HEALTH AND MEDICINAL APPLICATIONS

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Elements of the Periodic Table have been known since ancient times, even before elements were known and recognized as such. No doubt Gold, Silver and Copper were the first of such metals, and were generally used in jewelry and coins, and in some cases also as weapons (Cu). By the time the Periodic System was tabulated in 1869, one was already aware that some elements and metal-containing compounds were needed for life (like Fe) and others were known to be very toxic, like As, Hg.

Already in the ancient times, some of the elements were used to treat diseases, like colloidal gold. The dosage of many of such metallic elements to humans, to cure or prevent diseases has been a subject of study for many decades. In the last 50 years the usage of metal compounds to diagnose or cure diseases has been rapidly grown.<sup>1</sup> The Periodic Table shown below, has elements that are known to play a role in health of humans bold printed.

Elements needed for live and used in curing and diagnosis

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
<b>H</b>																	He
<b>Li</b>	Be											<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	Ne
<b>Na</b>	<b>Mg</b>											<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	Ar
<b>K</b>	<b>Ca</b>	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	Br	Kr
<b>Rb</b>	<b>Sr</b>	Y	Zr	Nb	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	Rh	Pd	<b>Ag</b>	Cd	<b>In</b>	<b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	Xe
Cs	<b>Ba</b>	<i>Ln</i>	Hf	<b>Ta</b>	<b>W</b>	Re	Os	Ir	<b>Pt</b>	<b>Au</b>	Hg	Tl	Pb	<b>Bi</b>	Po	At	Rn
Fr	<b>Ra</b>	<i>An</i>	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lanthanoids:		La	Ce	Pr	Nd	Pm	<b>Sm</b>	Eu	<b>Gd</b>	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinoids:			Ac	Th	Pa	U	<b>Np</b>	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

In the lecture examples of drugs to cure diseases will be presented, with a focus on treatment of cancers by metal compounds, in particularly by certain platinum compounds.<sup>2,3</sup> The mechanism of action of such compounds will be discussed as well.

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## MENDELEEV'S GIFT TO EDUCATION (AND TO ME)

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2019 has been declared the International Year of the Periodic Table in celebration of the 150th anniversary of Dmitri Mendeleev's first publication of his Periodic Table.<sup>1</sup> The purpose of this lecture is to demonstrate that Mendeleev's genius was to create something that anyone can use as a highly flexible framework for expressing their chemical ideas. I shall do this by giving examples of a whole variety of periodic tables ranging from one of the oldest surviving examples of periodic table intended to be shown in a lecture theatre<sup>2</sup> to the periodic table recently devised specifically by the European Chemical Society (EuChemS) for the IYPT, highlighting some of the elements which are becoming scarce.<sup>3</sup> I shall also highlight how the Periodic Table has impacted my own career and research, as well as mentioning our own contribution to the debate about designs of the periodic table.<sup>4</sup>

Acknowledgements: I thank all of my colleagues, collaborators, co-workers as well as our technicians. In particular, I thank Professor Mike George, Brady Haran and Neil Barnes. I also thank the Engineering and Physical Sciences Research Council, The Bill and Melinda Gates Foundation and The Garfield Weston Trust for financial support.

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## FROM MATERIALS INNOVATIONS TO NEW SUSTAINABLE BATTERY CHEMISTRIES

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Research's progresses in rechargeable batteries are driven by ever increasing demands for portable electronic devices as well as for powering electric vehicles and providing load-leveling for mass storage of renewable energy. Li-ion batteries are the systems of choice for the aforementioned applications. Therefore, for this to fully happen, new concepts and new sustainable chemistries are sorely needed, and this is what this presentation will address.

Firstly, regarding new concepts, we will show how the discovery of a new Li reaction mechanism that involves the anionic network with the reversible formation of dimers (O-O) represents a transformational approach for creating electrode materials with exacerbated capacities. Towards, higher energy density systems, recent advances on solid state Li batteries will be discussed. Concerning new chemistry, our new findings with the Na-ion chemistry which enlists novel materials/electrolyte designs together with the assembly of 18650 prototypes together with our work on Zn-MnO<sub>2</sub> aqueous systems will be presented. Lastly, an indirect way to enhance simultaneously energy density and sustainability via the use of sensing and self-healing functionalities will be introduced. Through these examples, the importance of materials design will be emphasized together

Altogether, these examples have been selected to show that the future of battery offers new opportunities for materials scientists as long as we are willing to play with the Mendeleev table and explore new risky paths. .

## BIOMASS CHEMISTRY: BIOFUELS AND BIOPLASTICS

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The lecture is devoted to the analysis of the achievements and trends in the renewable raw materials conversion into energy carriers and biomaterials.

The demand for new technologies for producing fuels and polymeric materials is determined by the raw materials sources growing shortage and the need to create fundamentally new large-scale environmentally acceptable methods for chemical industry.

The lecture discusses:

- Trends in the development of biofuels production and use;
- Biomethane and biohydrogen, chemical processes and the basis of technology for biogas production;
- Catalytic ethanol conversion processes;
- New fuels based on bioresources;
- Biotechnological processes for the butanol, acetone, other organic solvents and fuels production;
- Obtaining "bio-oil" and "synthesis oil" by biomass and polymeric materials pyrolysis;
- Biocatalytic synthesis of organic acids and plastics based on them;
- Polyhydroxyalkanoates - natural biodegradable polymers;
- Polyamides based on natural amino acids solid-phase polymerization;
- Bacterial cellulose - biocatalytic synthesis and use;
- Natural rubber - new biotechnological synthesis methods.

The rates of new renewable resource sources development, qualitatively new biofuels and bioplastics properties are considered.



# **SECTION 3**

## **PHYSICAL CHEMISTRY OF METALLURGICAL PROCESSES**

## PHYSICAL AND CHEMICAL MODELING AND OPTIMIZATION OF TECHNOLOGIES FOR PRODUCTION OF CLEAN STEELS

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The concept of clean steels appeared at the end of the last century, when it became clear that restrictions on the concentrations of individual impurity elements alone could not provide high service characteristics of modern high-strength steels. One of the most important controlled characteristics of pure steels is the minimum content of non-metallic inclusions with control of their composition, morphology and size distribution. The development and optimization of industrial metallurgical technologies for the production of clean steels is a complex process, requiring significant material and time costs. Mathematical computer simulation of technologies allows minimizing costs significantly if the developed models adequately describe the real high-temperature chemical and physical processes in metallurgical aggregates.

Therefore, the development of complex dynamic models of melting and refining units, including models of individual aggregates, is a very relevant area of research. The models and digital twins developed on their basis will allow to optimize production technologies and in the future to create flexible control systems for a fully robotized metallurgical enterprise. This will reduce the cost of steel, ensure high stability of production and competitiveness of the enterprise in the metal market, increase resource savings and lead to a reduction in harmful emissions.

The presentation will show the possibilities of the developed method of fractional gas analysis for monitoring non-metallic inclusions in steel. The capabilities of the models developed using the nonequilibrium thermodynamic equations and software for optimizing the ladle treatment technologies of steel will be demonstrated. Examples of analysis and optimization of smelting and after-furnace processing technologies for various steel grades in the current production conditions will be given.

## WORK AT KTH ON INCLUSION CHARACTERISTICS TO ENABLE AN IMPROVED STEEL QUALITY DESIGN

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Work at KTH Royal Institute of Technology (Stockholm, Sweden) focusing on steel quality design (SQUID) with an emphasis on non-metallic inclusions is presented. Laboratory experiments have been carried out to study the influence of ferroalloys on the inclusion content<sup>1-4</sup> and clusters<sup>5</sup> in steels using the 3D electrolytic extraction method in combination with SEM and EDS. Moreover, experiments have been carried out to determine how the lime dissolution into slags can be improved<sup>6</sup> and how the slag penetration into refractories can be decreased<sup>7</sup>. In addition, plant trials have been carried out to determine the inclusion characteristics in steels. Studies of the influence of the top slag composition of the steel and treatment times on the inclusion characteristics during vacuum degassing has shown that too long treatment times can lead to an increase of the oxygen and inclusion contents.<sup>8-10</sup> Plant trials have also been carried out to study the influence of the final stirring during the vacuum treatment on the inclusion characteristics. The results show that it is possible to lower the amount of especially large inclusions by lowering the gas stirring intensity during the final vacuum treatment period.<sup>11-13</sup> Initial studies have also been carried out to use on-line methods such as the pulse distribution analysis with optical emission spectroscopy (PDA/OES) method to determine the inclusion characteristics in steel under industrial conditions.<sup>14-16</sup>

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## STRUCTURE AND MECHANICAL PROPERTIES OF HEAT-RESISTANT ALLOYS ON THE BASIS OF NIOBIUM

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Alloys based on niobium, hardened by particles of silicides, carbides and other refractory compounds are currently considered as the basis for the creation of a new generation of particularly heat-resistant alloys for gas turbine engines. The report provides an overview of the state of research in this area and presents the results obtained at the Institute of Physics and Technology of the Russian Academy of Sciences with the participation of VIAM in studying alloys of the Nb-Si and Nb-C systems of the eutectic type. The structure, short-term mechanical properties were investigated, long-term strength tests were conducted in the temperature range of 1200–1500 °C. The results showed that the limiting temperatures at which complex-alloyed alloys of the Nb-Si system can be used do not exceed 1300 °C. The limitation is due to the creep resistance of the proper strengthening phase Nb<sub>5</sub>Si<sub>3</sub>. Nb-C system alloys can operate at higher temperatures. So the samples of the alloy Nb<sub>40</sub>Mo<sub>40</sub>C<sub>20</sub> retain high long-term strength at 1500 °C, due to the higher creep resistance of the NbC phase. On the basis of the data obtained on the dependence of the creep rate on stress, the values of the creep activation energy and the parameter *n* characterizing the dependence of the creep rate on stress are determined. Assumptions are made about the mechanisms of high-temperature deformation of the investigated alloys.

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## METHODS OF PRODUCING HIGH NITROGEN STEELS

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A brief review and own results on the methods of developing Metallurgy under (gas) Pressure – MP, in the production of High Nitrogen Steels – HNS, have been presented. MP represents a new metallurgy that has started its development at the end of the XX century. Nitrogen is the work medium – the most important, highly efficient and cheapest alloying element with practically inexhaustible resources.

The research and industrial results in the Republic of Bulgaria and in the former USSR – Russian Federation (RF), have proved that are achieved, in comparison to the conventional analogs: up to 4 times higher Re, preserving the other characteristics; 3.2 times lower electric power consumption; avoiding or reducing the use of expensive alloying elements (Ni, Co, Mo, W, V.); expanding the metallurgical range in the table of D. I. Mendeleev by effective and environmentally friendly alloying of HNS and conventional steels with easily evaporable and/or toxic elements (Ca, Zn, Pb, Mn); high economic efficiency; high ecology; sustainable development. Similar research was conducted in Germany, Austria, France, USA, China, India and other countries, where remarkable results were achieved in power generation, aircraft building, defense industry, etc. Various methods were applied but practically at present the method of Electro Slag Remelting under Pressure (PESR) (Austria, Germany) remained in industry. More than 13 international scientific conferences devoted to HNS and methods of its production were held (in France, Bulgaria (1989), Germany, RF (2006), China, India, Germany and other countries).

Now the debatable problem has arisen – which method to use further on? We consider that the method of the Big Steelmaking Bath is most prospective on the grounds of the following facts (compared to PESR): the rate of nitrogen alloying is more than 66 times higher; the productivity is 11 times higher; the power consumption is 3.2 times lower; 100% assortment against ≈10%.

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## MODELING AND SIMULATION OF METAL-OXIDE MELT INTERACTION

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Calculation of equilibrium phase composition is one of the stages (along with kinetics analysis) of building an end-to-end physical and chemical model of real processes.

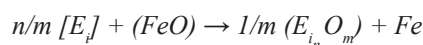
Thermodynamic patterns of oxidation-reduction reactions on the metal-slag melt interface are also taken into account when building phenomenological models of real welding, facing, and metallurgical processes.

The first part of this paper deals with calculating an equilibrium phase composition for a specific reaction. A method proposed herein also takes into account an interaction among any number of chemical reactions in the metal-oxide melt interface that form an equilibrium phase composition.

Multiple chemical reactions proceed in the interphase boundary. Hence, we need to know the equilibrium constant values for all potential processes, and also the details of material balance for all of the reactants. It should be noted that the choice of reactions is quite arbitrary.

We will attempt to describe system equilibrium by assuming that one common reactant is involved in all of the reactions. For iron-based melts, this should be iron oxide (FeO), which is always present in oxide melts.

Chemical reactions of all common reactant-containing metal phase components in terms of 1 mole (FeO) are as follows in general:



Thermodynamics analysis of oxidation-reduction reactions between metal melt and slag provides answers to certain practical issues such as the path of specific chemical reactions, final (equilibrium) phase composition, and the elements that are reduced and oxidized at given physical parameters. Although considerable, this is obviously not enough to analyze real technological systems, because the required equilibrium cannot be normally achieved despite high temperatures of welding and metallurgical processes. Hence, a dynamic problem has to be resolved here, which is calculating phase composition as a function of time. This cannot be achieved without knowing the rates of element concentration changes in each and every phase, and also technological parameters of the process. The second part of this paper analyzes special kinetic features of physical and chemical processes in the metal and oxide melt interface.

## POWDER METALLURGY OF NANOMATERIALS

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To date, powder metallurgy technologies have been developed, which make it possible to obtain powders of metals and their compounds with a given dispersion, nonporous structural and functional materials, as well as porous materials with adjustable porosity, pore size and shape, and desired properties<sup>1,2,3,4</sup>.

Porous nickel is used in many technical applications, such as heterogeneous catalysis, in heat exchangers, solid-state fuel cells. In recent years, methods for their production by powder metallurgy methods using temporary fillers of pore-forming agents have been actively developed. In this case, the processes of pressing mixtures of metal powders and a blowing agent, removing a blowing agent, and sintering metal powders are consistently carried out. Of particular interest are materials having a multimodal pore size distribution, otherwise materials with hierarchical porosity. Powder metallurgy in the process of sintering-evaporation for the first time synthesized permeable highly porous material based on nickel nanopowder, which has a pronounced hierarchical structure and contains pores of three spatial scales: macropores, their connecting windows and interparticle micropores in the walls of macropores<sup>5</sup>.

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## PARADOXICALITY IN SOME GROUPS OF METALS OF THE PERIODIC SYSTEM IN THE MODERN VIEW

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The anomalies connected with some groups of metals which are present at the Periodic law of D.I. Mendeleev and his table is connected with some discrepancies of physical and chemical properties in complex metal compounds with the location of elements in groups which first of all treat metals with a different valence. There was a possibility of a new view on structural changes of metals, alloys and their compliances with mechanical properties, and the present time with connected of development of technical means and conditions of level analytical devices. At the same time it is possible to explain some contradictions which took place in the first versions of the Periodic Table especially in groups of metals.

It is carried out the analysis of the archive materials of the Mining museum of Mining University in St. Petersburg connected with D.I. Mendeleev's activity concerning researches in the field of metallurgy. We are studied of contemporary records of the Freiberg technical academy in which were open indium and germanium. Studying of various methods of forecasting of arrangement of chemical elements in D.I. Mendeleev indicates that some discrepancies in groups of metals were eliminated in the course of its formation. An analytical research of papers of the Russian scientist methods of his forecasting of some elements («ekoboron», «ekosilizium», «ekoaluminium»), are proved and confirmed with the subsequent discoveries of scandium, germanium, gallium. There are considered that the some elements was studied on an example on advantage unvalued D.I. Mendeleev's generalizations such as the changing properties of elements of rather transitional metals, existence of functional dependence of atomic weight at compliance with the theory of numbers as instrument of judgment of frequency. Modern methods of the analysis of properties of some metals indicate system approach in creation of the Table of D.I. Mendeleev.

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## DEVELOPMENT AND EVOLUTION OF PHYSICAL AND CHEMICAL METHODS OF MODELING OF TECHNOLOGICAL PROCESSES IN FERROUS METALLURGY

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Modern experience in the use of information systems for the management of metallurgical enterprises shows that they are a powerful means of improving the efficiency of modern production in the field of ferrous metallurgy. The use of information technology significantly affects the organization of management processes for any plant and for a vertically integrated company as a whole. Information systems are capable not only to increase controllability and validity of decision-making, but also to reduce direct costs of production activity, to increase competitiveness of the enterprise in domestic and foreign markets.

Mathematical modeling of metallurgical processes allows reducing the share of expensive industrial experiments and thus facilitating the solution of various tasks to improve existing production, as well as to develop new technological schemes for processing and utilization of non-traditional ores and various industrial wasters. In this regard, the complex of software with the uniform database is developed for end-to-end calculations in the field of ferrous metallurgy. The basis for the creation of an integrated information system is the results of previous research in Institute of Metallurgy of Ural Branch of RAS on mathematical modeling of heat and mass transfer processes in metallurgical units<sup>1-2</sup>.

During implementation of a goal tasks of the choice of tools and software for engineering design and support of applications of an information system were solved, algorithms of mathematical models for the forecast of technical-economic indices are developed and improved for the main metallurgical processes. Variants of the solution of various technological problems are given.

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## PHYSICOCHEMICAL AND THERMAL BASES OF PROCESSING OF TITANOMAGNETITE CONCENTRATES WITH DIFFERENT CONTENT OF TITANIUM DIOXIDE

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Russia possesses the world's largest stocks of titanomagnetite ores. The Kachkanarsky group of fields of titanomagnetite ores consists of two fields: Gusevogorsky and actually Kachkanarsky. Now JSC EVRAZ NTMK processes titanomagnetite agglomerate and the pellets received from ores of the Gusevogorsky field<sup>1,2</sup>. For processing of titanomagnetite ores of actually Kachkanarsky field taking into account their specific features, in particular, the raised content of TiO<sub>2</sub> in iron ore concentrate from 2.5 % to 3.6 %, it is required to make changes in technology of blast furnace smelting. In this regard research of metallurgical properties of the agglomeration of iron ore raw materials received from concentrates with the different content of titanium dioxide is realized. For clarification of phase components of pellets the method of X-ray phase analysis was used. Results of calculation of viscosity of the received slags have shown that it is in limits, typical for viscosity of real blast furnace slags, that is violations of slag mode it is not expected. According to calculations with use of technique<sup>3</sup> increase of hot durability and temperature of the beginning of softening of pellets with the raised content of titanium dioxide will effect positively to the main technical and economic indicators of blast furnace smelting - coke consumption and productivity.

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## CONTROL OF STRUCTURE FORMATION IN A HIGH-STRENGTH NITROGEN-BEARING AUSTENITIC STEEL UNDER THERMOMECHANICAL TREATMENT

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The production of nitrogen-containing steels is associated with a number of technological difficulties, such as providing the required nitrogen content in steelmaking, the formation of cracks during hot deformation, etc. In industries, it is also necessary to ensure stable production of semi-finished metal with a given level of mechanical and performance properties. Of paramount importance is studying steel structure formed during thermomechanical processing<sup>1</sup>.

The research work established the relationship between various technological parameters and processes occurring in nitrogen-bearing steel grade 04Cr20Ni6Mn11Mo2NWNb during thermomechanical and heat treatment<sup>2,3</sup>. The obtained patterns served as the basis for the development of technologies for the manufacture of sheet and rolled metal, forgings of various sizes and ensured the production of semi-finished steel in industrial conditions.

The technological principles for the control of the structure formation of nitrogen-containing steel were developed for all production stages making it possible to obtain semi-finished products of various sizes with a wide range of mechanical and service properties within the composition of a single steel grade.

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## ASSESSMENT OF NON-METALLIC INCLUSIONS AND CLUSTERS IN CA-TREATED STEELS BY USING DIFFERENT MODERN ANALYTICAL TECHNIQUES

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Modification of different non-metallic inclusions (NMI) and clusters by Ca addition was investigated in Al-killed steel samples. After electrolytic extraction (EE) of NMI from the metal samples, the characteristics of undissolved inclusions and clusters (such as the morphology, size, number and composition) in steels before and after Ca addition were evaluated by using a scanning electron microscope (EE+SEM method).<sup>1-2</sup>

The results obtained from the current investigations of inclusions after electrolytic extraction of steel samples were supplemented by Fractional Gas Analysis (FGA) investigations.<sup>3-4</sup> The compositions and volume fractions of the main oxide inclusions in metal samples before and after Ca addition were investigated by using the FGA technique.

In this study, the FGA and EE techniques were successfully applied for the investigations of NMI and clusters in steel samples obtained from laboratory experiments and from different stages of steelmaking. The results obtained from both techniques agreed well. Moreover, these methods complement each other well with respect to the evaluation of inclusion modifications during Ca treatment of different steels.

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## THERMODYNAMICS AS A BASIS FOR IMPROVEMENT OF COMPOSITION AND PROCESSING TECHNOLOGY OF STEELS AND ALLOYS

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On the example of steels and alloys the capabilities of thermodynamic modeling for solving various metallurgical tasks have been shown: 1) forecast of the advanced aluminum-silicon alloys compositions for semi-solid processing (SSP)<sup>1</sup>, 2) controlling of  $\delta$ -ferrite nature in high-nitrogen steels for enhancing their technological properties during the hot plastic deformation<sup>2</sup> and welding<sup>3</sup>, 3) interpretation of the nature of nonmetallic inclusions in steels<sup>4</sup>.

On the basis of the fundamental curve “liquid fraction versus temperature” the criteria to forecast the advanced alloys for SSP technology have been developed<sup>1</sup>.

Via thermodynamic modeling methods, the critical parameters determining the behavior of  $\delta$ -ferrite during solidification and subsequent cooling of solid high-nitrogen steel during its production and welding have been revealed. The Schaeffler diagram has been improved and its more advance alternative has been proposed<sup>2-3</sup>.

A step-by-step method for the thermodynamic interpretation of the non-metallic inclusions nature both single and combined into the clusters by chemical composition found by the automatic feature analysis using the SEM EDS method has been developed<sup>4</sup>.

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## CORROSION RESISTANCE OF NITROGEN-CONTAINING STEELS

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Nitrogen-alloyed austenitic steels exhibit high static and cyclic strength, corrosion resistance. Using the own and literature data, the corrosion resistance of nitrogen-containing steels was considered, including the influence of nitrogen concentrations and the main alloying elements on the composition of the steel, the features of the corrosion behavior of nitrogen-containing steels in various media. The empirical dependences of the effect of nitrogen and other alloying elements on the critical temperatures of pitting and crevice corrosion, formulas for pitting formation equivalents, and data on the correlation of these equivalents with the electrochemical potentials of pitting formation are given. Attention is paid to the influence of the structural-phase state of nitrogen-containing steels on their corrosion resistance. The processes leading to the release from the solid solution of excess nitride phases reduce the corrosion resistance of nitrogen-containing steels.

The positive effect of steel doping with nitrogen consists in blocking anodic dissolution due to repassivation and changes in the mechanism of development of the nascent pitting. Nitrogen is absorbed on the surface of the forming passive oxide films, which are enriched in the surface layer with nitrogen, the stronger, the higher the nitrogen content in the bulk of the material. Studies of anodic potentiodynamic polarization in chloride-containing solutions of austenitic nitrogen-containing steels have shown that nitrogen concentrates on the surface of the metal oxide, causing repulsion of chlorine ions; Nitrogen ions, interacting with  $H^+$  ions in solution, increase the pH of the medium, which, in turn, slows down the corrosion of steel. This affects the intensity of crevice and general corrosion. The presence of nitrogen ions can prevent the pitting nucleation by suppressing the adsorption of chlorine ions on the surface of the passive film. With this in mind, when assessing the corrosion resistance of nitrogen-containing steel, one should take into account the amount of nitrogen in the solid solution.

The presented report contains the results of studies and tests in chloride-containing media of steel Fe- (18-20) Cr- (0.4-1.2) N; Fe- (21-22) Cr-15Mn-8Ni-1.5 Mo-0.5N; Fe-16Cr-5Ni-0.12N. Their advantage on corrosion resistance to nitrogen-free analogues has been demonstrated.

## PYROMETALLURGY AS AN ELEMENT OF IMPROVEMENT OF HYDROCHEMICAL PROCESSES FOR THE EXTRACTION OF METALS FROM ORES

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Specific features of the world practice in the metallurgy is that the technology of modern production of metals consists of a few phases:

- ore mining and processing of raw materials (enrichment, sintering, production of concentrate);
- metallurgical processing;
- utilization of metallurgical production wastes by processing dumps and slags for return to the main production.

At each of these stages, as a rule, it is possible to distinguish pyro- and hydrometallurgical methods of obtaining the target product or their combination. Difficulty and multi-stage technological schemes of complex processing of multicomponent mineral raw materials depend on the concentration of the metal in the raw materials, the content of various impurities in it, the requirements for the purity of the metal or its chemical compound, economic feasibility and justification of the proposed options<sup>1</sup>.

An ecologically safe technology of using high-titanium slags to obtain titanium dioxide pigment for the "Crimean Titan" plant has been proposed. The technology of germanium production from various ores and industrial wastes using pyro- and hydrometallurgical methods of its extraction (technology of reducing-sulphiding smelting of ash with subsequent leaching from the ash residue) are considered. For vanadium-containing raw materials, the necessity of using thermal roasting and sintering with alkaline reagents for selective leaching and obtaining highly concentrated vanadium pentoxide is shown. An assessment and justification of various combined schemes for the integrated use of bauxite in the production of alumina for the variants with the extraction of valuable rare-earth components, the production of commercial metal and slag suitable for the needs of the construction industry are given.

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## PROSPECTS OF DEVELOPMENT OF GRANULAR METALLURGY

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The development of modern technology requires the creation of products with enhanced performance characteristics under complex high-temperature loading, exposure to aggressive environments, wear, which can be very effectively obtained by the methods metallurgy of granules<sup>1</sup>. To obtain granules by the method of centrifugal spraying, a family of specialized technological equipment CSM has been developed. To increase the yield of fine granules (<100 microns), the installation of a new generation CSMT-9 has been developed<sup>2</sup>.

One of the most modern and promising technologies for additive production is the technology of selective electron beam melting (SEBM). In JSC «Kompozite» a powder was obtained from alloy VT6S of a fraction of 40-100 μm with a peak of a particle size distribution of 60-70 μm. Samples for mechanical tests were obtained from this powder by the SEBM method (Table 1).

Table 1. The results of mechanical tests

	Tensile strength $\sigma_b$ , МПа	Yield strength $\sigma_{0.2}$ , МПа	Relative elongation $\delta$ , %	Contraction ratio $\phi$ , %
VT6S manufactured by JSC «Kompozite» (SEBM + HT)	1234	1066	9,02	19,9
Grade 5 manufactured by Arcam AB (SEBM + HT)	1020	950	14	40
Rod VT6S according to GOST	755–935	-	6–9	15–22

Analysis of the data presented shows that the samples obtained by the SEBM method from powders produced by JSC „Kompozite” are comparable in properties to Grade 5 alloy obtained by a similar method and are superior to VT6S alloy obtained by standard technology.

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## THERMODYNAMIC OF NONMETALLIC INCLUSIONS FORMATION IN THE PIPE STEEL MELTS

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Problems of the alloys producing with the given properties is directly connected with deep understanding the characters of alloy components interaction with the present impurity elements. In this research a thermodynamic analysis of the phase equilibria in the Fe-Mn-Si-Ca-Al-Cr-V-Nb-Ni-Mo-P-S-O system at the temperatures of molten metal existence was performed. The concentrations of some elements were fixed ( $[Mn]=0,5$ ;  $[Si]=0,2$ ;  $[V]=0,05$ ;  $[Cr]=0,1$ ;  $[Nb]=0,03$ ;  $[Ni]=0,5$ ;  $[Mo]=0,1$ ;  $[P]=0,01$ ,  $[S]=0,005$  wt %).

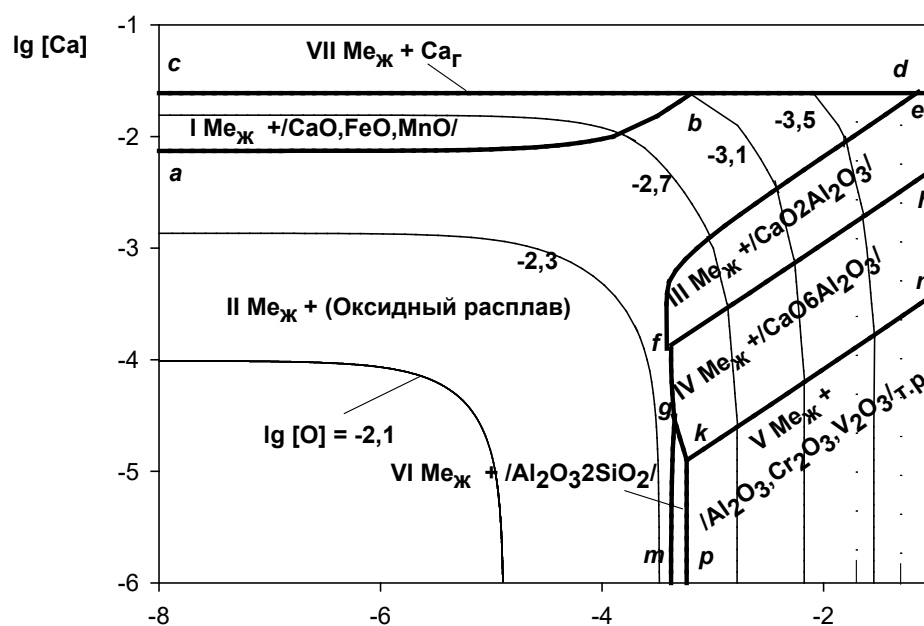


Fig. Phase equilibrium Fe–Ca–Al–Mn (0,5)-Si (0,2)-Cr (0,1)-V (0,05)-Nb (0,03)-P (0,01)-S (0,005)-Ni (0,03)-Mo (0,1)-O (wt. %) system ( $T=1873$  K)

It is found that at the temperature  $T = 1873$  K depending on the concentrations of calcium and aluminum in equilibrium with the liquid metal may be an oxide solid solution based on CaO (region I), oxide melt (FeO, MnO, SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrO, V<sub>2</sub>O<sub>3</sub>, VO) (region II), bi- and hexo- calcium aluminates (regions III and IV), oxide solid solution based on corundum (region V), mullite (region VI) and the gas phase consisting mainly of gaseous Ca (region VII).

## PHYSICO-CHEMICAL PHASE COMPOSITION MANAGEMENT OF TECHNOGENIC FORMATION AND OFF-GRADE ORE UNDER COMPLEX PROCESSING

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In present-day the metallurgical industry of Russian Federation is experiencing an increasing shortage of scrap metal for the needs of the steelmaking industry, as well as the depletion of traditional iron ore deposits and a content decrease of iron compounds in the ore. Thus, the issues of using non-traditional sources of iron-containing raw material in steelmaking have become topical. Non-traditional sources of iron-containing raw material include technogenic and natural formations of poor iron ore raw materials.

The complexity of processing such technogenic and natural iron-containing formations lies in the fact that, with an insignificant content of iron oxides, they are still strongly connected with silicate minerals, which does not allow the iron extracting with the standard methods of enrichment. In addition, a significant content of silicate minerals in these products creates an additional environmental pressure, since silicate minerals are not involved in processing, and after iron is removed, they are dumped.

The phase composition management of technogenic formations during the process of pyrometallurgical processing allows separating silicate and iron-containing minerals and ensuring their complex processing with complete iron extraction and conversion of silicate products into mineral binders or refractory products.

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## THE UNIFICATION OF SHEEPBUILDING STEELS

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Competitiveness of the Russian products, growing demand for their characteristic improvement call for new solutions, when creating structural materials with unique combination of properties, such as high ductility at specified high strength, cold resistance and corrosion resistance. Creation of the new chemically unified steels with minimal alloying will enable us to introduce more efficient welding technologies and assembly of marine technical equipment that will favour development of shipbuilding, nuclear power engineering, oil and gas complex and other key sector of the Russian economy.

The development of the structural steels production together with the increase of industrial equipment automation helps considerably limit the content of high-value alloying elements in steels and compensate the share of alloying in a high physical-mechanical properties and resistance to brittle and ductile fractures by using special high precision technological impact<sup>1</sup>.

The full scope of investigation, including hot plastic deformation modeling, design and development production, as well as structural studies on different levels<sup>2</sup> help us create unique steels with less alloying levels, as compared to the existed steels. In addition, there is possibility of wide unification of chemical elements of steels with adjusted strength degrees as well as a range reduction of steels applied for all industries. The total number of steel grades that differ in chemical composition can be reduced by 4 or 5 times, without losing the required quality indicators of the rolled metal assortment, which is mostly needed.

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## MAIN DIRECTIONS IN DEVELOPMENT OF TECHNOLOGY AND STEEL GRADE CHEMICAL COMPOSITIONS FOR MANUFACTURING WELDED AND SEAMLESS PIPES

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Steady progress in metallurgical technologies, one hand, and growth of technical requirements from main groups of key customers, other hand, define modern development of pipe and tube industries. Portion of pipe production in Russian domestic steel consumption is about one quarter, that is caused by high volumes of national oil and gas production and transportation. This has determining influence on technology development in pipe industry and metallurgy due to continuous growth of technical requirements and reliability improvement under severe and critical operation conditions. Moreover, determining condition of competitiveness of steel products is cost saving due to reasonable chemistry design and implementation of effective strengthening methods.

The results and future prospective of technology development related to welded and seamless pipe manufacturing are presented and discussed including:

- hot pipe rolling using continuous cast billets directly for seamless products for different applications;
- chemistry design and heat treatments routes for high grades with an improved fracture behavior at low temperatures;
- main fundamentals of alloying and microalloying of steel for pipes and tubes strengthened by quenching and tempering;
- the influence of chemical and phase composition of steel for tubing and casing sustainable to environments containing hydrogen sulfide and carbon dioxide;
- strengthening flat products using microalloyed steels and thermomechanical controlled processing;
- main approaches and methods providing strength, plasticity and ductility in different areas of joints in welded pipes.



## MODERN APPROACHES TO IMPROVING THE CORROSION RESISTANCE OF MODERN STEELS IN AQUEOUS MEDIUM

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Much attention is paid to the issues of improving the corrosion resistance of carbon and low-alloy steels operated in aqueous media (oilfield pipelines, marine conditions, etc.). It is shown that the optimization of the chemical composition and structural state of steels, as well as ensuring the purity of steel for certain types of non-metallic inclusions are important conditions for increasing the corrosion resistance of steel in such conditions.

The evolution of the non-metallic inclusions composition, concerned with the development of metallurgical technologies, caused the fact that in modern steels, non-metallic inclusions based on aluminum spinel have a complex chemical and phase composition. The oxide component of such inclusions may contain calcium, magnesium, aluminum and some other elements in different ratios. The corrosion activity of inclusions and, correspondingly, the corrosion resistance of steels depend on the ratio of the content of these elements. Thus, it is possible to increase the corrosion resistance of modern steels by optimizing the technology of steelmaking not only to increase their purity in non-metallic inclusions, but also to form non-metallic inclusions of favorable chemical and phase composition that do not have a negative impact on corrosion resistance.

During the development of the technologies rolling redistribution of steels in operation, each required in aquatic environments, it is necessary to provide the technological methods, preventing formation of unfavorable components of the structure, that have a negative impact on the corrosion resistance is a bone. These components include nano-sized selection of excess phase with unfavorable morphology, ferritic-pearlitic foliation etc.

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## IRON AND STEEL HARDENING WITH AIR OXYGEN

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Manufacturing of oxide dispersion-strengthened (ODS) steels includes mechanical treatment of mixture of steel powders and oxides in a ball mill. At this stage grinding and dissolution of sufficiently large initial oxides in a steel matrix occurs. The subsequent high-temperature sintering of the mechanically alloyed powder leads to formation of the necessary strengthening nanosized oxides of yttrium, titanium, iron, etc. The specific feature of the proposed method is that surface oxides formed in the process of preliminary air oxidation of iron or steel powder are used as a carrier of oxygen. The work represents the process of deformation dissolution of oxides and other phases at low and cryogenic temperatures (when diffusion is carried out mainly as a result of migration of interstitial atoms) using Mössbauer spectroscopy, electron microscopy and resistometry methods. Fig. 1 shows the structure of iron strengthened with FeO particles of  $\sim 2.5$  nm in size.

The structure was obtained after: (i) iron powder pre-oxidation, (ii) processing in the ball mill, (iii) sintering at 1000 °C and 80 MPa voltage, (iv) cold rolling with 88% compression and (v) recrystallization annealing at 1100 °C. It is shown that in the absence of any alloying elements, except for air oxygen, recrystallized samples of ODS-iron have increased strength characteristics ( $\sigma_{0.2} \sim 570$  MPa,  $\sigma_B \sim 632$  MPa).

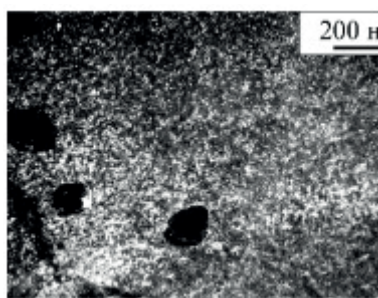


Fig. 1 The structure of the iron strengthened with dispersed iron oxides (dark-field image taken in the FeO reflection)

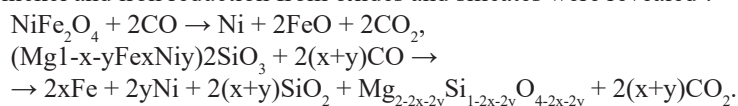
*The work was performed within theme “structure” № AAAA-A18-118020190116-6 supported in part by the RFBR project № 18-03-00216.*

## MASS-EXCHANGE PROCESS UNDER REDUCTION OF OXIDIZED NICKEL ORES

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The sequence of transformations during heating of the main types of the Ural oxidized nickel ores in inert and reduction conditions was revealed by methods of thermal analysis, X-ray phase and X-ray spectrum microanalysis. The temperature dependences of nickel and iron reduction from oxides and silicates were revealed<sup>1</sup>:



The use of coke as a reduction agent makes it possible to separate iron and nickel (fig.) from serpentinites at temperatures above 1200 °C.

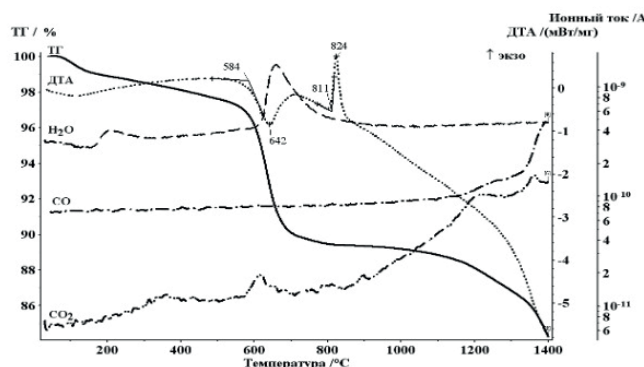


Figure. Thermogram of the ore and coke (10 %) mixture during heating (10 deg/min) in a stream of argon and data of mass spectrometric analysis of gases

The obtained data were used to substantiate the operating parameters of roasting and electric furnaces during smelting of ferronickel from oxidized ores of Serovskoe, Sakharinskoe, Buruktalskoe and Kulikovskoe deposits.

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## PHYSICS AND CHEMISTRY AND TECHNICAL CONCEPTS OF IMPROVING ALLOY-TREATED STEEL AND ALLOY PROCESSING TECHNOLOGY

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The Electrostal smelter has founded alloy-treated steels and alloys using forced blast of metal bath with oxygen gas for several decades. The melt temperature is relatively low with this technology, so much chromium was spent in the oxidation period, and significant quantities of low-carbon ferrochrome had to be added. We had to conduct thermodynamic and kinetic studies of oxidation.

The equilibrium constant of carbon oxidation at temperatures from 1,600°C to 2050°C dropped from  $6 \cdot 10^7$  to  $1,5 \cdot 10^7$ , i.e. by 4 times, remaining at Level 107. The equilibrium constant of liquid chromium oxidation declined from  $1,1 \cdot 10^6$  to  $1,4 \cdot 10^4$ , or two orders less. The ratio of constants increases 200 times. This thermodynamic analysis underlay the development and implementation of the high-temperature version of the oxidation technology when founding alloy-treated steels and high-chromium alloys. Raceway oxygen pressure was increased to 14.

Linear function of oxygen solubility in liquid metals, such as Ni, Co, Fe, Mn, Cr, and standard Gibbs energy for oxidation of these metals at different temperatures was established. The equations were proposed and the calculations of excessive chemical potentials of oxygen and the energies generated by mixing of these liquid metals with oxygen were carried out.

Equilibrium oxygen activities at the end of oxidation in experimental founding and actual oxygen activities were calculated based on measurements of electromotive forces by oxygen electrochemical sensors. The driving forces of oxidation were calculated for this founding processes and the possibility of calculated forecasting of carbon concentration at the end of oxidation was demonstrated in terms of non-equilibrium thermodynamics.

Kinetic studies enabled to establish the oxidation rate constants and critical concentrations of elements, to produce the equations to calculate the oxidation duration in each founding and to incorporate these calculations into the process guidelines.

Implementation of technical concepts enabled cost saving during steel making.

## INJECTION DEPHOSPHORIZATION OF HIGH-CARBON AND LOW-CARBON IRON MELTS

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There is a lack of researches of dephosphorization of iron melts containing different amount of carbon at comparable conditions. Dephosphorization of vanadium-containing iron and pig iron and high-carbon and low-carbon semi-products with 3-5 % slag-forming mixture injection during argon blowing was studied under laboratory conditions. Correlation between phosphorus content after slag-forming mixture injection and initial phosphorus content was established for all studied systems.

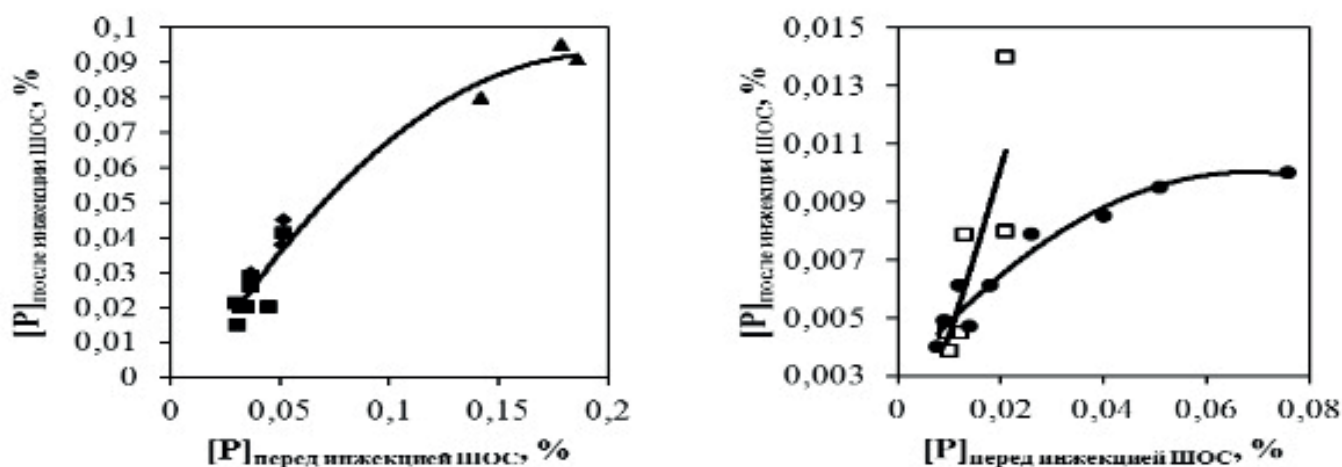


Figure 1. Correlation between phosphorus content after slag-forming mixture injection and initial phosphorus content - vanadium-containing iron, - pig iron, - high-carbon semi-product (after blowing of vanadium-containing iron), low-carbon semi-product (after flux-free blowing of vanadium-containing iron), - low-carbon semi-product (after blowing of pig iron)

Slag-forming mixture provides both desiliconization (90-95 %) and dephosphorization (45-50 %) of pig iron (4,1-4,5 % C, 0,40-0,45 % Si, 0,14-0,19 % P). The degree of dephosphorization of vanadium-containing iron (4,3-4,7 % C, 0,07-0,10 % Si, 0,04-0,05 % P, 0,40-0,45 % V) and high-carbon semiproduct (2,2-3,1 % C, 0,07-0,08 % V, 0,03-0,04 % P) in case of usage slag-forming mixture ( $\text{CaO-FeO-CaF}_2$  или  $\text{CaO-Na}_2\text{CO}_3$ ) was 25-40 %. Deep dephosphorization of low-carbon semi-product (0,04-0,12 % C, 0,008-0,076 % P) with final phosphorus content 0,004-0,005 %, was shown to be possible.

The research was performed in accordance to State assignment of Metallurgy (UB RAS) as part of State Academies Basic Research Program.

## THE DEVELOPMENT OF ANTIMONY PRODUCTION IN RUSSIA ON THE BASIS OF INNOVATIVE TECHNOLOGIES

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Russia has a leading position on antimony market in the world. Three provinces are the most abundant by antimony such as Sakha (Yakutia), Krasnoyarsk and Transbaikalian edges. Nowadays, the basic resources for antimony production in Russia are concentrated in Sakha Republic (Yakutia) and presented by Zhipkozinsky and Solonechensky deposits, while in Krasnoyarsk region the Olimpiadinsky deposit is perspective.

In the present work the efficiency of computer technology and chemical programs in order to study the behavior of collectors in flotation of antimony, arsenic and Au (I, III) minerals was shown. Perspective collectors for flotation antimony-gold-bearing ores on the basis of P (V) and compounds with S, O and N atoms were chosen. The mechanism of interaction with the mixtures of two or three components of collectors was studied. High recovery of antimony and gold were reached in processing of Au-Sb ores of Sarulah and Sentachan deposits in Sakha (Yakutia). X-ray radiometric methods of separation of antimony ores from of Transbaikalian edge deposits were proposed.

In order to choose the effective solvents for hydrometallurgical processing of Sb, Au-containing concentrates the method based on cluster formation between transition solvents and antimony minerals was suggested. The nature of losses Au was theoretically revealed in the sulfide-alkaline process. On the base of computational modelling the probable formation of various complexes of potassium-gold types (KAu): hydrosulphidic KAu, thiosulfates KAu Na<sub>3</sub>AuS<sub>4</sub>O<sub>6</sub>, antimony and arsenic KAu, trythiostibate (III) and trythioarsenate (III) KAu was established. The practice of processing of gold-antimony concentrates to produce high-quality antimony trioxide and antimony-gold containing alloy (AGCA) regarding to the special conditions of the Far North region was analyzed. The affinage of AGCA was recommended. Creative project development of antimony industry in Russia in order to produce antimony compounds and pigments, including pyroform compounds and flame retardants (antipirene,) was discussed.

## STEELS, ALLOYED BY NITROGEN

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Now alloyed by nitrogen steels of various structural classes are widely applied in various areas of industr<sup>1</sup>. Standard production technologies of steels with nitrogen were created. Steel with nitrogen distinguish on nitrogen-steels and high-nitrogen steels. Nitrogen steels melted with a normal pressure in ordinary steel-smelting units. High-nitrogen steels are melted with a pressure above atmospheric in special hyperbaric processes. At the same time nitrogen content in steel can be identical in both cases. To receive the high content of nitrogen in nitrogen steel, the content of chrome and manganese has to be much higher, than in high-nitrogen steel.

Nitrogen introduction even in small amounts leads to noticeable change of properties of steel, tab. 1<sup>2</sup>.

Table 1. Some nitrogen steels

Steel	HV, MPa	$\sigma_B$ , MPa	$\sigma_{0,2}$ , MPa	$\delta$ , %	$\psi$ , %	$M_s$ , °C
Cr18Ni10Ti, N $\leq$ 0,01	210	515	230	47	51	23
Cr18Ni10N, N=0,220 %	240	750	400	63	84	-15
Cr19Ni6Mn10Mo2N, N=0,310 %	300	926	690	33	84	-254

Perspective direction of development and application of steels, alloyed by nitrogen, can be the creation of the new steels with special functional properties<sup>1</sup>, such as high resistance in bioactive environments, bactericidal action, high durability, etc.

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## THE DATABASE AND MATHEMATICAL MODEL OF REE JOINT EXTRACTION IN THE SYSTEM HCL-NACL-H<sub>2</sub>O-CYANEX 272-P-507-TBP FROM THE CHLORIDE MEDIUM

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The joint extraction of rare earth elements (REE) (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y) from chloride solutions by the extractants: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P-507), bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and their mixtures in presence of tri-n-butyl phosphate (TBP) is investigated. The extraction isotherms of REE are obtained by a standard technique. Initial solution of the sum of the REE was prepared by dissolution of carbonates of the sum of the REE of cerium and yttrium subgroup in hydrochloric acid.

Content of rare earth elements in samples was determined by an emission spectral method with the inductively coupled plasma. In an atomic emission spectrometer Shimadzu ICPE-9000 the echelle optical system is implemented, the spectral resolution is less than 0,005 nanometers at 200 nanometers, the range of wavelengths is 167-800 nanometers. Concentration of an element in unknown sample was determined by comparison of the measured intensity of the chosen spectrum line in sample with the measured intensity of this line in the standard solution containing the identified element with known concentration.

The 1018 distribution coefficients of individual REE are measured at various concentration of extractants, pH, extent of saponification at their joint extraction. The isotherms of an extraction of the sum of the REE and individual REE for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y are obtained. Factors of separation of couples of the REE are calculated. It is established that within the broad range of initial concentration of REE chlorides the separation factors of the adjacent couples are acceptable for separation of the REE of cerium and yttrium subgroup by the corresponding extractant.

The extraction solvate numbers of REE chlorides of cerium and yttrium subgroups are measured. On the basis of the received results the mechanism of reactions of an extraction and solvation of extractible complexes in an organic phase is offered and the mathematical model of an extraction of the REE which is adequately describing experimental data within experimental errors is developed.



## PHASE DIAGRAM OF DISORDERED ALLOY MO-W

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On the basis of method<sup>1</sup>, that allows to study the properties of binary composition alloy, the phase diagram of molybdenum and tungsten alloy:  $\text{Mo}_1 - \text{W}_C$  have been obtained. Here  $C$  is the atomic concentration of W. The pairwise interatomic interaction is presented in the form of the Mie-Lennard-Jones potential:  $\varphi(r) = [D/(b-a)] \cdot [a(r_0/r)^b - b(r_0/r)^a]$ , where  $D$  and  $r_0$  are the depth and the coordinate of the potential minimum,  $b > a > 1$  are parameters, that are defined by the method from<sup>1</sup>. For Mo:  $r_{0\text{Mo}} = 0.272$  nm,  $a_{\text{Mo}} = 1.87$ ,  $b_{\text{Mo}} = 6.82$ ,  $D_{\text{Mo}}/k_B = 48950$  K; for W:  $r_{0\text{W}} = 0.274$  nm,  $a_{\text{W}} = 2.6$ ,  $b_{\text{W}} = 7.2$ ,  $D_{\text{W}}/k_B = 40000$  K. Here  $k_B$  is the Boltzmann constant. For calculation of the solidus temperature ( $T_s$ ) and the liquidus temperature ( $T_l$ ) the following expressions are used<sup>1</sup>:

$$T_s(C) = T_m(W)P_W(C) \cdot [m(C)/m_W] \cdot \{ [c(C)\Theta(m)]/[c_W\Theta(m_W)] \}^2 [X_{LW}/X_L(C)]^2 + T_m(\text{Mo})P_{\text{Mo}}(C),$$

$$T_l(C) = T_m(\text{Mo})P_{\text{Mo}}(C) \cdot [m(C)/m_{\text{Mo}}] \cdot \{ [c(C)\Theta(m)]/[c_{\text{Mo}}\Theta(m_{\text{Mo}})] \}^2 [X_{L\text{Mo}}/X_L(C)]^2 + T_m(W)P_W(C).$$

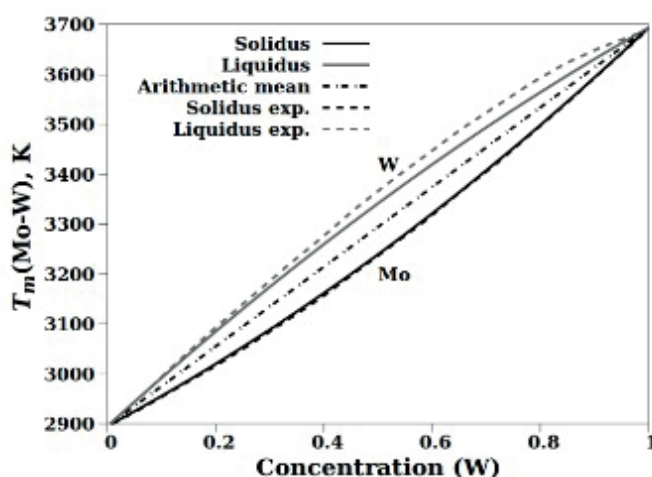


Figure 1. Phase diagram of the Mo-W solution.

Here  $T_m(i)$  is the melting temperature of  $i$ -th component pure lattice:  $T_m(\text{Mo}) = 2896$  K;  $T_m(\text{W}) = 3693$  K.  $c(C)/c_i$ ,  $\Theta(m)/\Theta(m_i)$ ,  $X_L(C)/X_{Li}$  are relations of the distances between the centers of the nearest atoms, the Debye temperatures and the Lindemann parameters in the solution lattice and in the pure  $i$ -th component lattice. Functions  $P_{\text{Mo}}$  and  $P_{\text{W}} = 1 - P_{\text{Mo}}$  are geometric probabilities of finding the atom Mo and W in the alloy<sup>1</sup>. The fig. 1 shows the dependencies of the solidus and liquidus temperatures of the Mo-W alloy on the atomic concentration of W. Solid curves – calculation result, dashed curves – experimental values<sup>2</sup>, dash-and-dot line – arithmetic mean of the melting temperatures of pure Mo and W lattices with respect to the concentration:  $T_m(C) = T_{mW}C + T_{m\text{Mo}}(1 - C)$ .

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## CHANGE OF GOLD ELASTIC PROPERTIES AT NANOCRYSTAL SIZE REDUCTION

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Based on the previously tested method<sup>1</sup> that allows to calculate both macroscopic ( $N = \infty$ ) and size properties of a substance, the dependences of the elastic modulus  $B_T = -V(\partial P/\partial V)_T$ , and its pressure derivative  $B_T'(P) = (\partial B_T/\partial P)_T$  on the number of atoms  $N$  in the nanocrystal are obtained. The calculations were made for fcc gold at an isothermal-isobaric (i.e., at  $T = \text{const}$  and  $P = 0$ ) decrease in  $N$  for a cubic nanocrystal.

The pairwise interatomic interaction is represented by the Mie-Lennard-Jones potential:  $\phi(r) = [D/(b-a)] \cdot [a(r_0/r)^b - b(r_0/r)^a]$ , where  $D$  and  $r_0$  are the depth and the coordinate of the potential minimum,  $b > a$  are the parameters. These parameters were determined by the method from<sup>2</sup>. For the fcc Au we obtained ( $k_B$  is the Boltzmann constant):  $r_0 = 0.28751$  nm,  $a = 2.93$ ,  $b = 12.82$ ,  $D/k_B = 7411.5$  K.

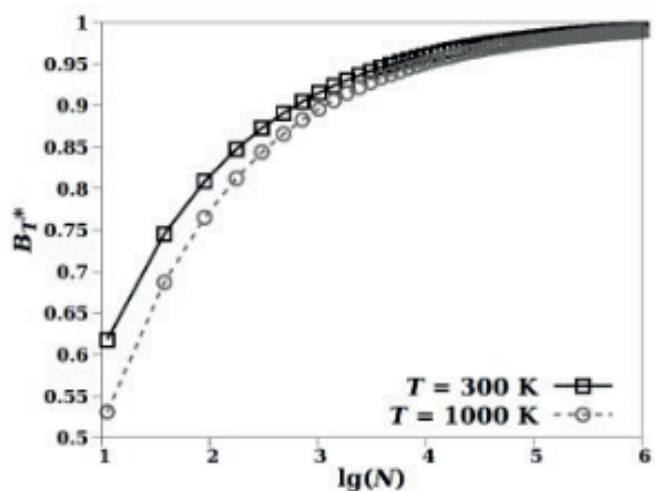


Figure 1. Size dependence of  $B_T^*$ .

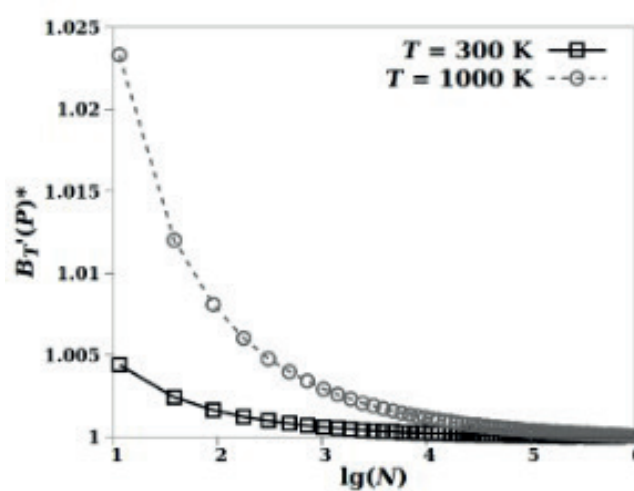


Figure 2. Size dependence of  $B_T'(P)^*$ .

Figures 1 and 2 show the isomorphic-isothermal-isobaric dependences of the normalized (on the value for a macrocrystal) functions  $B_T^*$  and  $B_T'(P)^*$  on  $N$  for Au nanocrystal of a cubic form. It is seen from the figures that with the decreasing of a nanocrystal size, the value of  $B_T^*$  decreases, and the value of  $B_T'(P)^*$  increases. With isomorphic-isobaric temperature rise, the size dependences of these functions are enhanced.

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## YTTRIUM REE SUBGROUP EXTRACTION BY MIXTURES OF CYANEX 272 AND P-507 FROM CHLORIDE MEDIUM

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The extraction process of rare-earth elements (REE) of the heavy-group rare-earth elements (HREE) from chloride solutions a mixture of extractants 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) and bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) + 10 volume % TBF in isopar – 1 with a mass concentration of P-507 + Cyanex 272 – 15, 30, 50 % was investigated. The molar ratio of extractants is 1:1<sup>1</sup>. The head solution of REE chlorides was prepared by dissolving the HREE carbonates in hydrochloric acid.

Set of 1012 concentration of individual REE in aqueous and organic phases in the range of concentration of the sum of chlorides of the REE 0.05-1.70 mol/dm<sup>3</sup> are measured. The isotherms of the extraction of the REE sum, individual REE (Eu, Gd, Tb, Dy, Y) at their joint extraction are received. The separation factors of pairs Gd/Eu, Tb/Gd, Dy/Tb, Y/Dy are calculated. It is shown that in the broad range of initial concentration of REE chlorides the partition coefficient of yttrium exceeds the dysprosium partition coefficient in 6 times, the separation factor a dysprosium/terbium reaches 3. It is established that the equimolar mixture of P-507 and Cyanex 272 can be used in the extraction separation technology of dysprosium and terbium.

Solvate numbers S of HREE are determined with the mixed extractant with various percentage by weight: 15% S=2.7, 30% S=3.1, 50% S=4.1. By IR (400-4000 cm<sup>-1</sup>), NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) spectroscopy, and dielectric methods were used to study yttrium solutions in extractant P-507. On the basis of the analysis of the dependences of the NMR signals shifts, changes of IR spectrums and dielectric permittivity of solutions on concentration of yttrium the mechanism of extraction reactions and solvation of extractible complexes suggested.

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## MICROHETEROGENEITY AND CONDITIONS OF CRYSTALLIZATION OF LIQUID STEEL 110Г13Л

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High-manganese austenitic wear-resistant steel 110Г13Л (Hadfield steel) has the following chemical composition, wt.%: C(0.95-1.50)-Mn (11.5-15.0). Viscosity  $\eta$ , density  $d$ , surface tension  $\sigma$  and electrical resistivity  $\rho$  of liquid steel 110Г13Л were measured in the temperature range from 1640 to 1970 K in the heating mode and subsequent cooling of the sample. A discrepancy was found between the temperature dependences of  $\eta$ ,  $d$ ,  $\sigma$  and  $\rho$  corresponding to the heating and cooling modes of the sample (hysteresis). The results are discussed in the framework of ideas about the microheterogeneity of liquid alloys. The heating temperature was determined from the point of view of the destruction of the microheterogeneity of liquid steel 110Г13Л  $T^*=1770$  K. An assessment was made of the characteristic size of a viscous flow structural unit - the size of microheterogeneity -  $s_0 = 3 \cdot 10^{-10}$  m. Relationship between the structurally sensitive properties of the melt and  $\eta$ ,  $d$ ,  $\sigma$ ,  $\rho$  is being researched in context of studying conditions for existence of microheterogeneity. The effect of manganese on the viscosity and supercooling of Fe-Mn melts was studied. It has been established that a change in the manganese content in the Fe-Mn alloy from 1 to 10% does not have a significant effect on the melt supercooling, the temperature  $T^*$  of irreversible destruction of microheterogeneity. A comparative metallographic study of the microstructure of 110Г13Л steel ingots, selected before and after heating the melt above  $T^*$ , was carried out. The heterogeneity of austenitic dendrites by chemical elements was revealed, which is the result of segregation during solidification, which agrees with the data on microhardness for an ingot that is superheated before crystallization.

## PHYSICO-CHEMICAL PROPERTIES OF LIQUID HIGH-ENTROPY ALLOYS

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We have studied temperature dependences of the physicochemical properties of liquid multicomponent alloys of equiatomic composition that are considered to be highly entropic: kinematic viscosity  $\nu$  of Cu-Bi-Sn-In-Pb, Cu-Sn-Bi-Pb-Ga melts, the specific electrical resistance  $\rho$  of the Cu-Sn-Bi-In-Cd melt, and surface tension  $\sigma$  of the melt Cu-Bi-Sn-In-Pb. There was found discrepancy between polytherm of heating and cooling  $\rho$  and  $\nu$ , which the authors interpret within the framework of the concepts of micro-inhomogeneous structure of metal melts: when passing through the liquidus line, no uniform solution at the atomic level is formed immediately and the micro-inhomogeneous state is maintained when heated to temperatures determined for each composition  $T^*$ . For all melts, we determined the temperatures at which an irreversible structural change in state of the melt occurs:  $T^*$  and  $T^\#$  (with  $T^* > T^\#$ ). Temperature  $T^*$  was determined from the beginning of coinciding part of the temperature dependences  $\nu$  and  $\rho$ , which were measured during heating and cooling of the melt. When heated to  $T^\#$ , the melts drastically changed characteristics of a viscous flow: the activation energy of a viscous flow and the entropy factor in Arrhenius equation. For all melts tested, viscosities during cooling were equal to or lower than corresponding values recorded during heating. Heating the melt to  $T^*$  also led to a sharp increase in values of  $\rho$ ; upon subsequent cooling, values of temperature coefficient of resistance  $d\rho/dT$  were close to zero, indicating an increase in the tendency of the metal to amorphize. Polytherms  $\sigma$  in heating and cooling modes coincide. The temperature coefficient of surface tension is the specific entropy of the surface  $d\sigma/dT = \gamma$  and is close to zero in absolute value. Value of  $\gamma$  decreases with increasing number of components in the melt, i.e. appearance of long-range order in a multicomponent melt is achieved in a more economical way.

## THE DIOXINS AND FURANS BEHAVIOR DURING REMOVING ZINC AND LEAD FROM EAF-DUST

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Electric steel production leads to the formation of metallurgical dust containing non-ferrous metals, which is associated with the use of galvanized scrap<sup>1</sup>. EAF-dust is a secondary resource suitable for extracting non-ferrous metals.

The chlorine and organic compounds content in metallurgical charge can lead to the dioxins and furans formation in the process of electric smelting with their subsequent sedimentation on electric arc furnace dust<sup>2</sup>.

The work experimentally confirmed the presence of D&F adsorbed on dust; a methodology for conducting an experiment, which makes it possible to study the behavior of D&F during metallurgical dust heating was developed.

In the course of the experiment, the intervals of D&F desorption from the surface of EAF-dust were revealed, and the dependence of the D&F removal rate on the dust heating temperature was determined.

The obtained data allowed us to develop recommendations for the reduction of D&F emission in the process of electric smelting. The study revealed the need of consideration of the dioxins and furans presence during development of technologies aimed at metallurgical dust processing.

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## SPECIFICITY ION EXCHANGE RECOVERY OF RHODIUM(III) FROM CHLORIDE SOLUTIONS

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Sorption of rhodium(III) from the individual and multicomponent chloride solutions on strong base anion exchange resin Purolite A500, weakly base anion exchange resins Purolite A111 with tertiary amino groups, Purolite S984 and Purolite S985 with polyethylene polyamine functional groups and ion exchange resins Purolite S914 and Purolite S920 with thiourea and thiouronium functional groups, respectively, hereinafter referred to as the A500, A111, S984, S985, S914 and S920 was investigated.

It has been established that in their selectivity to rhodium(III) the ion exchange resins with polyethylene polyamine and thiouronium, and thiourea functional groups substantially exceed the strongly base anion exchange resin and anion exchange resin with tertiary amino groups. It was shown that the preliminary keeping of the initial solutions at elevated temperature leads to a noticeable increase in the distribution coefficients of rhodium(III) during sorption on S984, S985, S914 and S920 resins from both its individual and multicomponent chloride solutions. By the rate of sorption of rhodium(III) S984 resin significantly exceeds S914 resin. An increase in temperature leads to a significant increase in the rate of sorption of rhodium(III) on the ion exchange resin with thiourea functional groups. It was concluded that the rate of sorption of rhodium(III) on S984 resin is limited mainly by internal diffusion, and the rate of sorption of rhodium(III) on S914 resin apparently, at the same time, both the internal diffusion rate and the chemical reaction rate occurring during sorption of rhodium(III).

The possibility of deep recovery of rhodium(III) from multicomponent chloride solutions previously aged at elevated temperature on S984 resin under dynamic conditions at room temperature and on S914 resin under static conditions at elevated temperature was shown.



## PLATINUM BEHAVIOR AT HEATING AND MELTING OF COPPER-NICKEL SULFIDE MATERIALS

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The platinum extraction from copper-nickel sulfide ores is a multistage process. Cu-Ni solid and impregnated sulfide ores were selected as the material for the study. Heating and melting of the ore were carried out in corundum crucibles placed in a resistance furnace. Using the obtained melting products, we prepared polished sections, which were studied using optical and scanning electron microscopes equipped with an energy dispersive attachment. Platinum in the matte was found to be in the form of chemical compounds with iron (tetraferroplatinum) and in the form of intermetallic compounds with Fe and Ni. Tetraferroplatinum is a needle formation with a length from 20 to 500 microns and a thickness of up to 10 microns. It is located in the shell of intermetallic compounds. The size effect is revealed: the content of impurities in tetraferroplatinum (Cu and Ni) increases as its thickness decreases. In the slag only Pt – Fe – Ni intermetallic compounds of sizes not exceeding 5–7  $\mu\text{m}$  were detected. These compounds float from the matte with bubbles of sulfur containing gas. The drops of matte with a diameter of up to 1.5 mm are also carried into the slag by bubbles. Such flotation leads to the loss of valuable components, in particular, platinum.

Modeling in the Equilibrium Compositions Module of the HSC Chemistry 9.0 package was performed to predict the phase composition considering changes in the temperature and carbon concentration. The calculation showed that most of the chemical reactions in sulfide ore occur in the temperature range of 200–600°C. As a result, the contents of C,  $\text{Fe}_7\text{S}_8$ ,  $\text{CuFeS}_2$ ,  $\text{Fe}_3\text{O}_4$  and PtS fall quickly, and intermetallic compounds (including those with Pt) appear. This fact is experimentally confirmed. In the specified temperature range the intermetallic compounds with platinum exist independently of changes in the phase composition of the starting material.

The data is extremely useful for improving the technology of ores and man-made materials processing and increasing the degree of platinum extraction.

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## ANALYSIS OF MANUFACTURING TECHNOLOGY ULTRALOWCARBON STEELS WITH BAKE HARDENING EFFECT

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For production steel with bake hardening effect IF-BH (Interstitial Free – Bake Hardening steels), it is requirement the presence of strictly specified quantity of carbon in  $\alpha$ -Fe solid solution. Bake hardening effect is steel aging, caused by interstitial atoms (carbon and nitrogen) fixing on dislocations. Nitrogen has ability to fix on dislocations at room temperature, due to that fact BH-effect should be controlled by dissolved in steel carbon. Based on many researches optimal quantity of carbon in  $\alpha$ -Fe solid solution is within 15-25 ppm. It can facilitate significant hardening during the heating and avoid occurring yield line in steel sheet during warehousing.<sup>1-2</sup>

Today best practices of ultralowcarbon steels production allow to reach concentration of interstitial elements less than 30 ppm of carbon and 30 ppm of nitrogen in final steel sheet, due to that fact steels is very formable.<sup>3-4</sup> Russian metallurgy manufacturers works with large quantities of interstitial elements 30-60 ppm of carbon and 30-70 ppm of nitrogen.<sup>5</sup>

The paper compares the production technologies of ultralowcarbon IF-BH steels at Russian metallurgy manufacturers, shows the main reasons for the high carbon and nitrogen contents in steel, defines the principles for developing an optimal after-treatment process, and gives practical recommendations.

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## **OPTIMIZATION OF THE TECHNOLOGY OF MANUFACTURE OF THE CONTINUOUSLY LITTED PREPARATION OF TRANSPORT METAL FOR THE PRODUCTION OF RAILWAY RAIL WITH THE PURPOSE OF TECHNICAL AND ECONOMIC EFFICIENCY OF USING NEW MATERIAL**

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One of the directions of development of modern metallurgical technology is to obtain stable service properties of metal products while striving to reduce material and energy costs for production.

In 2017, after the modernization of the continuous casting machine №1, the electric steel-making shop of JSC Ural Steel began the development of the production of transport metal, continuously cast billets for the further production of railway rails.

Melting on the exhaust steel 120 tons. Installation of stainless steel on the «ladle-bake» installation and installation of vacuuming chamber-type steel.

The technology of steel production in the electric steel-making shop implies the use of FeSi65 grade ferrosilicon, FeMn78 grade ferromanganese, and MnC17 grade ferrosilicon manganese for alloying steel with silicon and manganese.

In order to improve the production technology of rail steel E76F, a series of pilot heats were carried out, where the metal was alloyed to the required GOST R 51685-2013 silicon content in steel using the universal deoxidizer URS-94 steel.

## MELTING OF STEEL TRANSPORT METAL IN AN ARC STEEL MELTING STEEL USING DIFFERENT COMPOSITION OF METAL FLASH

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Steel production is associated with the use of significant quantities of various materials, which consist of metal charge, fluxes, inert gases (argon, nitrogen), refractories, electrodes.

The consumption of each of these materials along with the cost of electricity affects the cost of steel. More than 60% of the cost of steel is determined by the cost of the raw materials used, primarily by the consumption and cost of the metal charge.

To determine the influence of the composition of the metal charge, which provides a higher stability for obtaining the required steel composition, quality indicators of the steel produced by the transport metal and the economic efficiency of using a certain type of raw material, a comparative analysis of steel production was carried out using the metal stock: scrap metal, metalized pellets, liquid iron.

## HIGH STRENGTH CORROSION RESISTANT WELDABLE LOW MAGNETIC NITROGEN CONTAINING STEELS FOR THE ITEMS OF RESPONSIBLE APPOINTMENT

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New corrosion resistant steel of HS-5T grade has recommended itself not only as a base material, but as a perspective material, used for the production of high performance filters of high capacity for obtaining drinking water in terms of long sailing of ships and also in cities medical institutions.

The steel has passed the check out in industrial conditions (pulp and paper mills, geothermal stations etc.). Nitrogen containing austenitic steels are perspective as nonmagnetic materials of high strength for using from cryogenic (-296 °C) to high (up to 1000 °C) temperatures.

For the purposes of oil- and gas extraction industry the rods, shanks and also the bodies of inclinometers for directional drilling of wells from the 04H20N6G11M2AFB grade steel were made.

Due to the economic profitability of sea transportation of natural gas over long distances, a fleet of gas carriers, including independent ice navigation, is currently actively developing. High-strength nitrogen-containing steels can reduce the metal structure and thereby increase the speed of ships compared to the traditionally used cryogenic alloys.

When studying the behavior of nitrogen-containing austenitic steels in the region of cryogenic temperatures, it has been shown that steel has high strength, ductility, and crack resistance in the region of cryogenic temperatures.

The development and development of offshore hydrocarbon deposits requires the construction of more powerful nuclear-powered icebreakers capable of providing year-round pilotage on the Northern Sea Route. At the same time, corrosion-erosion wear of the vessel's ice belt material inevitably increases, therefore the use of austenitic steel 04H20N6G11M2AFB, which is more durable and corrosion-resistant than steel of type 316L, is promising.

It is shown that the resistance of clad steel to separation is 750-790 MPa, and the resistance to shear is from 500 to 630 MPa in the absence of a tendency to ICC.

## PERFECTION OF PRODUCTION TECHNOLOGY COBALT IN KOLA MMC

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In Russia, Kola MMC is the main producer of cobalt. It is produced by hydrochloride extraction-electrowinning technology from cobalt hydrate concentrates<sup>1</sup>. The industrial development of cobalt extraction with tertiary amines began 20 years ago at the Severonikel combine of the Kola MMC, where, firstly, cobalt salts were obtained at the pilot plant, and then had converted to electrolyte metal during next period. Since 2016, a new production with a capacity of 3000 tons of electrolytic cobalt per year has been operating in Kola MMC. The metal is produced from chloride solutions by electrowinning; in it case usually cobalt contains more than 99.95% of Co and mainly corresponds to the K1Ay grade. However, in the production of cobalt, we confronted with difficulties of quantity (output) and quality of the electrolyte metal. In particularly, the formation of the third phase during extraction and formation of deposits on the surface of the heat exchange equipment did not allow to achieve maximum performance in cobalt, and some of the cobalt batches had high nickel concentration.

Advanced extraction mixtures with tertiary amines have been developed with an eye to increasing the of cobalt extraction and decreasing of nickel concentration in the end – product. It enabled to increase the capacity of the extractant for cobalt and increase the rate of phase separation in extractors.

For increasing the performance of the cobalt unit, a new scheme of solution feeding for evaporation was developed. It enabled establish conditions under which evaporators deposits is decreasing because of decreasing concentration of silicic acid and inhibition of extraction agent adsorption with silica.

Also influence of various factors on the morphology of the surface of cobalt cathodes were investigated for improving quality of cobalt. Different conditions for obtaining cobalt with a surface stability against air oxidation were found.

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## EXTRACTION TECHNOLOGY OF FERRIC CHLORIDE FROM SOLUTIONS NICKEL PRODUCTION

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Ferric chloride is widely used in various areas of the chemical industry, metallurgy, building, and is also widely used for the treatment of industrial and domestic waste water. In practice, the solution of ferric chloride is usually produced by chlorination scrap iron. In the processing of copper-nickel sulfide ores in the Kola MMC iron is currently not produced in the form of finished products and is taken out of production in the form of waste hydrated iron cake. This leads to loss of non-ferrous metals and environmental pollution with heavy metals. At the hydrochloride processing of high iron intermediate products of nickel production the problem of cleaning solutions from iron becomes increasingly more serious.

To prevent the loss of non-ferrous metals with iron cakes and to obtain additional iron-containing products the extraction of iron from nickel chloride solutions have been studied in this work. Various kinds of extractants and their mixtures have been tested to extract iron. As a result, it was found that aliphatic ketones have the highest selectivity with respect to iron (III), the use of ketones allowed developing a new method of extraction of iron from chloride solutions<sup>1</sup>. The extraction of iron (III) from solution hydrochlorination of magnetic fraction of copper-nickel feinsteel containing, g·dm<sup>-3</sup>: 196.0 Ni, 20.6 Fe(III), 3.8 Co, 0.05 Cu, 247.0 Cl by 2-undecanon was tested on the cascade of laboratory extractors. Extracting included 3 extraction, 2 washing by HCl and 3 stripping stage. As a result, a ferric chloride solution was obtained, purity of the solution corresponds to reactive salt are chemically pure.

Based on the tests, the flow diagram for the extraction purification of hydrochloride solution from iron and the technological regulations for the production of 7000 tons of iron in the form of a 40% solution of ferric chloride have been developed.

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## THERMODYNAMIC ASPECTS OF MODIFICATION OF NON-METALLIC INCLUSIONS WITH CALCIUM IN LOW-CARBON ALUMINUM KILLED STEELS

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Low-carbon steel, deoxidized with aluminum, is the main group of structural steels produced in Russia and the world, working in key sectors of the economy - construction, automotive, mining and transportation of minerals, etc. Deoxidation of steel melt with aluminum leads to the formation of non-metallic inclusions that can significantly affect the quality of rolled products and reduce the manufacturability of production due to the clogging of submerged entry nozzles during continuous casting. So, all other things being equal, only due to contamination of steel with non-metallic inclusions, the following differences in technical and economic indicators can be observed: defects of surface, defects of casting blanks, increasing the rate of corrosive wear, sorting by ultrasonic testing defects, etc.<sup>1-2</sup>.

The report discusses the thermodynamic aspects of the formation of non-metallic inclusions in low-carbon steels deoxidized with aluminum when modifying their calcium containing reagents. The calculation of the target range of calcium content to ensure the modification of inclusions to a liquid state, depending on the concentrations of aluminum and oxygen in the melt. The maximum concentrations of sulfur in the melt are calculated depending on the content of aluminum and calcium to prevent the formation of refractory sulfide shells on oxide non-metallic inclusions.

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## INTERPHASE DISTRIBUTION OF METALS DURING TWO-STAGE HIGH-TEMPERATURE ELECTROLYSIS OF LEAD-BISMUTH ALLOYS

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X-ray fluorescence analysis, emission spectral analysis and X-ray powder diffraction analysis were used to evaluate the compositions of products of high-temperature (550 °C) electrolysis (anodic polarization) of lead-bismuth alloy (9 wt% Bi) in the NaCl–KCl–PbCl<sub>2</sub>–ZnCl<sub>2</sub> melt. The patterns of phase distribution of elements are determined. The modes of stepwise process are substantiated.

At the first stage of electrolysis ( $U = 8\text{--}12$  B,  $i_a = 0,5$  A/cm<sup>2</sup>) the molten salt has saturated with lead up to 35 wt%. In the cooled electrolyte, the K<sub>2</sub>Pb<sub>2</sub>O<sub>4</sub> phase is revealed, which indicates the melt has reacted with oxygen. The second stage was the electrochemical processing in fresh electrolyte at a lower anodic current density ( $U = 5\text{--}8$  V,  $i_a = 0.3$  A/cm<sup>2</sup>) of the first stage anode product (26.7 wt% Bi, 73.1 wt% Pb). The second stage anode product is a rough bismuth, containing, wt%: 93.6 Bi, 4.1 Pb, 0.086 Ag, 0.0066 As, 0.006 Sb, 0.0013 Cu, 0.001 Sn, and 0.0014 Zn. About 93.0 % bismuth and 0.4 % lead are transferred from the original alloy into the product mentioned. The second stage cathode product is the rough lead, containing at least 97.2 wt% Pb, up to 2.7 wt% Zn, and 0.06 wt% Cu. The need for preliminary reagent purification of lead-bismuth alloy from impurities (Cu, Zn, Sb, As, and Sn) is indicated.

The combination of the advantages of pyrometallurgical refining of bismutic lead and the subsequent stepwise high-temperature electrolysis at elevated current densities makes it possible to consider the process as a promising way of separating Pb–Bi–Cu–Zn–Sb–As–Sn alloys.



## PRINCIPLES OF CREATION OF NEW FERRITIC STEELS WITH A UNIQUE COMBINATION OF PROPERTIES

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The original scientific principles of creation of new low-carbon steels strengthened by the dispersed ferritic structure and the system of nanoscale phase precipitates, primarily formed in the  $\gamma$ - $\alpha$  phase transformation of steel (inter-phase) were developed. In contrast to the existing widespread high-strength low-alloy and advanced automotive steels, elaborated steels combine, for the first time, simultaneously high strength, ductility, formability, fatigue and corrosion resistance, other properties, with a simple, economical composition (mass.%: C - 0.03 – 0.06, Mn - up to 1.5 %, Ti + Mo - up to 0.3-0.4) and manufacturing technology. It is established that the key parameters controlling the structural state and properties of steel is the cooling rate after rolling. At its relatively low values of 10-15 °C/s, a polygonal ferrite and an interfacial separation system are formed, and with its increasing up to ~30 °C/s a block (acicular) structure of steel and a system of ferrite nanoscale carbide precipitates are formed. In the first case, the resulting strength characteristics are slightly lower and the hardening of steel due to interfacial separation is prevalent. In the second case, the strength properties are higher, but the contribution is dominated by the acicular high dislocation structure of the ferrite. The possibility of an extreme complex of properties obtaining due to the simultaneous formation of an acicular structure and interphase precipitates is shown. The number of carbide secretions increases with Ti content increasing, and the presence of Mo in the steel composition significantly accelerates the nucleation and, on the contrary, reduces the rate of their growth.

In addition to Ti and Mo, a detailed study of steels separately or jointly micro-alloyed with V, Nb, Ti, Mo was performed. The ability of unique complex of properties obtaining is shown, including simultaneously high strength values up to 1000-1200 MPa, the ductility (elongation up to 20 – 25%), formability (hole expansion ratio ~100 %), operational reliability and other properties, while reducing the production cost and the metal consumption up to 15%, which is not possible for widely used steel types.

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## INFLUENCE OF THE COMPOSITION OF PRECURSORS AND REDUCTION CONDITIONS ON THE PROPERTIES OF MAGNESIOTHERMIC MO-W ALLOY POWDERS

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Previously, the possibility of obtaining Mo-W alloy powders with a high specific surface area by reduction of magnesium vapors of precursors in the form of complex oxide compounds containing refractory oxides was shown<sup>1,2</sup>. The use of complex oxides as precursors is based on the fact that the refractory oxide contained in the precursor forms additional interlayers between particles of the reduced metal, and these interlayers prevent coagulation of particles<sup>3</sup>. Magnesium oxide leaching gives rise to pores, the number and sizes of which determine the specific surface area of the powders.

In this work was to study the influence of precursor composition and reduction conditions on the characteristics of Mo-W alloy powders prepared through magnesium vapors reduction of molybdenum and tungsten complex oxide compounds.

The equipment, methods of conducting experiments and studying the characteristics of the obtained powders were similar to those used previously<sup>1,2</sup>. As precursors for the reduction process, we used the compounds  $\text{MeMo}_x\text{W}_{1-x}\text{O}_4$  (where Me is Mg or Ca) synthesized by sintering method<sup>2</sup>. The reduction process was run in the temperature range 750–850°C at a residual argon pressure in the range 5–15 kPa. The reduction products were treated with a 10% hydrochloric acid solution to remove the MgO and CaO. Powders of the Mo-W alloy were obtained; the average crystallite size of 10–50 nm. The separation of the reaction products was observed during the reduction of compounds  $\text{MeMo}_x\text{W}_{1-x}\text{O}_4$ . It was the deposition of the bulk of magnesium oxide outside the reaction zone.

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## PHYSICO-CHEMICAL MATHEMATICAL MODEL INTERACTION OF THE SLAG-METAL COMPONENTS DURING STEEL LADLE TREATMENT

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Modeling of the processes occurring during the melting and ladle treatment of steel is a complex task that requires the development of physicochemical models and mathematical algorithms that allow us to describe high-temperature processes occurring in open non-equilibrium metallurgical systems. Physico-chemical descriptions and mathematical models are needed, taking into account the composition of the interacting phases and thermal regimes, reflecting the dynamic characteristics of the melting, dissolving, mixing processes, the interaction speed between all components of the slag and metal phases, etc.

This work is devoted to the development of a correct physico-chemical description of the interaction between the components of the slag-metal system.

A physical and chemical description, mathematical model and a software, describing the process of interaction between the components of the slag-metal system have been created.

The input information for the software are: the geometrical dimensions of the ladle, the initial temperature, the mass and chemical composition of the slag and metal, the time and weight of the additives, the time and intensity of inert gas purge, the electrical mode, the thermodynamic database, etc.

The adequacy of the developed software was checked according to industrial data. Comparison of calculation results using the developed software showed good agreement with experimental data. The developed software can be used for dynamic modeling and optimization of metal processing technologies at the ladle-furnace unit, vacuum-oxygen decarburization units of corrosion-resistant steels.

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## EFFECT OF SULFUR CONTENT IN METAL ON THE DECARBURIZATION PROCESS OF CORROSION-RESISTANT STEEL BY OXYGEN CONTAINING PLASMA

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In the production of modern low carbon corrosion-resistant steels, it is necessary to provide thermodynamic conditions for the selective decarburization of steel and to ensure the reduction of the content of dangerous chromium oxides in the slag. The process of selective decarburization of chromium-containing melts in plasma-arc furnaces is assisted by the high temperature of the reaction surface of the melt and the removal of gaseous reaction products. The rate and completeness of the steel decarburization reaction are also influenced by the presence of surfactant components in the bath - oxygen, nitrogen and sulfur.

The study of the effect of sulfur content on the decarburization process of an alloy of the Fe-Cr-Ni-S system by oxidative plasma was carried out on a laboratory plasma DC furnace with an open circuit voltage of up to 140 V and an operating current of up to 300 A. At the same time, the size of the surface of the metal under study was active spot of the plasma arc.

It was shown experimentally that with a low sulfur content in the metal, the decarburization process of the corrosion-resistant steels goes to lower concentrations of carbon. During the oxygen-plasma decarburization of high-chromium steels, sulfur is removed from the melt better at low initial concentrations in the metal and the higher the partial pressure of oxygen in the plasma. The desulfurization of stainless steel occurs at the stage of intensive removal of carbon from the melt and stops when the carbon concentration is reached, when the order of the decarburization reaction becomes higher than the first one. The mass transfer coefficients and reaction orders in different reaction areas were experimentally determined depending on the concentration of carbon and sulfur in the melt.

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## ELECTROMETALLURGY OF HAFNIUM: PRODUCTION OF POWDERS, COATINGS OF HAFNIUM AND ITS COMPOUNDS IN MOLTEN SALTS

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The application of hafnium in recent years is expanding rapidly. Most of them belong to the latest achievements of technique and technology. The main industrial method of producing hafnium is the metallothermic reduction of hafnium tetrachloride with metallic magnesium (Kroll process).

The drawback of the abovementioned process is numerous stages and the necessity of processing intermediate products having a significant amount of impurities and wastes containing valuable components. The consequence is high production cost of the metal.

More promising are the ways, which allow getting the desired properties and quality of metal with minimum number of process stages from hafnium containing raw materials to the final product technology. One of these methods is electrolysis of halide, mainly chloride and fluoride-chloride melts. The work presents the results of laboratory and experimental-industrial tests of electrolytic production of hafnium powder. During pilot tests, the possibility of obtaining hafnium of nuclear purity by the electrolysis of chloride-fluoride melts without the use of iodide or electron-beam refining was shown<sup>1</sup>.

One of the rational ways of using hafnium is deposition coatings on the surfaces of the assemblies and mechanisms, i.e. obtaining composite materials<sup>2,3</sup>.

In this study, a numerous examples of creating materials with hafnium coatings and its compounds for various functional application are presented.

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## INVESTIGATIONS OF INCONEL 718 ALLOY SAMPLES ON THE ALL STAGES OF SELECTIVE LASER SINTERING TECHNOLOGY

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The performance properties of products made of heat-resistant Inconel type alloys significantly depend on the technology of their production: the purity of the used charge materials, methods of smelting, casting and crystallization conditions, technology of hot plastic deformation, subsequent thermal and mechanical processing.

The use of additive technologies for creating complicated products from high-alloyed metal alloys is currently an urgent task, since laser technologies make it possible to obtain parts of complex shape and isotropic properties with a minimum number of technological operations.

In this study, investigations of the chemical and phase composition, microstructure and microhardness of samples of INCONEL 718 alloy selected at all stages of the technology of selective laser alloying were carried out: from the original ingot, powder particles of different fractional composition after spraying, from the product grown using selective laser sintering (SLS) and after hot isostatic pressing (HIP).

The chemical composition and phases of the samples were studied on a Rigaku X-ray diffractometer, the microstructure and phase composition were determined on a Vega T-scan scanning electron microscope, and the microhardness of the particles and compact samples was determined on a Leco M400H microhardnessmeter.

Changes in the chemical composition, oxygen and nitrogen content, and the microstructure of the samples along the entire process chain were established. It was shown that the microstructure of the samples after SLS and HIP differs from the original alloy in smaller grain sizes, isotropy of properties and increased microhardness.

## SCIENTIFIC AND TECHNOLOGICAL BASES OF PROCESSING OF METALLURGICAL WASTE IN AN ACID INDUCTION FURNACE WITH SECONDARY METALLURGY PROCESSING METHOD OF THE RESONANT INTERMITTENT REFINING

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Currently, the processing of metallurgical wastes (magnetized grains of iron and steel slag heaps, the processing of scrap pallets and molds, etc.) is urgent. These types of waste are characterized by a high content of sulfur, phosphorus, an unstable structure of cast iron products obtained from a heterogeneous charge, and increased gas content in the metal. The technology of semi-synthetic iron melting was developed, including the processing both iron and steel scrap and waste. This technology was distinguished by the possibility to obtain castings with stable microstructure and mechanical properties of cast iron as well as operational performance of products made from the cast iron. Such high rates of products are mainly conditioned by use of thermal-time melt processing modes in this technology. Methods for determining the optimal temperature regimes were based on the approaches developed in schools by Samarin A.M., Baum B.A., Kudrin V.A. and Elansky G.N.

To obtain high quality products, the following problems were solved: 1. An integrated technology that allows to recycle a heterogeneous metal charge was worked out; 2. A method for reducing the sulfur content in acidic induction furnaces has been developed and implemented; 3. A method of neutralizing the harmful effects of phosphorus in gray iron has been developed; 4. The structure and properties of cast iron of induction melting are stabilized by the optimal modes of melting thermo-time processing; 5. The gas content of the metal is stabilized before the products are poured by the method of resonantly pulsating metal refining; 6. A mathematical model was built to conduct numerical experiments for studying the effect of phosphorus on the thermodynamic properties of iron.

## ANALYSIS OF PRODUCTION OF STAINLESS STEEL TYPE 08KH18N10T

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The objective of this research work was to conduct an analysis of the production of stainless steel grade 08KH18N10T according to the technological scheme «EAF-LF-VOD-Ingots casting».

As part of this work, the main stages of its implementation were identified:

- collection, analysis of heat reports for each of the process stages and analysis of technological parameters (chemical compositions, temperature, time);
- determination of the [O], [N], [C] и [S] contents in the metal samples taken according to the technological scheme of production «EAF-LF-VOD»
- metal structure analysis by optical metallography using an OLYMPUS PME 3 microscope integrated into the «Thixomet» image analysis system.

According to the results of the analysis of heat passports, deviations were identified according to a number of technological parameters, which indicates a deviation of the technological process of production from a rational operation. Increased carbon content directly affects the waste of materials and processing time on the VOD.

In the course of laboratory studies, an increased content of oxygen (> 100 ppm) and nitrogen (> 500 ppm) on LF was detected, which in general could affect the increased consumption of materials, as well as the quality of the finished steel. According to the results of metallography, oxide and nitride nonmetallic inclusions were found. The increased nitrogen content in the metal contributes to the formation of TiN in steel, which also degrades the quality of steel.

Thus, the results obtained can indicate the need for further improvement of this production technology in order to improve the quality of the metal, minimize the amount of production waste and the cost of consumables.

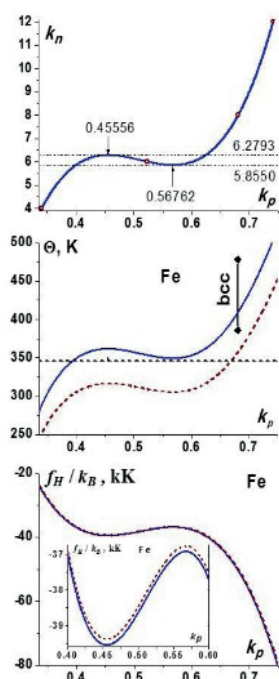
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## DEBYE TEMPERATURE CALCULATION FOR AMORPHOUS METALS

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To determine the amorphous structure it was used the dependence of the first coordination number ( $k_n$ ) on the packing factor ( $k_p$ ), obtained in<sup>1</sup> (it is show to Fig. 1):

$$k_n(k_p) = -71.76782 + 467.78914 \cdot k_p - 925.48451 \cdot k_p^2 + 603.01146 \cdot k_p^3 \quad (1)$$

At  $5.858 \leq k_n \leq 6.278$  and  $0.4 \leq k_p \leq 0.624$ , two or three  $k_p$  values correspond to one  $k_n$  value. Therefore, this area in<sup>1</sup> was defined as the “random packing” region for spherical atoms.

Using Eq. (1) and the method from<sup>2</sup>, the dependences of the Debye temperature ( $\Theta$  – Fig. 2) and the specific Helmholtz free energy ( $f_H$  – Fig. 3) on  $k_p$  for Fe were calculated. The calculations were performed at a temperature of 300 K for two distances between the nearest atoms:  $c/r_o = 1$  (solid line) and  $c/r_o = 1.0265$  (dotted line in Fig. 2 and 3). Here  $r_o(\text{Fe}) = 0.24775$  nm is the coordinate of the potential minimum in<sup>2</sup>. For amorphous Fe under these conditions, the following was obtained:

$$348.836 \leq \Theta_{\text{am}} \leq 361.322 \text{ K при } c/r_o = 1;$$

$$305.24 \leq \Theta_{\text{am}} \leq 316.16 \text{ K при } c/r_o = 1.0265.$$

This agrees well with the estimates from<sup>3</sup>:  $\Theta_{\text{am}} = 346.2$  K (horizontal in Fig. 2). For bcc-Fe, the Debye temperature is in the range:  $386 \leq \Theta_{\text{bcc}} \leq 478$  K (vertical in Fig. 3).

The values of  $\Theta_{\text{am}}$  for other metals were also calculated.

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## TECHNOLOGICAL BASES OF ZINC SULPHIDE FORM PROCESSING FROM SOME TECHNOGENIC FORMATIONS

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To extract zinc from its oxide forms, the waelz process is used, which is realized in rotary<sup>1</sup> or annular<sup>2</sup> furnaces.

In some technogenic formations, such as sludges from the synthetic fibers production, zinc is in sulphide form (ZnS). The zinc extraction from such technogenic formations by the waelz process is difficult, since it is based on the reduction of zinc oxide using carbon-containing material by reaction 1:



Calculation of the Gibbs energy change indicates that the occurrence of the reaction 1 is possible above the temperature of 1100 °C. Since in some technogenic formations zinc is in the sulfide form, its decomposition by carbon is possible by the reaction 2:



Thermodynamic calculations indicate that reaction 2 is possible only above the temperature of 1900 °C. This temperature is unattainable for the waelz process. In order to facilitate the extraction of zinc from the sulfide form, it has been proposed to convert it into oxide by reaction 3, followed by extraction of zinc by reaction 1:



That reaction is thermodynamically possible above the temperature of 1100 °C. This temperature is consistent with that required for reaction 1, and therefore will not require a significant change in the technology of the waelz process.

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## LAYERED STRUCTURE, CHARACTERISTICS AND REACTIVITY OF METAL SULFIDE SURFACES UPON THEIR OXIDATION AND LEACHING

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Metal sulfides are of vivid interest as semiconducting, optoelectronic, thermoelectric materials, including nanostructured and two-dimensional ones, and also as the main natural source of non-ferrous and precious metals. Physical and chemical properties of metal sulfides, in particular, so-called passivation of the hydrometallurgical leaching, are largely determined by compositional violations of real, that is oxidized and metal-depleted upon the exposure to the atmosphere and aqueous solutions, sulfide surfaces. We employed a set of spectroscopic techniques with varying probing depth (X-ray photoelectron spectroscopy (XPS), including hard energy HAXPES and cryo-XPS, X-ray absorption spectroscopy (XAFS), optical UV-, vis- and NIR absorption spectroscopy, etc., in combination with DFT simulation to examine composition and structure of the surfaces of natural sulfides of copper, iron, zinc, lead, and synthetic Cu<sub>1-x</sub>S nanoparticles. It was demonstrated for the first time that the reacted near-surfaces of the sulfidic phases are composed of “polysulfide” surface, “disulfide” layer, the thickness of which varied from few nm to hundred nm for different systems, and underlying heavily defective region with a relatively low metal deficit. The polysulfide surfaces, for example, at chalcopyrite CuFeS<sub>2</sub>, were calculated using DFT+*U* to be surprisingly stable under the oxidative conditions; this arrests the decay of metal sulfides yielding elemental sulfur, and promotes the growth of metal-depleted undersurfaces, causing “passivation” of metal sulfides in the reaction of oxidative dissolution. These conclusions were supported by cryo-XPS analysis of particulate minerals centrifuged and fast-frozen to liquid nitrogen at various stages of the oxidation in order to preserve volatile polysulfide species and elemental sulfur. The spectroscopy and DFT data imply that the electronic states of the surface polysulfide structures are delocalized; this effect can be responsible, in particular, for near-IR absorption maxima at copper sulfide nanoparticles that has been commonly attributed to surface-localized plasmon resonances.

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## STUDY OF THE KINETICS OF SECONDARY ALUMINUM OXIDATION AT A STEP OF BUCKET STEAM VACUUMING

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In the modern practice of manufacturing a wide range of steel grades, bucket processing is an integral integrated part of the technological process. To remove hydrogen and nitrogen from deeply deoxidized steel, its vacuum is applied immediately before casting.

In the electric steel-making shop of the casting complex of the Vyksa Metallurgical Works JSC, deoxidized steel is processed in a vacuum chamber under refining slag in a 160-ton pouring ladle.

In the course of studying the kinetic features of the process of aluminum oxidation during the evacuation of the melt in a steel-teeming ladle, statistical processing of an array of technological parameters of 464 low-carbon steel melts was carried out.

The exponential dependence of the change in the concentration of a component on time is characteristic of a first-order reaction, which is expressed by the following equation:

$$C = C_0 \times e^{-k\tau},$$

where  $C$  is the calculated concentration of the component after the time  $\tau$ , %;

$C_0$  is the initial concentration of the component ( $\tau = 0$ ), %;

$k$  is the reaction rate constant,  $s^{-1}$ .

The magnitude of the reaction rate constant in this case is  $k = 0.035 \text{ s}^{-1}$

The rather high degree of reliability of the proposed dependence is confirmed by the close to normal distribution of deviations of the calculated values from the actual ones. Thus, based on the results of a statistical study, it was shown that the initial oxidation of aluminum in steel under vacuum is significantly influenced by both the initial content of the latter and the duration of the vacuum.

## RECOVERY OF PLATINUM GROUP METALS AND GOLD FROM SULFIDE ORE CONCENTRATE

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The purpose of this research is a selection of method for recovery of precious metals (PM) and copper from a sulfide concentrates those were obtained from Viksha ore deposit (Republic of Karelia). The composition of main components in the concentrates is shown in table 1.

Table 1. Content of the main elements in Viksha ore concentrates

Pd	Pt	Au	Ag	Cu	Fe	S
g/t	g/t	g/t	g/t	%	%	%
80-160	25-50	20-40	40-70	12-20	17-20	10-15

Two different methods for main components recovery from ore concentrate were tested: consequential selective leaching of copper and precious metals and direct chloride leaching of these metals. The first method consists of a conventional pressure oxidative leaching (POX process) for copper recovery into solution followed by cyanide leaching of PM. The second method consists of direct chloride autoclave leaching of copper and PM followed by sulfide precipitation.

Oxidative pressure leaching allowed to completely recover copper into solution, however, a partial dissolution of platinum and palladium was observed. Following cyanide treatment of oxidized residue makes possible to recover more than 96 % gold, but palladium and platinum recoveries were about 80 % and 45 % respectively.

Copper and precious metals were recovered more than 96 % into solution using chloride autoclave leaching. Special conditions for separate extraction of copper and precious metals from pregnant solutions by using sulfide precipitation were found.

## EFFECT OF OXYGEN PARTIAL PRESSURE ON THE METALS REDUCTION DEGREE AT REDUCING ROASTING OF LIMONITE NICKEL ORE

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Results of research devoted to the study of the mechanisms of solid-state and gas reducing processes of oxidized nickel ore (ONO) are presented. The theoretical background for the selective reduction of nickel and cobalt, based on the difference of the equilibrium oxygen partial pressure over MeO-Me systems, for Ni, Co and Fe is shown. The effect of oxygen partial pressure on metals reduction degree is defined experimentally under laboratory conditions. Such conditions are modelling the reducing processes in the tubes furnaces or in the Gerreshoffe furnaces.

The parameters of roasting ensuring recovery of non-ferrous metal from oxide to metallic phase at high iron storage in oxidized form are recommended.

The possibility of decreasing the iron metallization degree with the high metallization degree of nickel and cobalt is confirmed. During the experiments solid carbon-bearing reducing agents as well as different gas mixtures (CO<sub>2</sub>-H<sub>2</sub> or CO<sub>2</sub>-Co) are used.

Also it is shown that in the conditions of the ONO roasting ( $T = 700 - 800^{\circ}\text{C}$  degree,  $\log P_{\text{O}_2} = -19,0 - -17,8$ , which corresponds to  $\alpha$  blast of 0,6 – 0,8) the reduction degree of nickel and cobalt reaches 80 and 70 % rel. accordingly, while reduction degree of iron does not exceed 13-5% rel.

## EXPERIMENTAL STUDY AND CALPHAD MODELING OF THE AU-CU-IN TERNARY

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Au, Cu and In are the components of a number of multi-component alloys which have applications in various fields.

Phase equilibria in the (not studied before) Au-Cu-In ternary at 500°C were examined experimentally using metallography (SEM), XRD, EPMA and DTA. The results obtained were used, together with CALPHAD assessments of bounding binaries<sup>1-3</sup>, for the CALPHAD calculation of the ternary.

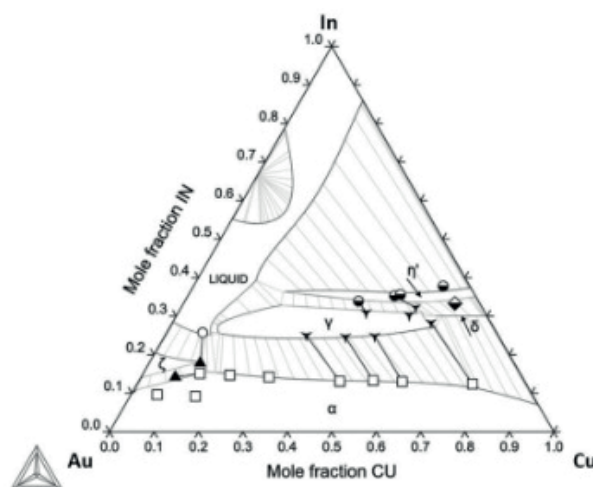


Figure 1. Isothermal section of the Au-Cu-In ternary at 500°C:  
black points and conodes – experimental, gray lines and conodes – calculated

It proved to be necessary to revise the descriptions of the Au-In and Cu-In subsystems for unification of stability parameter of fcc In as well as of the models of the  $\gamma$  brass phase. For description of the liquid and solid solutions the Muggianu extrapolation with ternary interactions was used.

The results of CALPHAD description of the Au-Cu-In ternary are in good agreement with experimental data.

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## DETECTION OF FORMER AUSTENITIC GRAIN IN MARTENSITIC STEELS

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Identification of former austenitic grain in low carbon steels is an actual problem of practical metallurgy. This is due to the fact that the grain size of high-temperature austenite before the onset of  $\gamma \rightarrow \alpha$  transformation<sup>1</sup> is one of the main parameters determining the complex of operational properties of high-strength steels.

To identify the former austenitic grain and to estimate their size, in the present work, methods of vacuum etching and diffraction of back reflected electrons (EBSD) were used.

The question of changes in the sizes of austenitic grains during heating and aging in a vacuum remains controversial. In this regard, it seems appropriate to carry out comparative studies of vacuum etching and the method of identifying the boundaries of the former austenitic grain according to the orientations of the crystallites of the transformed structure taking into account the peculiarities of crystal-geometric relations in the  $\gamma$ - $\alpha$  transformation (EBSD method<sup>2</sup> developing at the NRC «Kurchatov institute» - CRISM «Prometey»).

After conducting research, no correspondence of the transformed microstructure was revealed on the same area of the sample under study before and after vacuum etching. It was established that the size of the former austenitic grain decreases after vacuum etching, both according to the data obtained using optical microscopy, and according to EBSD. The vacuum etching method does not adequately reveal the size of the former austenitic grain, while the EBSD method can be recommended for determining the size of the former austenitic grain.

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## MATHEMATICAL MODEL OF THE FORMATION AND REMOVAL OF NON-METALLIC INCLUSIONS IN DEOXIDIZED STEELS IN A LADLE FURNACE

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At the present day there are several mathematical models that describe the processes of formation, growth, modification and removal of non-metallic inclusions. Usually these models describe one of these processes. There are no models that describe the entire chain of processes from formation to removal of inclusions. The main purpose of this work is the development of this model. An analysis of the currently existing mathematical models of the birth and removal of non-metallic inclusions was carried out. The models that most widely describe the processes of formation, growth, and removal of inclusions among the considered mathematical descriptions were selected. Based on these models, an integrated iterative algorithm was developed<sup>1</sup>. This algorithm allows to determine the number of generated non-metallic inclusions and their subsequent removal.

With the program developed on the basis of the algorithm the number of formed inclusions and their removal were calculated. Optimal purge intensity and time taken to remove inclusions from aluminum deoxidized steel in the ladle furnace were determined<sup>2</sup>. A comparison of the results of the program with real industrial data was made. Based on the comparison a conclusion about the adequacy of the program was done.

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## STRUCTURE AND MECHANICAL PROPERTIES OF NI-AL-BASED ALLOY PRODUCED BY SLM METHOD

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Chemical stability, high strength and incorrodibility at high temperature and other unique physical and chemical characteristics make it possible to use Ni-Al-based alloys thermally loaded parts of aerospace industries. But Ni-Al-based alloys are very crushable at indoor conditions. This fact makes it impossible to use standard methods of mechanical metal-working. One way to solve this problem is additive technologies. This technology makes it possible to produce the complex shape parts and to downgrade to minimum or refuse outright the mechanical processes.

Selective laser melting technology (SLM) limited to size range of used powder ( $<\mu 60$ ). In connection with this the powder was produced by vacuum induction melting inert gas atomization. The elemental composition of raw material are presented in the table 1.

Table 1. The elemental composition of Ni-Al-based alloy

Элемент	Ni	Al	Cr	Hf	ост.
% вес	65,9	28,7	4,4	65,9	0,8

In the course of the research process parameters of atomization was selected experimentally. Selection of SLM parameter process have conducted on the additive machine SLM 280 HM produced by SLM Solutions. Microstructures of powders and parts produced from them were obtained by optical and electron microscopy. Strength and ductility properties were determined on quenching and deformation dilatometer DIL 805 A/D. Showed that production of Ni-Al-based parts with dense structure is possible.

## MORPHOLOGICAL FEATURES OF VARIOUS GENESIS TANTALUM PENTOXIDE

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About a third of the tantalum produced in the world is used in the form of powders in the production of electrolytic capacitors<sup>1</sup>. Since the development of technology requires the constant miniaturization of electronic equipment, the magnesium-thermal reduction of tantalum pentoxide is becoming more widely used, since it allows obtaining powders with a high specific surface area and, accordingly, the high specific charge of capacitor anode<sup>2</sup>. Due to the large heat generation of the reaction, the reduction is carried out with magnesium vapor; therefore, as in other heterogeneous processes<sup>3</sup>, the morphology of the precursor has effects on the morphology of the final product<sup>4</sup>.

In the present work, the influence of the genesis and morphological features of tantalum pentoxide, used as a precursor, on the characteristics of magnesium powders of tantalum was studied. It was shown that depending on the method of producing pentoxide, particles of different morphology are formed (Fig. 1a, 1b). The obtained tantalum powders differed not only in the shape of the particles, but also in their particle size distribution (Fig. 1c), flowability, and shrinkage of the powder compacts after sintering.

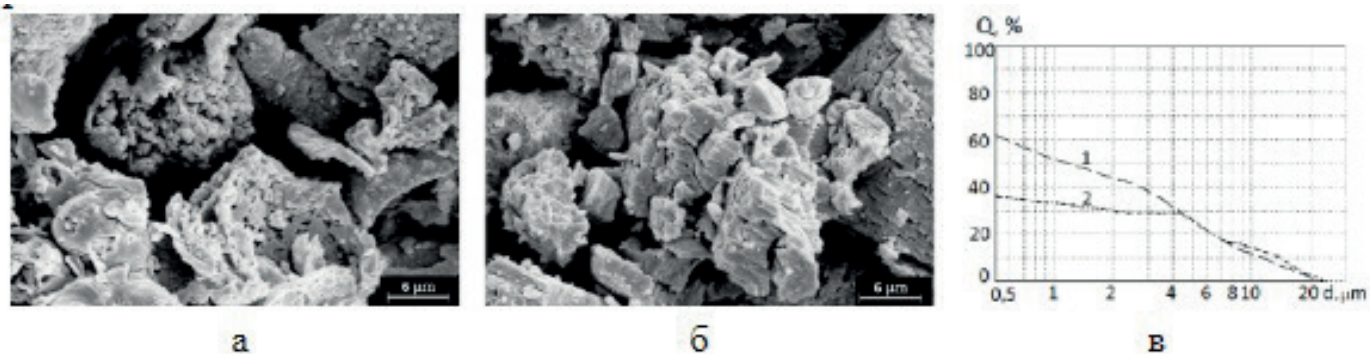


Figure 1. SEM image of Ta<sub>2</sub>O<sub>5</sub> particles obtained by calcining hydroxide (a) and burning tantalum scrap (wire trimming) (b), and integral particle size distribution curves (c), the precursor obtained: 1 - waste incineration, 2 - from hydroxide

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## PHYSICAL AND CHEMICAL BASES OF TECHNOLOGY PRODUCTION OF NITROGEN ALLOYED STEELS

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The physicochemical, physicomechanical and operational properties of a number of modern nitrogen-alloyed steels with an equilibrium and super-equilibrium nitrogen concentration are considered. In particular, attention is paid to the compositions Fe-Cr-N, Fe-Cr-Mn-N, Fe-Cr-Ni-Mn-N, Fe-Cr-Ni-N of developed or already used commercial steels. The optimal intervals for alloying them with nitrogen are presented, and the contribution of nitrogen to the formation of the structural-phase state and the complex of their properties is estimated. When alloying steel with nitrogen, it is important: to determine the maximum possible level of its solubility in the metal, to create conditions for its introduction into the liquid metal and preserving nitrogen in the solid metal. The difference in the content of nitrogen in the liquid and solid metal is taken into account using the concept of compositionally stable nitrogen content and composition stability factor. The main thermodynamic factors affecting the solubility of nitrogen in steel are considered: its chemical composition, temperature and pressure at which the alloying process proceeds.

Attention is paid to the advantages and disadvantages of the production of nitrated steels in open furnaces. The main technologies of electroslag remelting are considered. It is noted that the electroslag remelting (ESR) process makes it possible to preserve nitrogen in the process of melting nitrated steels, to ensure its uniform distribution over the height and cross section of the ingot, to obtain ingots with a good surface and a dense structure with a radial-axial orientation without shrinkage character. ESR can reduce the sulfur content in the metal by 2-3 times, oxygen by 3-7 times, non-metallic inclusions (NMI) by 2.5-3 times, which contributes to the improvement of ductility and toughness of nitrogen-containing steel, improving its processability.

Considered, incl. with specific examples, features of the method of electro-slag remelting under pressure (PESR), including its capabilities, which allow: - to obtain the nitrogen content in the metal above the equilibrium (under standard conditions) and ensure its preservation in the process of crystallization; - to obtain a more dense structure of the ingot and less developed dendritic structure (especially at high concentrations of nitrogen); - reduce the content of NMI (especially oxides); - reduce the waste of alloying elements (almost to zero) and provide an almost perfect ecology of production.

## STUDIES OF SURFACE GASEOUS NANOSTRUCTURES AND THEIR IMPACT ON HYDROPHOBILITY AND FLOATABILITY OF METAL SULFIDES

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Gaseous nanostructures (“nanobubbles”) on the interfaces between hydrophobic solids and aqueous media attract increasing attention in recent years due to their particular importance for a wide range of processes and phenomena. However, the studies are largely restricted by model substrates like highly oriented pyrolytic graphite (HOPG), “solvent exchange” for preparation, and atomic force microscopy and spectroscopy (AFM/AFS) for characterization of the nanostructures. We studied signatures of nanobubble formation upon chemical treatment with flotation collectors and other reagents, temperature difference (“hot” substrate and “cold” water), changing the solvent (acetone, ethanol – water) on the surfaces of main sulfide minerals, silica, HOPG, Au and some other metals employing AFM/AFS, quartz crystal microbalance (QCM), measurement of static and dynamic contact angles at sessile and falling water droplets, captive and floating air bubbles, cryo-XPS, etc. It was found that, in addition to tapping AFM imagination that is helpful only on smooth surfaces, the presence of nanobubbles can be indicated by a strong capillary attraction upon the probe retraction in AFS. The increase in the resonance frequencies of QCM sensors with Au coatings contacted with colder water was found to retain after the temperature equilibration and was explained in terms of a high stability of the surface nanobubbles similar to those produced via a solvent exchange. Gaseous nanostructure exerted relatively moderate effects on wetting the surfaces as determined with contact angle measurement but critically affected the rates of attachment of floating air bubble to substrate surfaces. Application of the temperature difference technique producing the gaseous nanostructures on metal sulfides allowed to enhance reagent-free floatability of pure sulfide minerals and the collective flotation performance of Gorevski Pb-Zn sulfide ore, including with xanthate as a collector.

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## ELECTRON-ION EXCHANGE IN PLASMA BETWEEN SOLID REAGENTS DURING REDUCTION OF METALS FROM ORE

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The existing theories of contact and indirect solid-phase carbothermal reduction of metals when they are extracted from ores are based on atomic-molecular concepts of the chemical processes and they do not explain the high rate of processes observed in the condensed phases. The high rate of processes was explained in the framework of the electronic theory of reduction developed by the authors.

In metallurgical furnaces at temperature of about 2000°C reducing plasma is formed at the surface of the solid reagents, which consists of electrons, ions, atoms, molecules, and their associations. The initial impulse to plasma formation in the reagent layer is thermionic emission from the carbon surface of the reducing agents, which is quantitatively described by the Richardson – Dashman formula  $I_0 = AT^2 \exp(-\Phi/kT)$ , where A is the coefficient depending on the surface state,  $\Phi$  is the electron work function and k is the Boltzmann constant. The thermoelectronic emission occurs from the surface of any heated body; however, in this case, the emission from the surface of the reducing agent prevails, since its external electrons are less bound to the atomic nucleus.

The emitted reducing electrons are attracted by the more electropositive metal cations and they are bonded by cations of the oxide phase replacing the less strong cation – anion bonds in the oxide and facilitating the removal of the oxygen anion from the oxide lattice with formation of the anion vacancy and “free” electrons by the reaction  $[C^{2+}, 2\bar{e}] + (Fe^{2+}, O^{2-})_{oxide} = CO_{gas} + (Fe^{2+}, 2\bar{e}, V_{an})_{oxide}$ . With a small width of the gas gap between the ions of solid reagents, the Coulomb interaction promotes not only separation of the individual ions from the surface of the oxide and reducing agent, but also fragments of their crystal lattices with incompletely compensated charges. The transfer of such complexes from the surface of one reagent to the surface of another leads to formation of the carbide shells on the surfaces of both reagents, which accurately repeat the surface relief, close the surface of the reagents and decrease the rate of the electron-ion exchange.



# RESEARCH AND IMPROVEMENT OF THE PROCESSES OF CASTING AND SOLIDIFICATION OF HEAVY INGOTS WITH THE PURPOSE OF IMPROVING THE QUALITY OF ENGINEERING PRODUCTS

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The development of atomic energy, heavy machinery, necessitates the need for large products of large mass, the initial billet for which is a heavy forging ingot. In the process of long-term solidification of heavy volumes of metal many physical and chemical phenomena take place, contributing to the formation and development of internal defects that cannot be removed at subsequent stages of forging, mechanical processing, etc.<sup>1,2</sup>

To improve the quality of the cast metal ingots, casting methods have been developed that allow producing forged ingots with controlled development of internal defects. To obtain hollow forgings by computer modeling, a model of the form has been developed  $D_{o.p.} \% = f(H/D; K_{mold}; V_{hot\ top}; K_{hot\ top}; T; \lambda_{thermal\ insulators}; \lambda_{exothermic})$ , allowing to choose the ingot geometry, which leads to the accumulation of defects of segregation and shrinkage origin in the extended axial part. The favorable location of shrinkage and segregation defects makes it possible to remove them during forging, which makes ingots suitable for hollow forgings. To obtain solid forgings, a method was proposed for casting ingots in vacuum with the transformation of a jet of molten metal into solid droplets. The introduction of solid droplets leads to the separation in the cast metal of ingots of the A segregation into smaller components, thus reducing the segregation of chemical elements: by 1.8 times carbon; sulfur and phosphorus 1.2 times. Increasing the chemical homogeneity of the cast metal of the ingot and the forging leads to stabilization of the mechanical properties along the length and cross section of large-sized forged products by 2–3 times.

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## INVESTIGATION OF BISMUTH SOLUBILITY IN IRON AND IRON-BASE ALLOYS

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Much data is available in the existing literature on the effect of bismuth on quality characteristics of steel, but its solubility in iron and iron-base alloys is studied poorly.

The difficulty of determination of solubility is due to the physical and chemical properties of bismuth, viz. low melting temperature (271 °C), boiling temperature lying below the temperature of molten steel (1560 °C), high vapour pressure, and high density (9.750 kg/m<sup>3</sup>). So to obtain reliable experimental data the following conditions must be fulfilled: sealing of the workspace, providing and maintaining high temperature (up to 1700 °C) for a long time, uniform heating of the whole crucible height, providing high pressure in the reaction zone, obtaining a quenched ingot after the end of the melting period, and automated control of the experiment. To carry out such experiments, an experimental unit for investigation of solubility of low-melting and low-boiling elements in liquid and solid iron alloys was projected and built up at the Engineering and Technology of Material Production Department of the South Ural State University.

Liquid pure iron was saturated with bismuth through the gas phase in a closed molybdenum container with a ground-in cover that was placed into a graphite crucible with a screw-top cover. Experiments were carried out in the argon atmosphere in the temperature range 1550–1620 °C with a 10 °C step. Duration of experiment was 60 minutes.

Similar experiments were carried out in the temperature range 1550–1650 °C with a step of 25 °C to study the effects of the following elements on bismuth solubility in liquid iron: copper (up to 4.262 %), aluminium (up to 3.60 %), carbon (up to 1.08 %), molybdenum (up to 5.47 %), tungsten (up to 2.11 %), titanium (up to 0.294 %), tin (up to 7.64 %), cobalt (up to 4.73 %), niobium (up to 1.89 %), vanadium (up to 1.52 %), chromium (up to 24.14 %), manganese (up to 15.02 %), silicon (up to 2.78 %), and nickel (up to 12.68 %).

First and second order interaction parameters for bismuth were determined. The liquidus temperatures for bismuth-bearing steels were calculated.

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## ASTM E 2283 APPLICATION FOR NONMETALLIC INCLUSIONS ASSESSMENT IN SUPERDUTY STEELS

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Large nonmetallic inclusions (NMIs) in superduty steels have an overwhelming influence on the properties of products made from such steels, for example, railway wheels or forgings from super-large ingots for the nuclear industry.<sup>1-2</sup> It is known that for the estimation of such NMIs, a method based on the statistics of extreme values is used. It is described in ASTM E 2283 and implemented in Thixomet image analyzer.<sup>3-4</sup>

ASTM E 2283 method covers only indigenous nonmetallic inclusions, however, this paper shows that it can be used for: 1) revealing single exogenous inclusions in a pattern of indigenous or 2) separation of indigenous and exogenous inclusions, if the latter have a systemic source of penetration into the melt. The sizes of each type of NMIs are described by its own Gumbel distribution.

In contrast to large exogenous NMIs, the single appearance of which on a cross section is random, small indigenous oxides and sulfides are rather uniformly distributed throughout the volume, therefore their dimensions are well described by the Gumbel distribution. But if there is a systemic source of exogenous NMIs during production of steel, for example, mixing of slag from a tundish, then the sizes of the largest exogenous NMIs will be also described by the Gumbel distribution, but with parameters specific for these slag inclusions.

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## IN-SITU DETECTION OF CRYSTALLIZATION PROCESSES AND THEIR APPLICATION FOR PURPOSEFUL SEED SELECTION IN HIGH TEMPERATURE SOLUTIONS

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Solution growth is a powerful tool for single crystal growth of various materials and particularly useful for basic research in solid state physics and chemistry. A decrease of the formation temperatures of the desired compounds by several hundred degrees as well as high diffusion rates can be achieved<sup>1</sup>. Accessing the exact nucleation temperature on the other hand and thereby the instant of nucleation remains almost impossible. A prediction of this instant gets also hampered by the uncertainties of the published liquidus temperatures (if available at all). This gets aggravated by supercooling, which stays completely undetected during the growth procedure. The difference between the displayed furnace temperature and the actual sample temperature makes this even more difficult.

Here we present a way to accurately measure the complete time-temperature profile including small temperature changes caused by dissolution or nucleation. Without the necessity of a reference crucible, the signal-to-noise ratio approaches the level of conventional DTA-signals. The detection of nucleation enables crystal selection using oscillations within a well-defined temperature range. The setup can be applied to all common growth systems including aqueous solutions and has been proven up to 1300°C. The reaction chamber can be flooded with inert gas, while a direct contact between solution and sensor is avoided.

Single crystals of the component PdBi successfully enlarged by seed selection are shown in comparison to conventionally grown crystals.

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## FEATURES OF THE FORMATION OF THE MACROSTRUCTURE IN CONDENSED SYSTEMS

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Currently, the majority of multicomponent lead - zinc and copper-zinc ores belong to the class of refractory. However, when developing technologies in metallurgy, it is not always taken into account that the crystalline forms in which the base metals are found may differ not only in terms of the structure of mineral formations, but also due to differences in the physical properties of minerals, which are defined as identical due to texture, degree metamorphism and structural features at the nanoscale. These differences, as a rule, are not taken into account in the formation of technological schemes for the enrichment of multicomponent ores, which can lead not only to the production of middling products having their own physical and chemical characteristics, but also to the loss of valuable metals. In technological processes of flotation, not only concentrates with their own characteristics are formed, but also middling products that require changes in the technological parameters of their processing. If you do not take into account the peculiarities of minerals containing base metals, the irretrievable losses can reach quite significant values. Extraction of metals from the difficult-to-be sulfide middling requires changing the technological regimes in accordance with the structure and physicochemical state of the compounds containing the base metal. For example, in nature, more than 300 lead minerals are known, and more than 140 are zinc. In ores, these metals usually accompany each other. The main minerals of lead - zinc ores, galena and sphalerite, account for more than 90% of lead and 95% of zinc in the estimated ore reserves. The analogy of crystallization of microstructures and macrostructures of various scales was made. It has been suggested that the incorporation of graphite into the structure of sulfide minerals may be the result of retrograde decay. It is shown that crystallization of microstructures may be similar to the formation of crystallization of macrostructures of a certain type. Features of the process of transition of microstructures into a macrostructure must be used for the development of technological processes in metallurgy.

## EXTRACTION OF SCANDIUM FROM WASTE OF PRODUCTION MASTER-ALLOY AL - SC 2%

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Currently, scandium is mainly used in the form of a master-alloy Al - Sc 2% in the production of aluminum alloys. The production of master-alloy is carried out by aluminothermic reduction of  $\text{Sc}_2\text{O}_3$  under a layer of fluorinating flux at a temperature of 850 - 900 °C. Wastes production are sublimate and spent flux.

In the sublimate composition, particles up to 5  $\mu\text{m}$  are predominantly present, but there are some large particles up to 200  $\mu\text{m}$  in size. Sublimate contains ~ 35% Al, two polymorphs of  $\text{AlF}_3$  (57% total), corundum and 0.3-0.4% scandium<sup>2</sup>. To extract Sc from sublimation, its treatment by the 10% caustic soda solution at 80°C has been proposed, which it possible to prepare a fluoride concentrate containing 3-11% Sc. The concentrate consists a mixture of  $\text{AlF}_3$  and  $\text{Al}_2\text{O}_3$  (corundum and  $\gamma\text{-Al}_2\text{O}_3$ ), graphite,  $\text{Sc}_2\text{O}_3$  and  $\text{ScF}_3$ , and can be further processed by known methods to produce  $\text{Sc}_2\text{O}_3$  or  $\text{ScF}_3$ .

The spent salt flux consists of 80% of a mixture of KCl and NaCl, complex fluorides Al and ~0.3% Sc. It is established that as a result of its water-leaching, it is possible to obtain KCl and 1.5% scandium concentrate; when leaching a concentrate with an F<sup>-</sup> - containing solution, the degree of Sc leaching is 95% without dissolution the main mass of the concentrate. Based on the kinetic study data (the reaction order for the reagent was determined, the activation energy, the rate constant, the kinetic equation, the limiting stage), the process parameters were optimized. From the leaching solution, scandium is released in the form of  $\text{ScF}_3$  with a yield of 6 kg / ton of spent flux.

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## ORGANIZATION OF UNUSUAL CHEMICAL REACTIONS USING UNSTEADY ENERGY IMPACTS

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In the study, we took as a basis the general conclusions from the works of M. Faraday, who are now beginning to play a decisive role in the development of ideas about the nature of chemical bonding and the practical application of electrochemical processes. In the 20th century, a huge amount of experimental material was accumulated, confirming the practical significance of M. Faraday's views on the effects of electric current on chemical reactions. In particular, the key points and main points of the works of M. Faraday were used:

1. The identity of energy manifestations in the interaction of material objects.
2. The discrete nature of the electric current.

The concept of the discrete nature of electric current led to the discovery of an electron as a "carrier" of electrical energy. The discreteness of the electron flow allows a combination of the parameters of the electric current over a wide range, the shape of the electrical signal, the rate of influence of the flow of electrons on chemical systems, etc. This makes it possible to organize unusual chemical reactions.

The provision on the identity of energy manifestations in the interaction of material objects provides the basis for the revision of scientific statements on the mechanism of realization of processes between material objects. This requires an in-depth study of the micro-macro properties of substances on the size of its constituent structural elements as a single interconnected material object.

Based on these fundamental setups, we have carried out a series of experiments on the organization of chemical reactions, which under normal conditions cannot be carried out. For example:

1. The dissolution of metallic molybdenum in an alkali solution with a concentration of less than 10%.
2. The division of the oxide melt into components with a change in viscosity and conductivity.
3. Reacting the oxide melt with carbon monoxide gas phase with the oxidation of the melt.
4. Reaction of oxide melt with inert gases (argon).
5. The reaction of the formation of sulfides, sulfates, etc. in a solution of sodium alkali with a concentration of from 0.5 M to 2.0 M at room temperature and electric current with low technical parameters.

## BASICS FOR MATERIAL STUDIES ON EFFICIENCY FOR THE ARCTIC

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Brand new marine equipment engineering for the Arctic with efficient materials of extended applications is linked with a challenge to guarantee specified characteristics of shipbuilding steels of various strength at cost reduction manufacture.

The paper suggests a complex approach to develop requirements for Arctic cold resistant steels by choosing efficient alloying, microalloying and specified structure formation of permissible heterogeneity and anisotropy of rolled plates' thickness depending on their fabrication technology, thickness up to 100mm and strength category between 315 MPa and 750 MPa. These requirements have to do with the “Arc” index steels that provide guaranteed strength and cold resistant characteristics, such as impact energy (KV) at temperatures between  $-60^{\circ}\text{C}$  and  $-80^{\circ}\text{C}$ , ductile-to-brittle transition temperatures  $T_{kb}$ , nil ductility (NDT), and fracture toughness by CTOD criterion.

The guaranteed characteristics of the rolled plate serviceability can be reached through the restriction of structure parameters and their maximum permissible difference by thickness of the rolled plates in terms of morphology and balance of structural constituents (with estimation of dislocation density, volume share of carbide precipitations within the grain and its boundaries as well as subgrains and degree of anisotropy), as well as the share of low and high angle boundaries, maximum and average structural constituents ( $D_{\max}$  and  $D_{\text{av}}$ ), as well as the portion of the structural constituents of specified size  $D$  at given tolerance angles of  $\theta t=5^{\circ}$  and  $\theta t=15^{\circ}$ , and grain average curvature  $GAM_{\text{av}}$ .

The investigations greatly expand the idea of interaction features of alloying composition with the structure and the properties of low alloyed and economically alloyed cold-resistant steels, obtained by different TMCP schemes.

## COMPLEX UTILIZATION OF THE ASH FROM COAL THERMAL POWER STATIONS BY AUTOCLAVE HYDROCHLORIC LEACHING METHOD

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Annually, ~230 thousand tons of coal fly ash (CFA) are generated at TPS-4 in Omsk after burning coal from the Ekibastuz deposit, Republic of Kazakhstan<sup>1</sup>. This ash contains up to 30 wt.% of alumina, which makes this type of raw material the most promising as an alternative to bauxite in the production of alumina, the main material for the production of metallic aluminum. Aluminum in ash is submitted in the mullite. This mineral is poorly soluble in hydrochloric acid. In this study, an autoclave process was first used to leach Al from CFA by hydrochloric acid.

In this research, the preliminary enrichment of ash and the further hydrometallurgical treatment of the non-magnetic fraction were studied. The enrichment included CFA magnetic separation to production the magnetite concentrate. The magnetite content in the magnetic fraction increased from 5 wt.% to 23 wt.%. Carbon was removed by flotation. Kerosene and diesel fuel were used as a collector. Methylisobutylcarbinol was used as a blowing agent. The optimum volume of the collector was determined. It's received a concentrate with a carbon content of ~ 30 wt.%.

When leaching non-magnetic fraction of CFA with hydrochloric acid under autoclave conditions, the effect of temperature, HCl concentration, solid/liquid ratio and process duration on the degree of aluminum extraction into solution was studied. By optimal parameters, the degree of extraction of aluminum in the solution exceeded 90%.

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## NEW APPROACHES IN CREATING SIMULATION MODELS OF PHASE FORMATION IN HYDROMETALLURGY

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In calculations of the regions of formation of solid phases from aqueous solutions of metal salts, the known solubility product rule is used, the less known molecular solubility rule [1] and the even less used condition for the selection of the priority phase [2]. In [3-6], we have given a broad definition of the molecular solubility rule and shown its areas of application. These works show the necessity of sharing the above rules and the conditions for selecting the priority phase, as well as applying the proposed new condition – the solubility rule for the intermediate [3, 4] for calculating areas of solid phase formation in the form of thin films or sediments with the same stoichiometry, but without overlapping their formation regions.

We have proposed a simulation model, software products and databases that, based on the experimental data, allow for manual or automatic calculations: the number of particles in the system; equilibrium constant values; the establishment of functions describing random processes necessary for estimating the uncertainty of parameter values.

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## PROMISING APPROACHES TO INCREASING THE LEVEL AND STABILITY OF PROPERTIES AND QUALITY OF STEEL

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Modern steels become more and more high-tech, science-intensive materials, due to the rapid growth of indicators of the level and stability of technological and service properties, as well as quality together with production costs reducing. It is important that at present, and especially in the future, it is necessary to provide extremely high values of not one, but the whole complex of difficulty-combining properties. This requires the development and usage of original approaches to the creation of a new generation of steels and their production technologies. Based on the results of detailed studies, it is shown that they should be based primarily on the establishment and use of almost unexplored principles of kinetics of processes, phenomena and transformations in the processing of liquid and solid metal, first of all, the formation and evolution of non-metallic inclusions, phase precipitates, structural components, the presence of impurities. This is especially current task resulting from the progress in metallurgical technology, creating additional opportunities for the formation of new elements of the structural state of steel of complex composition and small, in many cases, nanometer sizes, the impact of which on the performance of the properties of the metal can vary greatly or be extreme, depending on the characteristics.

Using the presented high-tech approaches, a new generation of different types of steels with a fundamentally improved complex of properties and effective technologies for their production was created. Among them there are the most promising and popular ones: high-ductile (elongation to 50%) and formable low-carbon and ultra-low-carbon IF-steels; high-strength (up to 1200 MPa) automotive low-alloyed, dual-phase ferritic-martensitic steels; cold-resistant, corrosion and corrosion-mechanical failure resistant tube steels; steels for hot stamping of high-strength products up to 2300 MPa; special alloy steels with guaranteed pre-stressing group 66 and 66T, corrosion-resistant, wear-resistant, clad and other steels.

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## PROSPECTS OF USAGE OF HIGH-CARBON FERROCHROME SLAG FOR OBTAINING REFRACTORY MATERIALS

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At present conditions of chrome-containing ferroalloys industry has a stable trend for decrease of natural mineral raw quality. It leads to significant increase of dump slag volumes. Currently about 500 thousand tons of dump slag is formed annually in Russia. Infusibility (refractoriness) is a feature of high-carbon ferrochrome slag, which allows supposing of alternative ways of utilizing of such slag in refractory industry.

Researches carried out on this kind of slag showed that its refractoriness exceeds 1770 °C and its preferred phase are forsterite, spinelides, silicon dioxide and glass phase enriched with such impurity as silicon, calcium and iron oxides. The calcium and aluminum oxides may be most deteriorating because they form fusible compounds as follows: monticellite  $\text{CaO-MgO-SiO}_2$  (melting point is 1498 °C), diopside  $\text{CaO-MgO-2SiO}_2$  (melting point is 1390 °C), cordierite  $2\text{MgO-2Al}_2\text{O}_3\text{-5SiO}_2$  (melting point is 1450 °C), anorthite  $\text{CaO-Al}_2\text{O}_3\text{-2SiO}_2$  (melting point is 1550 °C).

The presence of large amount of glass phase in researched slag (from 12 to 40 %) makes impossible obtaining high-refractory materials from waste only and leads to necessity of adding of excess of magnesium oxide (for shift of material crystallization region to forsterite region) or aluminum oxide (for shift of material crystallization region to spinelede-periclase region).

In order to obtaining of high level of strength and resistance to metal and slag in metallurgical melts conditions it's necessary to add a magnesia component (from 10 to 50 weight %) to high-carbon ferrochrome based refractory materials. Slag may be used without MgO addition in non-critical zones (on a taphole, for example).

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## ASPECTS OF HIGH TEMPERATURE DESTRUCTION OF PROTECTIVE COATINGS AND THE SATURATION OF WELD WITH ITS BREAKDOWN PRODUCTS

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Often, the pertinent tasks of connecting the prefabricated elements within steel structures, many of which are protected by various coatings, are carried out both inside and outside the factory through welding. The physicochemical processes occurring in protective coatings under the high temperature effects and the electric arc impact, as well as composition and technological parameters of coatings affecting the quality of the connection, were rarely addressed in literature. In a number of cases, the effects of electric arc welding on metallic, glass-enamel and paint-and-lacquer materials were specified. But the range of coatings used in the industry is not limited to materials listed above.

In this work, experimental studies were conducted using epoxy and organosilicate coatings. To determine the state and degree of coatings destruction, depending on the distance to the weld, temperature fields, thermal cycles and periods of stay in a range of different temperatures were calculated by method of boundary elements<sup>1</sup>. The model verification was performed by empirically obtained thermal cycles using thermocouples. XPS methods were implemented to examine the coating's distinctive fragments that were removed from the metal surface and subjected to varying degrees of thermal and electric arc effects. The research covering the distribution and composition of coatings breakdown products located in the weld metal was conducted using EDX, XRD techniques and by an optical microscope and SEM.

The destruction degree regularities of epoxy and organosilicate coatings were determined depending on the proximity of the weld. The data on the basic chemical transformations in the material occurring at high temperatures (up to 1400 °C) is related to the data on the coatings composition after welding. A link between the composition and thickness of the protective coating and the number and nature of non-metallic inclusions, pores and weld shape defects was established.

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## COMPOSITION FORECAST OF THE DUPLEX CORROSION-RESISTANT STEELS BY THERMODYNAMIC SIMULATION

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Duplex Stainless Steels (DSS), in which austenite and ferrite are in equal fractions [1], thus providing for a favorable combination of mechanical properties along with high corrosion resistance of these steels, are currently widely used in the petrochemical industry.

The development of new DSS compositions is a searching of a compromise. Increasing the chromium content in steel provides its higher corrosion resistance, but in order to maintain phases balance, nickel concentration has to be raised [1], that causes the formation of undesirable sigma phase [2]. To exclude its formation nickel is replaced with nitrogen [3] which induces the formation of unfavorable chromium nitrides [2].

In the present work thermodynamic criteria for the reasonable choice of chemical compositions of advanced DSS have been developed: 1) austenite and ferrite should be in equal fractions at the beginning of the rough rolling; 2) the temperature of the  $\sigma$ -phase initiation should be below the temperature of the finish rolling; 3) the onset temperature for the formation of chromium nitrides should be minimal.

The influence of the DSS chemical composition on the developed criteria has been summarized as the multiple regression equations. To illustrate the reasonable choice of new advanced DSS compositions with a predetermined corrosion resistance the examples of the joint solution of these equations have been provided.

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## DEVELOPMENT OF UNBAISED ESTIMATION METHODS FOR NONMETALLIC INCLUSIONS IN STEELS FOR TRANSPORT INDUSTRY

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Nonmetallic inclusions (NMIs) in railway wheels and rails determine their metallurgical and useful qualities. It has been shown that the assessment of NMIs, carried out in industry today, is biased and requires the development of new approaches for acceptance test, including test between processing stages, as well as to improve these steels production technology.

The methods based on the statistics of extreme values for valid forecasting the probability of large NMIs occurrence have been developed. 1

The relationships of the NMIs pattern distribution across the section of continuously cast billets (CCBs) to prove CCBs sampling for the NMIs assessment have been established. 2

Data on the chemical composition, size and volume fraction of a representative amount of NMIs in ready-made railway wheels produced by different technologies have been accumulated by automatic feature analysis implemented in the SEM-EDS method. 3-4 These data have been processed by the developed method of NMIs clustering by chemical composition. The nature of NMIs (primary, secondary or tertiary) for each cluster found using thermodynamic modeling has been established. On the basis of the obtained results, the recommendations for reducing the nonmetallic impurity rating of these steels have been proposed and successfully tested in industry.

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## EFFECT OF ADDITION SODIUM AND POTASSIUM CARBONATE ON THE PROCESS OF SOLID-PHASE CARBOTHERMIC REDUCTION OF RED MUD

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The production of alumina by the Bayer method accompanied, along with the main production, a large amount of iron-containing waste that called red mud. By some estimates, from 1.9 to 1.5 tons of this waste is generated. More than 600 million tons of red mud have been accumulated in Russia, and near 5–8 million tons are stored each year. [1] Only small amount of red mud are processed.

Red mud contains a large amount of iron (up to 60%), and aluminum, titanium and rare earth metals. The presence in red mud of valuable components and a harmful impact of their storage on environment, stimulates the development of technologies for their complex recycling.

Solid-phase carbothermic reduction of red mud with the extraction of iron by magnetic separation is the most promising way. The main hinderance is too small size of the reduced iron particles that leads to low efficiency of magnetic separation [2]. Addition sodium and potassium carbonate in the process solid-phase carbothermic reduction of red mud is the best way for growth of iron grains.

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## METAL PLASTICITY AND THE MENDELEEV PERIODIC TABLE

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A possible correlation of mechanical properties of solids with their position in the Mendeleev periodic table is very important scientific problem. Similar correlations have been examined and explained earlier for the elastic moduli<sup>1</sup>. In this study the plastic properties were investigated<sup>2</sup> for Mg, Al, Ti, V, Fe( $\alpha, \gamma$ ), Co, Ni, Zr, Nb, Mo, Cd, In, Sn, Hf, Ta, Pb. The relations were established between mechanical properties and the position of elements in the Mendeleev periodic table.

As it follows from autowave model of plastic deformation<sup>2</sup>, which is in progress today, the principal feature of plasticity is their localization. On this reason, it is convenient to describe the plastic flow with the help of the product of the length of localized plasticity autowave on the propagation rate,  $\lambda V_{aw}$ . The positions of metals in Periodic table were determined by the period number  $N=3, 4, 5, 6$ , and number of electrons of conductivity in the unit cell,  $n$ .

In this case, the following linear relationship is existed

$$(\lambda V_{aw})^{-1} \approx C + D_n \quad (1)$$

where the constants  $C$  and  $D$  are different for 3-6-th periods. For example,

$$D \approx D_0 \exp(-q/N) \quad (2)$$

and besides  $D_0$  and  $q$  are constants, which can be found from the experimental data.

Thus, the parameters of plastic flow localization are defined by the position of metal in the Mendeleev periodic table. It is manifested as the dependence of macroscopic characteristic of autowave plasticity development,  $\lambda V$ , on  $n$  and  $N$  values simultaneously. The interpretation of the experimental data on the base of plastic flow autowave model is maintained in this article.

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## PRODUCING OF NIOBIUM-RARE-EARTH SLAG AND PHOSPHOROUS CAST IRON IN THE REDUCING ROASTING OF ORES OF THE CHUKTUKON DEPOSIT

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Rare-earth metals (REM) are used in the production of magnets, phosphors, superconductors, etc. Niobium is used in the production of corrosion-resistant, heat-proof and other alloys. The growth of production and consumption of these metals largely affects the competitiveness of the economy as a whole<sup>1</sup>.

One of the promising sources of rare-earth metals and niobium is the Chuktukon deposit. Its ores contain 3-7 % of oxides of rare-earth metals and up to 1,5 % of niobium oxide. Due to the presence of a large amount of iron (40-70 %), hydrometallurgical methods of processing these ores are ineffective<sup>2</sup>. For their processing, a combined pyro-hydrometallurgical scheme with producing phosphorous cast iron and niobium-rare-earth concentrate is most acceptable.

At the IMET, RAS, studies of reducing roasting of ore were conducted. It has been established that at temperatures over 1400 °C and a flow rate of the coke above 11% by weight of the ore is observed best separation of metal and slag. At the same time, iron and up to 90 % of phosphorus almost completely are passed into the metal phase (cast iron). Niobium, rare-earth metals and more than 80 % of manganese are concentrated in the slag.

As a result, the content of niobium and rare-earth metals in the slag increases by 4 times and, accordingly, decreases the material flows during its subsequent hydrometallurgical processing. As a by-product, it is obtained phosphorous cast iron, which is used for the production of brake pads of railway transport.

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## PHISICO-CHEMICAL PROPERTIES OF THE ZR-AL-NB-TA LIGATURE ALLOY

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Alloys alloyed with rare metals (superalloys), are widely used in the technology of rocket and aircraft technology. One of the options for the production of alloys and master alloys can be an aluminothermic process in controlled temperature conditions.

The limited information available in the literature on the physicochemical properties of Zr - Al alloys containing rare refractory (Nb, Ta) elements, in particular, on density and surface tension, does not fully improve the methods for producing such alloys and master alloys and the processing of metal waste. For example, the study of surface characteristics and density is relevant for metallothermic processes. At the same time, surface tension and density not only affect the separation of the metal and oxide phases, but also are properties that make it possible to judge the structure of the melt. Complex metallothermic processes, as a rule, are multistage and flow at interphase boundaries. Therefore, in this work, we studied the effect of niobium and tantalum additives on the surface tension ( $\sigma$ ) and density ( $\rho$ ) of Zr-Al alloys, which is necessary to evaluate the interfacial properties.

The study of the physicochemical properties of Zr-Al alloys showed that an increase in the concentration of niobium and tantalum in the alloy influenced the growth of surface tension and density. The addition of Ta promoted a maximum increase in the surface tension value, with a simultaneous addition of 5% Ta and 5% Nb, as well as 5% V, a slight change in  $\sigma$  was observed. The dependences of surface tension on temperature were linear. At the same time, the values of temperature coefficients changed insignificantly.

The density study showed that the base alloy Al-Ti has the lowest density. With increasing temperature, there is no significant change in density for most alloys. The most significant decrease in density during heating occurs when tantalum is added to the alloy.

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## COMPLEX TREATMENT OF TITANOMAGNETITE CONCENTRATES OF THE GREMYAKHA-VYRMES DEPOSIT

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Russia ranks second in reserves of titanium raw materials in the world after China. However, more than half of the reserves are concentrated in the poor ores - titanomagnetite ores. Today, titanium magnetite ores are used as iron ore to extract iron and vanadium as associated component. For example, in Russia low titanium titanomagnetites of the Kachkanarsky deposit are used at the Nizhny Tagil Metallurgical Plant using blast furnace smelting, as a result of which iron and vanadium slag are obtained, which are then processed into steel and vanadium pentoxide. Abroad (China, South Africa, Canada, etc.) two schemes are implemented for processing such raw materials - blast-furnace smelting and electric smelting, the latter being used when the  $\text{TiO}_2$  content is more than 4%. At the same time, regardless of the technology, titanium is irretrievably lost with waste slag. In this connection, the technology of complex processing of titanomagnetite raw materials with the extraction of not only iron and vanadium, but also titanium is necessary. One of the promising deposits is the ilmenite-titanomagnetite deposit Gremyakh-Vyrmes, with the enrichment of ores of which it is possible to produce two concentrates - ilmenite and titanomagnetite. Ilmenite concentrate is suitable for further processing to titanium and its compounds. At the same time, the resulting rough titanomagnetite concentrate requires additional enrichment. In IMET RAS conducts research on the processing of high titanium magnetite titanium raw materials with the extraction of several valuable components - not only iron, but also titanium and vanadium. Enriched titanomagnetite concentrate is subjected to recovery to obtain two products - iron and titanium-vanadium slag. The obtained granulated metal (1.92% C,  $\text{V}_2\text{O}_5$  0.28%) is a marketable product and can be processed into converters to produce high-quality steel. The slag contains about 40% of  $\text{TiO}_2$  and 2.7% of  $\text{V}_2\text{O}_5$ , which makes it possible to use it for further processing with the successive extraction of vanadium by the lime-sulfuric acid method and titanium by leaching.

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## HIGH TEMPERATURE LEACHING OF COPPER AND ZINC FROM SUBSTANDARD CONCENTRATE

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Currently, metallurgy is faced with the problem of the depletion of high-grade ores, which forces to process ores that are unsuitable for producing conditioned concentrates<sup>1</sup>. Hydrometallurgical technologies may be promising for processing substandard sulfide concentrates. The goal of the present work was to conduct high-temperature leaching (90°C) of substandard polymetallic concentrate containing 6.22% copper, 7.30% zinc, 24.4% iron, 1.7% arsenic, and 38.6% sulfur. Pyrite, chalcopyrite, tennantite, and sphalerite were the main minerals of the concentrate. The leaching was carried out in four variants: with 1% H<sub>2</sub>SO<sub>4</sub> solution, with 1% H<sub>2</sub>SO<sub>4</sub> solution supplemented with 1 M NaCl, with 0,5 M solution of Fe<sup>3+</sup> ions (in the form of ferric sulfate), 0.5 M solution of Fe<sup>3+</sup> ions supplemented with 1 M NaCl. The rate of zinc extraction during the leaching with 1% H<sub>2</sub>SO<sub>4</sub> solution was about 35%, while in other variants of the experiment, it comprised about 50%. The rate of copper leaching with solutions without Fe<sup>3+</sup> ions was about 2-3%, while leaching with 0,5M solution of Fe<sup>3+</sup> ions and 0,5 M solution of Fe<sup>3+</sup> ions supplemented with 1 M NaCl was 13 and 20%, respectively. The residue of the leaching with a 0,5 M solution of Fe<sup>3+</sup> ions was then leached with a 0,5M solution of Fe<sup>3+</sup> ions supplemented with 1 M NaCl. 3 cycles of the residue leaching made it possible to extract about 49% and 92% the copper and zinc, respectively. The rate of arsenic leaching in all experiments was low and did not exceed 7%, which indicates the low efficiency of tennantite leaching. The results obtained demonstrated that oxidative leaching with Fe<sup>3+</sup> ions may be a promising approach for the processing of substandard polymetallic concentrates, but its practical application will require the development of combined technologies, including, for example, a stage of sulfide leaching for arsenic removal from tennantite.

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## COMPOSITION OF THE PR AND ND COMPLEXES IN THE SYSTEM 2-ETHYLHEXYL PHOSPHONIC ACID MONO-2- ETHYLHEXYL ESTER (P507) - TBP - ISOPAR-L

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Spectra of Nd solutions in extraction system on the basis of P-507 are presented on figure. Addition of metal reduces polarity of all bonds around atom of phosphorus and shifts absorption peaks in visible and the Infrared range to the long-wave area. Explicit asymmetry and observed splitting of a peak in an extract absorption spectrum in a visible band on 575,5 nanometers is explained by strengthening of an oscillatory component of absorption and demonstrates coupling of  $\text{Nd}^{3+}$  with  $\pi$ -bond.

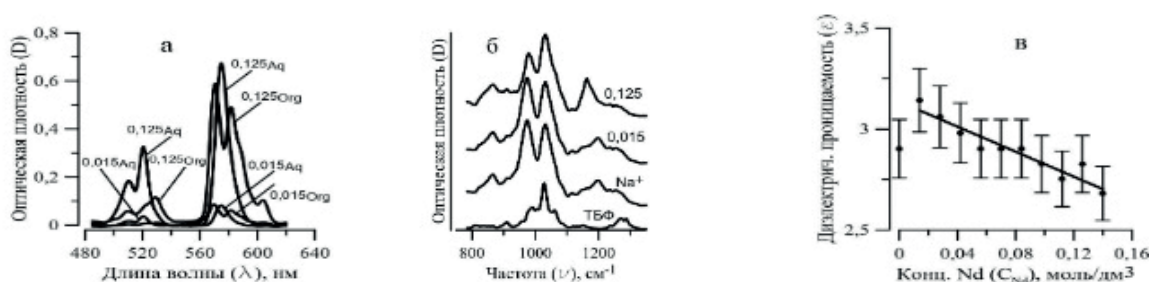


Figure. Visible (a), infrared (b) spectra of Nd. Dependence of dielectric permittivity of P-507 solution on concentration of neodymium (c).

Shift of a peak of absorption in the Infrared range about 1200 cm<sup>-1</sup> demonstrates formation of the integrated intermolecular P=O-Nd system with phosphoryl oxygen. At low concentration of metal (0,015 mol/dm<sup>3</sup>) the coupling is not observed. Peak of absorption on 1280 cm<sup>-1</sup> for tri-n-butylphosphate (TBP) belongs to the P=O group. Disappearance of a peak of TBP added to extraction system indicates solvating of a complex of metal in organic phase by TBP.

Shift of the NMR signal of <sup>31</sup>P in a range 30 → 35 ppm of agreed with the assumption of formation of the P=O-Nd bond.

Based on the analysis of the dependences of the NMR signals shifts, changes of IR spectrums and dielectric permittivity of solutions on concentration of Nd and Pr the mechanism of extraction reactions and solvation of extractable complexes suggested.

## INVESTIGATION OF INGOT SOLIDIFICATION KINETICS ON THE BASIS OF PHYSICAL MODELING OF MELT CASTING AND CRYSTALLIZATION

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Steel casting and solidification are the most important stages of ingot production. Currently the investigation of the processes which occur during the solidification of an ingot or a cast product are extremely difficult, which requires to apply solidification modeling methods based on physical models with transparent substances. Such methods present a fairly common laboratory research technique.

The paper reports findings on the processes which occur inside the ingot when it is poured into a mold; the pouring is accompanied with the transformation of a part of the molten metal stream into hard particles (inoculants). A simulation technique is used to model solidification in physical models.

Sodium thiosulphate crystals are used as inoculants; their content being 1, 3, 6 and 12% of the melt used to pour the model ingot. Sodium thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (crystalline hyposulfite) was used to model liquid metal.

It was established that when inoculants are added, the directional effect of solidification improves. Besides, the thickness of the two-phase area is reduced, crystallization rate grows and the thermal center shifts due to the decrease of melt overheating.

When hard particles (inoculants) are introduced at the amount of 6 and 12%, the solidification time of model ingots decreases. An increase in the amount of inoculants introduced into the stream results in the prevalence of the vertical solidification front over the horizontal one.

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## PROCESSING OF VANADIUM PRODUCTION SLIMES WITH VANADIUM EXTRACTION

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In Russia about 2 million tons of vanadium-bearing waste of the plant “Evraz Vanadium Tula” company pentoxide vanadium producing are saved up and it contain more than 2.0 - 3.5% of  $V_2O_5$ . Every year about 120 thousand tons of slimes (on dry weight) fill up open sludge collectors which contain 40-70 thousand tons of  $V_2O_5$ , from which 1.2-4.2 thousand tons are the water-soluble compounds that creates a serious problem for the environment, in particular for the region water resources.

Considering large volumes of such waste and their ecological threat for environment, research of utilization and neutralization possibility of a vanadium-bearing wastage is a relevant task. The slimes are rich vanadic raw materials and can be efficiently used for vanadium extraction.

In work results of researches on vanadium extraction from vanadium containing dump slimes of  $V_2O_5$  production from lime-sulfuric acid technology converter slags, on the example of 3 samples of slimes with the  $V_2O_5$  content of 2.2-3.3% are presented. It is established that in a water-soluble form there are 3-6% of  $V_2O_5$ . Influence of concentration of sulfuric acid within 0.5-10% for vanadium extraction in solution at a slimes leaching is studied. It is shown that there is enough 3% sulfuric acid leaching for the almost complete extraction of soluble vanadium. Effect of leaching temperature and durations is studied at 3% sulfuric acid. It is determined that it is possible to reach 60.9% of vanadium extraction in solution carrying out process at 60 ° C within 60 min. Further pure vanadium pentoxide obtained from solution by precipitation and prerefining can be applied to titanic alloys production and in other industries. In Russia pure vanadium pentoxide production is practically absent.

*The work was carried out within the framework of the program of fundamental research of the Presidium of RAS №39 «Fundamentals and energy-efficient, resource-saving, innovative technologies of mineral processing, recycling of industrial and household waste» (registration number of R & d AAA-A18-118032690052-5).*

## OXIDATION KINETICS AND PHASE TRANSFORMATIONS DURING THE OXIDATION OF SILICON-DOPED ELECTRICAL STEEL IN THE AIR IN THE TEMPERATURE RANGE 540-720 °C

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The article shows the results of investigating the patterns of silicon-doped electrical steel oxidation in the air in the temperature of 540-720 °C for a period of 33 hours. The kinetics of electrical steel oxidation in the air was investigated using the thermogravimetric method. It has been found that steel oxidation in the given temperature range is governed by the exponential law  $\Delta g^n = K \cdot \tau$ . The calculated activation energy value at  $\approx 8$  kJ mole<sup>-1</sup> attests to the diffusion control of the oxidation.

The oxidized surfaces of the samples were examined with Scanning Electron Microscope JEOL JSM-7001F. It showed that the oxide content on the steel surface depends on the oxidation temperature. It has been found that within oxidation temperature as low as 540-580 °C, the steel surface forms predominantly independent chaotically distributed nuclei of silicon oxide SiO<sub>2</sub>.

In the range 580-6200C, the oxide scale consists of SiO<sub>2</sub> and ferrous oxide. If temperature is further increased, SiO<sub>2</sub> reacts with the ferrous oxides to form fayalite Fe<sub>2</sub>SiO<sub>4</sub>, which is consumed by the growing scale of ferrous oxides as soon as the oxidation continues.

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## RESEARCHING OF SELECTIVE NICKEL AND COBALT EJECTING PROCESS FROM BURUKTAL LIMONITE ORE

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Oxidized nickel ores contains more than 70% of world nickel (160 million tons)<sup>1</sup>, but processing of these ores in modern times is low profitability. Oxidized nickel ores separates in two groups by chemical composition: magnesium silicates (saprolitic) and ferrous (limonitic). Limonite ore consist of: 35 – 47% Fe<sub>total</sub>, 0,8 – 1,3% Ni and 0,04 – 0,2% Co. Due to the high ferrous content, saprolitic ores processing technology is not suitable to limonite ores. Industry uses high pressure autoclave leaching (HPAL) and ammonia-carbonate leaching (Caron-process). These methods had number of serious drawbacks<sup>2</sup>.

Consequently, our laboratory of IMET RAS carries out the research to develop new process of selective ejection of nickel and cobalt from Buruktal limonitic ore. The core subject of this process is using the reductive roasting at temperature 400-900 °C in reducing atmosphere followed by atmospheric leaching of roasted ore at temperature 60-95 °C by low-concentrated sulfur acid solution for selective extraction of nickel and cobalt to leachate.

Addition of roasting stage to process should allow transition of nickel and cobalt from oxides to metallic state and reduce ferrous oxides to Fe<sub>3</sub>O<sub>4</sub> that sparsely soluble in low-concentrated sulfur acid. Ejection of nickel and cobalt is reaching 87-99% and 80-91% respectively at optimal arrangements of reductive ore roasting and leaching the cinder. The specific sulfur acid consumption is amount 100-140 kg/tonn of ore.

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## MORPHOLOGY OF SPHERICAL TINI POWDER PRODUCED BY EFFECT TO THE THERMAL PLASMA

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A special feature of additive manufacturing is the ability to manufacture geometrically complex products using 3D models with significant savings of consumables compared to traditional production methods. The raw material used is a powder consisting of spherical particles with a uniform particle size distribution. Producing such powders is an actual problem, the solution of which will facilitate to the development of additive production<sup>1</sup>.

In this paper, TiNi powder angular form (Fig. 1a) was sifted through laboratory sieves FRITSH with a mesh size of 45  $\mu\text{m}$  to exclude fine particles that can glue to larger particles during the spheroidization process to form satellites (Fig. 1b). The spheroidization of the powder occurred due to the effect of the thermal plasma.

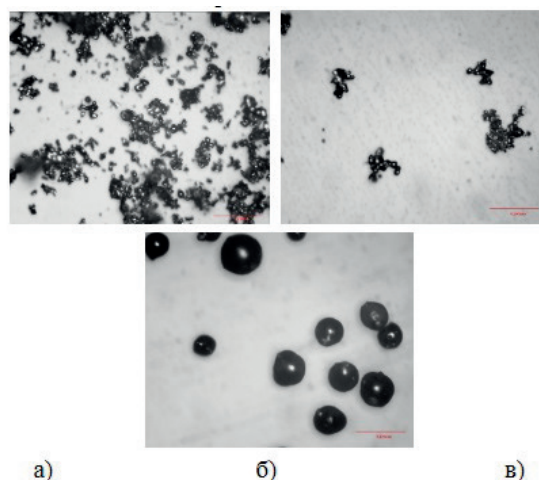


Figure 1. The morphology of the powder particles (a – initial, b – sifted, c – spheroidized).

As a result of the thermal plasma effect, particles acquired a spherical shape with satellites on their surface (Fig. 1c).

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## NEW ASPECTS IN INVESTIGATION OF PHYSICAL AND CHEMICAL FOUNDATIONS OF TUNGSTEN METFL PRODUCTION BY GAS-PHASE FLUORIDE METALLURGY

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The paper studies kinetic characteristics of a process of tungsten hexafluoride reduction by hydrogen at atmospheric and reduced pressure of (1-2) kPa in the temperature range of (500-1200)° C and hexafluoride concentration in a gas mixture from 0 to 100 mole %.

The original components were purified.

The tungsten deposition rate dependence on the process temperature and gas mixture composition at atmospheric pressure was studied in the temperature range of (500 ÷ 1200) °C and tungsten hexafluoride content in the gas mixture of (0 ÷ 100) mol.%. When the content of WF<sub>6</sub> is (30 ÷ 35) mol.%, this dependence is close to linear. In the range of the tungsten fluoride concentrations of (35 ÷ 55) mol.% a growth rate changes slightly, and its maximum value becomes (4.8 ÷ 5.0) mm/h. At the content of more than 55 mol.%, the growth rate decreases to zero and takes negative values at (85 ÷ 90) mol.%. An etching rate in pure WF<sub>6</sub> varies from 1 mm/h to 2.5 mm/h at the temperatures from 600° C to 1200° C.

The study of the kinetic characteristics under the reduced pressure of (1 ÷ 2) kPa showed that with increasing in the tungsten hexafluoride content in the gas mixture, a tungsten deposition rate is growing and reaches the maximum value, and then it is decreasing to zero and to the negative values.

The maximum tungsten deposition rate of ~ 2.6 mm/h is at a temperature of 1200°C and tungsten hexafluoride concentration of ~ 35 mol. %. The maximum etching rate (0.5 ÷ 0.6) mm/h is also at 1200°C.

The process activation energy in the kinetic area was (54.5 ± 2.1) kJ/mol.

The conditions of the process transition from the kinetic area to the diffusion one were determined. While reducing the pressure in the reaction volume, the kinetic reaction area is expanding.

Some structural-physical properties of the tungsten sediments were studied.

## THERMODYNAMIC SIMULATION OF PHASE FORMATION IN THE MO-14.5V-13.2SI ALLOY, DOPED WITH YTTRIUM

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Thermodynamic analysis was performed using the HSC Chemistry 6.12 software package, the database of which contains information about values of the  $\Delta H_f$ ,  $\Delta S$  and  $c_p$  coefficients. Equilibrium phase formation models were calculated for the Mo-V-Mo<sub>3</sub>Si-V<sub>3</sub>Si-Y system in the temperature range 25–2000 °C. Inert atmosphere - argon. The addition of metallic yttrium to the hypoeutectic Mo-14.5V-13.2Si (at. %) alloy, which was taken as the basis, varied from the calculation of its content in doped samples to 5.0 at. %. The choice of the alloy is based on knowledge of its chemical and phase composition, as well as a number of its physicochemical properties<sup>1</sup>.

When performing model calculations, the possibility of the formation of silicides was taken into account in accordance with the state diagrams of the Mo-Si and V-Si binary systems. Additionally, the missing thermal characteristics of V<sub>3</sub>Mo, VMo double intermetallic compounds and Y<sub>2</sub>Mo<sub>3</sub>Si<sub>4</sub>, V<sub>3</sub>Si<sub>2</sub>Mo<sub>3</sub> and VSi<sub>3</sub>Mo<sub>4</sub> ternary silicides were entered into the program database:  $\Delta H_f$  values were borrowed from source<sup>2</sup>, and  $\Delta S$  and  $c_p$  coefficients were calculated using known methods. According to the obtained models, in addition to the solid solutions (Mo,V)<sub>ss</sub> and (Mo,V)<sub>3</sub>Si, there can be silicides of yttrium and elemental yttrium in the equilibrium composition of Mo-14.5V-13.2Si-(0-5.0)Y alloys. Taking into account the formation of micron-sized particles, representing the eutectic of Y<sub>5</sub>Si<sub>3</sub> silicide with Mo<sub>3</sub>Si, which are concentrated along the grain boundaries of the silicide phase of the Mo-15.3Si-Y ternary alloys<sup>3</sup>, we can expect a similar distribution of yttrium in the structure of Mo-14.5V-13.2Si-(0-5.0)Y quadruple alloys.

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*The reported study was funded by RFBR according to the research project № 18-33-00797 mol\_a*

## OXIDATION OF MOSS – MO<sub>3</sub>SI ALLOYS DOPED WITH SC AND ND

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In the area of hypoeutectic compositions (up to 25 at% Si) of Mo – Si diagrams, composites are formed consisting of the solid solution Mo<sub>ss</sub> and Mo<sub>3</sub>Si. They are the basis of promising high-temperature alloys. Test doped samples (0.5–3.0 at % REE) were obtained from the Mo – 15.3at% Si alloy by the vacuum-arc melting. According to XRD, SEM and EPMA, the Mo<sub>ss</sub>/Mo<sub>3</sub>Si volume ratio increases by 1.4-1.6 times due to the addition of Sc or Nd. Besides in the structure a third component is formed consisting of REE silicides and Moss, at that their ratio varies proportionally with the concentration of Sc and Nd On the DSC line of the Mo – 15.3 at% Si alloy (Figure) heated in a stream of gas (20% O<sub>2</sub> – Ar), two exoeffects at 775 and 800 °C related to the oxidation of the main phases were detected. The mass gain was observed in the range of 400-820oC, further the MoO<sub>3</sub> was beginning to sublime.

The REE effect is to increase in the oxidation rate at the initial stage of process (Table), at that to a lesser extent for Sc and significantly in the case of Nd. The results can be useful in the development of heat-resistant composites and heat-protective coatings.

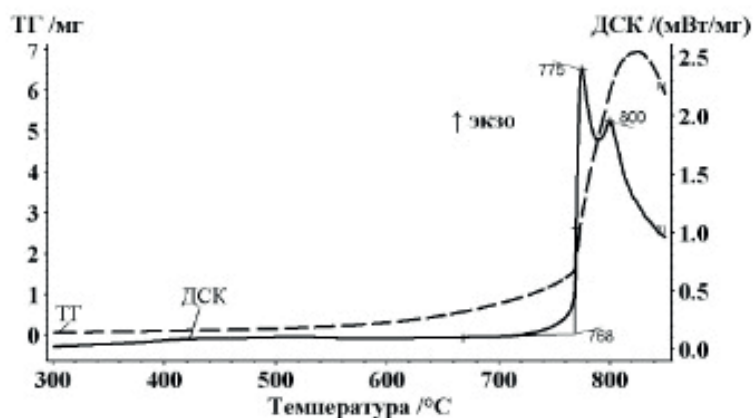


Figure. Changes in mass (TG) and heat flux (DSC) during Mo<sub>ss</sub>–Mo<sub>3</sub>Si is heated in a stream of O<sub>2</sub>-Ar (20% O<sub>2</sub>) gas mixture at a rate of 10 °C / min)

Table. The oxidation rate of alloys based on Mo-15.3.% Si

T, °C	Скорость окисления сплавов, ·10 <sup>4</sup> (мг/мм <sup>2</sup> )/мин		
	Mo-Si	Mo-Si-Nd	Mo-Si-Sc
500	0.94	1.22	1.28
600	3.19	3.39	4.22
690	13.16	26.59	14.16

The work was supported financially by the Russian Foundation for Basic Research (project A No 18-03-00648)

## CORROSION RESISTANT AUSTENITIC STEEL 25CR-11MN-5NI WITH 0,5 % N AND HIGH NICKEL ALLOY K-500 TESTS AS A MATERIAL FOR THE PETROLEUM SHAFTS EQUIPMENT

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For the manufacture the oil pump shafts, MPMS shafts and pumps mine pressure maintenance station, electric centrifugal pumps shafts, working in aggressive environments, parts for submersible electric motors, e.t.c traditionally using high cost heat-resistant alloys Monel and Inconel, such type as Alloy 925, Alloy 718, Alloy K-500, which is nickel base. They have high corrosion resistance and durability. Up to the temperature of 900 oC this alloy is distinguished by the high impact viscosity and durability, and at the low temperatures (to -78 oC) not sensitive to the notchings.

This work involves the replacement option for the expensive nickel alloys with more economically alloyed corrosion resistant, low carbon nitrogen austenitic steels 25Cr-11Mn-5Ni with nitrogen containing of 0,5 % (mass.). Nitrogen alloying increasing resistance to local types of corrosion and MCC, promote to hard solution and deform steel strengthening. The results of comparison investigations of mechanical properties of 25Cr-11Mn-5Ni with 0,5 % N steel bars and alloy K-500 (25N60D30UGT) showed in the table 1.

The results of 25Cr-11Mn-5Ni steel tests to hydrogen sulphide stress corrosion cracking according to NACE TM 0177-2005 (method A) in the area of  $H_2O, H_2S + 0,5\%NaCl + 0,5\%CH_3COOH$  (concentration  $H_2S - 2730$  ppm, temperature  $24 \pm 2$  °C) at constant load 0,7 from liquidity limit also proved satisfactory – the samples failure did not occur.

Table 1. Mechanical properties of nitrogen steel and alloy K-500 bars (Ø 25 mm, cold deformed, calibrated, polished)

Material	$\sigma_e$ , MPa	$\sigma_p$ , MPa	$\psi$ , %	$\delta$ , %	KCU, MJ/m <sup>2</sup>
05Kh25AG11N5	1902	1790	49	11	0,73
Alloy K-500	1412	1074	40	12	0,79

## STUDY OF WELDED JOINTS OF AUSTENITIC HIGH-STRENGTH STEEL WITH 0.57% N RECEIVED BY TIG WELDING BY MEANS OF THREE TYPES OF WELDING ADDITIVES

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Austenitic stainless steel with a high nitrogen content (~0,5% wt.) in the equilibrium state is a high-strength, corrosion-resistant and wear-resistant material. In classical fusion welding of steels with a high nitrogen concentration, a number of different phenomena are possible: nitrogen desorption; cracking during crystallization in the welding zone; appearing of liquation cracks in the heat-affected zone; forming of porosity and, as a result, deterioration of mechanical and corrosion properties. Named problems can be overcome by developing a suitable welding procedure.

In present work, we investigated welded joints of austenitic cast steel 05Kh22AG15N8MF (0,57% by weight. N) obtained by argon-arc welding with a non-consumable electrode according to the following modes: strength of current - 70-110 A, voltage - 10-11 V, using filler materials 05Kh22AG15N8MF (~0,57% N, I), 10Kh20N18M3APS (~0,2% N, II) and 25Kh25N16AG7 (~0,1% N, III).

The microstructure of the base metal is cast austenite grains, 500-700 μm in size, with a δ-ferrite content of not more than 0,6%. The weld is characterized by a cellular-dendritic structure with a grain size of 4–20 μm, with a δ-ferrite content of up to 0,16%.

The selected welding mode made it possible to avoid nitrogen losses in the welds, the nitrogen concentration in the welded joints was: I – 0,55%; II – 0,22%; III – 0,11%. The mechanical properties of tensile samples cut along the welds were 1,5–2 times higher than that of the base metal ( $R_m$  of welded joints was 915 (I), 800 (II) and 792 (III) MPa versus 709 for the base metal).

Testings of Charpy samples with a notch along the fusion line showed the presence of a viscous fracture in all welded joints; KCV = 58 (I); 74 (II); 45 (III) J/cm<sup>2</sup>.

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The work was carried out according to the state assignment No. 075-00746-19-00.



## LEACHING OF NONFERROUS METALS WITH EXTRACTANT-CONTAINING MICROEMULSIONS

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The strong interest in the application of nanomaterials and nanostructures, for example, microemulsions, for the extraction and separation of substances has grown for the last decades. Nanomaterials and Nanotechnology Department of D.I. Mendeleev University of Chemical Technology of Russia has developed the method of microemulsion leaching, which involves the recovery of substances from a solid material with an extractant-containing microemulsion. The main advantage of this method is the combination of the leaching of substances from a solid phase with the selective extraction of required components into microemulsion droplets in the single process.

Microemulsions are thermodynamically stable and isotropic mixtures of water and oil with nanoscale domains stabilized by surfactants. Microemulsions for the leaching process should have a wide region of existence, contain a sufficient amount of an extractant to achieve the high extraction rate and recovery of required components, be stable at high temperatures during the leaching process.

It was shown that microemulsions in sodium bis-(2-ethylhexyl)phosphate (NaDEHP) – extractant – kerosene – water and sodium dodecylsulfate (SDS) – 1-butanol – extractant – kerosene – water systems are capable for the leaching of metals from oxide materials. These microemulsions contain extractants bis-(2-ethylhexyl)phosphoric acid (DEHPA), caproic acid, or the mixture of tributylphosphate (TBP) and acetic acid. The leaching of copper, cobalt, nickel, and iron from the oxidized cobalt-copper concentrate with NaDEHP microemulsions containing DEHPA or TBP+  $\text{CH}_3\text{COOH}$  was studied. The recovery of copper was 72,1% after the 5 hours of microemulsion leaching with microemulsion containing 0,174 mol/l of DEHPA. The application of SDS microemulsions for the leaching of copper was investigated on the model system with CuO.

The results of the presented work may be exploited for the development of methods of the metal recovery with extractant-containing microemulsions from ores and secondary raw materials, for example, galvanic sludges.

## STUDY OF THE POSSIBILITY OF REDUCING THE CARBON CONTENT DURING THE TANTALUM POWDER HEAT TREATMENT

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Modern capacitor tantalum powders are characterized by a highly developed surface. To maximize its preservation, capacitor manufacturers reduce the temperature and sintering time of powder compacts, which work as capacitor anodes. There are no conditions for additional purification of the powder from impurities, in particular carbon. The latter, due to the low value of solubility in tantalum, has a significant impact on the electrical characteristics of anodic tantalum oxide<sup>1</sup>.

Since heat treatment with the purpose of agglomeration is an integral part of the process of producing tantalum capacitor powders, we studied the possibility of reducing the carbon content in the powder at relatively low temperatures.

Thermodynamic analysis of the processes of carbon interaction with hydrogen released during heating of tantalum hydride showed that carbon interacts with atomic hydrogen to form CH<sub>4</sub>. Removal of CH<sub>4</sub> from the reaction zone results in the purification of the metal from carbon. This was practically confirmed by heat treatment of tantalum hydride powder, produced by grinding of ingot, in a stream of high-purity argon<sup>2</sup>.

This paper presents the results obtained by heat treatment of magnesium thermal powders of tantalum with a large specific surface area, containing up to 0.5% hydrogen. The maximum heat treatment temperature was 800 °C. The process was carried on both in a stream of pure argon and at a certain partial pressure of hydrogen in the system.

The results of the study showed that maintaining the required partial pressure of hydrogen contributes to a more complete removal of carbon. The carbon content in the tantalum powder as a result of heat treatment decreased by 2-7 times. The proposed method is very promising for the decarburization of fine tantalum powders.

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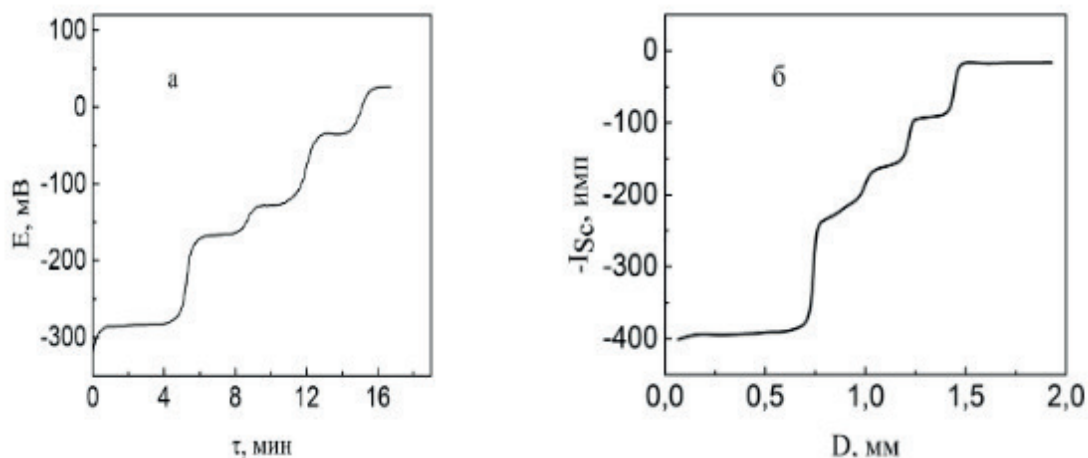
## INTERACTION OF SCANDIUM WITH ALUMINUM, COPPER AND LEAD: STRUCTURE AND PROPERTIES OF MULTI-PHASE ALLOYS

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Scandium alloys are of great interest for materials chemistry and metallurgy due to their unique properties caused by formation of intermetallic phases with controlled structure<sup>1</sup>.

Here, the results of experimental investigation of the direct interaction of metallic Sc with Al, Cu, Pb (under various conditions) are presented. Figure (a) shows the time dependence of the electrochemical potential  $E$  of the  $(L + Pb_{50}Sc_{50}) | LiCl-KCl + ScCl_3 | Cu-Sc$  (s) galvanic cell at 893 K. The structure of Cu-Sc multi-phase alloys was studied by measuring of the SEM-EDX signal of scandium at linear scanning across the interaction layer (with thickness  $D$  up to 2 mm). The intensity curve (b) is shown with the reverse sign ( $-I_{Sc}$ ).



The «potential-time» and «coordinate-intensity» dependences show a close mutual correlation. It allows one to identify the regions of phase diagram corresponding to the areas of the electrochemical potential stabilization, and to determine the thermodynamic properties of the alloys.

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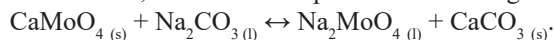
*The work was carried out according to the state assignment for IMET UB RAS.*

## RESEARCH OF THE INTERACTION OF CALCIUM MOLIBDATE WITH SODIUM CARBONATE SOLUTIONS

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Calcium molybdate  $\text{CaMoO}_4$  is an intermediate product in the processing of molybdenite concentrate and other molybdenum raw materials. For the leaching of molybdenum from this intermediate product, containing a whole range of impurities, it is advisable to use sodium carbonate solutions. In this case, the interaction proceeds according to the equation:



The dissolution of  $\text{CaMoO}_4$  in a solution of  $\text{Na}_2\text{CO}_3$  at a ratio  $S : L = 1 : 15\text{--}20$  g/ml under conditions ten times the stoichiometric required amount of  $\text{Na}_2\text{CO}_3$  in the ranges of soda concentrations  $1.4\text{--}2.5$  mol / l and the temperature  $60\text{--}90$  °C. Studied the equilibrium composition of liquid and solid phases, the parameters of the kinetic processes — constant velocity, energy activation are determined, and the limiting stage of the process is established. It is shown that the rate of dissolution of  $\text{CaMoO}_4$  in a solution of  $\text{Na}_2\text{CO}_3$  is proportional of stirrer speed up to  $8.3 \text{ s}^{-1}$ , therefore the kinetic parameters of the process are determined at  $n \geq 8.3 \text{ s}^{-1}$ . The process is accompanied by the formation of a dense  $\text{CaCO}_3$  shell and, depending on the selected conditions, a series of salts in the bottom phase ( $\text{CaMoO}_4$ ,  $\text{Na}_2\text{MoO}_4$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaCO}_3$  in the form of calcite and vaterite,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ ). The maximum degree of decomposition of  $\text{CaMoO}_4$ , reached at a temperature of  $90$  °C in  $2.5 \text{ M Na}_2\text{CO}_3$  solution, is  $80.4\%$ , while the concentration of molybdenum in the solution was  $0.24 \text{ mol / l}$ .

The obtained data allow us to optimize the conditions of molybdenum leaching from concentrates containing calcium molybdate by sodium carbonate solution.

## THERMODYNAMIC ESTIMATION OF MELTING OF COMPLEX ALLOYS THROUGH THE OSMOTIC COEFFICIENT OF B'YERRUM-GUGGENGEYM

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The Bjerrum-Guggenheim coefficient ( $\Phi_i$ ), known in the literature<sup>1</sup>, is closely related to the coefficient of activity of components in a binary system by the formula:

$$\ln j_i = (\Phi_i - 1) \cdot \ln x_i \quad (1)$$

Using the developed technique<sup>2</sup> for extracting thermodynamic information from their state diagrams, the activities of the components of various binary metallic systems were calculated using the B'yerrum-Guggenheim osmotic coefficient.

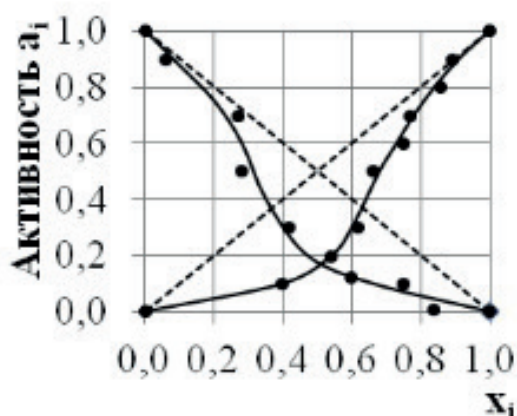


Figure 1. The activity of iron and manganese in the system Fe-Si at T = 1973 K  
(solid lines - calculation, points - initial literature data)

The dependences of  $\Phi_{Fe}$  and  $\Phi_{Si}$  on the ratio of activity in the liquid and solid phases are obtained:

$$\Phi_{Fe}^* = 1,36057 - 1,33189 \cdot a_{Fe}^L / a_{Fe}^S \quad (2)$$

$$\Phi_{Si}^* = -4,65745 + 2,16985 \cdot a_{Si}^L / a_{Si}^S \quad (3)$$

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## PHASE EQUILIBRIUM IN BINARY AND TERNARY SUBSYSTEMS OF THE FE-CU-AS-S SYSTEM

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The relevance of the research is determined by the need to develop and improve the process of arsenic-containing polymetallic ores treatment. Large amount of research works are devoted to the problem of arsenic removal from technological semiproducts and neutralization it into non-toxic forms for further storage. Despite certain scientific and technological results achieved in this area, this task is still far from being solved. The methods of dearsenization, involving the transfer of arsenic into sulphides and arsenides of various metals are the most effective, since they are nontoxic and convenient for transportation, storage and disposal. Thus, it is necessary to develop the effective ways for the conversion of arsenic to sulphide form and/or to As-Fe solution. Both sulfur and iron are essential components of arsenic-containing raw materials of non-ferrous and precious metals. Thus, the bonding of arsenic in compounds or solutions of the Fe-Cu-As-S system is practically justified, and knowledge of the phase equilibria realized in this quaternary system should develop the pyrometallurgical technologies for dearsenization metallurgical intermediates and subsequent neutralization of arsenic.

Using a complex of experimental physicochemical methods of research as well as analysis of previous experimental several boundary binary and ternary phase diagrams of Fe-Cu-As-S system have been constructed (excluding the area of high sulfur concentrations in some cases). The thermodynamic description of the systems is carried out. The database of thermodynamic data has been created, providing phase equilibrium calculations of these systems using FactSage software.

The obtained results will be the basis for construction the phase equilibrium diagram of the Fe-Cu-As-S quaternary system. The use of the obtained data gives the possibility for the development of a pyrometallurgical methods of dearsenization of ores and concentrates of heavy, non-ferrous and precious metals with the conversion of arsenic to a low-toxic sulfide or arsenide forms.

*The reported study was funded by RFBR according to the research project № 18-29-24166.*

OXYSULFIDE ION-EXCHANGE MEDIUM  
FOR PROCESSING ZINC-CONTAINING WASTE

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The processes of zinc extraction from ore raw materials are based on zinc reduction from their oxides. Man-caused materials (slag, dross, dust, sludge) that characterized by various occurrence forms of zinc can be involved in the processing. It would require the creation of conditions for efficient process behavior. The processing of zinc-containing materials, which contain sulfur compounds, for example, slags of autogenous smelting of copper-zinc concentrates<sup>1</sup> and blast-furnace dust<sup>2</sup> is represented as a great difficulty.

An ion-exchange medium based on the FeO-SiO<sub>2</sub>-FeS-CaO system allows implementing exchange reactions in order to intensify the processes. This ensures the transfer of ZnS to oxide melt, its dissociation, reduction and zinc concentration in the gas phase. High-iron slags of copper-smelting production, allowing to increase the diffusion coefficients of Zn<sup>2+</sup>, Fe<sup>3+</sup> and Fe<sup>2+</sup> ions (fig.), thereby to intensify mass transfer processes, were tested as an ion-exchange medium.

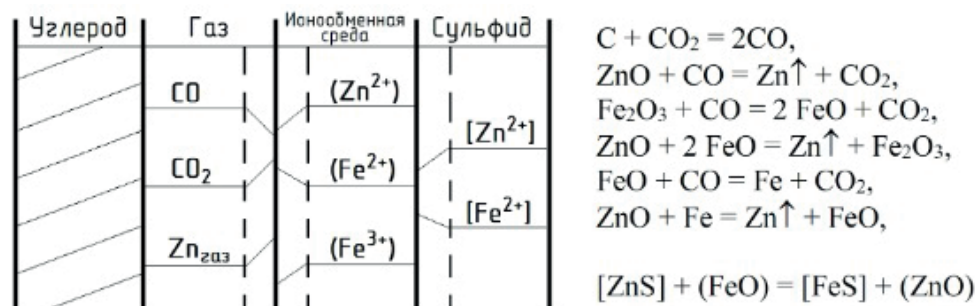


Figure. Diffusion layers in the carbon–gas–slag–sulfide system

The presented terms allowed to scientifically substantiate the technology that provides deep dezincification of industrial wastes with the production of requested marketable products.

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## THERMODYNAMIC MODELING OF THE METALS REDUCTION FROM OXIDE MELTS IN THE APPROACH OF OPEN SYSTEMS

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A method<sup>1</sup> that allows one to obtain data on the reduction of metals from an oxide melt in processes with periodic removal metallic phase and continuous removal gas phases has been developed. The method is used to analyze the reduction reactions in the  $B_2O_3$ -CaO-MeO-CO system (where Me is Ni, Zn, Pb, Cu). The information obtained is useful for predicting processes occurring during the extraction of useful components from the slags of non-ferrous metallurgy.

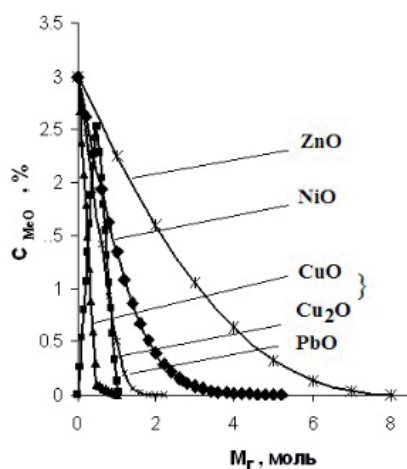


Figure 1. The effect of gas consumption ( $M_g$ , mol) on the content of metal oxides in the melt

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## SOLUBILITY OF OXYGEN IN MELTS OF THE NI-CO SYSTEM

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The thermodynamic analysis of oxygen solutions in melts of the Ni-Co system containing Cr, Mn, Si, Ti, Al was carried out. The equilibrium constants of deoxidation reactions of the studied melts with the given elements were determined. The activity coefficients at infinite dilution and interaction parameters in alloys of different composition were calculated. The concentration dependences of the oxygen solubility in the studied alloys on the content of cobalt and the deoxidizing element are obtained. The contents of deoxidizing elements at the minimum points on the oxygen solubility curves and the corresponding minimum oxygen concentrations were determined. The dependences of the oxygen concentration in the melt on the content of the deoxidizing element for melts of the Ni-Co system of various compositions containing Cr, Mn, Si, Ti, Al at 1873 K are shown in Figure 1.

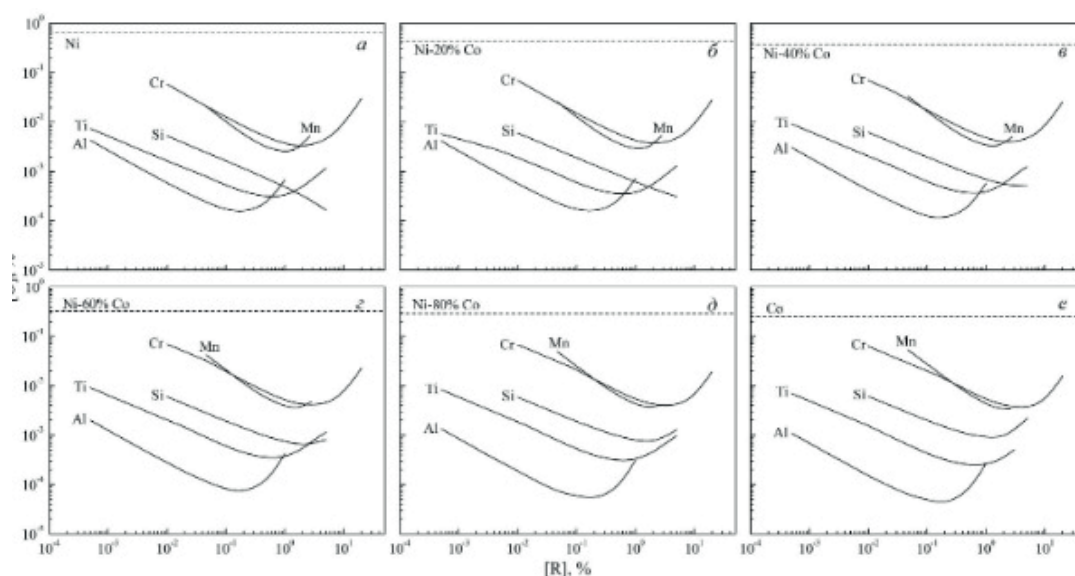


Fig. 1. Dependence of oxygen concentration in melts of the Ni-Co system on the content of deoxidizing elements (R) at 1873 K

The deoxidizing ability of aluminum increases from nickel to cobalt, the deoxidizing ability of titanium practically does not change, the deoxidizing ability of silicon and chromium decreases slightly, and the deoxidizing ability of manganese decreases markedly. Horizontal dashed lines show the solubility of oxygen in nickel-cobalt melts of a given composition at 1873 K.

## EVOLUTION OF NON-METALLIC INCLUSIONS' COMPOSITION AT VARIOUS STAGES OF METALLURGIC TECHNOLOGY DEVELOPMENT

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It is known that corrosion resistance of carbon and low-alloyed steels depends on several factors, including chemical composition of steel, characteristics of microstructure and purity of steel in terms of specific types of non-metallic inclusions.

Thus, from the middle of 1990s and till 2005-2007 the major reason for reduction of corrosion resistance of steels in aqueous media was high content of specific non-metallic inclusions based on calcium aluminate. Such inclusions generated during ladle processing of liquid steel, when non-optimal technological parameters are used, were called corrosion-active non-metallic inclusions (CANI).

Beginning from the middle of the first decade of 21 century CANI based on magnesium aluminates (magnesium aluminate spinel) with sulphide component (from manganous sulphide and calcium) were detected instead of calcium aluminate-based CANI in steels produced by various plants. The most probable reason therefore was change in composition of ladle lining. Numerous researches have shown that such non-metallic inclusions also caused acceleration of corrosion processes though to only a lesser extent than calcium aluminate-based CANI.

Over the last years emergence of new grades of steels and improvement of liquid steel processing technology, which includes complex deoxidation treatment, vacuum treatment and modification of non-metallic inclusions has resulted in a situation, where non-metallic inclusions based on magnesium aluminate spinel in modern steels have more complex composition, oxide component of such inclusions may contain calcium, magnesium, aluminum and some other elements in different proportions. Corrosiveness of inclusions and corrosion resistance of steels accordingly depends on content proportions of such elements. Therefore, corrosion resistance of steels can be improved to a large extent by optimizing steelmaking technology without rise in product prices.

## PRODUCTION OF A CAST IRON AND ALUMINATE SLAG BY SINGLE-STAGE RED MUD REDUCTION ROASTING PROCESS

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The main waste of aluminum production is red mud - an insoluble fine material formed during the leaching stage of aluminum production<sup>1</sup>. Due to the fact that there are no effective technological solutions for their processing, mud accumulates annually in special mud storage facilities, representing a serious technological threat to the environment<sup>2</sup>.

The aim of this work is the development of single-stage red mud reduction roasting with simultaneous production of pig iron and aluminate slag.

As a result of the conducted research, the optimal parameters of red mud reduction roasting were determined, providing the most complete transfer of iron to cast iron<sup>3</sup>. The effect of sodium and calcium carbonate additives on the phase composition of aluminate slag and on the separation of the metal and slag phases was studied. It was found that, under optimal roasting conditions, aluminate slag is formed, during the alkaline-carbonate leaching of which the degree of extraction of aluminum into the solution is more than 75%. Incomplete extraction of aluminum is associated with the formation of complex calcium aluminosilicates, mainly of gellenite.

The study is carried out by a grant from the Russian Science Foundation (project No. 17-73-10414).

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## INTERACTION OF EXOGENOUS REFRACTORY NANOPHASES WITH IMPURITIES OF SAS IN IRON MELTS AND THE INFLUENCE ON THE CAPILLARY PROPERTIES OF METAL

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One of the trends in the development of the physicochemistry of metal melts of the iron triad is the use of nanoparticles of refractory phases (NPRP) in liquid metal, both in the form of reagents for melt refining from surfactants, and in the form of inoculators, affecting the crystallization process and the structure of the solid metal. In this regard, earlier<sup>1</sup> proposed and experimentally confirmed the hypothesis of heterophase interaction of NPRP with surfactants in melt with the subsequent formation of hypothetical Me + (NPRP-surfactant) ensembles and their removal from the metal at the Me-gas/ceramics/slag interface.

The heterophase interaction of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiN}$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{SiC}$ ,  $\text{TiN}$ ,  $\text{TiCNO}$  nanoparticles with surfactants (S, Cu, Sn, Sb) was studied in model Fe-surfactant melts and industrial alloys. It was shown that the degree of removal of the surfactant ( $\alpha_{\text{Surf}}$ ) is influenced by the lyophilic and lyophobic properties of the contact, the composition and size of the NPRP, the concentration in the melt and the kinetics of interaction with the surfactant. The processing of time dependences of surfactant removal is satisfactorily described by second-degree polynomial functions with the minimum extremum values for the systems: Fe-S -  $\alpha_s = 33.8$  rel.%; Fe-Sn -  $\alpha_{\text{Sn}} = 23.3$  rel.%; Fe-Sb -  $\alpha_{\text{Sb}} = 30.3$  rel. %; Fe-Cu -  $\alpha_{\text{Cu}} = 16.8$  rel.%. Using the large drop method, we studied the effect of NPRP on the capillary properties of melts and showed that, first, the values of  $\sigma$  of melts without NPRP, as a rule, are higher than with additives. Secondly, the values of  $\partial\sigma/\partial T$  change with the inverse of the values. Thirdly, as a rule, the degree of melting of the melts is greater with the introduction of NPRP into the metal. Investigated the removal of surfactants from steels of type 12Ch18N10T produced by Metallurgical Plant "Electrostal", JSC, and under laboratory conditions showed that after entering NPRP,  $\alpha_{\text{Cu}}$  values were up to 23 rel.% depending on the residence time of NPRP in the melt (240-1200 s.) and their concentration (0.06-0.18 wt.%).

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# **PHYSICAL - CHEMICAL BASES FOR THE CREATION OF NEW TECHNOLOGICAL SOLUTIONS FOR THE PRODUCTION OF HIGHLY STRENGTH CONSTRUCTIONAL STEELS IN THE PROCESSING OF PHOSPHORUS CAST IRON**

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In conditions of limited reserves of high-quality iron ore deposits and the presence of huge deposits of iron ore with a high phosphorus content, it becomes necessary to involve it in the processes of iron and steel production. The features of the chemical composition of phosphorous cast irons, the need to expand the grade composition of steel and the ever-increasing demands for its quality require special basic research aimed at developing the physicochemical and technological bases for the production of high-strength structural steels. Based on theoretical and experimental studies of the physicochemical features of oxidative processes and slag formation processes during the processing of phosphorous cast irons and the physicochemical properties of slags of the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-B}_2\text{O}_3$  system, formed on the ladle-furnace installations (CGP), physico-chemical fundamentals of deep dephosphorization of cast iron in a converter and direct microalloying processes with boron steel, combined with metal desulfurization, under basic boron-containing slags in the UCP. The developed technology provides improved technological and technical and economic indicators of redistribution of phosphorus iron in converters, boron content at the level of 0.001-0.008% and sulfur 0.004-0.0144% in the studied steel grades, reduction of manganese ferroalloys consumption by 0.3-0, 6 kg/t of steel, the formation of fine-grained structure and high strength properties of metal-roll structural steels of a wide brand composition. In particular, the strength properties of metal-roll tube steel grade 17G1S containing 1.4% manganese, 0.014% phosphorus, 0.006% boron and 0.003% sulfur corresponded without heat treatment to the strength class X 80.

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## COMPLEX EUDIALYTE PROCESSING

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The development of industrial processing of rare metals and rare-earth metals (REM) technology is one of the priority tasks of the whole industrial complex of the Russian Federation (RF). To this end, new deposits should be developed and new processing technologies introduced.

Eudialyte ores of the Lovosero Massif (Kola Peninsula, Murmansk region of RF) are actually unlimited supplies of zirconium, niobium, titanium, REM and manganese. The REM concentration in these ores can reach the value of 4 %, what exceeds that one of loparite and apatite.

To develop complex eudialyte processing, in this paper has been studied the influence of the sulfuric acid concentration and addition of the ammonium sulfate (percentage of the eudialyte concentrate mass) upon the extraction and distribution of the most valuable eudialyte components (Zr, Nb, Mn, REM et al.) between the solution and precipitate.

There had been found conditions of extraction of zirconium, niobium and manganese into the solution at the total its cleaning of silicon. In this case, 90 % of REM is concentrated in the silica precipitate (Fig. 1). Subsequently, zirconium, niobium and manganese can be extracted from the solution and REM –from the silica precipitate.

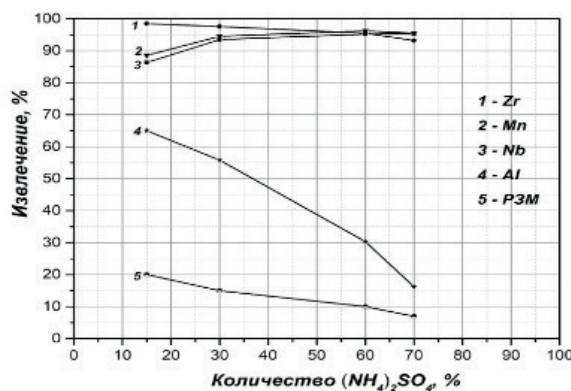


Fig. 1 – Influence of the ammonium sulfate percentage upon the extraction of Zr, Nb, REM, Al and Mn.



## RECOVERY OF HIGHLY PURE LEAD FROM LEAD BATTERY SCRAP

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Pyrometallurgical processing of lead battery scrap produces mainly lead of S2 and S1 grades.

Serious environmental problems caused by pyrometallurgical methods for processing of secondary lead-containing raw material have led to the development of various process schemes including hydrometallurgical operations. Our previous studies report recovery of lead metal from various technogenic lead wastes by electrolysis of carbonate melt.<sup>1-3</sup> To improve the purity of lead metal, in this work a combined technology is proposed.

It comprises the following steps:

1. Hydrochemical preparation of lead chloride from sulfate-oxide paste of waste batteries.
2. The lead chloride obtained was additionally purified by chlorination of molten  $\text{PbCl}_2$ .
3. Electrolysis of molten lead chloride.

Lead current efficiency was up to 98 %. Variations of temperature in the range 521–526 °C, cathode current density in the range 0.6–1.0 A/cm<sup>2</sup>, and anode current density in the range 0.24–0.40 A/cm<sup>2</sup> did not produce an effect on lead current efficiency. The lead obtained with respect to the content of impurities is similar to highly pure lead of S00 grade according to GOST 22861-93. The increase of the electrolysis current intensity did not influence the content of impurities in lead. The main impurities were Zn, Bi, Sb, Fe; their content was in the range  $(1-6) \cdot 10^{-4}$  mass %. The content of other impurities was in the range  $(1-8) \cdot 10^{-5}$  mass %.

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## TWO-STAGE SULFURIC ACID LEACHING OF PYRRHOTINE CONCENTRATES

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A progressive two-stage technological scheme for the processing of pyrrhotine concentrates and other types of poor copper-nickel raw materials is proposed.

Laboratory studies of two-stage sulfuric acid leaching of poor copper-nickel raw material - low-nickel middling ("MMC "Norilsk Nickel") with hydrolytic purification of the recycled solution from dissolved iron were carried out<sup>1,2</sup>. Autoclave hydrolytic purification of solutions from ferrous sulfate, as a separate operation between two leaching stages, allowed removing the iron without influence on sulfide concentrate - solid part of the pulp<sup>3</sup>. The oxidized ferrous cake (with a minimum content of non-ferrous and platinum metals), sulfide concentrate and pure recycled solution without iron were obtained. Then, in the second stage, the leaching of sulfide concentrate was carried out with a pure recycled solution, supported by sulfuric acid<sup>4</sup>.

It is shown, that for the full cycle - two stages - there are 60% of low-nickel middling leaches and only 40% remains in the form of a sulfide concentrate, containing 60-65% of elemental sulfur.

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*The work has been carried out according to the state task number 075-00746-19-00*

**THE ACTIVITY OF OXYGEN IN NICKEL MELTS,  
DEOXIDIZED BY ELEMENTS IIIA PERIOD OF THE PERIODIC TABLE  
D.I. MENDELEEV, AT  $P = 0.1$  MPa**

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A significant improvement in the service properties of the new nickel alloys for GTE blades is realized by obtaining in them a nanostructured state of the metal<sup>1</sup>. For this purpose, the melt is refined, deacidified and microlengthened AEM and REM in a vacuum induction furnace (VIF) to reduce concentrations of harmful impurities (oxygen, nitrogen, etc.) less than 0.001 wt. % of each to ensure the response of finishing REM with minimization of the formation of non-metallic inclusions and the creation of the necessary conditions for nanostructuring.

Oxygen is always present in the metal since the appearance of the liquid bath during the melting of the charge in the VIF. Therefore, the control of this element throughout the entire cycle of obtaining material is necessary. The method of instantaneous fixation of electromotive forces using certified Celox II Standart sensors was used to test  $a_{[O]}$  in Ni-O melts with the deoxidation of Mg, Al, Y, and REM (La, Ce, Pr, Dy) to 0.2 wt. % each at 1560 °C and was described the changes in  $a_{[O]}$  from the deoxidizer concentrations by logarithmic dependencies. When deoxidizing Mg, Al, Y (0.1 wt.% each), the values of  $a_{[O]}$  were calculated and showed an increase in the deoxidizing capacity of Mg by 5.4 times, Y in 3 times as compared to the deoxidizing ability of Al. When introduced into the metal (La, Ce, Pr, Dy (0.1 wt.% each)), the values of  $a_{[O]}$  were calculated and showed a change (increase) in the deoxidizing ability of La by 0.95 times, Ce by 8.4 times, Pr is 4.2 times, Dy is 6.1 times compared with the deoxidizing ability of Al. It can be used to determine the amount and order of introduction of rare-earth metals in nickel melts.

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## ANALYSIS OF CHANGES DIFFERENT TYPES OF NONMETALLIC INCLUSIONS DURING LADLE TREATMENT AND CASTING IF-STEEL

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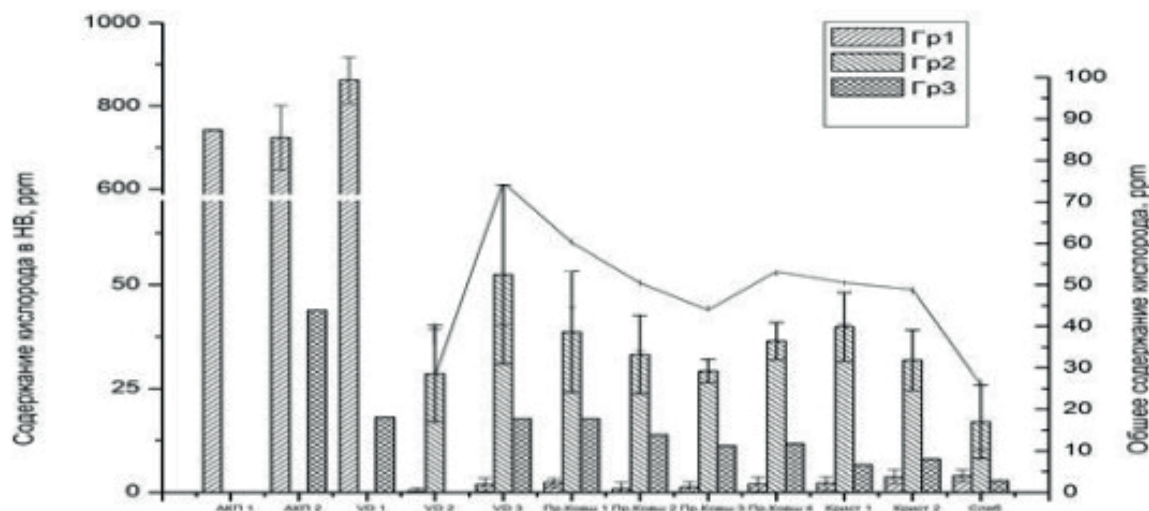
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To modern sheet steel for deep drawing make high demands on the plastic characteristics and strength of the finished metal. Non-metallic inclusions significantly affect the properties of finished steel, forming a variety of surface and internal defects.

In this paper analyzed the passports of the heats and selected metal samples at the stages of smelting, secondary treatment and casting. Using the methods of optical and electron microscopy and fractional gas analysis, the dynamics of changes in the content of the main types of nonmetallic inclusions in samples at various technological stages and their transformation is shown.



Three main groups of nonmetallic inclusions are distinguished: 1 — silicates, 2 — aluminates, 3 — spinels. The results of the study showed the possibility of improving technology in order to improve technical and economic indicators and product quality.

## PROCESSING OF BISMUTOTALITE CONCENTRATE BY MINERAL ACIDS

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Earlier authors studied a possibility to use solvometallurgical method to a complex extraction of niobium and tantalum from the perovskite of the Afrikanda deposit, the loparite of the Lovozero deposit, the plumbomicrolite of the amazonite deposit Ploskaya gora and the pyrochlore of the Beloziminsky deposit. In this paper we present development of a new technology for processing of bismutalante concentrate (BTC) with obtaining of tantalum, niobium and bismuth.

Samples of BTC contain, wt%:  $\text{Ta}_2\text{O}_5$  – 35.5;  $\text{Bi}_2\text{O}_3$  – 43.8,  $\text{Nb}_2\text{O}_5$  – 5.1. We have shown a possibility to extract niobium and tantalum at a low-temperature decomposition of BTC by hydrofluoric acid or a mixture of hydrofluoric and sulfuric acids. The process continues without heating due to a heat of an exothermal chemical reaction. We have determined conditions for an effective BTC decomposition that provides recovery of niobium and tantalum at a rate 97-99 % with the sum concentration in the solution not less than 160-190 g/l. Natural radionuclides U(IV) and  $\text{ThO}_2$  almost completely turn to poorly soluble fluoride compounds and concentrate in an insoluble bismuth fluoride cake. This happens at use of both pure hydrofluoric acid and a mixture of acids.

As an alternative, we have shown a possibility to extract niobium and tantalum together at a non-aqueous low-temperature decomposition of BTC by n-octanol hydrofluoric extract (solvoprocess). Direct recovery of niobium and tantalum to an extract during one chemical stage exceeds 99%<sup>1</sup>. At this bismuth concentrates in an insoluble fluoride cake. After sulfation of the cake and subsequent dissolution in nitric acid bismuth is released as a concentrated solution of bismuth nitrate.

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## COMBINED TREATMENT OF CHROMIUM ORE BY MICROWAVE IRRADIATION AND ACIDS

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Treatment of ore materials under microwave irradiation for maximum extraction of metals is one of the largely used and environmentally friendly methods. Combination of microwave irradiation with chemical treatment of ore let's possible to get more effective yield of metals.<sup>1,2</sup>

The optimal conditions for chromium extraction from ore of Shorzha deposition, Armenia, were obtained. The ore treatment by pure acids, as well as mixtures of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ , isn't effective for extraction of chromium. The most effective results were detected by using mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ .

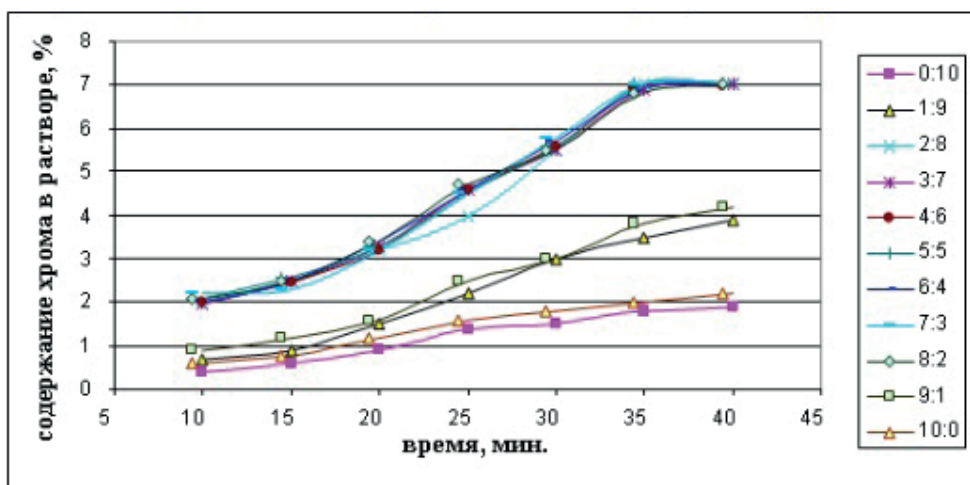


Fig. 1. Chromium content in solution vs. ore destruction time.  
Numbers in right are ratio of volumes (ml)  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ .

It was established experimentally that maximum destruction of chromium ore was detected at 503 K after 35 min., at power of heating 700 Wt and at ratio of  $V_{\text{H}_2\text{SO}_4}:V_{\text{HClO}_4}$  - 2 : 8; 3 : 7; 4 : 6; 5 : 5; 6 : 4; 7 : 3; 8 : 2 (Fig. 1).

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SOLUBLITY OF THE SYSTEM  $\text{Na,Ca//SO}_4\text{,CO}_3\text{-H}_2\text{O}$  AT 500C

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Solubility method investigated system  $\text{Na,Ca//SO}_4\text{,CO}_3\text{-H}_2\text{O}$  at 500C in order to determine the concentration parameters of the position of its geometric images and the ratio of the crystallization fields of the individual equilibrium solid phases. Experiments were performed according to the method of before saturation<sup>1</sup>. The establishment of equilibrium was determined by the invariance of the phase composition of the sediments for 50-100 hours. The results of crystal optical analysis of the equilibrium solid phases (micrographs), the composition of saturated solutions characterizing equilibria on invariant fields monovariant curves and nonvariant points as well as the solubility diagram of the system itself are presented in<sup>2</sup>. The table shows only the compositions of saturated solutions, characteristic of nonvariant points of four component level.

Table. System solubility  $\text{Na,Ca//SO}_4\text{,CO}_3\text{-H}_2\text{O}$  in nonvariant points at 500C

Composition of the liquid phase, mas. %					Precipitation phase composition
$\text{Na}_2\text{SO}_4$	$\text{CaSO}_4$	$\text{Na}_2\text{CO}_3$	$\text{CaCO}_3$	$\text{H}_2\text{O}$	
1.52	0.14	3.74	—	94.6	Te+Br+Gb
3.71	—	13.98	0.003	82.30	Cx1+Br+Pr
8.92	0.16	—	0.004	90.91	Gp+Cc+Gb
—	0.13	2.77	0.004	97.09	Cc+Pr+Gb
6.17	—	9.01	0.006	84.81	Gb+Br+Pr

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## EXTRACTION OF VANADIUM FROM THE SLUDGES OF THERMAL POWER PLANTS FROM BURNING FUEL OIL

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Sludges of thermal power plants from burning fuel oil are not only environmentally hazardous waste products, but perspective source of vanadium and nickel. In sludge storage different TPP of Russia has been accumulated tens of thousands this sludges, which content significant amount of water soluble toxic substances of vanadium.[1] Thus, finding an effective way method of recycling and disposal this sludges with extraction of vanadium and nickel makes it possible to obtain valuable commodity product and improve the ecological situation in the area of the sludge storage. The work was investigated sample of sludge with TPP in Konakovo with  $V_2O_5$  and NiO content 7,8% and 0,6% respectively and Italian sludges of TPP in Cagliari, in which the content of  $V_2O_5$  and NiO 50,0% and 4,2% respectively. The studied method of extracting vanadium and nickel into solution includes the preparation with addition of sodium carbonate, oxidative roasting, sequential water and sulphate leaching. In this work, the influence of the type of mixing (dry and wet), the effect of direct steam on oxidative roasting, the effect of  $Na_2CO_3$  addition, the duration of oxidative roasting were investigated. As a result of the research, the maximum degree of extraction of  $V_2O_5$  and Ni for Russian sludge was 75.6% and 58.0%, respectively. 96.3% of  $V_2O_5$  and practically all Ni were recovered from Italian sludge.

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## OBTAINING AL-B ALLOYS BY REDUCTION OF BORON OXIDE IN THE CRYOLITE MELTS

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When producing Al-B alloys, it is of interest to use boron oxide  $B_2O_3$ , instead of  $KBF_4$ , as a source of boron because this component is cheaper and enriched with boron. However, attempts to obtain the Al-B master alloy directly in the aluminum electrolysis cell at a temperature of about 960 °C were unsuccessful due to the process instability and the large sludge of the bath with the aluminum oxide.

Research in the field of the physicochemical properties of low-melting mixtures based on the potassium cryolite, containing  $B_2O_3$ , revealed that the  $Al_2O_3$  solubility in the  $KF-AlF_3$  and  $KF-AlF_3-(5 \text{ mol.}\%)B_2O_3$  melts is comparable. Therefore, the aluminothermic and electrolytic reduction of the  $B_2O_3$  were carried out in these electrolytes.

The Al-B alloy with a low boron content (0.13 wt%) was produced during the aluminothermic synthesis using the  $B_2O_3$  as a boron-containing raw material and the  $KF-AlF_3$  salt flux with  $X_{KF}/X_{AlF_3}=1.5$  at 800 °C. The micrographs of the alloy cross-sections, whose microstructure was analyzed using a DMAX-2500 analyzer (Rigaku) and a JMS-5900LV scanning electron microscope with INCA Energy 200 microanalyzer and INCA Wave 250 energy dispersive microanalyzer (JEOL), revealed a high content of the  $Al_2O_3$ . Indeed, the  $Al_2O_3$  can be formed as a result of several reactions, at interaction of the  $B_2O_3$  both with liquid Al, and with potassium cryolite:



The electrolysis in the  $KF-AlF_3-B_2O_3$  melt with  $X_{KF}/X_{AlF_3}=1.3$  at a temperature of 700 °C was steady, and within 24 hours the Al-B alloy with a boron content of 7.5 wt% was obtained. The process is accompanied by a continuous electrochemical reduction of the  $Al_2O_3$ , i.e. the electrolyte regenerates in situ. Analysis of the alloy microstructure indicated the presence of intermetallic  $AlB_2$ .

## MUTUAL IMPACT OF COMPLEX FLUOROMETALLIC ACIDS $\text{H}_2\text{SiF}_6$ AND $\text{H}_2\text{TlF}_6$ AT THEIR EXTRACTATION BY NEUTRAL PHOSPHORUS - AND OXYGEN CONTAINING EXTRAGENTS

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A rare-earth raw material is usually processed by a hydrofluoride method. Niobium, tantalum and titanium from the raw material pass into solution as complex fluorometalate acids along with silicon during the processing. It is possible to concentrate and separate these acids by solvent extraction. Thus, study of behavior and mutual impact of fluorometalate acids in extraction processes in fluoride media is important and relevant.

We have researched extraction of complex fluorometalate acids (fluorotitanium (FTA) and fluorosilicate (FSA)) both separately and together with monohydric aliphatic alcohols of various isomers ROH ( $\text{R}=\text{C}_5\text{-C}_{10}$ ), with a mixture of alcohols and with addition of tributyl phosphate.

We have demonstrated that effective extraction of pure FTA by aliphatic alcohols depends on the nature and isomer of alcohol, and on titanium concentration in the initial solution. We have studied density, viscosity and conductivity of aliphatic alcohols extracts containing  $\text{SiO}_2$ . These properties were shown to depend on aliphatic alcohol structure, electrolyte concentration in extracts and the acid dissociation rates. When both FTA and FSA are present in a solution, fluorometalate acids mutually impact each other, which leads to suppression of FSA extraction and improvement of FTA extraction by studied extractants. FSA decreases a degree of pre-evaporation of FTA during a technology of fluoride extraction of titanium. This allows us to extract titanium effectively from solutions with neutral extractants at lower concentrations. The latter will lead to a decrease in process energy consumption.

## RESOURCE-SAVING ELECTROCHEMICAL TECHNOLOGY OF PROCESSING DRAINS OF METALLURGICAL PLANTS

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Processing, cleaning and utilization of highly mineralized sewage from metallurgical production are currently one of the most pressing environmental problems. According to the implementation of the national project «Ecology» of the Russian Federation in 2018-2024, it is necessary to develop environmental standards for the disposal of industrial waste, to develop and implement energy-saving technologies for processing and cleaning the effluents of industrial enterprises.

Various technologies for wastewater treatment exist and are used: physicochemical, reagent methods, mechanical,<sup>1</sup> electromembrane and others. In this work, the electrochemical method (electrodialysis with bipolar membranes)<sup>2</sup> of wastewater treatment was used.

The object of the study was the solution that simulates the effluent of vanadium production (containing heavy metal ions and sulfate ions) with a sulfate concentration of 20-22 g/l. The experiments were carried out on a multi-chamber electrodialysis cell EDS. The membrane package of EDS was made with ion-exchange membranes of domestic production: monopolar MA-41, MK-40 and bipolar MB-3 with a working size of 5 cm \* 20 cm = 100 cm<sup>2</sup>.

Thus, it was possible to process more than 90% of the initial vanadium-containing solution. According to the standards, the purified solution (sulfate concentration less than 2 g/l) is allowed to be used for technical purposes. The concentrated solution is supposed to be further processed for the selective extraction of vanadium and other valuable components. Analysis of the research data indicates the possibility of creating a promising, resource-saving, environmentally friendly technology for processing the effluents of metallurgical enterprises.

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## USING N,N,N',N'-TETRAOCTYLDIGLYCOLAMIDE IN SCANDIUM EXTRACTION

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N,N,N',N'-tetraoctyldiglycolamide (TODGA) was considered as the extractant for processes of scandium extraction from complex multicomponent solutions.

The effects were studied on the values of the distribution coefficients (D) of scandium, lanthanum, ytterbium, thorium and calcium by various diluents (chloroform, dodecane, hexachlorobutadiene, linear alkyl benzene, decanol, toluene, CCl<sub>4</sub>, pseudocumene, p-xylene, fluoroheptanol) in the extraction with 0.1 mol/L TODGA from 1 mol/L HNO<sub>3</sub>. It is found that the minimum values of the Sc distribution coefficients are observed for chloroform, the maximum values are observed for dodecane, decanol and toluene. In most cases, the order of extractability is as follows: Ca < La < Th < Sc < Yb. There is no correlation with the polarity of the diluents considered.

Scandium extraction from nitric acid, hydrochloric acid and sulfuric acid solutions were investigated for 0.1 mol/L TODGA in dodecane. It is found that almost complete extraction of scandium occurs at a concentration of nitric acid more than 2 mol/L; the scandium extraction factor from hydrochloric acid solutions does not depend significantly on the concentration of hydrochloric acid and does not exceed 60%; in the case of the use of sulfuric acid at a concentration of H<sub>2</sub>SO<sub>4</sub> 2-3 mol/L, the scandium extraction factor is not more than 40%.

Throughout the considered mineral acids concentrations range, hydrochloric acid and sulfuric acid are not extracted by TODGA, there is only an insignificant transition HNO<sub>3</sub> into organic phase.

The effect of salting-out agent (LiNO<sub>3</sub>) on Sc extraction from aqueous solutions containing 0.5 mol/L HNO<sub>3</sub> was investigated; at a concentration of LiNO<sub>3</sub> > 3 mol/L, the Sc extraction factor into the organic phase exceeds 98%. The scandium liquid extraction possibility with TODGA from mixed nitrate-sulfate solutions is also considered. The presence of different LiNO<sub>3</sub> concentrations in 3 mol/L H<sub>2</sub>SO<sub>4</sub> does not lead to a significant increase in D Sc, the its maximum extraction factor does not exceed 44%.

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## PROPERTIES OF TUNGSTEN IN DIFFERENT P-T CONDITIONS

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The formalism from<sup>1,2</sup>, tested on iron, diamond, silicon, germanium, and molybdenum, was used for calculations of the thermodynamic properties of bcc tungsten. The four parametric potential of Mi – Lennard – Jones was used To describe the pair interatomic interaction:

$$\phi(r) = D/(b - a) [a(ro/r)b - b(ro/r)a], \quad \text{where } D, ro, b > a > 1 - \text{parameters.} \quad (1)$$

In this work parameters (1) are determined by optimization according to the isotherm of the equation of state  $P(V/V_0, T = 300 \text{ K})$  and by the volumetric coefficient of thermal expansion<sup>3</sup>:  $\alpha_p(P = 0, T = 300 \text{ K}) = 13.01 \cdot 10^{-6} \text{ K}^{-1}$ .  $V/V_0$  – crystal volumes ratio at  $P$  and  $T$ , and at  $P = 0$  and  $T = 0 \text{ K}$ . Thus we have obtained parameters values of potential (1):  $r_o = 2.7365 \cdot 10^{-10} \text{ m}$ ,  $D/k_B = 40000 \text{ K}$ ,  $a = 2.6$ ,  $b = 7.2$ , where  $k_B$  – is the Boltzmann constant. Our calculations (solid line) for  $P(V/V_0, T = 300 \text{ K})$  and literature data are shown at fig. 1. We also calculated the pressure dependencies for: Debye temperature; three Grüneisen parameters; isothermal bulk modulus; specific surface energy и  $\alpha_p(P)$  (shown at fig. 2) along two isotherms 300 and 3000 K. Baric dependencies of pressure derivatives for indicated properties at 300 and 3000 K are obtained at first time.

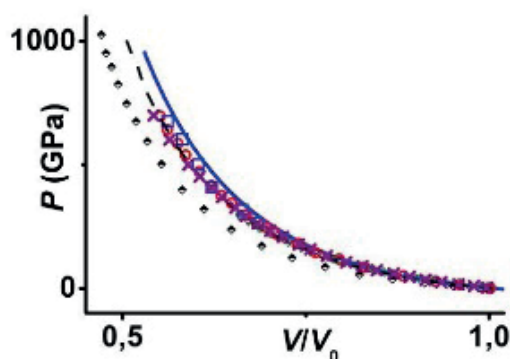


Figure 1. Tungsten EOS isotherm at  $T = 300 \text{ K}$ .

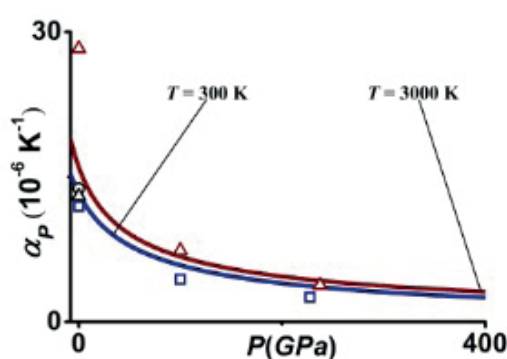


Figure 2. Baric dependencies of  $\alpha_p(P)$ . Symbols – literature data.

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## BARIC DEPENDENCE OF NIOBIUM MELTING TEMPERATURE FOR MACRO AND NANO-CRYSTALS

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Formalism from<sup>1</sup> was used for bcc-Nb melting temperature  $T_m(P)$  baric dependence calculations. The four parametric potential of Mi – Lennard – Jones was used to describe the pair interatomic interaction, potential parameters are:  $r_o = 2.8648 \cdot 10^{-10}$  m,  $D/k_B = 30200$  K,  $a = 2.3$ ,  $b = 6.2$ , where  $k_B$  – is the Boltzmann constant. Based on the Lindemann melting criterion and the state equation obtained by us, for the dependence  $T_m(P)$  we obtained<sup>2</sup>:  $T_m(P) = T_m(0)[V(P)/V(0)]^{2/3}[\Theta(V(P)/V(0))/\Theta(V(0)/V(0))]^2$ , where  $T_m(0)$  and  $V(0)$  – melting temperature and volume at  $P = 0$ ,  $V(0) = N \pi r_o^3 / (6 k_p)$ ,  $k_p$  – packing factor.

We have calculated  $T_m(P)$  and  $T'_m(P)$  for macrocrystal ( $N = \infty$ ) and nanocrystal of cubic form with  $N = 83$  atoms, using for Nb<sup>3</sup>  $T_m(0) = 2742$  K. Method from<sup>2</sup> has been used for nanocrystal properties calculations.

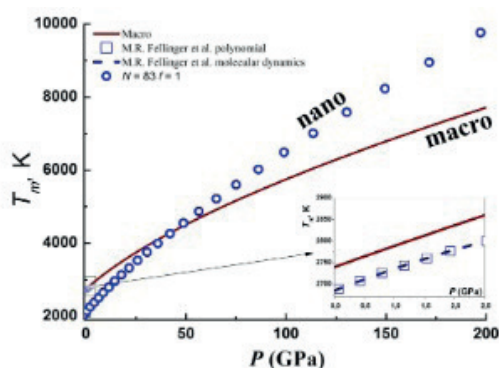


Figure 1. Our calculations of  $T_m(P)$  – solid curve. circles – calculations for nanocrystal (at  $N = 83$ ). Squares and dotted curve – data from<sup>3</sup>.

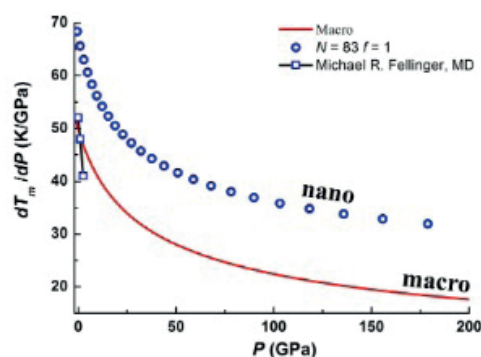


Figure 2.  $T'_m(P)$  dependence. Circles – our calculations for nanocrystal (at  $N = 83$ ), solid curve – for macrocrystal. Symbols – data from<sup>3</sup>.

We compared  $T_m(P)$  and  $T'_m(P)$  with the results of<sup>3</sup>, since there is no experimental data for  $T_m(P)$  of Nb macrocrystal in literature.

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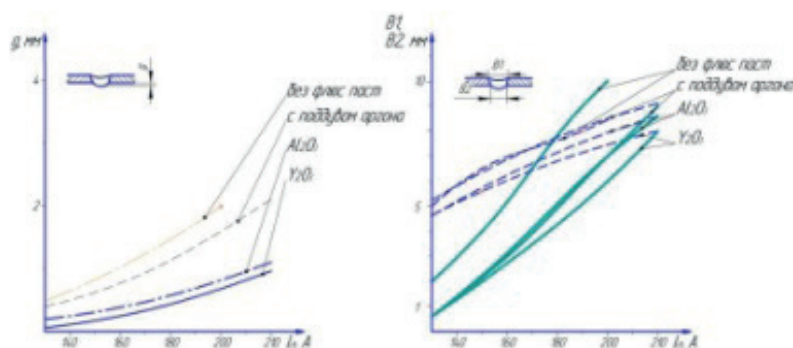


THE USE OF SURFACE-INACTIVE SUBSTANCE TO STABILIZE  
THE PARAMETERS OF WELDED JOINTS

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The shape of the seam made with full penetration of the edges, in accordance with the static equilibrium scheme adopted in the works<sup>1,2</sup>, is determined by the condition of equilibrium forces acting simultaneously on the molten metal bath (gravity, arc pressure and surface tension). Changes in the weld pool, arc pressure, surface tension coefficients or radii of curvature of the free surfaces of the molten weld pool metal, which can be caused by a variety of reasons, should lead to a change in the main dimensions of the weld and, in particular, its sagging (strengthening or weakening) as with arc side and root side<sup>2</sup>.



Picture 1. Effect of welding current ( $I_w$ ) on geometric parameters reverse roller with different composition and without surface-inactive substances:  $S = 3$  mm, GOST 14771-76 C2,  $L_{arc} = 2$  mm;  $V_w = 16$  m / h;  $d_e = 4.0$  mm; protective gas Ar.

The use of surface-inactive substances (PIAV), applied to the back side of the butt joint when welding low-alloyed steels, allows you to control the size of the resulting root weld layer and increase the range of welding currents, ensuring its defect-free formation.

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## ELECTROCHEMICAL MACHINING UNDER THE CONDITIONS OF THE ELECTRODE-TOOL SPATIAL DISPLACEMENTS

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Electrochemical machining (ECM) is one of the methods of processing difficult-to-work materials. The best results were achieved when using ultra-small interelectrode gaps (IEG), of the order of  $1\text{ }\mu\text{m} - 30\text{ }\mu\text{m}$ . However, at such values of the IEG, the electrolyte flow is difficult or impossible. In this connection, the need arises to use the ECM in pulse-loop mode, i.e. in the moving electrode-tool (ET) to the flushing gap ( $1\text{ mm} - 2\text{ mm}$ ), which leads to a decrease in the overall performance of the ECM.

It is possible to use an ECM mode under the condition of the ET spatial displacements to preserve the constancy of the interelectrode environment properties and regeneration of the electrolyte. At the same time, the electrolyte will be regenerated due to the moving of ET to a new treatment area. The use of this machining mode makes it possible to reduce the power consumption of the machining by reducing the treatment area, as well as to improve the overall performance of the machining as compared to the pulse-loop mode.

The velocity of ET displacement along the treatment surface is one of the important parameters of this ECM mode, as it determines the velocity of electrolyte regeneration in the IEG.

Experimental studies were carrying out on steel grade 12X18N10T GOST 5632-72. The electrode tool was made of brass of the LO 70-1 GOST 15527-70 brand with a ratio of the areas of the treatment surface and the working part of the tool 12:1. The velocity of ET displacement varied from  $50\text{ mm / min}$  to  $300\text{ mm / min}$ . The value of the IEG was  $30\text{ }\mu\text{m}$ , the electrolyte was 10 %  $\text{NaNO}_3$ .

An analysis of the experimental results showed the following: the highest current density was achieved at a displacement velocity of  $300\text{ mm / min}$  and was  $135\text{ A / cm}^2$  versus  $80\text{ A / cm}^2$  at a velocity of  $50\text{ mm / min}$  (area ratio 12:1), which indicates an improvement in the evacuation conditions of the treatment products and about updating the electrolyte.

Thus, the application of the proposed ECM mode will allow to increase the performance of the machining, as well as reduce its power consumption.

## CALCIOTHERMIC REDUCTION OF ZIRCONIUM OXIDE COMPOUNDS

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Calciothermic reduction of  $\text{ZrO}_2$  is one of the industrial ways to produce zirconium powder. The process is conducted at 900-1300 °C. In order to reduce the content of oxygen in the powders an excess amount of calcium, prolonged holding time (1-5 h) and addition of  $\text{CaCl}_2$  are used to dissolve the by-product  $\text{CaO}$ <sup>1,2</sup>.

Thermodynamic analysis with the application of program complex TERRA made it possible to calculate adiabatic temperatures of calciothermic reduction of  $\text{ZrO}_2$  и  $\text{CaZrO}_3$  (1252 and 767 °C correspondingly) and demonstrate the possibility to conduct the process at the temperatures below the temperature of melting Ca. In the present work, the possibility to produce Zr powders at the temperatures below 850 °C is studied.

The source materials for the reduction were powder of  $\text{ZrO}_2$  with surface area of 0,7 and 35 m<sup>2</sup>/g and powder of  $\text{CaZrO}_3$  zirconate (0,45 m<sup>2</sup>/g). The excess amount of reductant, for which Ca grain with the particle size of 0,04-2,0 mm was used, constituted 25-50% of stoichiometry.

The reduction was performed in a retort made of high-temperature steel where niobium containers with prepared mixture were placed. The scheme and description of the device are presented in the work<sup>3</sup>. The reactor was vacuumized, filled with argon and heated to 700-850 °C, following which the holding was performed for 1-3 h. To remove the excess amount of Ca and by-product CaO the reduction products were processed with the solution of hydrochloric acid.

As a result, the conditions were defined experimentally, which allow to produce the zirconium powder with a low content of hydrogen at temperatures 700-750 °C. By the reduction of  $\text{ZrO}_2$  and  $\text{CaZrO}_3$  at 700 °C the powders were produced correspondingly with specific surface on the level 0,6 and 1,5 m<sup>2</sup>/g, where the content of hydrogen is 0,7 and 1,5 %.

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## PROCESSING OF HEAVY TUNGSTEN ALLOYS WASTE BY DC/AC ELECTROLYSIS

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Nowadays, tungsten recycling is an important scientific task. Waste of heavy tungsten alloys, widely used in the production of subcalibre armor-piercing ammunition is of particular interest<sup>1</sup>.

The process of tungsten electrochemical extraction from the heavy tungsten alloy of NVG type (90% W, 7% Ni, 3% Fe) by the using of direct current (DC) in alkaline solutions slows down with a passage of time. This leads to a need of activating the surface of dissolved alloy, enriched in nickel and iron<sup>2</sup>. The most promising way of alloy surface depassivation is the electrolysis under the influence of an alternating electric current (AC). The effect of AC on nickel and iron electrodes leads to the formation of ultra microdispersed powders of these metals in alkaline solutions<sup>3</sup>.

In this work, an environmentally safe hydrometallurgical process of valuable components regeneration from heavy tungsten alloys was studied as an example of NVG alloy in alkaline solutions under the influence of direct and alternating electric current. The high degree of tungsten extraction into solution is achieved by DC polarization of alloy with current efficiency close to 100%. AC polarization of alloy results in depassivation of its surface and concentration of microdispersed powder, based on nickel and iron, in the electrolytic residual. Commercial products (ammonium paratungstate, tungstic acid and etc.) are produced from tungsten electrolyte; electrolytic residual can be used as a catalyst for the production of carbon nanostructured materials after hydrogen reduction stage.

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## THE STUDY OF OPTIMAL PARAMETERS OF SOLID-PHASE RECOVERY OF THE IMMENITE CONCENTRATE OF THE MALYSHEVSKOE DEPOSIT

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Titanium belongs to a group of metals, the unique properties of which ensured their widespread use in leading industries. Despite the wide variety of deposits, industrial reserves of titanium are mainly represented by ilmenite and rutile, the main minerals of which titanium, its pigmented dioxide and other compounds are produced on a large industrial scale.

Today, the most common method for producing titanium is the Kroll method, the first stage of which is the ore-thermal smelting of titanium charge at a temperature of  $1800 \pm 100^\circ\text{C}$ <sup>1</sup>. As a significant disadvantage of this stage, we can note the high energy consumption, the duration of the process and the large losses of fine raw materials resulting from its transportation. In order to reduce energy consumption and loss of expensive raw materials in the process of pulverizing the fine fraction of ilmenite concentrate, it is advisable to use less energy-intensive two-stage technologies, the essence of which is solid-phase reduction of ilmenite concentrate granulated with a reducing agent, followed by grinding and separating the reduced iron fraction by magnetic separation.

The aim of the presented work was to determine the optimal parameters of the solid-phase reduction process of the ilmenite concentrate of the Malyshevskoe deposit.

As a result of the studies performed, the optimal particle size characteristics of ilmenite concentrate and the temperature and time parameters of reductive roasting of ore-coal briquettes, ensuring the most complete extraction of iron in the metal phase, are established. It was shown that without using additional methods to intensify the process of reducing iron oxides, the optimum temperature range of the process was 1300-1350°C.

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## THERMODYNAMICS OF PHASE TRANSITIONS IN THE IRON-OXYGEN SYSTEM

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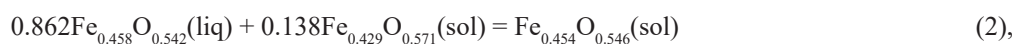
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There are three stable solid compounds in the iron–oxygen system: iron (III) oxide  $\text{Fe}_2\text{O}_3$  – hematite, iron (II, III) oxide  $\text{Fe}_3\text{O}_4$  – magnetite (melting point at 1870 K), iron (II) oxide  $\text{FeO}$  – wustite<sup>1</sup>. Wustite, a non-stoichiometric phase, is formed by the peritectic reaction:



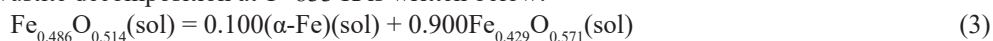
Reaction (1) is written in a formal way and not balanced.

It is proposed to write chemical formulas per mole of atoms of the compound, i.e.  $\text{Fe}_{2.000}\text{O}_{3.000}$ ,  $\text{Fe}_{3.000}\text{O}_{4.000}$ ,  $\text{FeO}$  at peritectic transition temperature  $T=1697\text{ K}$  –  $\text{Fe}_{0.454}\text{O}_{0.546}$  (oxygen-rich wustite). Using the level rule, equation of peritectic reaction should be written as follows:



Reaction (2) is balanced, the total mass of the reactants equals the mass of the product.

Equation of eutectoid reaction of wustite decomposition at  $T=833\text{ K}$  is written below:



Considering the area of homogeneity of magnetite at high temperatures, reaction of hematite formation at  $T=1730\text{ K}$  is:



Magnetite  $\text{Fe}_{0.429}\text{O}_{0.571}$  is characterized by more negative values of Gibbs free energy of formation ( $\Delta G_{1000} = -113.1\text{ kJ}\cdot\text{mol}^{-1}$ ) in comparison with hematite  $\text{Fe}_{0.400}\text{O}_{0.600}$  ( $\Delta G_{1000} = -112.9\text{ kJ}\cdot\text{mol}^{-1}$ ) in the temperature range of 1000–1800 K, thus, the correlation indicated by Kubaschewski and Evans<sup>2</sup> is observed.

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## PERSPECTIVES OF THE INDIVIDUAL COMPLEX PROCESSING OF HIGH PYRITOUS CONCENTRATES

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Presented work is dedicated to development of physico-chemical and technological bases of the individual complex processing of the high pyritous lead concentrates, by the method of the blast furnace reducing melting<sup>1</sup>. Sulphide lead concentrates, used in our research, have been obtained by means of flotation of hardenrichable Filizchay polymetallic ores. In large-scale laboratory conditions was, obtained the qualitative high feriferous lead sinter. The reducing melting of the obtained lead sinter has been carried out in laboratory conditions by use of conversed natural gas or natural gas in mix with water vapours as a reducer.

Possibility of the effective processing of Filizchay lead concentrates according to proposed technology is confirmed by means of results of industrial trials of high pyritous lead concentrates processing by the blast furnace reducing melting method. With use of the results of our investigations. The results of plant processing have indicated, that low lead losses with the slag can be achieved with the moderate sinter throughput – 50 ÷ 60 tonnes/m<sup>2</sup> with a CaO/SiO<sub>2</sub>=0.70 – 0.74 and FeO concentration in the slag in the ranges of 38.4÷41.0 wt.%. The concentrations of CaO and SiO<sub>2</sub> in the lead sinter are above of 6.5 – 7.5 and 10.0÷12.0 wt.% respectively. The plant slangs liquids temperature is estimated to be ~1170°C. Elaborated technology of the individual complex processing of high pyritous lead concentrates is of a great aconomic importance for an increase of extraction of lead, silver and bismuth into the lead bullion, the low content of the lead losses slag obtaining of burning gases “rich” in SO<sub>2</sub>, that is necessary for the sulphuric acid production an an output of additional volume of commodity product at the ax pence of high composition of noble metals and bismuth.

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## PRINCIPLES OF PROCESS CONTROL FOR PRODUCING AMORPHOUS WIRES FROM THE MELT FOR MEDICAL USE

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Amorphous metal wires 20 to 150 microns in diameter endowed with a complex of unique mechanical, biochemical and magnetic properties have a great future in the manufacturing of new medical instruments and products. The Ulitovsky-Taylor method is the exclusive one to produce amorphous wires over a wide diameter range. A laboratory set-up prototype was made to produce rapidly quenched wires. The prototype unit is equipped with the set of high-precision machinery and instruments, the software package has been developed. Analysis of the factors, that maintain automatic process control and manufacture of long-length geometrically stabilized amorphous wires with high level mechanical properties, has been carried out<sup>1</sup>. The process maintenance method has been implemented based on continuous template matching in area, shape, and position of the melt drop in the inductor. The key parameters, having control over manufacturing from the melt of the given diameter amorphous wire, are determined. Fixed parameters being: area, geometric shape, and the melt droplet temperature, the position of the droplet relative to the inductor and to the surface of the quenching device, the temperature of the quenching fluid, the speed of the winding wire. Variable parameters to be regulated automatically: displacement speed of the core precursor and of the glass tube. The current values of the glass tube and precursor displacement speeds, the underpressure values, the specified wire diameter, the temperature of the replenished melt drop, the drop shape and volume, the deviation from the specified graphical template are continuously recorded on the monitor and are stored in the computer memory. A pilot series of long-length flexible amorphous wires 50 to 150 microns in diameter was made from the Co-alloy. The wires obtained are taken for the manufacturing of medical devices prototypes.

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## STRUCTURE, MECHANICAL AND CORROSION PROPERTIES OF COLD DEFORMATION NITROGEN AUSTENITIC STEELS

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The Arctic reclamation is the most significant economic direction in Russia. Taking into account the influence of aggressive environment and negative temperatures materials with special behaviors are required for development seacoast and offshore area infrastructures. One of the problems solving for marine construction building including for arctic service can be austenitic stainless steels using.

Austenitic stainless steels have a good combination of ductility and toughness included in low-temperature range. Strength properties of austenitic stainless steels rise is provided by cold deformation which is employed for rolled sheets and pipe productions. But in the same time strain-induced martensite can form in the steel structure. It makes worse ductility, magnetic and corrosion properties.

The cold deformation influence researches on structure, mechanical and corrosion properties was carried out on nitrogen austenitic stainless steels compared with Fe-18Cr-10Ni steel. Fe-20Cr-6Ni-11Mn-2Mo-N-V-Nb and Fe-18Cr-10Ni alloys were cold rolled at the room temperature from 15 to 47%. The deformation increasing led to hardening both steels. The nitrogen austenitic stainless steel yield strength reached 1300MPa while yield strength of Fe-18Cr-10Ni steel didn't exceed 1000 MPa with the same values impact toughness. Optical microscope examination has revealed that both steels had austenitic structure which is stable to strain-induced martensite formation. It was observed that percent reduction increasing promoted elongation grains and dislocation density growth. Corrosion testing was shown that cold deformation nitrogen alloyed stainless steels is less susceptible to pitting corrosion as opposed to Fe-18Cr-10Ni steel. Correlation between corrosion rate and degree of reduction has a non-monotonous character.

The cold plastic deformation of Fe-17Cr-7Mn-N and Fe-18Cr-10Ni steels at low-temperature was carried out with plane sample tension. There was 9% martensite deformation in nitrogen steel and 20% martensite deformation in Fe-18Cr-10Ni steel. For martensite detection metallography, EBSD-analysis and magnetometric methods (determining the amount of ferromagnetic phase and permeability measurement) was used. Corrosion testing was shown that martensite presence (different for each steels) increased pitting potential and further rise of martensite amount adverse affected on the corrosion resistance.

## DETERMINATION OF THE PHASE COMPLEX OF THE SYSTEM Na,K//SO<sub>4</sub>,CO<sub>3</sub>,HCO<sub>3</sub>,F-H<sub>2</sub>O AT 0°C IN THE NAHCO<sub>3</sub>) CRYSTALLIZATION REGION

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Nahcolite (NaHCO<sub>3</sub>) is an equilibrium phase in 6 out of 14 four –component systems and in 4 out of 6 five –component systems that make up the six –component systems under the study, which the regularities of the phase equilibria rationalize the conditions of complex processing of natural polymineral and complex technical crude. Phase equilibria in the research system at the 0°C in the crystallization region of NaHCO<sub>3</sub>, determined by the method of translation<sup>1</sup>, which was recognized by experts, one of the most universal<sup>2</sup> in the study of multicomponent systems.

It is set in that nahcolite (NaHCO<sub>3</sub>), participates in the formation of 18 divariant fields, 16 monovariant curves, and 5 nonvariant points. Based on the data obtained, a closed phase diagram (phase complex) of the system under study at 0°C in the region of crystallization of nahcolite (NaHCO<sub>3</sub>), which is fragmented by divariant fields<sup>3</sup>, was constructed.

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# **ACTIVITIES OF OXYGEN IN METALLIC SOLUTION FE-CR-NI-MN-C-O FOR OXIDATION PROCESS ANALYSIS IN TECHNOLOGY OF ALLOYED STEEL PRODUCTION.**

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For the standard state of oxygen dissolved in a liquid metal was adopted pure gaseous oxygen at pressure  $P_{O_2}^{\frac{1}{2}} = 1$  on reaction  $\frac{1}{2}O_2 = O$ , for dissolved carbon - pure solid carbon, for solvent metal - pure liquid metal.

The oxygen activity in a multicomponent metallic solution in equilibrium with the slag components and with gaseous phase  $P_{CO}=1P_{CO}=1$  in the oxidation in reactions of the metallic components with gaseous oxygen is calculated by the equation

$$a_{O(equil)} = (\sum a_{MeO} + P_{CO}) / (\sum K_{MeO} a_{MeO} + K_{CO} a_C) \approx (\sum x_{MeO} + 1) / (\sum K_{MeO} x_{Me} + K_{CO} x_C)$$

At the end of the oxidation period of experimental melt of alloyed steel Cr18Ni10 in 20-ton arc furnace the samples were taken from metal and slag, the activity of oxygen in the metal is equal to  $a_{O(equil)} = 1,04 \cdot 10^{-4}$ .

The actual activity of oxygen in the liquid metal at this experimental melt was calculated by the result of the measurement  $E = -0,08$  V by electrochemical oxygen sensor Cr-Cr<sub>2</sub>O<sub>3</sub>|ZrO<sub>2</sub>(MgO) is equal to  $a_{O(ET)} = 1,67 \cdot 10^{-4}$ .

In none equilibrium thermodynamics<sup>1</sup> the driving force of the oxidation process A was calculated as difference between the actual and equilibrium chemical potentials of oxygen

$$A = \mu_{O(E,T)} - \mu_{O(equil)} = RT \ln a_{O(ET)} - RT \ln a_{O(equil)} = RT \ln (a_{O(ET)} / a_{O(equil)}) = 9 \text{ kJ/mole}$$

Results of calculations show that it is possible to use the theory of oxygen activity in multicomponent metal solutions to analysis the completion level of the technological processes of alloyed steel oxidation.

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## DENDRITIC CRYSTALS OF PRIMARY AUSTENITE IN GREY CAST IRON AND MECHANICAL PROPERTIES OF CASTINGS

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Gray cast irons with flake graphite, with eutectic degree from 0.82 to 1.0 were investigated. The base of industrial tests included 142 specimens of cupola melting and about 70 specimens of cast iron of induction melting. The chemical composition of the studied cast irons corresponded to pearlitic class from SCh 15 to SCh 35 (Russian state standard specification 1412-85). The amount of carbon was ranging from 2.98% to 3.47%, silicon from 1.75% to 2.85%, and manganese was characterized by almost constant value of 0.79%, the content of sulfur and phosphorus corresponded to 0.1% and 0.14%.

The relationship between tensile strength  $\sigma_B$  and Brinell hardness HB of different grey cast irons was investigated. It was found that at the same hardness values the tensile strength of different specimens may differ by almost two times. It was shown that the mentioned above tensile strength scatter is caused by the different volume fraction of dendritic crystals of a primary austenite  $f_{dc}$ .

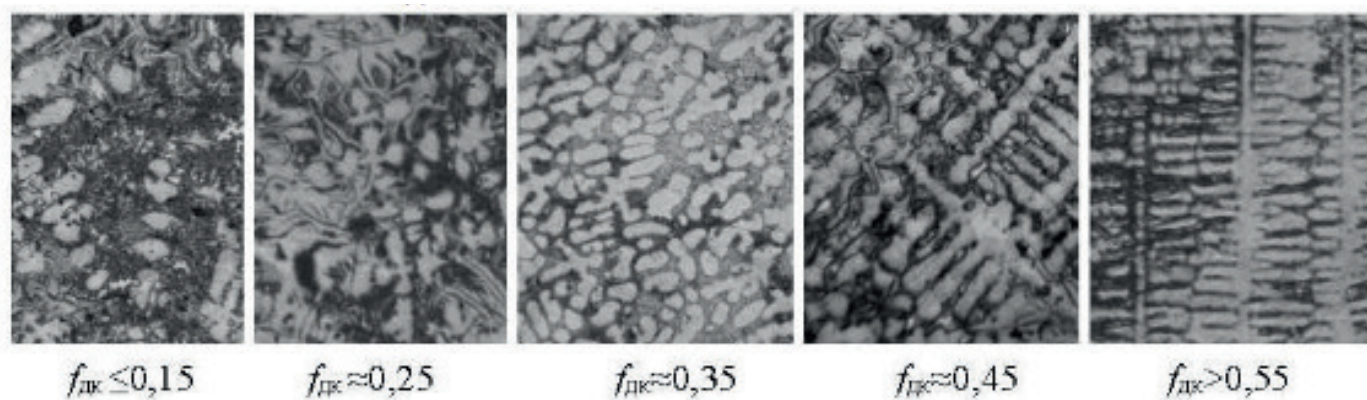


Fig. Dendritic structure of the investigated grey cast irons x 90.

The quantitative relationships between  $\sigma_B$  and  $f_{dc}$  for in situ tensile strength assessment were established. The comparison of  $\sigma_B$  values calculated through Brinell hardness HB and through volume fraction of dendritic crystals  $f_{dc}$  shows that the latter method developed in the present paper provides more reliable results. The received relationships between  $\sigma_B$  and  $f_{dc}$  make it possible to carry out express assessment of strength  $\sigma_B$  both under production and operation, and at clarification of causes of grey cast iron machine parts fracture. Besides, possibilities for search of new ways for quality improvement of grey cast iron details extend, which is a relevant scientific and practical problem of modern mechanical engineering.

## THE INFLUENCE OF THE DEGREE OF COMPRESSION DURING ROLLING TO CHANGE THE LATTICE PARAMETER OF THE ALUMINUM LAYERS LAMINATED COMPOSITE AMG6-AD1-VT1-0

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For particularly critical parts in aircraft and rocket science are used in permanent connections of dissimilar materials. However, the development of complex technological processes, including the production of such compositions and their subsequent processing, is constrained by the lack of data on the deformation ability of compositions and patterns of changes in the structure and properties in the process of their subsequent deformation.

The effect of the degree of deformation on the change of the lattice parameter ( $a$ ) of aluminum layers in the explosion-welded composite AMG6-AD1-VT1-0 subjected to cold rolling on samples with compression ( $\varepsilon_{\min}=3\%$  и  $\varepsilon_{\max}=22.5\%$ ) was studied. The degree of distortion of the crystal structure of aluminum layers in the near-surface zone (OSH) of Ti-Al composite was estimated by precision measurement of the parameter ( $a$ ). Recording the characteristic x-ray lines of Al (400) at the velocity meter of 0.25 deg/min and the chart tape 1800 mm/h in increments of elevation angles of 0.05 deg.

Changes in the parameter ( $a$ ) for the alloy AMG6 and aluminum AD1 showed that the nature of the redistribution of the unit cell size is largely determined by the degree of deformation. In AMG6, at small compressions, the crystal lattice period decreases near the interface (removal is less than 0.6 mm) and its constant value is maintained in remote areas. When the maximum deformation is observed a General increase in the lattice period and 0.4086 nm, with the exception of near-field zone, where he is reduced to 0.4082 nm, which is probably connected with the action of compressive stresses from the side of AMG6. The dependence of the aluminum crystal lattice parameter is more complex. With minimal de-formation near the boundaries of the compound with AMG6 and VT1-0, an increase in the lattice period to 0.4056 and 0.4055 nm, respectively, is observed, while in the center of the layer the period is at the level of the standard. At the maximum degree of deformation there is a sharp decrease ( $a$ ) near the near-field zone alloy AMG6 and its gradual increase to the boundary with VT1-0. The obtained results showed complex mechanisms of size change ( $a$ ) in the aluminum and aluminum alloy lattice associated with the redistribution of the dislocation structure on certain sliding planes of the HCC lattice.



## SYNTHESIS OF MAGNETITE CONCENTRATE WITH DEALKALIZATION OF RED MUD

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The production of alumina from bauxites is accompanied by the formation of a large amount of wastes. Worldwide alumina production capacities grow constantly, and the volume of discharged mud also increases. Deterioration in the quality of processed bauxites also contributes to the accumulation of mineral feedstock in disposal fields. The basic component of red mud (RM) of Ural enterprises processing local bauxites is hematite – 43-46%  $\text{Fe}_2\text{O}_3$ . The content of underextracted alumina is as much as 15-16%  $\text{Al}_2\text{O}_3$ . The technologies for complete processing of mud developed recently are based on modular solutions<sup>1</sup>. Magnetic concentration for the extraction of iron concentrate encounters difficulties in view of an increased content of weak-magnetic hematite, hydrogoethite, chamosite<sup>2</sup>. Leaching of alumina ( $\text{Al}_2\text{O}_3$ ) from alkaline sludge pulp at temperatures above 250°C requires a nonconventional equipment.

Autoclave extraction of alumina from red mud was studied in this work at different temperatures and proportions of active lime and sodium hydroxides<sup>3</sup>, as well as in the presence of iron (II) salts. The parameters of almost complete (not less than 80%) extraction of alumina from RM at temperatures admissible for operating alumina shops (below 250°C) have been determined. As a result, silicon compounds are bound in calcium silicates, and the major part of iron compounds is converted into magnetite.

The realization of these developments in industry will make it possible to recover minimum 1 t of  $\text{Al}_2\text{O}_3$  from 8-10 t of RM and to convert a greater part of iron compounds into a form convenient for magnetic separation with production of a concentrate containing more than 50% of iron.

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*The work was performed in accordance with the state assignment for the Institute of Solid State Chemistry UB RAS.*



THERMOKINETICS OF REACTIONS INTERACTION OF WOLFRAMITE  
WITH SODIUM AND POTASSIUM CARBONATES

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An important element of the technology for processing wolframite raw materials is its sintering with carbonates of alkali metals to convert tungsten from  $\text{Fe}_x\text{Mn}_{1-x}\text{WO}_4$  to water-soluble  $\text{Na}(\text{K})_2\text{WO}_4$ . According to the thermal analysis data (Netzsch STA 449 C Jupiter, Netzsch Thermokinetics package), the interaction of wolframite with  $\text{Na}(\text{K})_2\text{CO}_3$  proceeds via a two-stage mechanism. In  $\text{Fe}_x\text{Mn}_{1-x}\text{WO}_4 - \text{Na}_2\text{CO}_3$  mixtures, the first stage proceeds in the diffusion mode ( $E_1 = 243$  kJ/mol), and the second corresponds to the n-th order reaction with autocatalysis ( $E_2 = 212$  kJ/mol). For the system  $\text{Fe}_x\text{Mn}_{1-x}\text{WO}_4 - \text{K}_2\text{CO}_3$ , these values are 176 and 302 kJ/mol, respectively.

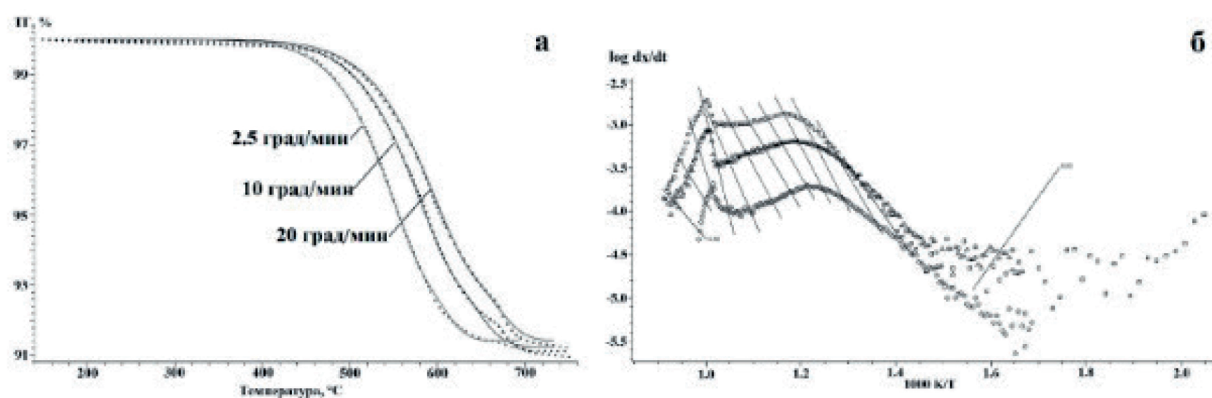


Figure. The change in mass of a mixture of wolframite with sodium carbonate when heated in air (a) and the results of data processing by the method of Friedman (b)

The obtained data was used to improve the processing technology of concentrates extracted from the ores of the Orlovsky and Kalgutinsky deposits.

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## ANALYSIS OF MELTING TECHNOLOGY AND LADLE TREATMENT OF PIPE STEEL K56

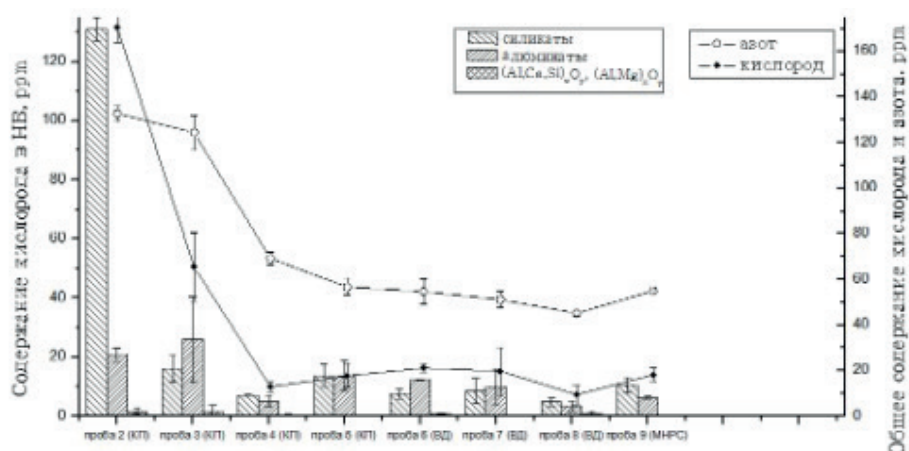
Pogodin A.M.<sup>a,b</sup>, Zykova A.S.<sup>b</sup>, Elistratov A.U.<sup>a,b</sup>, Komolova O.A.<sup>a,b</sup>, Grigorovich K.V.<sup>b</sup>

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Increasingly stringent requirements are imposed on the content of non-metallic inclusions in pipes of modern brands, which are the cause of various defects that affect the performance properties. Therefore, an urgent task is to increase the purity of pipe steel for non-metallic inclusions with a high content of  $\text{Al}_2\text{O}_3$ .

Metal samples were taken for the entire production technology of pipe grade K56 steel and an analysis of the production technology was carried out. Selected samples of the metal were analyzed using the methods of quantitative metallography, electron microscopy and fractional gas analysis and the main types of non-metallic inclusions formed in the metal during smelting and ladle treatment were identified. The results of the fractional gas analysis of the investigated metal samples of one of the analyzed heats are presented in the figure.



There is an increase in the content of nitrogen and non-metallic inclusions in the sample of the metal during casting, this indicates a secondary oxidation of the metal during casting. The analysis made it possible to make recommendations for improving the secondary treatment technology.

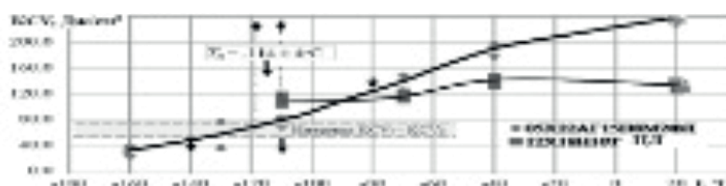
## COLD RESISTANCE ESTIMATION OF NEW HIGH NITROGEN STEEL 05KH21AG15N8M2FL

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To the modern steels, operating in the North condition, also to the nitrogen containing (NC), high requirements to resistance at the low temperatures are require. On the basis of own and literature data, the conditions for the choice of composition of cold-resistant cast steel were formulated. Including, to ensure cold resistance cast NC limit liquidity  $\sigma_{0.2}$  should be  $\geq 300$  MPa (1) at +20 °C. Cast austenitic steel (AS) nitrogen alloying limits narrowed by its minimum concentration, necessary for solid solution hardening and fulfillment of the condition (1); by its maximum concentration the excess of which leads to an increase the critical temperature of the viscous-brittle transition  $T_K$  ( $T_{DBTT}$ ) above the specified value.

New cast steel 05Kh21AG15N8M2FL with 0,5% N have liquid limit  $\sigma_{0.2}$  at +20 °C from 370 to 480 MPa. For it, for the first time, the temperature dependence of the impact toughness was constructed with a decrease in the temperature to -160 °C. Comparative tests on the impact bending of the samples of the laboratory steel 0,5Kh21AG15N8M2FL and the industrial centrifugal cast steel 12Kh18N10-TsL showed that in the whole range of climatic temperatures and up to -90 °C the proposed NC steel exceeds the nitrogen-free. The critical temperature of the viscous-brittle transition  $T_K = T_{DBTT} = -114 \pm 4^\circ\text{C}$  is determined for the steel 0,5Kh21AG15N8M2FL. According to the ferritometry and microstructural analysis, in the NC steel, unlike the steel of type 18-10, deformation and cooling martensite are not formed.



*The work was carried out as a part of RAS program 1.55 P «Arctic».*

## EXTRACTION OF RARE EARTH METALS WITH THE $\alpha$ -BRANCHED CARBOXYLIC ACID HYDRAZIDES AS INFLUENCED UPON BY ANIONIC COMPOSITION

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Low fractions of rare-earth metals (REMs) and their rather complicated chemical and mineralogical compositions appear to be a peculiarity of available raw materials in Russia. The extraction agents which are able to extract REMs from the sulfuric-acid and mixed media are of great interest.

A preliminary investigation in the extraction ability of the hydrazine and  $\alpha$ -branched acid (fractions C10 and C15-19) derivatives in the sulfuric-acid media evinced the DH 1519 (an isoacid hydrazide with C15-19 radicals) to have the largest extraction capacity.

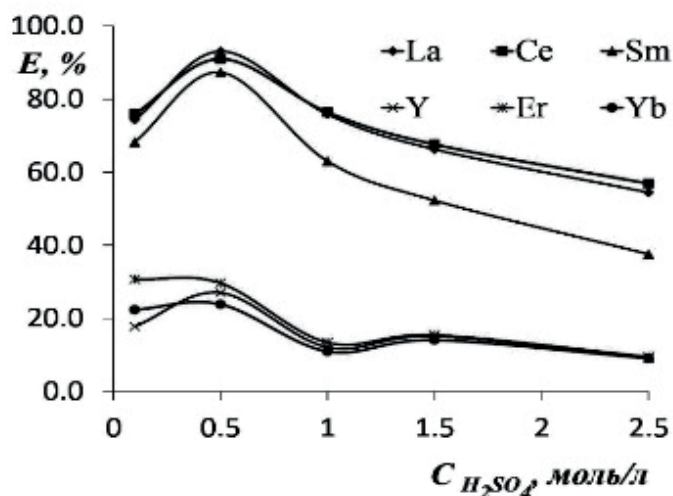


Figure 1. Dependence of the REM extraction rate ( $E, \%$ ) on concentration of  $H_2SO_4$  in the aqueous phase. The content in the 10 ml aqueous phase, mg: La-5.5; Ce-7,8; Sm-6.4; Y-8.4; Er-8.5; Yb-8.7. The REMs were introduced as a nitrate form. The extractant: 0.5 mol/l solution of HD1519 in kerosene. Vorg: Vaqu = 1:1. Shaking for 5 min, phase disengagement for 5 min.

As follows from the obtained findings, La, Sm and Ce are extracted appreciably better than Y, Er and Yb over the entire acidity interval; for example, in 0.5 mol/l of  $H_2SO_4$ , the separation factor  $\beta$  of the Sm-Er pair  $\approx 2.9$ .

*This work was financially supported by the RFBR (Grant Nr. 19-03-00039).*

## EXTRACTION OF SILICON FROM SOLUTIONS OF FLUORIC HYDROGEN ACID BY TRIBUTYL PHOSPHATE

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Today in Russia the main source of metals and compounds of tantalum and niobium continues to be loparite concentrate of the Lovozersky mining company. At the same time, Russia's need for ferroniobium is mostly met by imports. Providing the domestic industry with its own niobium raw materials can be achieved through the development of domestic niobium deposits<sup>1</sup>.

One of the most effective methods for extracting and concentrating niobium is extraction, widely used in technology. The ore concentrate is decomposed with a mixture of acids (78% HF + 22% H<sub>2</sub>SO<sub>4</sub>). In addition to Ta, Fe and Mn, all the elements contained in the accompanying minerals pass into the solution in the form of complex fluorides, for example, H<sub>2</sub>SiF<sub>6</sub><sup>2</sup>.

Despite the knowledge of the extraction behavior of Nb and a number of accompanying elements from fluoride solutions with tributyl phosphate (TBP), very little attention has been paid to the behavior of such an impurity as silicon<sup>3</sup>.

So, when leaching 18% HF niobium containing cakes, obtained after acid autoclave leaching of the Chuktukon ore, up to 83% of silicon goes into solution. Reducing the concentration of HF to 4% and using it in a mixture with 55% H<sub>2</sub>SO<sub>4</sub> during leaching of the cake led to a decrease in the extraction of silicon in the solution to 64%. Thus, niobium-containing solutions (up to 3.5 g/l Nb), coming to the extraction stage, contain 6-8 g/l of silicon. This silicon content, which is almost twice the niobium content, can significantly impair the extraction of the latter at the extraction stage.

Extraction equilibrium when extracting silicon TBP from HF solutions is achieved within 40 minutes. The study confirmed the extraction of silicon from solutions of hydrofluoric acid TBP. The TBP capacity for silicon is determined. The effect of the parameters on the degree of silicon extraction of TBP on the concentration of HF, the concentration of H<sub>2</sub>SO<sub>4</sub> in the mixture (HF + H<sub>2</sub>SO<sub>4</sub>) was studied.

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## CONCEPTUAL COMPLEX APPROACHES TO THE DEVELOPMENT OF LATERITE NICKEL DEPOSITS

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In recent years, due to the high cost of production and environmental problems the production of nickel and cobalt from lateritic ores became unprofitable and was discontinued in many plants. Production efficiency can be achieved only with a conceptual integrated approach to the use of all types of lateritic nickel ores (saprolite, limonite, mixed and hematite) of the developed deposit with the introduction of new technologies.

In this regard in the period 2012-2018 in IMET RAS a complex of studies was conducted on the development of new pyro- and hydrometallurgical processes for the processing of various types of lateritic nickel ores with high technical and economic indicators. The improved version of steel ball technology for processing of saprolite and mixed ores has been developed which has been tested by industrial tests. The resulting steel ball contains 10-20% Ni with the extraction degree of its - 90-98%. The process of selective extraction of Ni and Co from limonite ores according to the «reductive roasting - weak acid leaching» scheme has been developed. In comparison with the industrial Karon process it differs by 2 times smaller specific material flows in solutions and 1.5 times higher in the extraction of metals (up to 87-99% Ni and 80-91% Co). As an alternative the process of metallurgical enrichment of limonite ores according to the «reductive roasting-magnetic separation» scheme has been proposed. The magnetic concentrate contains up to 8.3-10% Ni and 0.4-1.0% Co with their extraction degree are 92% and 84% respectively. For the processing of hematite ores high-temperature reduction roasting is offered with direct production of granulated nickel iron (2.0-2.5% Ni) and aluminosilicate slag (40-42%  $\text{Al}_2\text{O}_3$ , 20-25% CaO, 25-27%  $\text{SiO}_2$ ) that suitable for use as a complex flux additive in the process of making ferronickel from saprolite ores.

*The work was carried out on state order № 075-00746-19-00.*



## THE NEW APPROACHES TO PROBLEM SOLVING OF COMPLEX USE OF TITANOMAGNETITES

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Titanomagnetite is the main raw material for the production of vanadium. They are processed using flux melting in blast furnaces and ore-smelting electric furnaces to produce vanadium iron and titanium slag. At the same time, all titanium and some amount of vanadium (20-35%) are sent to the dumps with the slag. The loss of titanium is especially noticeable when using titanomagnetites with a high content of  $\text{TiO}_2$  (8–15%). Due to the use of a large amount of flux (quartz sand, limestone or dolomite), the content of  $\text{TiO}_2$  in the slag does not exceed 22-24% during blast furnace smelting and during electric smelting - 29-32%. The low content of titanium and its form in the slag greatly complicate the technology of its extraction. The irretrievable loss of titanium in terms of  $\text{TiO}_2$  with such slags is at least 1 million tons in year. At present, over 100 million tons of titanium slags have been accumulated in the dumps of large producers of vanadium, which creates a serious environmental problem for the environment.

Considering the huge reserves of titanomagnetites containing a large amount of titanium dioxide in Russia, the research of IMET RAS is aimed at solving the problem of their complex use as mass iron-titanium and vanadium raw materials. The titanomagnetite concentrate is subjected to flux-free (or with a small addition of limestone) smelting reduction with producing vanadic cast iron and titanium-vanadium slag. In this case, the extraction of vanadium into cast iron can change in the range of 35-60%. Vanadic cast iron is sent to the converter redistribution, and titanium-vanadium slag, depending on the chemical and phase composition can be processed in two ways. In the first way vanadium is selectively extracted from the slag according to the «oxidative roasting - acid leaching» scheme, and the titanium-containing residue is leached in an autoclave with producing of synthetic rutile for the production of pigment  $\text{TiO}_2$  by the chlorine method. In the second way the slag is subjected to sulfuric acid leaching for cleaning from  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{Al}_2\text{O}_3$ , etc., then the titanium-containing residue (70-90%  $\text{TiO}_2$ ) is fed to decomposition with sulfuric acid to obtain pigment  $\text{TiO}_2$ . Vanadium is produced from the solution by extraction with obtaining of pure  $\text{V}_2\text{O}_5$  (99.5-99.7%).

*The work was carried out on state order № 075-00746-19-00.*



## THE THERMODYNAMIC SIMULATION SILICOTHERMAL REDUCTION OF CHROME

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Thermodynamic modeling of silicothermic reduction metals from oxygen the  $\text{CaO-SiO}_2\text{-Cr}_2\text{O}_3\text{-FeO-MgO-MnO-Al}_2\text{O}_3$  system was conducted. The HSC Chemistry 6.12 software package developed by Outokumpu Research Oy (Finland)<sup>1</sup> was used for simulation. The information of CrO is introduced additionally in the database and it adjusted for  $\text{CaCr}_2\text{O}_4$ . The chemical composition of the original oxide components is, mass. %: 25-37,5 CaO; 12,5-25  $\text{SiO}_2$ ; 25  $\text{Cr}_2\text{O}_3$ ; 5 FeO; 14 MgO; 3 MnO; 3  $\text{Al}_2\text{O}_3$  and basicity  $(\text{CaO})/(\text{SiO}_2)$  is 1, 2, 3. As a reducing agents used FeSi45 and FeSi65. The amount was 110% of the stoichiometric required for the reduction of Fe, Mn and Cr. The calculations were performed in the range of 1500-1700 °C.

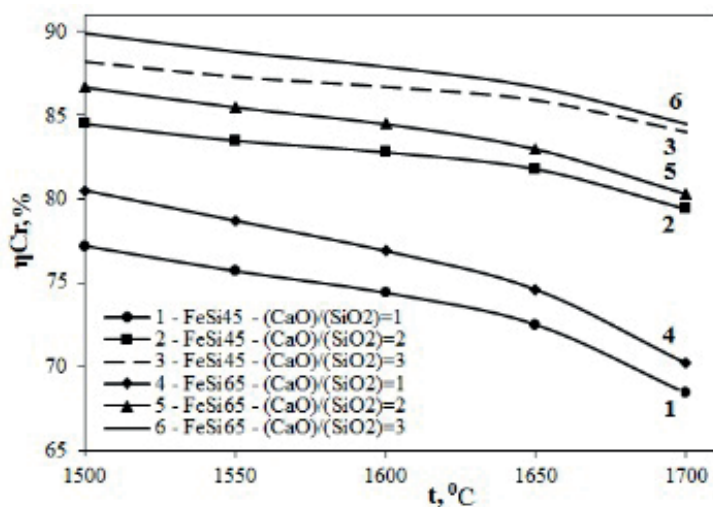


Figure 1. Change in the degree of chromium reduction ( $\eta_{\text{Cr}}$ ) by ferrosilicon (FeSi45, FeSi65) depending on temperature ( $t$ ) at  $(\text{CaO})/(\text{SiO}_2)$

The positive effect of increasing the basicity from 1 to 3 and increasing the silicon concentration in the reducing agent on the  $\eta_{\text{Cr}}$  showed at Figure 1. The obtained data are consistent with the  $\eta_{\text{Cr}}$  indices when using FeSiNi<sup>2</sup>.

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## ELECTROCHEMICAL OBTAINING SEMI-CONDUCTIVE ALLOYS RE-CU-SE

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Rhenium (Re) is a heat-resistant metal, which has won great acclaim as a high-tech material, which shows an exceptional combination of properties. This metal has some specific properties and finds its application in various fields of semi-conducting industry. In recent years a sphere of using these compounds was substantially widened space technique, electronics.

Rhenium chalcogenide alloys are semi-conductor materials and can be used as a photosensitive element in visible region of spectrum.

The present work is made aiming to research the appropriate processes, to determine scientific base of electro-deposition of rhenium chalcogenides and to define physico-chemical properties of produced thin films.

To study mechanism of electrolytic deposition of semi-conductor layers from different solutions obtained by electrolysis method potentiostatic, cyclic voltammetric methods has been used, but for studying the chemical and phase composition of alloys X-ray diffraction method has been applied.

The study was carried out from sulfurous solution containing selenous acid, potassium perrhenate and copper chloride. Kinetics of the processes was controlled using measurement methods of cyclic voltamperimeter at IVIUMSTAT. According to the researches of voltammetric dependences during co-electrodeposition of calium perrhenate ions (VII), selenium (IV) and copper (II) from sulphate electrolytes on Pt electrode the conditions of potentiostatic deposition of thin films in the system Re-Cu-Se were established. To study the morphology of films on platinum and copper substrates the surface of an electrode was studied at SEM JEOL JSM7600F in different amplifications, as well as was subjected to elemental analysis using a detector Oxford X-MAX 50. Scanning of the sample was carried out in the mode of secondary electrons at accelerating voltage ~15 keV. It was determined that agglomerates consisting of spheric particles with average size of ~20-25 nm are observed on the surface of an electrode.

## THE USE OF SYNTHETIC ION EXCHANGERS FOR THE RECOVERY OF VALUABLE COMPONENTS FROM THE ACIDIC WASTE SOLUTIONS OF COPPER SMELTING PRODUCTION

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Specialists LLP «Kazgidromet» was held the scientific-research work on the development of technology for recovery of valuable components (copper, rhenium, Nickel) from waste solutions of the Balkhash copper-smelting plant of «Kazakhmys Smelting». The composition and amount of acidic effluents are given in table 1.

Table 1. The average composition of acidic effluents

The name of the stand	Volume, m <sup>3</sup> / year	Ratio, % relative	Content, g/dm <sup>3</sup>		
			Cu	Re	Ni
Washing sulfuric acid	468026	82,58	0,02	0,0037	0,002
Spent electrolyte from the 84-series	7224	1,27	9,10	0,00	1,41
The solution after obtaining copper sulphate	24300	4,29	30,0	0,00	3,97
Electrolyte after deep electroextractions	27086	4,78	1,43	0,00	1,10
The rich solution after filtration of slime	19723	3,48	31,74	0,00	1,19
Poor the solution after filtration of slime	20387	3,60	18,30	0,00	0,08
TOTAL per year	566746	100	2,49	0,0031	0,15

Taking into account the multicomponent composition of solutions for the extraction of valuable components, ion-exchange sorption methods on synthetic ionites of a new generation were used, which showed their technological and economic efficiency in the processing of this type of waste.

### Literature:

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## STUDY OF PHYSICO-CHEMICAL PROPERTIES OF RED MUD AND OILY SCALE FOR JOINT UTILIZATION

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With the aim of improving the technology of co-processing of red mud (RM) and oily mill scale free (OMS) using co-temporal methods and apparatus, including using equipment of the center «Ural-M», studied the physico-chemical properties of industrial wastes.

The main components of RM are: Fe (35.7 %) in the form of hematite and complex hydroaluminum, Ca (11.0 %) in the form of calcite and hydro-aluminosilicates, Al (6.8 %) and Si (4.7 %) in the composition of hydroaluminum, Na (2.8 %) in the form of hydroaluminum, carbonate and hydroxide, Ti (2.5 %) in the form of rutile. The sludge moisture content was 11.9 %.

The main components of the OMS are: Fe (71 %) in the form of magnetite, wustite and hematite with a very small amount of fayalite. The contents of Si (in the form of quartz), Al and P (non-forming phases) are within 1-3 %. Humidity OMS – 16.3 %, the content of indelible organic matter – 4.0 %.

Granulometric composition of RM is characterized by high dispersion. With an average diameter of 1.6  $\mu\text{m}$ , all particle sizes are in the range of 0.5-12  $\mu\text{m}$ . Granulometric composition of OMS is characterized by complexity. With an average diameter of 8.6  $\mu\text{m}$ , maxima of 0.9  $\mu\text{m}$  and 15  $\mu\text{m}$  and a minimum of about 1.2  $\mu\text{m}$  are observed in the particle size distribution. The specific surface area of the materials is equal to RM 23.7  $\text{m}^2/\text{g}$ , and OMS – 1.9  $\text{m}^2/\text{g}$ .

The change of waste properties after exposure to aqueous solutions of alkalis and acids neutralizing the effect of organic (OMS) and alkaline (RM) surface compounds was studied. Neutralization of aqueous suspension with HCl solution leads to removal of alkaline film from the surface. As a result of the impact of reagents, there is a decrease in the content of water-soluble components in the processing products. At the same time, the average particle sizes of RM and OMS increase to 2 and 14  $\mu\text{m}$ , respectively, and the specific surface area to 25.7 and 2.3  $\text{m}^2/\text{g}$ . The distribution of particle size of RM is almost constant, and the OMS is approximately 5 and 10 % of the smoothed maximum and minimum in the area of at least 0.5 and 15  $\mu\text{m}$ .

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## PYROMETALLURGICAL EVALUATION OF THE SCHEME FOR PROCESSING ALUMINUM-MADE INDUSTRIAL WASTE

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As a result of the research, the metallurgical properties of pellets and briquettes were studied, obtained from mixtures of dross and red mud:

- strength;
- recoverability;
- softening temperature range.

Using the information system «Interactive calculations in ferrous metallurgy»<sup>1</sup>, the effect of iron ore material on the main technical and economic indicators of pyrometallurgical transformation in the metallurgical processing is estimated: energy consumption, productivity, chemical composition of the metal and slag.

To determine the optimal conditions for obtaining iron-containing alloys and alumina slags available for the production of alumina-cement clinker.

X-ray studies of the phase composition of concentrates, briquettes and pellets, metal alloys and alumina slags were carried out.

Analyzed and evaluated various options for utilization of industrial wastes of metallurgical production (red mud and oily scale) according to various schemes, taking into account the economic efficiency for each metallurgical redistribution.

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## EXTRACTION OF REE FROM APATITIC CONCENTRATE

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A large part of the balance reserves of rare earth elements (REE) of Russia is associated with the Khibinsky apatite deposits of the Kola Peninsula.

The report summarizes the results of research on the scientific substantiation and development of technologies for extracting REE from the products of the sulfuric acid processing of apatite concentrate: phosphogypsum, extraction phosphoric acid (EPA), as well as improving the technology for extracting REE during nitric acid processing. The peculiarities of REE extraction from phosphopoluhydrate of the production of various enterprises, phospho-dihydrate, methods of extraction of the dihydrate process from extraction phosphoric acid are considered. It has been shown that economically expedient extraction of REE from phosphorups is possible only with sulfuric acid leaching of REE, phosphorus and fluorine simultaneously with the production of a gypsum product suitable for the production of binders and cement. Effective leaching of phosphorus and fluorine is achieved only with percolation leaching, but not with agitation. Methods for extracting REEs from leaching solutions have been developed, which ensure the production of high-quality REE-free carbonate concentrates that are not contaminated with radionuclides. The results are confirmed on a pilot scale. Methods have been developed for the disposal of solutions containing phosphorus and fluorine, which virtually eliminates the formation of liquid wastes.

Methods for the extraction of REEs from EPA are proposed and investigated: precipitation of double sulfates with sodium, precipitation of REE in the form of fluorine-phosphate concentrate, sorption by sulfonic cation. Their advantages and disadvantages are estimated. The sorption method for extracting REE from a solution obtained by the nitric acid processing of apatite has been improved.

It is proposed to carry out the extraction of REE from fluorine-phosphate concentrate, as well as phosphate concentrate, resulting from the nitric acid processing of apatite concentrate by the developed method of sorption conversion. In all cases, solutions have been found for the separation of REE and thorium, which exclude the formation of radioactive products requiring special storage.

## **SORPTION OF METALS BY SULFOCATIONITE FROM WEAKLY SOLUTIONS OF COMPLEX COMPOSITION**

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The experimental data on the sorption of simultaneously present alkaline, alkaline-earth, rare-earth elements, aluminum, titanium, iron (III), thorium and uranium by sulfoconite from the solutions of complex composition obtained during the acid processing of various types of rare-earth raw materials using low-concentrated solutions of nitric, sulfuric hydrofluoric acids, concentrated solutions of orthophosphoric acid are analyzed

During sorption from solutions of complex composition, as a rule, the distribution coefficient for sorption of rare earth metals  $K_d$  is maximal, which allows them to be concentrated with the separation of a part of impurities already at the stage of acid decomposition of concentrates. This determines the prospects for the use of sorption processes in the processing of many types of rare-earth raw materials. The  $K_d$  values are influenced by the acidity of the solution, its anionic and cationic composition, and the sorption temperature. The efficiency of sorption of individual metals often does not correlate with the values of their ionic potentials  $z_{Men+}/r_{Men+}$ , where  $z$  and  $r$ , respectively, the magnitude of the charge and radius of the  $Men+$  cation, which determine the strength of the bond of the sorbed cation with the functional group of the sorbent. This is especially characteristic of solutions containing phosphate ligands, in which the  $K_d$  values of trivalent metals, thorium and uranium are significantly reduced, apparently due to the formation of durable phosphate complexes by these metals. The presence of fluorine in solutions in the absence of phosphate ion only slightly affects the efficiency of sorption of rare-earth metals, alkali and alkaline-earth metals, but significantly reduces the efficiency of sorption of metals-fluorine acceptors: Al, Ti, Fe, Th and U. The fluoride medium Ca, Th, U, and REE had high  $K_d$  values, which indicates their existence in such a solution in the cationic form. The data on sorption allow us to qualitatively estimate the features of the complexation of a number of metals in solutions of the studied compounds.



## RESEARCH PROCESSING RED MUDSWITH RECEIVING ALUMINUM-IRON COAGULANTS

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Currently, red muds are mainly thrown into the sea, or stored in sludge fields near alumina refineries. In this regard, the urgent task is to find effective methods for the disposal of red mud.

The aim of our research was the processing of red mud with the production of aluminum-iron coagulants<sup>1</sup>. The object of the research was the red mud of the Ural Aluminum Plant and the Romanian plant «Alum», the chemical composition of which was as follows (%):  $\text{Al}_2\text{O}_3$  – 14-21;  $\text{SiO}_2$  – 9,1-9,4;  $\text{Fe}_2\text{O}_3$  – 40-44;  $\text{CaO}$  – 4,6-14,2;  $\text{TiO}_2$  – 2,9-4,1;  $\text{Na}_2\text{O}$  – 3,8-7,1.

Aluminum-iron coagulants were obtained by decomposing red mud with sulfuric and hydrochloric acids<sup>2</sup>. Studies were performed using a red mud decomposition reactor, a vacuum filtration plant, and drying equipment. The degree of extraction of aluminum oxide in the solution was: 79,67-80,73%; iron oxide – 38,68-39,19%; sodium oxide – 93,43-95,66%. The degree of extraction of trace elements was, (%): scandium – 67,46-70,44; vanadium – 49,35-54,45; gallium – 66,54-67,78; yttrium – 74,81-82,30; zirconium – 66,38-70,33; cerium – 42,63-65,50; neodymium – 43,42-56,65; terbium – 61,72-72,14; ytterbium – 73,13-79,93; lutetium – 75,10-81,02, which will provide an opportunity to extract these elements by leaching of red mud. NII VODGEO showed high coagulation properties of the obtained alumina-iron coagulants.

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## REDUCTIVE SMELTING OF NEUTRALIZED RED MUD: IRON & ALUMINA-CONTAINING SLAG PRODUCTION

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Research of the smelting the neutralized red mud (RM) from the Ural Aluminum Plant with a reducing agent (carbon) has been conducted. Using the program FactSage v.7.1, a thermodynamic calculation of the  $\text{Al}_2\text{O}_3$ -CaO-SiO<sub>2</sub>-TiO<sub>2</sub>-FeO system was carried out in the temperature range of 1300-1800 °C. The liquidus exists in the range of 1500-1600 °C. In order to decrease the melting point, a flux additive: CaO and SiO<sub>2</sub> were used.

Experiments on the smelting of RM were carried out at T = 1500, 1550, 1600, 1650, 1750 °C and a duration time of 10-30 minutes in the Tamman furnace. The RM was mixed with carbon in the amount of 10 wt.% and loaded into graphite crucibles. Fluxes were added in the following amounts: 5-15 wt.% CaO and 3-15 wt.% SiO<sub>2</sub>. Experiments have shown that with the use of 7.5 wt.% CaO and 6, 9 wt.% SiO<sub>2</sub>, large drops of metal are formed, however, due to the high melt viscosity, the drops do not coagulate in one ingot and do not down to the bottom of the crucible. An increase in the process temperature from 1500 to 1600 °C did not affect the melt viscosity decrease. The best result was obtained when melting without fluxes at a temperature of 1650-1750 °C.

The results of the experiments showed that the addition of calcium oxide and silica significantly increase the surface tension between the metal and slag, which does not allow the metal to coagulate completely and precipitate into the bottom of the crucible. It is shown that the strong overheating of the slag above the melting point by 100-200 °C made it possible to reduce the surface tension and viscosity of the slag melt, which led to a complete separation of the metal from the slag.

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## INTEGRATED PROCESSING OF KAOLIN RAW MATERIALS BY CHLORINE METHOD

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Coal-mining and coal benification wastes from the “Bogatyr” quarry of the Ekibastuz coal deposit were used as kaolin raw materials. Mineral composition of the waste products (in %): 83-85 kaolinite, 10-12 quartz, 1.0-1.5 siderite, 0.2-2.0 pyrite and 1-3 albite and calcite. The reducing agent was evenly distributed throughout the coaly rock volume and was available in the necessary quantity (14-26 %) for chlorination. Reducing agent concentration deviation from stoichiometry (80 to 160 %) result in increase in chlorination degree of the oxides of aluminum, nitrogen, and iron. However, the conditions of preferential chlorination of the aluminum oxide, contained in carbonaceous rock, are of practical interest in the preparation of aluminum chloride. Acid enrichment of the rock was used to obtain rough alumina, laced with  $\text{Fe}_2\text{O}_3$  ( $1.5 \div 2.5$  %) and  $\text{SiO}_2$  ( $0.5 \div 0.9$  %). The optimum acid concentration was:  $\text{H}_2\text{SO}_4$  - 26 %,  $\text{HCl}$  - 20 %,  $\text{HNO}_3$  - 40 %. The derived rough alumina is sent for chlorination at  $800 \div 900$  °C over a catalyst - oil coke. Despite the general morphology of the aluminum oxide formation during decomposition of the crystallohydrates under study, the development of  $\text{Al}_2\text{O}_3$  phase composition occurs at different rates and depends on the precursor nature.  $\text{Al}_2\text{O}_3$  reaction capability toward chlorine increases in the following order: nitrate  $\rightarrow$  chloride  $\rightarrow$  sulfate; and the degree of chlorination reaches  $98 \div 98.7$  %<sup>1</sup>. Based on the results of this research, aluminum production flow scheme was proposed, the main stages being: (I) acidic enrichment of the mineral part of carbonaceous rock, which allows to remove silica almost completely from the rock and to send to the cement production then; (II) - after thermal decomposition crystallohydrate of aluminum salts are placed for chlorination in fluidized bed furnaces; (III) - electrolysis of the purified melt of aluminum chloride<sup>2</sup>.

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## ALKALI-CHLORINE COMPLEX PROCESSING OF NEPHELINES

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Nephelines are among the most promising types of non-bauxite Al-containing ores, but the direct chlorination of nepheline is ineffective. The proposed alkali-chlorine processing method of extraction of the Kola nepheline heads involves sintering of nepheline with limestone using conventional alkaline technology. Belite sludge produced by leaching of sintered mass mixture enters on cement manufacturing after scrubbing action. Aluminum hydroxide, produced via the Bayer process, was extracted by carbonizing from non-crucified aluminate solutions;  $\text{Al}(\text{OH})_3$  is mainly represented by gibbsite at  $T > 600\text{ }^\circ\text{C}$ , and by bayerite at  $T = 400\text{ }^\circ\text{C}$ <sup>1</sup>. The primary difference between bayerite and gibbsite in reactivity with chlorine lies in the fact that at the same heat treatment temperature the different alumina modifications are formed. Phase composition and the phase ratio of  $\text{Al}_2\text{O}_3$ -modifications are affected by fabrication conditions for obtaining the aluminum hydroxide precursor. Soda solutions, by-produced when carbonization, are used to obtain soda, potash, and gallium. Aluminum hydroxide, containing 2.0-2.5 mass. % of sodium hydroalumosilicate, is exposed to calcination at  $700\text{ }^\circ\text{C}$  to obtain crude alumina. Its fluid chlorination at  $800 - 900\text{ }^\circ\text{C}$ , over petroleum coke as reducing agent, results in high chlorinity level of aluminum oxide - up to 94.2 %. Moreover, the formation of  $\text{NaAlCl}_4$  eutectic compound (melting point  $\sim 164\text{ }^\circ\text{C}$ ) diminishes the dust losses. The dispersed phase of the  $\text{NaCl-AlCl}_3$  melt is formed in the fluidized bed apparatus reaction zone, this phase adsorbs aluminum particles that carried away by the gas stream. As a result, the duration of stay of  $\text{Al}_2\text{O}_3$  in the fluidized bed increases, that enables the reduction of losses with dust and the increase in the degree of chlorination<sup>2</sup>.

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## SORPTION THIOUREA COMPLEX OF PALLADIUM(II) CATION EXCHANGE RESIN KU-2-8

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Thiourea complexes Pd(II) are found in the processes of elution and reextraction, as well as in the analytical practice of this element. Under conditions of excess thiourea (Thio) in such solutions there is a stable cationic complex  $[\text{Pd}(\text{Thio})_4]^{2+}$ . Unlike anionic complexes, the sorption of cationic Pd(II) complexes was studied to a much lesser extent, so it seemed appropriate for us to investigate the patterns of sorption of  $[\text{Pd}(\text{Thio})_4]^{2+}$  - ions with cation exchange resin KU-2-8.

Sorption under static conditions was carried out in glass tubes at room temperature, mixing was carried out manually,  $[\text{Pd}(\text{Thio})_4]\text{Cl}_2$  was used as the starting compound. The concentration of Pd (II) ions in the initial solutions varied from  $2,0 \cdot 10^{-3}$  to  $1,3 \cdot 10^{-2}$  mol/l,  $\text{CHCl} = 0.01 - 6$  M, the mass of sorbent ( $m_{\text{sorb}}$ ) –  $0.05 \pm 0,0005$  g., solution volume - 10 ml.

The sorbent is characterized by a slow kinetics of establishing constant sorption values – of 2 days, however, it exhibits a high static capacity of 3,18 mmol/g. It is noted that the growth of  $\text{CHCl}$  leads to a significant decrease in the values of capacity (up to 0.08 mmol/g in 6 M  $\text{HCl}$ ). In the process of sorption, the phase of the sorbent is painted in bright orange color. In the IR spectrum of the sorbent with sorbate, the absorption bands present are characteristic of the  $[\text{Pd}(\text{Thio})_4]^{2+}$  - ion. Free Thio in the filtrate under conditions of quantitative sorption of Pd(II) was not detected, which indicates the preservation of all 4 Thio molecules in the sorbate. The combination of the data obtained, as well as the comparison of the IR spectra of  $[\text{Pd}(\text{Thio})_4]\text{Cl}_2$ , sorbent and sorbent with sorbate, indicate cation-exchange sorption of  $[\text{Pd}(\text{Thio})_4]^{2+}$  - cations. However, difficulties in desorption of Pd (II) are observed. This is apparently due to the presence of hydrogen bonds between the hydrogens of the amide groups of the ligand and the oxygens of the sorbent sulfogroups, which lead to a firm retention of the sorbate in the phase of the sorbent. As a result of the thermolysis of the sorbent phase saturated with Pd(II) ions, porous black granules were obtained in air, in which the initial morphology of the sorbent is preserved, the phase composition: Pd ( $Fm3m$ ), PdO ( $P4n2$ ). These granules may be of interest as catalytic materials.

Samples were studied using the equipment of the Center for Scientific and Technological Control MIREA-Russian University of Technology

## INFLUENCE OF HEAT TREATMENT ON THE MAGNETIC PROPERTIES OF THE HARD MAGNETIC POWDER ALLOY FE-24%CR-15CO-1.5TI-3MO

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Hard magnetic materials made of ternary Fe-Co-Cr alloys based on the high atomic moment of the Fe-Co alloys and the miscibility gap occurring when Cr is added.<sup>1</sup> The development of such materials are explored not only for fundamental scientific research but also for technological applications. Due to good ductility in the as-quenched state and magnetic properties which are comparable with the same of cast Al-Ni-Co magnets, the Fe-Cr-Co alloy is an important magnetic material for different permanent magnetic applications.<sup>2</sup>

In this study the investigation of the magnetic properties of the hard magnetic powder alloy Fe-24%Cr-15%Co-1.5%Ti-3%Mo (wt.%) have been completed. The heat treatment was carried out by a two-stage continuous cooling above the  $\alpha_1+\alpha_2$  miscibility gap. The optimum cooling rate for the first step was found and examined (figure 1).

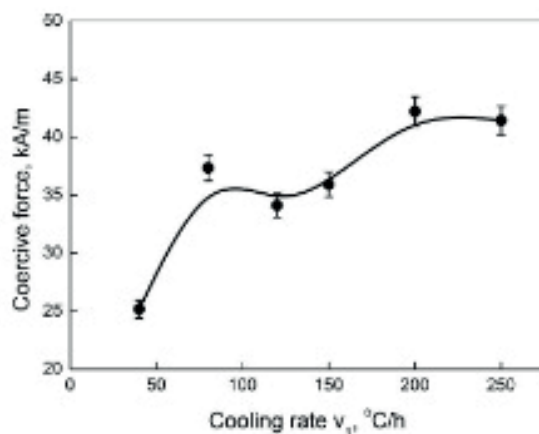


Figure 1. Magnetic properties of Fe-24%Cr-15%Co-1,5%Ti-3%Mo alloy vs. cooling rate

The magnetic properties  $B_r = 1.2$  T,  $H_c = 42.2$  kA/m,  $(BH)_{max} = 31.2$  kJ/m<sup>3</sup> have been achieved for studied alloy after cooling at rate 200 °C/h.

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## STRUCTURE AND PROPERTIES HIGH STRENGTH CORROSION RESISTANT NON-MAGNETIC STEEL AND HER WELDED JOINTS WITH HIGH NITROGEN STEEL

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Development of high nitrogen steel – perspective direction in building low alloyed high strength corrosion resistant materials. Nitrogen backpressure casting technology allows without expensive alloying elements (especially nickel) by introducing nitrogen – austenitic element – to form in steel based Fe-Cr-N austenitic structure without deterioration corrosion resistant and has low magnetic permeability<sup>1-2</sup>.

Steel smelting was done on the modernized setting «Prometey-A». Test high nitrogen steel has low magnetic permeability ( $\mu \leq 1,001$  G/Oe) and austenitic structure. Nitrogen alloying is increases the yield strength ( $\sigma_{0.2} \geq 800$  MPa) and preserves high plastic characteristics ( $\psi \geq 50\%$ ) and impact strength ( $KCV^{+20} \geq 100$  J/cm<sup>2</sup>).

The optimal percentage of nitrogen in steel has been determined – 0,7-0,8. With increasing nitrogen concentration the strength properties are increasing but at the same time lowers plastic characteristics.

Increased nitrogen content increases durability pitting corrosion (pitting resistance index PRE in 2 times higher than to steel Cr18Ni10Ti). Due to the tendency to intermittent austenite decomposition with the formation of chromium nitride colonies Cr<sub>2</sub>N pearlite type it is possible that ICC can occur.

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## THE KINETICS OF LEACHING OF NICKEL FROM LIMONITIC ORE USING A MODEL OF THE «SHRINKING CORE» (SHRINKING CORE MODEL)

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About 160 million tons of Nickel are concentrated in oxidized Nickel ores, of which about 70% are represented by limonites. In recent years, there has been a tendency in the world to increase the share of their use for the production of Nickel and cobalt, but the known hydrometallurgical processing methods have significant disadvantages and are ineffective. In Russia, significant reserves of oxidized Nickel ores are concentrated in the Buruktal Deposit (Orenburg region), which contains about 1377 thousand tons of Nickel, but in comparison with foreign deposits is quite poor in Nickel content (0,8-1,0%) and cobalt (0,04-0,07%). In this connection, IMET RAS is developing a new method of hydrometallurgical processing of this type of raw material with selective extraction of the Ni and Co into a solution using weak solutions of sulfuric acid at atmospheric pressure.

The kinetic parameters of the process and the features of dissolution of Nickel from the previously reduced limonite ore are determined. To describe the kinetics of dissolution of Nickel from the calcined ore, a new model of «Shrinking Core» (SCM) was used, which is widely used in modern studies of the kinetics of hydrometallurgical extraction of Nickel from various ores [1]. It was shown that the experimental data obtained in the temperature range 60-95 ° C are well interpreted by the SCM model. Taking into account the selected model «Shrinking Core» the relationship between the process time and the degree of extraction of Nickel in the solution will be described by the equation  $1 - 3 \cdot (1 - x)^{2/3} + 2 \cdot (1 - x) = k_d \cdot t$ . As a result, it is shown that Ni dissolution is associated with the rate of H<sub>2</sub>SO<sub>4</sub> reagent supply through the pores of the calcined ore to the metal particles of Nickel distributed over the oxide matrix.

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## FORECASTING THE THERMODYNAMIC CHARACTERISTICS OF ALKALINE EARTH METALS IN LIQUID ALLOYS

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Alkaline earth metal alloys, a.e.m., (Me — Ca, Sr, Ba) are obtained by electrolysis of salt melts on liquid metal cathodes — MI. Low-melting non-ferrous metals of groups II - IV of the Periodic Table are considered as MI. Their efficiency is determined by the excess thermodynamic characteristics of the a.e.m. ( $\Delta\bar{H}_{Me(MI)}^{ex}$ ,  $\Delta\bar{S}_{Me(MI)}^{ex}$ ) in alloys Me(MI). Values  $\Delta\bar{H}_{Me(MI)}^{ex}$  obtained for a.e.m. in dilute alloys Al, Cd, Zn, Sn are  $-(90-180)$  J/(mol·K), which indicates the ionic-metal nature of the bond. At the same time in diluted alloys, stable microgroups, MG, with composition of  $MeMI_v$  are formed. According to the methods used to describe the alloys of rare-earth metals<sup>1</sup>, the dependence of the form is obtained  $-\Delta\bar{H}_{Me(MI)}^{ex} = f(\Delta k, \bar{r}_m)$  for alloys a.e.m. It has been established that  $\Delta\bar{H}_{Me(MI)}^{ex}$  naturally increases with increasing difference of relative electronegativities MI and Me ( $\Delta k$ ) and their reduced radii<sup>1</sup> ( $\bar{r}_m$ ). It is shown that the values of the a.e.m.  $\Delta\bar{S}_{Me(MI)}^{ex}$  are determined for all alloys  $-(5,2 \pm 0,2) \cdot (v+1)$ . The excess values  $\Delta\bar{H}_{Me(MI)}^{ex}$  and  $\Delta\bar{S}_{Me(MI)}^{ex}$  obtained experimentally for a.e.m. in alloys with gallium are in good agreement with the predicted calculation.

This provides a basis for predicting the excess partial molar thermodynamic characteristics of Ca, Sr, Ba in unexplored alloys, including the limited use of experimental methods. The composition of MG (value  $v$ ) in a diluted alloy Me (MI) corresponds, as a rule, to the composition of the nearest intermetallic compound in the state diagram of the MI-Me system.

Thus, at 973 K, we can assume that  $\Delta\bar{S}_{Me(MI)}^{ex}$  for example, in alloys with indium will be  $-15 \pm 0,6$  for Ca and Sr, and  $-26 \pm 1$  J/(mol·K) for Ba. At a.e.m. with Bi, Sb, Pb ( $v = 1$ ) the excess entropy a.e.m. of  $-10 \pm 0,4$  J/(mol·K).

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# **SECTION 4**

**ENERGY EFFICIENCY,  
ENVIRONMENTAL SAFETY  
AND RISK MANAGEMENT OF  
CHEMICAL INDUSTRY**

## BEST AVAILABLE TECHNIQUES AND INDUSTRY ENVIRONMENT REFORM: INTERNATIONAL EXPERIENCE

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In Europe, the Best Available Techniques (BAT) concept has been the key policy tool used to prevent and control industrial emissions and thereby ensuring a high level of environmental protection since 1990s. In Sweden, BATs became recognised as early as in 1960s. The European Union (EU) Industrial Emissions Directive (2010) defines BAT as “the most effective and advanced stage in the development of activities and their methods of

operation, indicating the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where this is not practicable, to reduce emissions and the impact on the environment as a whole”<sup>1</sup>.

Sector-related requirements to BATs are established in Reference Documents on Best Available Techniques (BREFs) and BAT Conclusions. BREFs are developed by a special process (Sevilla process) based on the information exchange including sector-related benchmarking of environmental performance and resource efficiency of the EU installations. Economic feasibility and market availability of techniques are taken into account, too. There are 33 BREFs developed in the EU and used by the practitioners. In the Nordic countries, there are additional guidance documents addressing sectors not covered by the EU BREFs. Since 2010, BAT Conclusions have been used to set clear requirements to emissions, – BAT-associated Emission Levels (BAT-AELs)<sup>2</sup>. In the EU, there are over 52,000 installations obliged to comply with sector-related BATs and showing both such compliance and gradual enhancement of their environmental performance and resource efficiency.

The EU experience proves also that the application of the BAT concept helps to prioritise attention of the regulatory authorities and improve the state of environment but does not interfere the competitiveness of the EU industry. In Russia, Nordic countries and in particular Sweden run a number of projects aimed to support introduction of Integrated Environmental Permits and implementation of the BAT concept.

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## **CIRCULAR ECONOMY, ENERGY EFFICIENCY AND ENVIRONMENTAL SAFETY IN CHEMICAL INDUSTRY**

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Climate change, as well as smog/haze, are crucial environmental challenges of our time. Carbon emissions footprint is a key environmental accounting tool for business managers, policy makers and non-governmental organisations attempting to identify mitigation measures that reduce the threat of climate change. The society is increasingly engaged in carbon emissions footprint as a part of policy development and product design. The present plenary lecture discusses the key issues and tools for the integrated environmental and business performance of the industry, starting from footprints. They have reached worldwide popularity, and the environmental issues they are addressing become increasingly diverse, as climate change and smog/haze issues (Greenhouse gas including Carbon Emissions footprint), freshwater use (water footprint), land use (land footprint), material use (material footprint). Footprints are an essential tool for the development and assessment of the circular economy. They are invaluable for measuring and managing the industry's contribution to the achievement of sustainable development. They help meet the challenge of providing competitive results and products in the short term while trying to protect and preserve natural and human resources in the long term. The lecture further discusses crucial issues as chemical industry waste and emissions, waste avoidance based on circular economy principles as well as environmentally responsible behaviour. Biomass management, both dedicated (energy crops) and residual, is challenging. The entire life cycle needs to be taken into consideration for decision making, and the biogenic emission is yet to be defined. This is applied to either biomass for energy or green chemical as a molecule of CO<sub>2</sub> emitted has the same impact on radiative forcing whether it comes from other resources/feedstock or biomass. The feasibility of biomass utilisation/management needs consider different footprints (beyond GHG), and it is essential to include the temporal dimension in the assessment. The presentation concludes by underlining the need for human society to develop a strategy that fulfils its responsibility towards the living conditions and the environment both in regional and worldwide level. There are specific challenges to be overcome by science on the way to providing tools to practitioners and decision makers. In terms of methodology, it is vital to appropriately integrate the footprint indicators into the overall system models and evaluation procedures.

## BISMUTH-BASED LAYERED COMPOUNDS AS PHOTOCATALYSTS FOR ENVIRONMENTAL APPLICATION

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Bismuth-based semiconductors are regarded as promising photocatalytic materials due to their suitable band gap for visible light absorption, increased mobility of photogenerated charge carriers because of well-dispersed Bi 6s orbital, non-toxicity, and easy tailoring of their morphologies owing to their layered structure. In this study, we have explored a wide variety of bismuth-based semiconductors, namely  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{MO}_6$  ( $M = \text{Mo}, \text{W}$ ),  $\text{BiVO}_4$ ,  $\text{BiOX}$  ( $X = \text{Cl}, \text{Br}, \text{and I}$ ) and  $(\text{BiO})_2\text{CO}_3$  for environmental remediation. As a narrow band gap semiconductor,  $\text{Bi}_2\text{O}_3$  has five polymorphs:  $\alpha\text{-Bi}_2\text{O}_3$  (monoclinic),  $\beta\text{-Bi}_2\text{O}_3$  (tetragonal),  $\gamma\text{-Bi}_2\text{O}_3$  (body-centered cubic),  $\delta\text{-Bi}_2\text{O}_3$  (cubic), and  $\omega\text{-Bi}_2\text{O}_3$  (triclinic). Among them,  $\beta\text{-Bi}_2\text{O}_3$  has the strongest absorption in the visible light region with a smaller band gap ( $E_g = 2.0\text{--}2.4\text{ eV}$ ) and demonstrated a good photocatalytic performance than other polymorphs under visible light irradiation, and is inexpensive, nontoxic, and stable in acidic conditions. To further enhance its photocatalytic performance,  $\beta\text{-Bi}_2\text{O}_3$  was composited with  $\text{MoS}_2$  quantum dots and  $\text{Pd/PdO}$  nanoparticles, and doped with  $\text{Gd}^{3+}$  ions. Also, the  $(\text{BiO})_2\text{CO}_3/\text{Fe}_3\text{O}_4$ ,  $(\text{BiO})_2\text{CO}_3/\text{Bi}_2\text{O}_3$ , and  $(\text{BiO})_2\text{CO}_3/\text{Ag}/\text{AgBr}$  composites were synthesized to enhance the visible light absorption and improve photocatalytic performance for the degradation of various organic pollutants under visible light. The present work demonstrated that the bismuth-based photocatalytic nanomaterials have potential to be applied in wastewater treatment and air purification systems in the future.

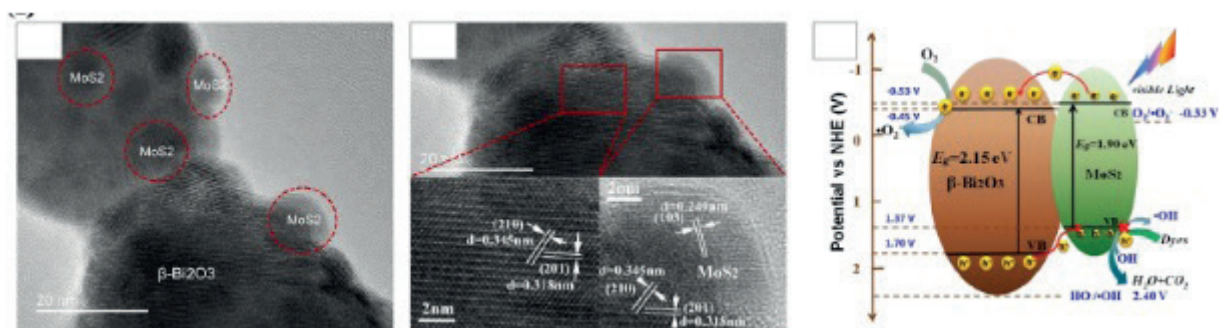


Figure 1. (a,b) TEM images of  $\beta\text{-Bi}_2\text{O}_3$  particles loaded with 1.0%  $\text{MoS}_2$  and (c) a schematic diagram of the photocatalytic mechanism and the photogenerated charge transfer process in  $\text{MoS}_2/\beta\text{-Bi}_2\text{O}_3$ .



## SUSTAINABLE CHEMICAL TECHNOLOGY IN BIOMASS VALORIZATION

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Biomass as a source of renewable energy and chemicals is attracting more and more attention. Utilization of woody biomass can lead, besides such biobased products as pulp and paper or furniture, also to chemicals and fuels.

Technological approaches to chemical treatment of lignocellulosic biomass are different depending on the target. One option is delignification giving cellulose and some residual hemicelluloses, which are further applied in production of paper or board, or the derivatives of cellulose. Thermal and catalytic treatment of biomass, e.g. thermal or catalytic pyrolysis, is viewed as the route to bio-based synthesis gas and bio-oil. Mild depolymerization of wood components (cellulose, hemicelluloses and lignin) results in formation of low-molecular-mass components such as sugars (Figure 1) or various aromatic hydrocarbons, which serve as building blocks for further chemical synthesis. Moreover, wood biomass contains many valuable raw materials for producing fine and specialty chemicals.

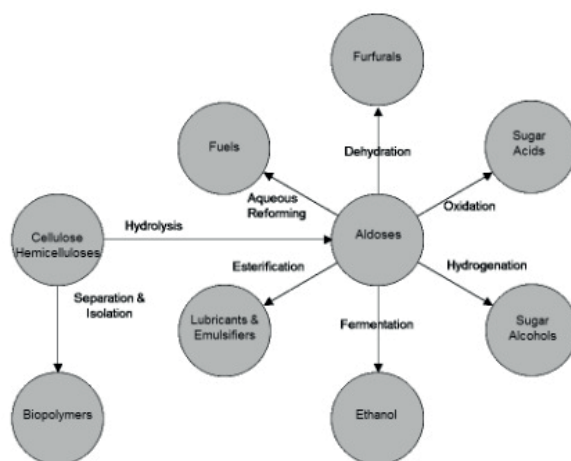


Figure 1. Chemicals from cellulose/hemicelluloses.

The current status of chemical technology for biomass valorization aiming at bio-fuels and chemicals will be reviewed in the lecture.



## **ENVIRONMENTAL AND ECONOMIC EVALUATION OF LARGE INTERNATIONAL ENERGY PROJECTS: THE CASE OF THE «ONE BELT ONE ROAD»**

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Large international energy projects are expected to boost the economic growth of the countries participating in the project, removing or alleviating poverty in underdeveloped areas and creating new markets for goods and services.

This analysis has been recently challenged with respect to China's «One Belt-One Road» project, as some countries begin to regard the considerable debt loads they might incur as financially unsustainable despite the expected economic boost.

A further matter of concern is the negative outcome on the environment due to increased energy demand and electricity generation, industrial activities, transportation. The clearing of forests for highways and railways, the possible destruction or degradation of ecosystems are additional sources of worries.

This presentation aims at providing general considerations about the relation between the expected growth in trade and infrastructures and the amount of investments in energy technologies required to guarantee environmental sustainability, as well as an estimation of whether the relevant financial burden would possibly generate a financially unsustainable debt load.

## ADVANCED MATERIALS FOR HIGH ENERGY DENSITY LI-ION BATTERIES

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Electrochemical systems are being thought as the solution for the vast demand for high energy density in both portable and stationary devices. Such systems hold a great promise, while pressure on researchers grows as the need for more “juice” in mobile device (from small hand held electronic to large mobile systems as electric vehicles (EVs) dramatically increase as technology is rapidly evolving.

In this talk, we will address both the anode and cathode materials in Li-ion batteries. Lightweight anode current collector made of CNTs (carbon nanotubes) tissue materials and metal fluoride coating applied by atomic layer deposition (ALD) of 5 volts Lithiated Mn spinel Ni doped cathode materials ( $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ) will be discussed in this talk. Synergism of both technologies will be presented in a flexible high energy Li-ion battery demonstration.

## IMPROVING THE EFFICIENCY OF AIR COOLERS BY IMPROVED DESIGN AND OPTIMAL ORGANIZATION OF COOLING FLOWS

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Analysis of the composition of heat exchanging equipment at petrochemical plants revealed that nominally more than 30%, and in fact about 50% of all equipment, is a heat exchange equipment, among which are also air-coolers (AC) that require replacement and reconstruction as a result of the end of lifetime or corrosion - erosion wear. Therefore, work aimed at improving the efficiency of air conditioning equipment are relevant<sup>1</sup>.

The existing problem of reducing the efficiency of air cooling in hot, calm weather is aggravated by the need for short-term air humidification with a humidifier mounted directly behind the fan wheel when air enters the diffuser. This dramatically increases the processes of corrosion and the formation of deposits on the surface of finned tubes (scale, fluff and dust).

We carried out a set of computational and experimental studies to assess the thermal efficiency of small-sized ACs of various designs using a universal experimental-industrial stand.

The results of the research have shown that the structures of air-handling units of a vertical-cylindrical design are more energy-efficient and less metal-intensive than standard horizontal ones and allow for the inflow of cold atmospheric air to the air-coolers in hot season.

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*The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No 18-29-24178*

## UTILIZATION OF HYDROGEN SULFIDE AND LOW-MOLECULAR THIOLS TO BIOLOGICALLY ACTIVE MONO- AND DISULFIDES

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Hydrogen sulfide (H<sub>2</sub>S) and low-molecular thiols (RSH) are toxic and corrosive waste from refining industries. The utilization of these compounds into asymmetric mono- and disulfides in N-methylpyrrolidone (N-MP) was researched. We proposed two approaches based on the use of one-electron oxidizers – sterically hindered o-benzo(imino)quinones (3,5Q, 3,6Q, imQ) and electro-mediators (o-aminophenols – APh) to convert H<sub>2</sub>S and RSH into practically useful compounds.

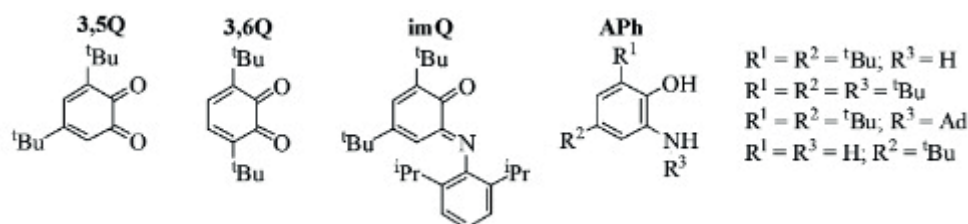


Figure 1. One-electron oxidizers used in the work

The introduction of these additives in N-MP containing sulfur components leads to the production of asymmetric biologically active mono- and disulfides (4,6QH<sub>2</sub>-3S<sub>n</sub>R, R<sub>2</sub>S<sub>2</sub>) under different reaction conditions. The yield of the target products varies from 4% to 97%.

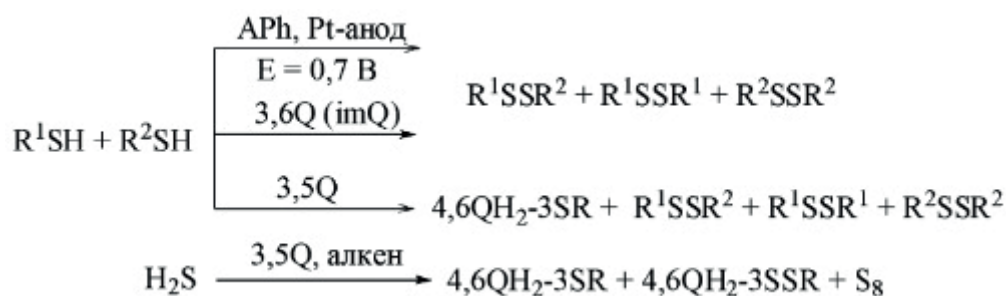


Figure 2. The utilization of thiols and hydrogen sulfide to mono- and disulfides

Thus, the possibility of involving toxic thiols and hydrogen sulfide to the synthesis of organic sulfur compounds has been shown.

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## SCIENTIFIC AND EDUCATIONAL COMPLEX FOR RESOURCE-SAVING MANAGEMENT OF LIFE CYCLE OF PROCESSES AND PROCESSING OF SECONDARY POLYMERIC MATERIALS

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Industrial engineering of the modern enterprises for the purpose of their modernization, improvement of quality of products and introduction of new manufacturing execution systems results in need of formation of highly skilled staffing [1] that is especially important for processes of processing of secondary polymeric materials (SPM) for decrease in environmental pollution and return of valuable raw materials to production. Processes of processing of SPM differ in a variety of technologies and complexity of management [2].

For resource-saving management of full life cycle of processes of processing of SPM the structure of engineering team (IT) included experts for providing a production cycle of processing of SPM, technical and economic assessment of life cycle, control and safety of the production environment and also automated management of production with use of digital technologies. The practical-focused educational modules of a scientific and educational complex which approbation is carried out on the basis of «Polymer-ecology» training center at cooperation with OC Plastic processing plant «Komsomolskaya Pravda» are developed for training of specialists of IT.

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## ORGANIZATION AND LOGISTICS MANAGEMENT OF URBANISTIC CHEMICAL-BOTECHNOLOGICAL CLUSTERS

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The special economic zone is an element of investment attractiveness, creating for residents the most favorable conditions for successful business and the effective development of their projects.

The positive dynamics of the formation of integrated structures in the industry is due to the higher efficiency indicators obtained by enterprises due to the effects of synergy and emergence from the association.

The special economic zone Dubna promotes business activity in the region and its socio-economic development. This is confirmed by the leadership of the SEZ in the first national rating of investment attractiveness of special economic zones in Russia in 2017.

The project of creating a biopharmaceutical cluster in the Moscow Region near Pushchino has been developed, its construction is scheduled to begin in May of this year.

Programs for developing entrepreneurial competencies, lack of administrative barriers allow companies not only to create competitive products, but also to create their own research and production complexes, cutting the path from idea to a specific business result.

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## ACQUISITION AND PREPARATION ALGORITHMS INFORMATION ON HAZARD INDICATORS FOR CLASSIFICATION OF CHEMICAL PRODUCTS

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Technological processes at hazardous production facilities are associated with the handling or storage of toxic, explosive and fire hazardous substances. The risk of emergency situations in the production, storage, use and disposal of chemical products is due to inadequate assessment and insufficient information to consumers.

Informing about the dangers of chemical products and precautions statements when using them is carried out with the help of safety data sheets and precautionary label applied to the packaging. For their development it is necessary to collect and analyze a sufficiently large amount of information, including data on the physicochemical properties, toxicity and ecotoxicity, first aid measures; measures and means of ensuring fire and explosion safety; measures to prevent and eliminate emergency and emergency situations and their consequences, etc. Thus, the information that should be contained in the safety data sheet goes beyond the competence of one specialist. Due to the large amount of information, systematization of methods for determining hazard indicators for chemical products and the development of a decision support system (DSS) to manage its safe handling is necessary.

Algorithms have been developed for determining the hazard indicators of chemical products using computational methods for the critical temperature, lower (upper) concentration limit of flame propagation, auto-ignition temperature, ignition, flare, and solubility in water. These algorithms have been tested on several substances: isobutan, trichloroacetic acid, 2-formylpyridin.

The functional structure, methods, models and algorithms of intelligent DSS for managing the safe handling of chemical products designed for the integrated solution of problems of identifying chemical products, assessing and classifying hazards to human health and the environment at all stages of the life cycle of their circulation have been developed.



## MODELING AND PARAMETRIC IDENTIFICATION OF THE CATALYTIC RECTIFICATION PROCESS OF THE ORGANOFLUORINE ESTERS AND ACIDS

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Using results of experimental investigation of the catalytic distillation<sup>1,2,3</sup> of the four-component system:  $\text{CF}_3\text{COOCH}_3$  –  $\text{CF}_3\text{COOH}$  –  $\text{BrCF}_2\text{COOCH}_3$  –  $\text{BrCF}_2\text{COOH}$  in production of bromodifluoroacetic acid in the presence of the sulfuric acid as a catalyst, modeling procedure of the continuous catalytic rectification with the conducting chemical reaction of bromodifluoroacetic acid formation has been proposed. Also, an original algorithm for identification of the binary interaction parameters for Wilson and NRTL, which takes into consideration chemical reaction taking place during experimental studies of a vapor-liquid equilibrium has been developed.

The computer models adequacy has been verified by comparing the results of the experimental studies with predicted isobaric data on phase<sup>2</sup> and chemical<sup>1</sup> equilibrium. Simulation of the continuous catalytic rectification process is carried out in stationary conditions in column apparatus of a tray or packed type<sup>4</sup>.

The results of the work can be used both to improve the methods of organofluorine esters and acids production as well as for developing rectification and distillation apparatus for their separation.

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## BEST AVAILABLE TECHNIQUES AND INDUSTRY ENVIRONMENT REFORM: EXPECTATIONS IN RUSSIA

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In Russia, the Best Available Techniques (BAT) concept has been developed since the 1970s though it was addressed as the concept of low-waste technologies. In 1990s, the first pilot projects aimed at evaluating opportunities for applying techniques identified as European BATs were implemented in glass, cement, ceramic industry, and pulp and paper sector.

In 2019, in accordance with the new Russian BAT legislation<sup>1</sup>, larger installations of the key industrial sectors will begin turning to BAT and Integrated Environmental Permits (IEP). Though both the legislation and Reference Books on Best Available Techniques (BREFs) were developed openly and discussed with wider stakeholders, there is a high level of misunderstanding and therefore wrong expectations. Let's consider them.

Yes, Russian BAT concept has many features in common with the European one. It is based on the continual development principle and open opportunities for the gradual enhancement of the environmental performance and resource efficiency in industry<sup>2</sup>.

Yes, BATs are the key instrument of the environmental industrial policy aimed at turning Russian industry to the innovative development, greening production and minimising environmental impacts.

No, Russian BREFs are neither translations of the European ones nor catalogues of technologies and equipment. In contrary, they are documents developed as the result of the national benchmarking, reflect the current state of art in the key industrial sectors<sup>2</sup>.

No, Russian BREFs do not jeopardise development of innovative solutions or require the compulsory implementation of any particular technology (technique). Instead, BREFs establish requirements to BAT-associated emission levels but not to technologies themselves<sup>2</sup>.

In 2019-2022, the first results of turning to BAT/IEP will be achieved by the key polluters (300 industrial installations) proving (or disapproving) positions described in this paper.

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## METHODOLOGY FOR THE DEVELOPMENT OF ENERGY RESOURCE EFFICIENT ENVIRONMENTAL AND SAFE CHEMICAL-TECHNOLOGICAL SYSTEM OF CLEANING WASTE WATER GALVANOCHEMICAL PRODUCTION

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The modern technological production of paint coatings includes plating shops, machine shops, assembling shops, a section of composite materials, a central factory laboratory and service shops.

During the service of such shop areas, liquid technogenic wastes are formed. This technogenic wastewater contains a wide range of harmful chemicals both organic (dibutyl phthalate, diphenylol propane, polyhydric alcohols, solvents like  $\text{CCl}_4$ , DMF etc.) and inorganic (heavy and non-ferrous metal ions:  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ , etc.) compounds, the discharge of which into the centralized water supply system is strictly limited. The maximum permissible concentration of them is 0.1-0.01 mg/L. The greatest amount of toxic substances comes from the plating shops, sections of paint coatings and composite materials.

The combined wastewater treatment is proposed to be used for solving this problem. The purification consists of sections of pre-treatment, desalting and concentrate utilization. Wastewater treatment is carried out on basis of treatment facilities of galvanic production.

The shop area of pre-treatment consists of a reactor, a settling tank, an electroflotter, a granular mechanical filter complex, a sorption filter complex, a filter press for sludge dewatering. The section of desalting and utilization includes an ultrafiltration plant, a reverse osmosis system, a module of thermal evaporation of the electrolyte ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ , etc.).

During the treatment up to 95% wastewater purified to the level of indicators GOST 9.314 (1 cat.) is returned to the process flow. A resource-saving way of the work of all basic elements has been developed.

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## ELECTROFLOTATION. THEORY, PRACTICE, PERSPECTIVES OF DEVELOPMENT

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Electroflotation technology in the last 20 years has become widespread when extracting from aqueous media sparingly soluble compounds of non-ferrous and rare-earth metals, organic emulsions, surfactants, petroleum products, highly dispersed carbon materials, including carbon nanocomposites. Industrial installations, installations for the extraction of the dispersed phase, emulsions, surfactants with a capacity of 1, 5, 10, 20 m<sup>3</sup>/h have been created and put into practice.

The main directions of fundamental research are related to the formation of the flotation complex H<sub>2</sub>O - dispersed phase - surfactant - emulsion - H<sub>2</sub> (O<sub>2</sub>), which has high flotation characteristics such as: the degree of extraction in the first 5 minutes  $\alpha_5$  (80 – 90 %), the maximum degree of extraction  $\alpha_{20}$  (90 – 99%), minimum electrical costs (0.1 - 0.5 kW·h·m<sup>-3</sup>). The role of gas saturation, the size and charge of particles and gas bubbles (H<sub>2</sub>, O<sub>2</sub>) in the efficiency of the electroflotation process.

The general laws governing the high efficiency of the electroflotation process have been established: for hydrophilic particles of the dispersed phase (hydroxyls of metals Fe, Al, Ti, Sc, rare earth metals), as well as highly dispersed carbon materials (OU-A, OU-B, CNP, BAU).

The factors that intensify the process include a positive value of the zeta-potential of the particles in the electrolyte, the hydrophobization of the surface of the particles due to the surfactant, the particle size of 10 - 100  $\mu$ m, the laminar mode of gas saturation.

Electroflotation process is suppressed for particles with negative  $\xi$ -potential (from -20 mV to -50 mV) and particle size less than 10 microns and more than 200 microns, with a high concentration of the dispersed phase (more than 500 mg/l) and surfactants (more than 100 mg/l).

*The study was carried out with the financial support of the Russian Foundation for Basic Research, project № 18-29-24010.*

## METHODOLOGY OF COMPLEX ANALYSIS OF GLOBAL CHEMICAL LOAD

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Chemical stress on the environment is one of the global challenges of our time as result of the exponential growth of production and use of chemicals<sup>1</sup>. Current approaches to the assessment of hazardous chemicals are mainly focused on individual areas and chemicals. Models for the estimation of a large number of chemicals are practically absent.



Figure 1. Mass of mercury, seen in freshwater bodies, g / cell

The paper presents a methodology for the integrated analysis of the global chemical load using the concept of a chemical footprint. The proposed approach has been implemented in practice to assess the impact on the environment of mercury and its compounds entering from various anthropogenic sources. Figure 1 shows the results of estimating mercury releases to freshwater bodies based on emission data reported by AMAP<sup>2</sup>. In this research work, estimates were carried out separately with the use of GIS on a grid with a size of 0.5 to 0.5°. Additionally, an algorithm to evaluate the movement of chemicals with water masses has been developed.

The results of this research work can be used to develop strategic decisions at a country level, for example, the relevance of such decisions on mercury can be associated with the development of national action plans required for the ratification of the Russian Federation of the Minamata convention on mercury.

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## AUTOMATED MONITORING SYSTEM OF POLLUTION OF ATMOSPHERIC AIR AND WATER OBJECTS BY ENTERPRISES OF THE CHEMICAL INDUSTRY

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The purpose of the automated monitoring system for water and air pollution (AUTOMATED MONITORING SYSTEM) is to provide environmental services with information on air pollution and support in making management decisions to improve the environmental situation<sup>1</sup>. The following elements can be distinguished in the AUTOMATED MONITORING SYSTEM: environmental data (measurement of the concentration of harmful substances); meteorological data (air temperature, wind speed and direction, pressure, humidity); information about the company; sensors for measuring; weather stations; network and terminal equipment; collection point; information processing subsystem; map or terrain map; emission data; operator or decision maker. The main tasks of the AUTOMATED MONITORING SYSTEM include: continuous collection of environmental and meteorological information; recording and storage of information; conversion of information into the most convenient form for analysis; making recommendations for making management decisions. The accumulation of environmental data on the server is carried out using stationary monitoring posts connected to the server through various communication channels. The AUTOMATED MONITORING SYSTEM allows operators to see current environmental information<sup>2</sup>.

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## MULTI-SCALE MODELING AS A BASIS FOR RESOURCE AND ENERGY SAVING IN THE CHEMICAL INDUSTRY

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The development of digital technologies for the chemical industry is a prerequisite for maintaining the competitiveness of Russian chemical enterprises at the global level. Digital technologies promote the basic goals and approaches of cybernetics of chemical-technological processes, such as mathematical modeling and system analysis, the foundations of which were laid under the direction of the academician V.V. Kafarov<sup>1</sup> at the end of the 20th century. System analysis allows to consider the processes at different scales: 1 - nano level (chemical interaction, material structure); 2 - micro level (research of diffusion of heat and mass transfer processes and phenomena); 3 - macro level (modeling of individual devices, technological schemes and work of the enterprise as a whole). Each level requires appropriate multi-scale modeling approaches, allowing to optimize processes at each level, which leads to resource and energy saving in general.

Using the example of the production of innovative material – aerogel<sup>2</sup>, which is called «solid smoke» and which is used as a composite material in rocket, aircraft, for thermal insulation in the Arctic, the use of multi-scale modeling is shown. The interrelation of models based on molecular dynamics, computerized cell-automaton models, mechanics of heterogeneous environments, as well as macro approaches to the design of technological schemes, enterprises, automation, logistics, ecology, and resource saving is shown.

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# THE INTEGRATED LOGISTIC SUPPORT OF EQUIPMENT AS A FACTOR OF SECURING OF ENERGY AND RESOURCES EFFECTIVENESS AND MANAGEMENT OF TECHNOGENIC RISKS

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According to GOST R 53394-2009, the ultimate goal of integrated logistics support (ILP) of equipment is to reduce operating costs. However, with regard to chemical industries, ILP, as an organizational and technological process, also provides energy efficiency<sup>1,2</sup> and quality of management of man-made risks. In this case, the quality of the ILP is determined by a similar characteristic of the execution of the procedures included in it. Currently, most of the procedures of ILP are carried out using disparate software, which significantly complicates their implementation and reduces the quality level.

The report presents the results of the development of problem-oriented system (hereinafter the System), which implements the functions of ILP and which provides high quality of ILP of process equipment. Quality improvement is achieved through the use of specially developed information and heuristic models, heuristic and computational algorithms, as well as the concept of an integrated information environment that allows you to automate:

- procedures for searching, entering and editing the source data;
- implementation of various engineering calculations;
- formation of passport-technical and operational documentation on the equipment;
- processing of the results of technical surveys;
- data exchange with external information systems.

The developed System is implemented at several chemical enterprises and has successfully established itself as a factor in ensuring energy efficiency and management of man-made risks.

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## ORGANIZATION OF RESOURCE-SAVING PRODUCTION SYSTEMS IN THE CONDITIONS OF DIGITALIZATION OF THE PETROCHEMICAL INDUSTRY

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In modern conditions, the main directions of improving the efficiency of resource-saving production systems is the use of digital technologies and automation of production and auxiliary processes. Using the procedure of factor analysis in the Statistica package, we carried out a grouping of indicators of the use of digital technologies into factors affecting the effectiveness of the resource-saving production system of petrochemical enterprises<sup>1</sup>.

The first integral factor with the conditional name "Information Systems Integration" is formed by five indicators: the share of organizations that had special software for managing sales of goods, the share of organizations that used ERP-systems, the share of organizations that used CRM-systems, the share of organizations that used electronic data interchange between their own and external information systems on the exchange formats, the share of organizations that used SCM-systems, which characterize the potential of industrial enterprises to use integrated control systems in the Supply Chain. The second integral factor with the conditional name «Electronic Commerce» is formed by two indicators: the share of organizations that placed orders for goods (work services) on the Internet and the share of organizations that had special software tools for managing the procurement of goods. The third integral factor with the conditional name "Electronic Communications" is formed by two indicators: the share of organizations using electronic document management systems and the share of organizations using open source operating systems provided by third parties, for example, Linux. The share of total variance in the explanation of the resultant for all three integral factors is 91%.

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## THE ELECTROCHEMICAL METHOD OF OIL-CONTAMINATED SOILS TREATMENT

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Electrochemical treatment of soil contaminated with oil and oil products allows cleaning them by reducing the concentration of petroleum hydrocarbons and other related pollutants, such as salt of formation water.<sup>1</sup>

It was found that transmission of amounts of charge through the soil (for chernozem -  $0.96 \cdot 10^7$ , for clay -  $0.63 \cdot 10^7$ , for loam -  $0.93 \cdot 10^7$ , for sand -  $1.34 \cdot 10^7$  C / kg of oil products) allows to achieve the efficiency of cleaning 75.67 - 84.52% of oil products for different types of soil.<sup>2</sup>

The calculation of the main electrical parameters of the cleaning process was carried out.<sup>3</sup>

The study of soil characteristics changes occurring by the small amperage treatment showed a slight decrease of the soil total organic matter, moderate soil compaction and an active decrease of chloride ions and humidity.

The effect of the electrodes material on the intensity of the process is studied.

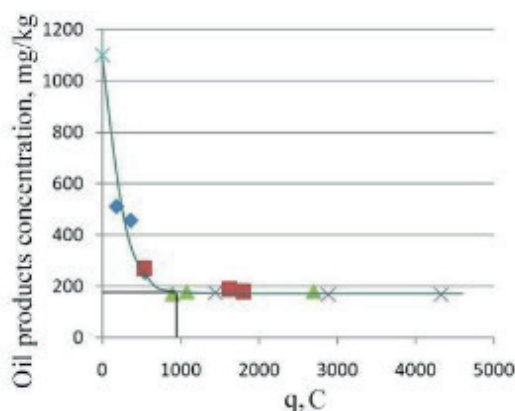


Figure 1. The decrease in the content of petroleum products in clay soil

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## PROCESS INTEGRATION EXTENSIONS FOR INCREASED ENERGY EFFICIENCY AND FOOTPRINT REDUCTION

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Large amounts of energy are used in industry, commercial and residential sectors, relying mainly on fossil fuels. The costs and emissions can be reduced by applying Process Integration (PI), which started as Heat Integration (HI) <sup>1</sup>. PI is a family of methodologies for combining processes or their parts for reducing the resource consumption and emissions <sup>2</sup>. HI has been extensively used in the processing (e.g. chemical, petrochemical, pulp and paper, food and drink) and power generating industries. It allows to reduce the amount of external heating and cooling, together with the related cost and emissions. It provides systematic design procedures for energy recovery networks.

The presentation discusses the implementation and Data Extraction issues, the Total Site Integration (TSI) targeting, accounting for individual process heat transfer characteristics, Total Site capital cost targeting, novel representation tools for retrofitting Heat Exchanger Networks, illustrated on a bromine plant example. The presentation then analyses the challenges and indicators to be considered, to enable sustainability evaluation and emissions impact of industrial sites. These include GHG and Water footprints, supplemented by investment and total cost targets. Further extensions to the methodology are also presented, allowing to design regional supply networks for renewable energy resources.

The final part of the presentation provides an analysis of the PI development trends, clearly showing the need for a unified modelling and workflow framework, as well as for the introduction of the essential indicators of the energy system performance – energy costs and environmental footprints.

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# ELECTROPLATING AND SURFACE TREATMENT: RESOURCE CONSUMPTION, CLASSIFICATION, SYSTEMATIC APPROACH TO THE SELECTION OF RESOURCE EFFICIENT TECHNOLOGIES

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The volume of production of electroplating coatings in the world (740 – 1700 thousand tons/year) and in Russia (25 – 44 thousand tons/year) was estimated.

On the basis of the concentration of ions of non-ferrous metals in a baths (ci) and the sum of the concentrations of all components of the baths proposed and used for electrodeposition coatings, the methodology of estimation of resource content and classification baths for the electrodeposition coatings<sup>1</sup>.

This technique is aimed at ensuring the environmental performance of the technology (in terms of the achieved level of concentrations of chemical compounds in technological solutions), corresponding to the technological indicators of the best available technologies, and can also be used in research activities, for example, in the development of new bath compositions for electrodeposition of metals and alloys.

Guided by the results developed self-regulating bath protective-decorative chromium plating on based complex compounds of trivalent chromium with a concentration of 0.3 mol/l, and HCOOH, KBr, H<sub>3</sub>BO<sub>3</sub>, NH<sub>4</sub>Cl The bath is additionally content a slightly soluble salt [Cr<sub>3</sub>(OH)<sub>2</sub>(HCOO)<sub>6</sub>]Cl·nH<sub>2</sub>O to maintain the effect of self-regulation with a decrease in the concentration of both chromium ions and formic acid. The bath can be attributed to the group with low resource consumption and recommend this composition for practical use.

A modified nonparametric-statistical method of SWOT analysis is proposed, which allows to quantify the reliability of the conclusions about the feasibility of changing technologies in the development of science-based strategies for the development of enterprises (industries)<sup>2</sup>.

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## SCIENTIFIC BASES OF ENERGY RESOURCE EFFICIENT PROCESSES AND APPLIED METHODS OF ENVIRONMENTALLY SAFE MICROWAVE PROCESSING OF OIL SLASH

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The results of the analysis of scientific papers and patent elaboration of the existing methods and technologies for the separation of water-oil emulsions made it possible to implement energy-efficient processes of microwave exposure to hydrocarbon-containing media.

Based on the analysis of existing mathematical models of the direct and reverse oil-water emulsions structure and evaluation of the behavior of oil-water emulsions in the microwave field, a mathematical model of the interaction of microwave energy with oil-water emulsions 1 has been developed.

The use of this model allows determining the most effective parameters of the microwave exposure for phase separation with different compositions and dielectric parameters of emulsions.

Computational experiments have been carried out to identify the dependence of the binding energy of water molecules and different grades of oil on the physicochemical properties of the emulsion and the technological factors of the sludge processing. An experimental installation of microwave sludge processing has been developed and manufactured, which allows determining the adequacy of the developed model.

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## PROTECTIVE CHROMATE-FREE CONVERSION COATINGS ON GALVANISED STEEL

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Hexavalent chromium compounds, which are included both in the composition of chromate solutions and in the composition of chromate coatings, are very toxic and are carcinogenic.

In recent years, nanoscale conversion cerium-, silicon-, zirconium-, titanium- and molybdenum-containing coatings are increasingly used as an alternative to chromating in world practice. Domestic developments in the field of deposition of these protective coatings do not exist<sup>1-3</sup>.

The present work is devoted to the development of the process of chromate-free passivation for galvanized steel.

The experiments made it possible to determine the concentration ranges of the components of the solution, as well as the process parameters in which it is possible to form good-quality coatings with high protective ability.

The solutions developed make it possible to form passivating protective coatings on galvanic zinc coatings deposited from various types of electrolytes galvanizing on hangers and in bulk in a drum. It has been established that the developed passivating coatings on zinc in terms of corrosion resistance and protective ability are comparable with rainbow chromate coatings. The developed coatings withstand high temperatures without deterioration.

Developed concentrates for the preparation of working solutions and their adjustment during operation.

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## DEVELOPMENT OF METALIZATION PROCESS THROUGH PCB HOLES

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The process of electrochemical metallization of through holes is an integral part of the production of printed circuit boards (PCB) and the reliability of products depends on the quality of its implementation. The complexity of the metallization of through holes in modern PCB is due to a decrease in the diameter of the holes and an increase in the ratio of the diameter to the thickness of the PCB with an increase in their accuracy class. To metallize holes in modern PCBs, more and more high-tech processes of galvanic copper plating are required, ensuring uniform coating in the holes and on the PCB surface. Therefore, the development of the electrolyte of copper plating of the holes, which provides the formation of a coating that meets modern requirements, is highly relevant.

This paper is devoted to the study of the effect of additives in copper sulfate electrolyte on the distribution of the coating in the through holes of printed circuit boards. Polymeric inhibiting additives ( $P_1$ ,  $P_2$ ,  $P_3$ ) and leveling additives, which are nitrogen-containing compounds ( $M_1$ ,  $M_2$ , C), were investigated.

A copper-plating electrolyte was developed (containing in g/l): 60  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 220  $\text{H}_2\text{SO}_4$  (96 %); 0,12 NaCl; 0,5  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; combination of additives 10  $P_2$  and 0,005-0,1  $M_1$ ; 10  $P_2$  and 0,005-0,1  $M_2$ ; 10  $P_2$  and 0,005-0,1 C; 5  $P_3$  and 0,005-0,1 C, not inferior to the foreign counterpart in dissipative ability and satisfying the uniformity of the coating in thickness in the holes and on the surface of the PCB (Figure 1).

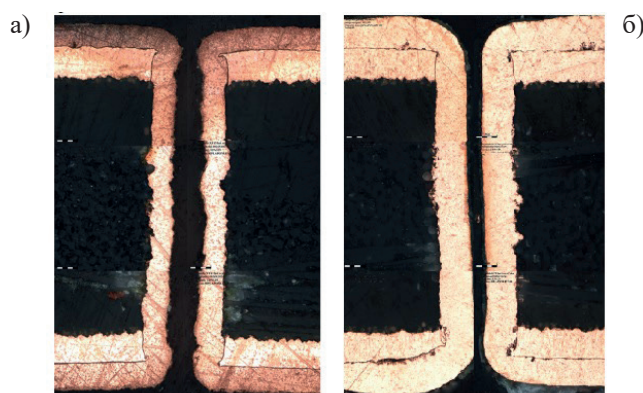


Figure 1. Photography (x2000) of transverse section of PCB with a hole  $\varnothing$  0,8 mm with copper coating deposited from:  
a) developed electrolyte containing  $P_2$  – 10 g/l,  $M_2$  – 0,1 g/l; b) from the electrolyte – foreign counterpart.

## USE OF THE BIOPLATO FOR REMOVAL OF RESIDUAL CONTAMINATION OF INDUSTRIAL DRAINS

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The modern state of the most water bodies and coastal zones does not comply with the maximum permissible standards. Water pollution indicates the need for water treatment systems. For this goal, the proposed were used of biological engineering structures with higher aquatic vegetation– bioplato (floating plant islands). The cleaning process occurs due to the natural ability of a number of living organisms and plants to absorb, decompose and recycle pollutants.

In the course of the experiment, a set of successively placed containers of wastewater containing certain concentrations of heavy metals and petroleum products was assembled. The imitation biosystem of the plant– microorganisms was represented by rhizomatous plants of the Iridaceae and Typhaceae family, represented *Tipha Gracilis* and *Iris Pseudacorus* L and anaerobic microorganisms.

A comparative analysis was made of data from the control group of plants and the working group. Also, data on the dynamics of cleaning bioplato on individual components and its combined action with the use of prolonged-action biologics and chelate complexes depending on the temperature profile, various regimes circulation of water flows and aeration.

The magnitude of bio – and phytomass needed for wastewater treatment has been revealed. The result was investigated the effects of various agents stimulating the extraction (accumulation) of plant contamination at various concentrations of heavy metals and petroleum products.

As a result, working approaches were obtained for the creation of highly efficient mobile combined floating bioplats adapted for temperate climate zone. A method of “building up” the root system was also proposed, which yields significant results from an active bacterial film necessary for cleaning wastewater. Creation of the process of degradation in the autumn-winter period through the use of strains of anaerobic microorganisms in the aggregate action with prolonged-action biologics.

*The study was carried out with the financial support of RFBR project No. 18-29-25068.*

## INVESTIGATION IN THE FIELD OF MASS TRANSFER DEVICES CONTACT ELEMENTS FOR INCREASE ITS ENERGY EFFICIENCY

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Increase of heat and mass transfer energy efficiency for industrial devices in chemical technology, petrochemical industry, power energetics and other is a modern urgent task. At least, partially it is possible by improvement of traditional and creation of new contact elements.

There are two main directions to improvement of contact elements – technological and constructive. In both cases they are technical solutions for significant increase of industrial processes with application those contact elements by simultaneous power consumption decrease.

Recently in Moscow State University of Environmental Engineering (former MICHM) multiple studies of new irregular and regular packing elements have been conducted. These packing elements have small flow resistance, large contact surface, high mass transfer coefficient values and consequently large energy efficiency.

In those investigations different types of ring and mini-ring, volume-lattice, combined (combination of irregular and regular) packing elements from different materials have been studied.

Summary of experimental and theoretical results and comparison of new packing with their foreign analogues are made. Recommendation for new packing application for different heat and mass transfer processes are proposed.

## METHOD AND INFORMATION TECHNOLOGY OF COMPLEX RISK MANAGEMENT IN HEAT-TECHNOLOGICAL SYSTEMS

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The complex nature of risk management in heat technology systems (FTS) is determined by the requirements not to exceed the permissible or critical level of disruption risk of various processes (both for processes in general and for individual stages of these processes).

A model of complex risk management is proposed while ensuring resource- and energy saving processes in FTS<sup>1</sup>. The structure of this model is cascade. It consists of the following fuzzy models: (i) models for the analysis at all stages of processes in FTS; (ii) models for estimating of resource- and energy efficiency, as well as models for estimating of disruption risks at all stages of the processes in FTS; (iii) models for estimating of disruption risks of the processes in FTS; (iv) models for estimating of the overall resource- and energy efficiency in FTS and models for estimating of the generalized disruption risk of processes in FTS as a whole<sup>2</sup>.

A method and information technology of complex risk management in FTS are proposed. The method is based: firstly, on the determination of various combinations of control parameters at each stage of the processes in FTS (taking into account limitations); secondly, on modeling and defining of parameters for increasing resource- and energy efficiency of processes in FTS (without exceeding of the permissible or critical level of disruption risk of these processes).

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## LEACHING OF NON-FERROUS METALS FROM WASTES OF POLYMETALLIC ORE DRESSING

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Ores dressing wastes are currently regarded as technogenic raw materials<sup>1</sup>. The goal of the present work was to study the leaching of non-ferrous metals from samples of old flotation tailings with sulfuric acid solutions (from 0.5 to 10%) and distilled water. Leaching was carried out using percolators and bottle agitator. Percolators were loaded with 100 g of old tailings, and leaching was performed with 100 mL of acid solutions. Pulp density during agitation leaching (S : L) was 1 : 5. The first sample of flotation tailings contained 0.26% of copper, 0.22% of zinc, and 17.4% of iron, and the second sample contained 0.36% of copper, 0.23% of zinc and 23.2% of iron. Percolation leaching made it possible to extract up to 43 and 47% of Cu and Zn from the first sample. Extraction was maximum during the leaching with 1 and 2.5% sulfuric acid solutions. During the agitation leaching, the maximum extraction rate was reached with a 2.5% sulfuric acid solution (52 and 54% Cu and Zn), but the leaching rate with all solutions and distilled water differed insignificantly. Percolation leaching made it possible to extract up to 54 and 37% of Cu and Zn from the second sample tailings, while agitation leaching made it possible to extract up to 34 and 68% Cu and Zn. The rate of non-ferrous metals extraction from the second sample with water did not differ significantly from that with acid solutions. In all experiments, the increase in the H<sub>2</sub>SO<sub>4</sub> concentration led to the increase in concentrations of iron ions in productive solutions, which impedes the extraction of non-ferrous metals from solutions. Thus, it was possible to reach selective leaching of non-ferrous metals and to obtain solutions with relatively low concentrations of iron ions. After leaching non-ferrous metals, old flotation tailings may be leached with acid solutions to produce productive solutions with high concentrations of Fe<sup>3+</sup> ions that can be used to leach metals from various raw materials, including technogenic ones (substandard concentrates, slags).

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FUNCTIONAL MODELING  
OF LIQUID MIXTURE SEPARATION PROCESSES

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Functional modeling provides the ability to build a structured, formal description of the production and management processes. An important advantage of functional modeling is the use of graphical language. This language is clear and understandable not only for technologists, but also for specialists in the field of management, information, quality. The formal language provides the possibility of automated verification and analysis of the functional models. Separation processes of liquid mixtures are technologically complex and the most energy-intensive stage of chemical manufacturing. Usually, the separation is subjected to a multicomponent reaction mixture containing in addition to the target product unreacted raw materials, products of adverse reactions, solvents, catalytic system, etc.

We have developed generalized functional models of both technological processes of separation of liquid mixtures and accompanying processes of quality control of the products obtained. As an example, a diagram describing the process of rectification is presented at fig.1.

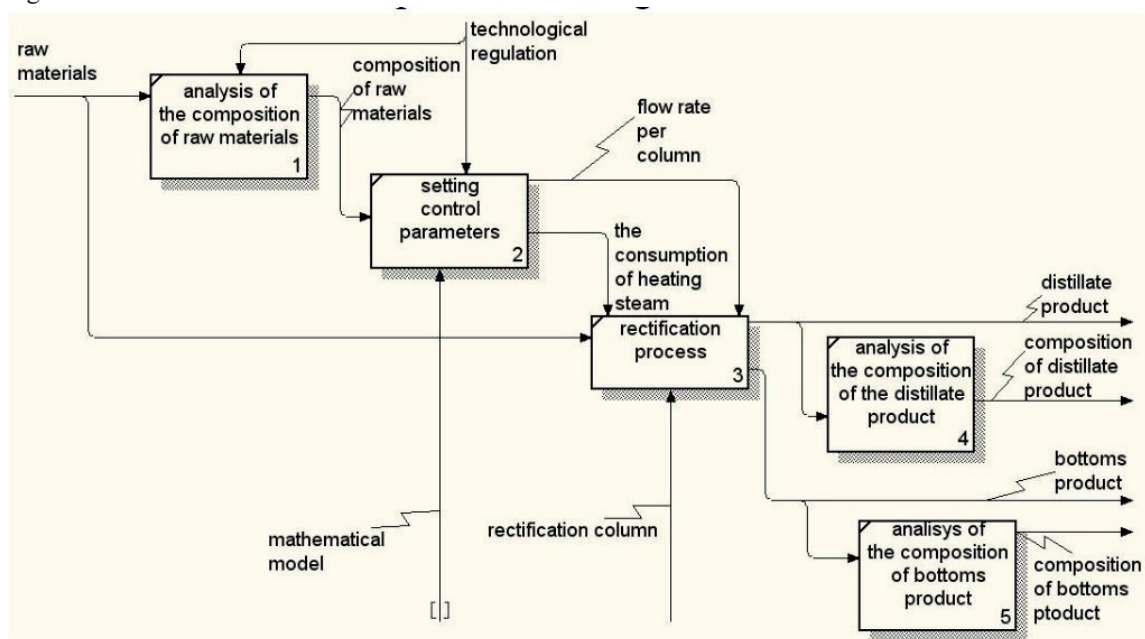


Figure 1. Functional diagram describing the process of rectification

The detailing of these models for the production of vinyl acetate from various raw materials (acetylene and ethylene).

## BIODETERIORATION OF FUELS AND LUBRICANTS INFLUENCED BY MICROORGANISMS-DESTRUCTORS OF HYDROCARBONS

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Currently, biodegradation of fuels and lubricants (FL) are serious problem. The cause of biodegradation is the development of hydrocarbon-oxidizing microorganisms. As a result of the vital activity of fungi and bacteria in petroleum products, a hydrocarbon composition changes, a biomass accumulates. Such changes lead to a deterioration in the quality of FL, clogging filters and fuel systems<sup>1</sup>.

The effect of biodegradation on the physicochemical properties of basic and commercial diesel fuels and fuels for jet engines, industrial and engine oils, and motor gasoline were investigated in this work. For this purpose, the investigated FL were infected with the association of active microorganisms-destroyers, which we had previously isolated from aviation fuel.

On the 25th day of the experiment, the most biostable turned out to be the gasoline. A change in color, intense turbidity of the fuel, formation of biofilms and accumulation of biomass were observed in the other FL. Indicators «content of mechanical impurities» and «general pollution» were higher than the permissible values by several times. The results of the study showed that, according to the degree of biodeterioration, the investigated FL form the following row: TS-1 > the diesel fuel > engine oil > industrial oil.

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## CATALYTIC DECOMPOSITION OF AMMONIA FROM COKE GAS

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Coke production that is the base of ferrous metallurgy entails to formed of toxic ammonia. For the prevention of it's emissions in atmosphere all the more commonly used *Carl Still* method with catalytically decomposed of ammonia vapors in the reducing medium.

By the thermodynamic limitations (the equilibrium ammonia concentration grows rapidly in inverse proportion to the temperature) and to prevent the poisoning of catalyst by sulphat (hydrogen sulphite concentration in ammonia vapors reaches ~8 % vol.) process of ammonia decomposition is carried under temperature nor less then 11000C in lined reactors (furnaces) with using special thermostable catalysts. Specially for that process BASF firm was producing the nickel magnesite catalyst G1-11 that was using in furnaces of ammonia decomposition H-6101 at PJSC *Magnitogorsk Iron and Steel Works (MISW)*.

Statistic analysis of data monitoring during 9 years G1-11 exploitation in both ammonia decomposition furnaces *MISW* show the nonreversible decrease in activity of G1-11 catalyst with stable rate it's deactivation that make feasible derive a reliable forecast of catalyst activity in exploitation.

With the purpose to substitute imported it is developed home-produced catalyst for ammonia decomposition KDA-18 (NIAP-13-06) that is a nickel oxide on a corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) base that is manufacture in forms of rings and grains 16,5 mm size with diminish resistance to the gas flow.

Exploitation NIAP-13-6 catalyst in furnaces ammonia decomposition H-6101 at *MISW* since 2017 indicate that the NIAP-13-6 catalyst compare favorably with G1-11 *BASF* catalyst in activity.

For using all known high-activity catalysts with a little size of it's grains it is designed a high-temperature axial reactor that has a central vertical combustion chamber surrounded by a circular horizontal layer of catalyst.

The technology of catalytic decomposition NH<sub>3</sub> that well developed for the treatment of ammonia from coke-oven gas may be employed in other fields of metallurgy for example in affinage production at JSC «*KRASTSVETMET*» instead two-stage oxidation of ammonia vapors which principally is unstable.

## CONCEPT OF A DIGITAL MODEL OF CHEMICAL MANUFACTURE RISK MANAGEMENT

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Any activity of the chemical industry is associated with threats not only in the environmental field and people's life, but also in the financial sector. Research in the field of risk management in this area will always be relevant and priority because of the specific nature of the activities of chemical plants, the complexity of technological processes and equipment.

Today there is a lot of specialized software based on the ERM-system, which emphasizes the high rate of implementation of this methodology in all types of organizations. Since each enterprise has its own specifics and internal corporate rules, the most effective option for implementing an automated risk management system in an enterprise is the development of its own software. When an organization plans to create an effective EPM program, it should adhere to general rules: having a strategic plan, a simple structure and a clear interface, the interest of top management, communication between risk management indicators and performance indicators, the cost-effective concept of the system's technological solutions<sup>1</sup>.

As a result of the research, we developed the concept of a digital risk management model which we divided into the following related subsystems: a monitoring and risk prediction system, a risk identification system, an alert and response system, a system of proposed remedial actions, a damage assessment system, a reporting system and journaling, knowledge base accumulation system. For each of these subsystems were written business requirements for all automated functions.

The using of such models will significantly increase the efficiency and safety of the activities of chemical plants.

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## HEAT EFFICIENCY IMPROVEMENT OF CHEMICAL PRODUCTION HEAT EXCHANGERS BY IMPROVING DESIGN AND MATERIAL PERFORMANCE

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A set of computational and experimental studies was carried out using a double-circuit laboratory test bench designed for comparative evaluation of hydraulic resistances and thermal efficiency of heat exchangers.



Figure 1. Dual Circuit Test Bench

Tests of a small-sized shell-and-tube heat exchanger with a collapsible involute-shaped tube bundle have shown its effectiveness in comparison with typical shell-and-tube and lamellar apparatuses<sup>1</sup>.

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## IMPROVING THE EFFICIENCY OF THE TECHNOLOGY OF MICROWAVE HEATING OF HEAVY OIL DEPOSITS, OIL SANDS AND BITUMEN

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Ultra-high-frequency and high-frequency methods of impact on the oil reservoir for maximum oil recovery, due to their environmental, economic and technical advantages, are the subjects of research for scientists in many countries.

Microwave heating has a significant disadvantage as a small depth of penetration of electromagnetic waves and, therefore, limited coverage of the formation by heating. In case of microwave effects, the formation will be heated in the same places, and the temperature near the antennas can rise to unacceptable limits. This is explained by the following circumstances: firstly, the antennas used in the bottom have a narrow radiation pattern, and secondly, the microwave energy at a wavelength distance is almost completely attenuated. Therefore, the microwave effect on the formation must be carried out in short time cycles. According to the results of computational experiments on the developed mathematical models of the reservoir heating process, confirmed experimentally on the physical model of the reservoir (up to 3 cubic meters), a fundamentally new microwave heating technology is developed, based on the replacement of the time cycle by the «spatial», which eliminates overheating of the reservoir near the antenna, while ensuring uniform heating of the reservoir throughout all the volume. The method of calculation of the scheme of formation drilling by injection and production wells is also proposed.

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## ELECTROFLOTATION EXTRACTON OF SURFACTANTS ON DISPERSED PHASE OF ALUMINUM AND IRON HYDROXIDES

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A large number of chemicals is produced for needs of modern industry; it is associates with their release into wastewater. One of the most common contaminates are surfactants. Adsorption of surfactants on the surface of dispersed phase of metal hydroxides with following electroflotation separation is promising method of wastewater treatment.

The table presents experimental data of influence of initial concentrations on sorption value of some surfactants on freshly formed sediments of iron and aluminum hydroxides.

Table 1. Comparative analysis of efficiency of adsorption ( $q$ , mg/g) for anionic, cationic and non-ionic surfactants on adsorbents:  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ .

Conditions of the process:  $\tau=60$  min,  $\text{pH}=7$ , adsorbent  $C(\text{Me}(\text{OH})_3) = 10$  mg/L

C, mg/L	q, mg/g					
	$\text{Fe}(\text{OH})_3$			$\text{Al}(\text{OH})_3$		
	NaDBS	DDAC	Synthanol	NaDBS	DDAC	Synthanol
50	25	60	5	215	50	205
100	40	82	50	225	280	370
250	355	380	125	405	662	945
500	825	940	175	430	1808	1175
750	905	900	70	215	2902	1285
1000	850	1116	80	245	3626	1200

It was established that the process of electroflotation of iron and aluminum hydroxides in the presence of surfactants proceeds efficiently. The time of electroflotation is 5-10 min; recovery is 95-99%; energy consumption is 0.5-1 kWh/m<sup>3</sup> of treated water.

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## RESOURCE-SAVING TECHNOLOGIES IN THE FIELD OF PRODUCTION AND APPLICATION OF CARBON NANOTUBES

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The process of production of carbon nanotubes (CNT) and hydrogen by the method of catalytic pyrolysis of hydrocarbons is considered. A kinetic scheme for the CNT synthesis has been developed. The kinetic parameters have been determined on the base of experimental studies. A mathematical model of a continuous screw reactor for the CNTs production has been developed and optimal conditions for their production (feed rate of hydrocarbons, catalyst, process temperature, the ratio between hydrocarbons and hydrogen) have been found.

The CNT application is considered for two cases: 1) in hydrogen fuel cells; 2) in the creation of ceramic composites with high mechanical properties.

A mathematical model of a hydrogen fuel cell (with a catalyst modified by CNT) has been developed, taking into account the degradation of the electrochemical active surface area (ECSA). The mechanism of ECSA degradation has been studied and modeled. It was found that the presence of CNT in the catalyst could significantly reduce the content of platinum at detention of the current-voltage characteristics.

Mathematical models of sintering processes (free sintering without application of pressure, spark plasma sintering) of ceramic-matrix composites based on  $\text{Al}_2\text{O}_3$  modified with CNT have been developed. The mathematical model of free sintering without the application of pressure is built on the basis of the neural network apparatus, the spark plasma sintering is based on the methods of mechanics of heterogeneous media. In order to solve the first-order partial differential equations a new absolutely stable difference scheme with the second order of time and pore size approximation has been developed.

The kinetic parameters have been determined from a comparison of the calculated and experimental data. The optimal temperature regimes of sintering processes, which provide production of ceramic-matrix composites with high mechanical properties have been found.

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## VEGETABLE RAW MATERIALS AS A BASIS FOR MEDIUM- TONNAGE AND BULK CHEMICAL PRODUCTS

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The chemical and technological aspects of using renewable (plant) sources of raw materials for the production of medium-tonnage and bulk chemical products are considered.

Starch- and sugar-containing crop, as well as oilseeds are used as a source of raw materials.

Starch and sugar, with high efficiency can be biotechnically converted into carboxylic acids (lactic, succinic, etc.) and bioethanol. The above listed bio-products can be used as raw materials for resource-saving chemical technologies for producing various chemical products, such as polylactic acid (biodegradable plastic), propylene glycol, “green” solvents, environmentally friendly plasticizers, ethyl acetate, etc.<sup>1-3</sup>.

Seed oils serve as a source of higher carboxylic acids, which can be efficiently processed into fuel hydrocarbons (including “bio jet fuel”)<sup>4</sup>, higher fatty alcohols<sup>5</sup>, and environmentally friendly plasticizers for PVC<sup>6</sup>.

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## INCREASING THE EFFICIENCY OF HEAT EXCHANGERS BY USING VOLUMETRIC INTENSIFIERS

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An important problem of increasing the efficiency of heat transfer processes is solved by using fine random metal packings in channels of the apparatus.

Physical modeling of heat transfer is carried out on an experimental stand in a “pipe-in-pipe” heat exchanger, using a random metal packing as an intensifier in the internal pipe when industrial oil is heated in the temperature range of 40–50 °C. Without the use of the packing, the flow of oil is laminar. Due to the packing, turbulization of the flow of oil occurs. A fine (~6 mm) metal packing (similar to the packing “Inzhekhim 2012”) with a specific surface area of 580 m<sup>2</sup>/m<sup>3</sup> and a free volume of 95% is experimentally investigated. It is found that when industrial oil of grade I-8A is heated through the pipe’s dividing wall with hot water by means of the use of the random packing, an increase in the coefficient of heat transfer from oil is by 14–15 times at the Reynolds number  $Re_M=170-270$  for oil and at  $Re_B=10^4$  for hot water. Comparison of experimental results for the coefficient of heat transfer from oil versus a known theoretical expression obtained by the Prandtl model is performed. It is established that agreement between calculated and experimental data is within ±5%.

Modified complexes are obtained for the comparative thermal-hydraulic efficiency of heat exchangers equipped with intensifiers and conclusions are drawn on the most efficient designs and operating modes of the apparatus.

Results of the obtained experimental and theoretical studies are used in engineering firms, design organizations as well as at industrial enterprises when creating compact heat exchangers.

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## IMPLEMENTATION INTO INDUSTRY OF MODERNIZED ENERGY- AND RESOURCE- SAVING APPARATUS FOR SEPARATION OF HYDROCARBON MIXTURES

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Based on application of methods of mathematical modeling of heat and mass transfer processes, scientifically grounded energy efficient technical and technological solutions for energy and resource saving modernizations of industrial heat and mass transfer devices and installations with the selection of import-substituting main and auxiliary equipment are developed.

The main methods of improving energy efficiency and energy saving are as follows: replacing outdated contact internals in industrial apparatus with more efficient domestic ones, which will ensure the intensification of heat and mass transfer processes; improving the products quality; reducing energy costs per unit of output; well-reasoned selection of energy-efficient technological regime in terms of minimizing energy costs for the given products quality and environmental safety of production; modernization or replacement of auxiliary equipment at heat and mass transfer units to ensure a high degree of energy-efficient cleaning of heat carriers, process streams, gas and liquid emissions; changes in heat technology schemes for the purpose of energy-efficient distribution of thermal loads. Import-substituting energy-efficient scientific-technical solutions for the modernization of more than ten distillation and absorption apparatuses at a number of enterprises of the oil and gas chemical complex of the Russian Federation are developed and implemented<sup>1</sup>. For example, in the production of ethylene, energy consumption is reduced by 8-10% per unit of output; in the production of motor fuels, desulfurization columns are modernized. A technical solution for the modernization of the crude topping unit is developed and implemented. As a result, the productivity of the gasoline plant is increased with an economic effect of more than 3 billion rubles per year.

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## INCREASING THE EFFICIENCY OF PURIFICATION OF WATER FROM DISSOLVED GASES

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Comparative characteristics of energy-mass transfer efficiency of water purification in devices realizing various methods of organizing the interfacial surface during interaction of liquid and gas (vapor) are obtained, and scientific-solutions are developed with the help of mathematical modeling methods for improving the efficiency of thermal deaerators and decarbonizers.

A scheme for upgrading a plant for water deaeration with an additional straight-flow packed turbulization device is patented. Increased purification efficiency is achieved by installing a mass transfer turbulization device with an intensifier (fine packing) to the water inlet pipe. Before entering the packed bed, air (decarbonization) or water vapor (deaeration) is supplied. Random packing provides intensive turbulent mode of air (vapor) interaction with water and crushing into small bubbles. Due to this, the specific contact surface of the phases is significantly increased and high efficiency of mass transfer (extraction of dissolved gases) is ensured.

Based on the diffusion model of the flow structure, a procedure is developed for calculating a straight-flow mass transfer turbulization device for determining the feasibility of its use. A decarbonizer with a packed straight-flow turbulization device is calculated. The calculation shows a decrease in the overall hydraulic resistance of the main apparatus due to a decrease in the required packed bed height, and an increase in the efficiency of purification from dissolved gases to the required level at high concentrations of them in the water in the supply line. At low concentrations at the inlet, a straight-flow packed device can be excluded from work by means of bypass of water and it is possible to conduct purification only in the main apparatus. Similarly, one can use a straight-flow mass transfer device also for the purpose of increasing the efficiency of the thermal deaerator<sup>1</sup>.

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## SYNTHESIS OF PHOTOCATALYTIC ACTIVE $\text{Fe}_3\text{O}_4\text{-TiO}_2$ CORE-SHELL COMPOSITES

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Synthesis of the  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  materials with magnetic and photocatalytic properties will solve the problem of the photocatalysts extracting from the liquid phase. The important points in the synthesis of  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  composites are the preparation of well-crystallized  $\text{TiO}_2$  with anatase structure and the preservation of the magnetite phase, which can be achieved by modifiers introducing.

The  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  core-shell composites with different Fe:Ti content were obtained by the hydrolysis of  $\text{TiOSO}_4$  in the presence of  $\text{Fe}_3\text{O}_4$  modified with citric acid and urea, under the hydrothermal conditions at 160 °C, followed by calcination at 400 °C.

The existence of  $\text{Fe}_3\text{O}_4$  and anatase of  $\text{TiO}_2$  phases was confirmed by the XRD and Raman results. Based on SEM and low-temperature nitrogen adsorption method characterizations, the  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  samples are mesoporous agglomerates with spherical shapes and diameter sizes between 2 and 5  $\mu\text{m}$ .

According to the first-order rate constants of methylene blue degradation under UV irradiation with main wavelength 365 nm, the apparent rate constants increase with the rise of the  $\text{TiO}_2$  content in the samples. The rate constant of  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  with Fe: Ti = 0.1 is 0.0105  $\text{min}^{-1}$ .

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## RECEIVING A NEW POLYMERIC REAGENT ON THE BASIS OF POLYACRYLONITRILE

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Waste in the production of synthetic fibers (PAN) is a promising polymer reagent for use in repair and insulation operations in wells of oil and gas fields.

The authors have developed process schedules for obtaining a new polymer reagent by hydrolyzing PAN fibers with sodium silicate (Figure 1) at a ratio of 1:15, provided that the poly-electrolyte anions are compensated with sodium ions at a temperature of 95 °C and a gel spatial structure forms with strong acids.

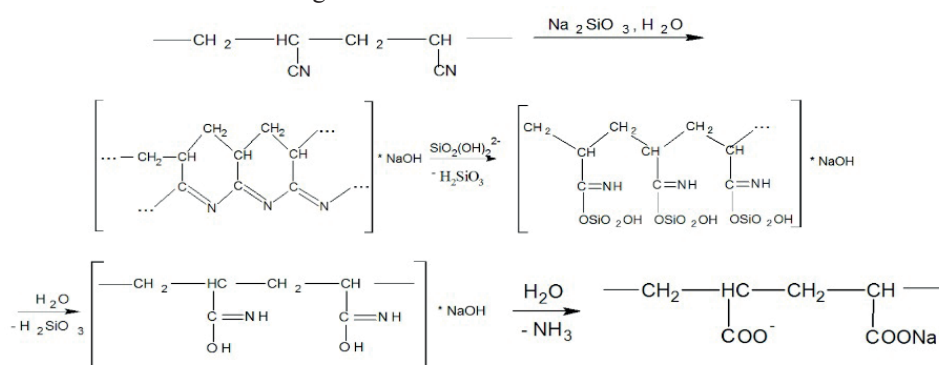


Figure 1. Scheme of hydrolysis of PAN in an aqueous solution of sodium silicate

The optimal concentration of the gel-forming composition<sup>1,2</sup> with a gelation time of 15-24 hours is substantiated based on rheological and physicochemical studies. The gelation mechanism of a new composition is proved, which exhibits high strength characteristics and stability to aggressive formation medium in simulated reservoir conditions.

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## PROBLEMS OF LARGE-SCALE UTILIZATION OF INDUSTRIAL WASTE

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One of the most important problems of the present-day world is the deteriorating environmental situation, lack of energy supplies and intensification of the adverse impact of natural and technogenic processes on the environment<sup>1</sup>.

Most of these problems can be solved by means of integrated utilization of mineral raw materials for new-generation composites production<sup>2,3</sup>.

Solving these problems is possible by using interdisciplinary and transdisciplinary approaches. Within the theoretical statements of geonics (geomimetics) the methodological basics for transforming industrial wastes into technological raw stuff were developed, and a wide range of composites for creating the comfortable human living environment was designed.

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## ALLOCATION OF A CONCENTRATE OF LANTHANUM AND CERIUM FROM THE EQUILIBRIUM FLUID CRACKING CATALYST IN THE FLUORIDE WAY

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Rare-earth elements (REE) use in high-tech industries. The equilibrium fluid cracking catalyst (e-FCC), brands Avangard, made on Omsk Refinery contains 1% of La and Ce that is comparable to their content in industrially processed ores, however now it is not processed. In work the technique of allocation of REE from e-FCC with use as the opening agents of  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4\text{F}$  is considered. As a result of interaction of  $\text{SiO}_2$  has to be removed quantitatively from e-FCC, and  $\text{Al}_2\text{O}_3$  to turn into easily soluble sulfate. The La, Ce and Mg connections pass into insoluble fluorides. Therefore after rest washing we receive a fluoride concentrate of La and Ce with Mg impurity from soluble connections. The study was carried out by the complete factorial desing (CFD). The mass of  $\text{NH}_4\text{F}$  ( $1.24 \div 1.46$  of g),  $\text{H}_2\text{SO}_4$  volume ( $1.06 \div 1.21$  of ml), duration ( $20 \div 40$  min.) and temperature ( $150 \div 200$  of  $^\circ\text{C}$ ) processings varied. For an experiment the hinge plate of e-FCC weighing 0.5 g was taken. The largest mass of the turned-out product - 0.1391 g, the smallest - 0.0075 g Was received mathematical dependence according to which residual weight is influenced more by the volume of  $\text{H}_2\text{SO}_4$  and duration of processing, to a lesser extent - temperature of processing and mass of  $\text{NH}_4\text{F}$ . By the SEM method with the EDS it was determined that concentration of REE increased in a concentrate at 5-10 times, Al and Si remained in number of 25-30% and 30-40% respectively. Mapping showed that elements, except for Mg and Ca, are distributed evenly. Mg and Ca meet in the form of silicates and sulfates. The maximum maintenance of La in tests - 3.8%, Ce - 0.8%, i.e. concentration of REE increases almost by 4 times. Residual content of fluorine in a concentrate of 5-6%. By methods of IK-spectroscopy and XRD it was determined that the main phases which are present at a concentrate were topaz -  $\text{Al}_2\text{F}_2\text{SiO}_4$  and dioxide of  $\text{SiO}_2$  silicon, were also revealed La and Ce fluorides.

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## PROSPECTS OF GLOBAL POLYOLEFIN CATALYST MARKET

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An overview of evolutionary development and current assortment of catalytic systems for industrial production of basic polyolefins – polyethylene and polypropylene – has been done. Comparative analysis of characteristics of polyolefin catalysts produced by the world leading chemical and petrochemical companies was carried out<sup>1</sup>.

Current state of the market and prospects of global polyolefin catalyst market are analyzed according to the basic market conditions (leading producers, market size, production, capacities, consumption structure, products export-import, regional markets, forecast for market development, etc.). Based on the analysis, it is concluded that there is a close link between the states of global polyolefin market and polyolefin catalyst market. The susceptibility of global polyolefin market to the innovations in the field of development of new catalytic systems for polymerization of polyethylene and polypropylene is also mentioned.

It is shown that the following high-priority trends in development of new catalytic systems for production of polyolefins are deduced in a long-term outlook:

- catalysts for production of polyolefins of definite microstructure and morphology;
- catalysts for homopolymerization and copolymerization of polar and nonpolar monomers allow the structure of polymer chains to be controlled;
- *in situ* synthesis of nano- and micro-filled composites for production of biodegradable polymer materials;
- development of catalysts corresponding to the rigid international rules, in that number to REACH (Registration Evaluation Autorization Chemicals) и FDA (Food and Drug Administration) programs.

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## IMPROVING THE RELIABILITY OF DRUMS OF ROTATING FURNACES BY STABILIZING THE TEMPERATURE MODE BY EXPOSURE OF ELECTROMAGNETIC WAVES

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Irregularity of the heat flow generated in the furnaces of the drums of rotary furnaces leads to the peak of the wall temperature due to radiant heat exchange implemented by the full coverage of the drum body with a flame that reaches 600-650 ° C. As a result, an uneven temperature field causes damage to the drum casing in the form of ring cracks, dents, overheating, etc., which leads to premature failure and an emergency situation in industries with rotary kilns. In particular, in the production of soda ash by the ammonia method, the final stage of production of which is the sodium bicarbonate calcination technology by the dry method; the reaction chamber is a soda furnace drum welded from sheet low-alloy steel with a thickness of 32 mm, a diameter of 2.8 m and the length of the cylindrical portion is 24.5m, and increasing the turnaround time remains an urgent task<sup>1</sup>.

We have developed an energy efficient method of extending the turnaround time by ensuring uniform temperature conditions by exposure of electromagnetic waves. The essence of the method lies in the use of electromagnetic waves to control the direction of the burner flame and the movement of heated combustion products (the effect of «ion wind») in the furnace, which allows uniform distribution of heat flux throughout the entire volume of the body.

In addition, by local influence on the flows of heated gases, it is possible to regulate local temperature fields in real time (in order to exclude uneven heating when carbonate raw materials stick to the drum walls).

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*The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No 18-29-24178*

## MONITORING THE PURITY OF THE SURFACE OF THE FELTED PIPES OF AIR COOLER FROM POLLUTION OF LUBRICANT COOLING LIQUID DURING MANUFACTURE AND OPERATION

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By production of pipes AVO the surface becomes covered with fatty pollution. As a result, the heat transfer coefficient decreases by 1.5 ... 2.0 times and reduces the efficiency of heat exchange equipment<sup>1</sup>. According to GOST 9.402-2004, the quality of degreasing is evaluated by the following methods for monitoring the degree of degreasing.

Table 1.

The degree of degreasing	The time to rupture of the water film when tested by methods of wettability, seconds	The presence of an oil stain on the filtered paper when tested drop method	The presence of a dark spot on the cloth when tested by the method of wiping
First	Over 30	Missing	Low grade, fuzzy
The second	Less than 30	Low grade, fuzzy	Explicit

These methods are labor intensive and do not allow to perform quality control of degreasing with high performance and accuracy. For a more accurate determination of the degree of degreasing of the surface of pipes, we have developed a device whose principle of operation is based on an optical method that allows us to express the intensity value of the light flux reflected from the surface of the pipe fixed by the photoresistor.

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*The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No 18-29-24178*

## THE MECHANISM OF SCALE INHIBITION BASED ON THE NOVEL FLUORESCENT-TAGGED ANTISCALANTS VISUALIZATION IN THE BULK AND ON THE REVERSE OSMOSIS MEMBRANE ALONG THE DESALINATION PROCESS

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Scaling in reverse osmosis facilities, boilers, heat exchangers, evaporation plants, and oilfield applications is a serious problem worldwide. In order to provide a new insight into the mechanism of the scale formation and inhibition, novel fluorescent-tagged bisphosphonate and polymer scale inhibitors were synthesized and applied for the fluorescent microscope visualization of gypsum crystals formation in supersaturated aqueous solutions and in reverse osmosis membranes.

The visualization location at gypsum crystals has demonstrated that the bisphosphonate molecules do not act as they are expected to do according to the current scale inhibition theory. At ambient temperature the gypsum macrocrystals are found to form, and then to grow without visible sorption of bisphosphonate on the crystal edges or any other gypsum crystal growth centers. A tentative nonconventional mechanism of scale inhibition in the bulk supersaturated aqueous solutions of gypsum is proposed.

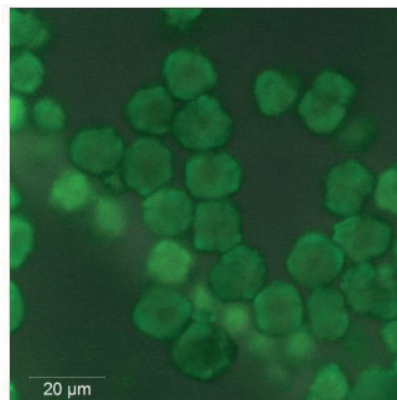
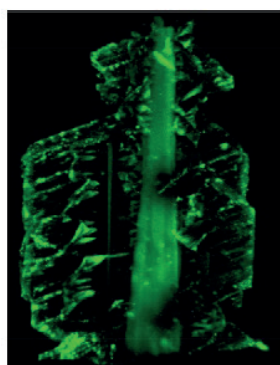


Figure 1. Images of a gypsum crystal and CSM 1812-100 GPD membrane after passing brine containing a fluorescent label through it made on a fluorescence microscope.

The process of desalination on a laboratory reverse osmosis unit with a CSM 1812-100 GPD membrane was studied using a fluorescent microscopy method on a model brine solution.

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## ENERGY EFFICIENCY SOLUTION OF WATER TREATMENT SYSTEMS IN RUSSIA USING HOME-MADE CHEMICAL REAGENTS

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Improvement of operational efficiency of heat power facilities is the most important task of the Russian economy. Economic calculations of tariffs in Russia in the early XXI century show that due to the deterioration of thermal conductivity according to hardness deposition on the condenser tubes 0.6 mm/year, the power unit with an electric capacity of 1000 MW loses up to 4% efficiency for the year, which corresponds to a loss of 175 rubles per 1 kW of installed power. In general, the country's heat power engineering waste about 30 billion rubles a year due to under-production of electricity<sup>1</sup>. However, 25-28 % of all national heating systems damage is caused by internal corrosion. The main way to solve the problems of corrosion and scaling is the use of appropriate reagents (inhibitors)<sup>2</sup>.

One of the leaders of the national chemical industry of reagents for industrial water treatment is a holding company family (EKOS-1, Travers, Fine Chemicals R&D Centre), that provides russian consumers with a wide range of reagents, including more than 400 items produced by an annual volume of 10,000 tons<sup>3</sup> and meets the best foreign samples<sup>4</sup>. In the field of fluorescent inhibitors development the holding has taken a leading position in the world over the past three years.

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## ELECTRON-BEAM TREATMENT OF WASTEWATER

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The problem of wastewater treatment is steadily escalating. An increase in the range and volume of chemical reagents, as well as an increase in the number of water purification stages, often not only fails to solve the problem, but also complicates it excessively. Over time, there is a growing awareness that the growth in reagent volumes and the number of stages is a deadlock way. Break-through approaches are needed to clean up wastewater safely without excessively bulky equipment and excess chemicals.

The solution of the problem can be based on the application of high energy chemistry methods, first of all, electron-beam methods. Electron-beam treatment (EBT), an advanced oxidation technology, consists of the effect of a beam of accelerated electrons on contaminated water, resulting in the formation of short-lived particles ( $OH$ ,  $H$ ,  $e^-_{aq}$ ,  $HO_2$ ,  $O_2$ ,  $O_3$ ,  $HO_3$ ,  $OH$ ,  $H_3O^+$ , and others) from the water, which can fast and irreversibly convert any impurities.

Conventional reagents have significantly lower chemical activity compared with short-lived radiolytic radicals and ions. No other method provides such a set of short-lived reactive particles. In addition, the residual radiolytic intermediates after the destruction of contaminants are again converted into water molecules. EBT has a universal effect, giving the opportunity to decompose any impurities without using any chemical reagents, catalysts and initiators.

Electron-beam treatment has an irreversible sterilizing effect, allows to repeatedly reduce the volume of vessels for finishing biological purification, as well as to obtain significant savings of reagents and materials. EBT can be easily integrated into digital control systems and detoxication quality control. ELO can serve as the basis for the creation of automated compact wastewater treatment plants of local application (home, quarter, microdistrict). The treatment of wastewater with accelerated electrons makes it possible to replace the usual long stages of oxidation and reduction by the instantaneous neutralization of impurities.

## MICROWAVE DRYING OF OIL AND GAS-CHEMICAL EQUIPMENT OF SHELL TYPE

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By manufacturing, repairing and operating of oil and gas equipment of shell type arises the problem for corrosion protection. The most widely used method of drying is the convective one. The disadvantage of this method is high energy consumption due to heat loss during the drying process because of the need to heat the apparatus and the environment, which significantly increases costs due to the difference in design and metal consumption of the equipment<sup>1</sup>. Currently, the microwave method has been widely used in heating and drying technologies. However, the microwave method in the drying of petrochemical equipment, has not been studied sufficiently, in particular, the parameters of the microwave wave, the modes and the drying time for its various sizes are not determined.

We have developed a mathematical model of the process of drying the equipment using the microwave method, depending on the size of the apparatus to be dried. The model allows calculating the wavelength, the required radiation power and drying time for a specific type of equipment. The temperature  $T$  of water thickness  $h$  at the bottom of the apparatus with radius  $r = a$  and length  $z = l$  is determined by the formula:

$$T = t \frac{E_0^2 \omega \varepsilon_0 \varepsilon''}{\rho C} \int_0^l \int_{\frac{3\pi}{2}-\varphi}^{\frac{3\pi}{2}+\varphi} \frac{\int_{a-h}^a e^{-2\alpha z} \sum_{i=1}^3 \left( J_0^2 \left( \frac{\eta_{0i} r}{a} \right) \right) dr d\xi dz}{\cos \left( \frac{3\pi}{2} - \xi \right)}$$

The report presents the results of calculations of the heating time, depending on the parameters of microwave radiation and the residual amount of water after crimping for cylindrical containers of different sizes.

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*The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No 18-29-24178*



## **SORPTION PURIFICATION FROM STRONTIUM OF NATURAL WATER BY SORBENT ON THE BASIS OF MANGANESE OXIDE (III, IV)**

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Currently, the problem of selective extraction of natural water from strontium is becoming more urgent. First of all, this is due to the involvement in the drinking water supply of large volumes of artesian water aquifers with a content of  $\text{Sr}^{2+}$  5-20 times higher than the maximum permissible value. Long-term use of such water leads to the development of morbidity among the population. There is no stage of purification from strontium ions in the technological schemes of water treatment at the treatment facilities of the Russian Federation. There is little information about the methods of removing  $\text{Sr}^{2+}$  from natural waters when solving the problem of water softening (the term “hardness” describes the total concentration of calcium, magnesium and strontium in equivalent terms).

The sorption method with the use of selective inorganic sorbents is the most promising, from the technological and economic points of view, to solve the problem of strontium extraction. A study on the preparation and study of the properties of the sorbent based on manganese oxide (III, IV), selective to strontium ions on the background of hardness salts ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ). The synthesis conditions are optimized in order to increase the sorption characteristics, in particular, to stabilize the selective capacity during operation in desorption cycles. The results of the studies have allowed to develop recommendations for the synthesis of sorbents for ions when extracting it from liquids of different composition.

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## SAPONIFICATION OF POLYETHYLENE TEREPHTHALATE WASTE BY CRUDE GLYCEROL

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Crude glycerol is the main by-product of fatty acid methyl esters (FAME) production facilities, and 100 kg of this waste produce with each one ton of FAME<sup>1</sup>. This product also includes many impurities, such as moisture, methanol, potassium soaps and so on. On this reason there is no commercial way of crude glycerol treatment. On the other hand, a method of saponification of polyethylene terephthalate (PET) by NaOH in presence of alcohol solvent is known<sup>2</sup>. The main product of this method is sodium terephthalate. Crude glycerol is a cheap feedstock and contains potassium terephthalate as well as glycerol. So it was decided to use crude glycerol as a saponifying agent at utilization of PET waste

The process was carried out at atmospheric pressure and temperature below boiling point of crude glycerol. Potassium terephthalate obtained during the saponification was solved into distilled water and then this solution was acidified with orthophosphoric acid. Conversion of PET and selectivity of potassium terephthalate were as high as 100% and 99,0-99,6% respectively.

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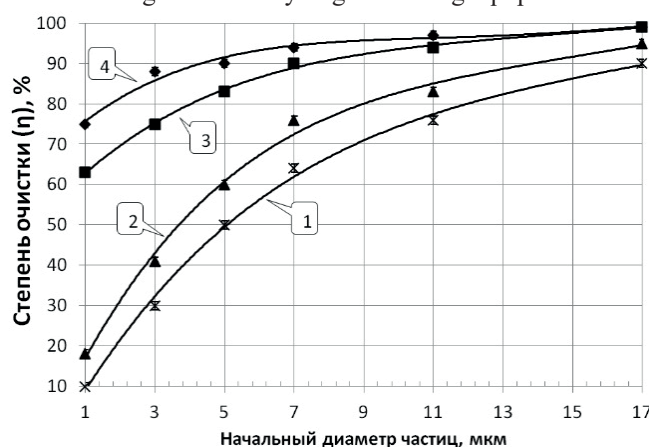
*The reported study was funded by RFBR according to the research project № 18-29-24009.*

## ULTRASONIC COAGULATION OF FINE-DISPERSION AEROSOL INTO RESONANCE INTERVAL

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Micron and submicron aerosol particles are a serious ecological problem and a threat to humans due to respiratory and blood supply diseases<sup>1</sup>. They get into the atmosphere due to anthropogenic influence. A perspective way to destruction of such aerosols is the use of ultrasonic influence. It gives dispersed particles of additional motion, contributing to their association (coagulation). It was shown that ultrasonic influence in a swirling flow directly in gas cleaning equipment is the most efficient<sup>2</sup>.



1 – only cyclone; 2 – agglomerator and the cyclone; 3 – agglomerator (+ ultrasonic influence) and the cyclone;  
4 – agglomerator (+ultrasonic influence) cyclone (+ultrasonic influence)

Figure 1. Fractional efficiency of ultrasonic coagulation

It was found that purification degree under the influence of ultrasonic vibrations can reach 85% for the most dangerous for human particle with size range PM 2.5. For comparison, the degree of purification does not exceed 20% without ultrasonic influence.

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## ENVIRONMENTALLY FRIENDLY SOLUTIONS OF RECYCLING OF MSW

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The limitation of planetary resources and the need for sustainable development of the technosphere predetermine the transition to a new technological order based on alternative and renewable energy, nature-like technologies and man-made mineral reserves (by analogy with natural) <sup>1</sup>.

The basis for the formation of man-made mineral reserves can be solid municipal waste (MSW), disposed of on the basis of natural (environmentally friendly) technologies of housing and communal services <sup>2,3</sup>.

Implemented technologies of MSW utilization in the Russian Federation are landfill storage and thermal processing. They need to be supplemented with nature-like engineering principles of sorting and processing of MSW, developed taking into account the fundamental foundations of man-made and natural cycles of substances and energy.

Introduction of nature-like engineering principles in landfill storage should be aimed at the transition from storage of man-made resources to storage of compacted man-made raw materials. The purpose of landfill storage should be the formation of reserves of man-made raw materials for their subsequent use.

The introduction of nature-like engineering principles into the technology of thermal processing should be aimed at creating nature-like energy industries focused on the output of products with associated carbon and hydrogen (the main components of greenhouse gases).

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## FLARE GASES UTILIZATION VIA LOW-TEMPERATURE STEAM REFORMING: CATALYST DESIGN, REACTION MECHANISM AND REACTOR ENGINEERING

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Nowadays, there is an urgent problem of gas flaring all over the world. Billions of cubic meters of gas are wasted in flare installations due to the lack of required transportation or refinery infrastructure or economical inefficiency. This includes associated petroleum gas (APG), separation gas from gas conditioning units at off-shore fields, shale gas and plant gas. These multi-component gas mixtures predominantly consist of methane and its homologues with some inert components such as CO<sub>2</sub>, N<sub>2</sub> and can neither be pumped to pipelines due to high dew point temperature, nor directly used as a fuel for internal combustion engines (ICE) due to high calorific effect (NCV) and detonation risk. Thus, an alternative way of APG utilization is necessary.

Low temperature steam reforming (LTSR) of flare gases (FG) represents a promising method of FG utilization. The process occurs at 250-350 °C and low steam to carbon molar ratio H<sub>2</sub>O/C<sub>C<sub>2+</sub></sub> 0.5-1 and therefore differs from conventional pre-reforming. Overall process converts C<sub>2+</sub>-hydrocarbons into CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>, which results in lowering net calorific value, Wobbe index and dew point temperature of the gas obtained.

However, complete conversion of C<sub>2+</sub>-hydrocarbons leads to excessive dilution of methane by CO<sub>2</sub> and H<sub>2</sub> according to equilibrium product distribution and to insufficient energy content of gas for fuel applications. In this case, kinetically controlled partial conversion of ethane, propane and butane provides a way to obtain methane-rich mixtures with desired calorific properties for various applications. This idea was verified experimentally. Kinetic study of C<sub>2</sub>H<sub>6</sub>-C<sub>5</sub>H<sub>12</sub> low-temperature steam conversion was performed. The model adequately described the experimental data on the conversion of model flare gas mixtures at various temperatures and flow rates and was applied to predict reaction conditions which would allow obtaining methane-rich mixtures with the desired properties for various applications from APG of different fraction C<sub>2+</sub>-hydrocarbons.

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## OBTAINING HIGH-PURE GLASSY SILICON-28 DIOXIDE

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One of the promising directions in the field of isotope-enriched substances is the manufacture and study of the properties of fibers based on silica glass with different isotopic compositions of silicon and oxygen. However, information about the preparation and properties of such glasses is limited.

A promising method for obtaining isotope-enriched glass is the sol-gel method. The advantages of sol-gel method are uniformity of samples, low sintering temperature and the ability to work with small amounts of matter.

The aim of this work is to obtain and study the properties of glassy  $^{28}\text{SiO}_2$  from  $^{28}\text{SiF}_4$ . Preparation of silicon dioxide was carried out according to the scheme:  $^{28}\text{SiF}_4 \rightarrow ^{28}\text{SiCl}_4 \rightarrow ^{28}\text{Si}(\text{OC}_2\text{H}_5)_4 \rightarrow ^{28}\text{SiO}_2(\text{гель}) \rightarrow ^{28}\text{SiO}_2(\text{glass})$ .

$^{28}\text{SiCl}_4$  synthesis was carried out according to the reaction  $^{28}\text{SiF}_4$  with aluminum(III) chloride under static conditions at 250-300 °C. The content of metal impurities in  $^{28}\text{SiCl}_4$  according to inductively coupled plasma mass spectrometry (ICP-MS) is  $n \cdot 10^{-4} - n \cdot 10^{-6}$  mass. %.

Synthesis of  $^{28}\text{Si}(\text{C}_2\text{H}_5\text{O})_4$  was carried out by reaction of  $^{28}\text{SiCl}_4$  with ethanol in a fluoroplastic container. Hydrolysis of  $^{28}\text{Si}(\text{C}_2\text{H}_5\text{O})_4$  was carried out by adding an aqueous ethanol solution to it in a quantitative ratio of 1:4:4. The solution was placed in fluoroplastic forms for gelation, then dried and calcined. The isotopic composition of silicon and the impurity elemental composition of the glasses were determined by ICP-MS. Transparent samples of glass  $^{28}\text{SiO}_2$  (light transmission >90% in the visible region) with an isotope content of  $^{28}\text{Si}$  99.85 % were obtained.

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## ECO-FRIENDLY EXTRACTION SYSTEMS IN THE PROCESS OF SUBSTANCE SEPARATION

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At present, the priorities of modern chemistry and technology is the development of new eco-friendly methods of extracting, separating and concentrating substances, among which extraction methods occupy an important place. At present, researchers pay great attention to the extraction of substances using systems without organic solvents<sup>1-6</sup>. Such systems include, for example, aqueous two-phase systems with water-soluble polymers. The advantages of such systems include the absence of polymer toxicity, the possibility of their decomposition by microorganisms, commercial availability and relatively low cost. The use of aqueous two-phase systems to obtain, extract and separate a wide range of organic and inorganic substances is a very important task, the solution of which is the aim of the present work.

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## CHLORINATION OF AUTOCLAVED CONCENTRATE

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Leaching of the quartz-leucoxene concentrate of the Yarega deposit with 20% NaOH solution was carried out at a temperature of 200 °C and a solid: liquid ratio of 1: 4 g / ml in a steel laboratory autoclave. In the leaching process, the SiO<sub>2</sub> particles located in the grains of leucoxene dissolve. The chemical composition of autoclaved concentrate is presented in table 1.

Table 1. Chemical composition of autoclaved concentrate

TiO <sub>2</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Прочие
93.76	2.86	2.01	0.88	0.08	0.05	0.37

The study of the chlorination process of the autoclave concentrate was carried out in a fluidized bed reactor. Calcined petroleum coke was used as a reducing agent.

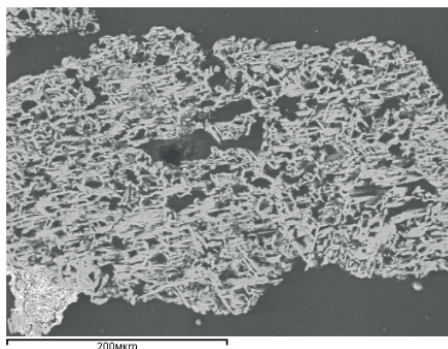


Figure 1. Polished grain of autoclave concentrate

Autoclaved concentrate grains have a porous structure (Fig. 1). However, in the process of chlorination, the inner surface of the grains does not take part in the reaction. The chlorination process proceeds sequentially from the periphery to the center, which leads to a decrease in the size of the grains. Reaction of gaseous intermediates with TiO<sub>2</sub> is fast, and therefore the reagents do not have time to penetrate into the grain reacting near the outer surface. The gaseous compounds formed on the surface of TiO<sub>2</sub> act as carriers of titanium and oxygen to the surface of carbon.

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## STUDY OF THE QUARTZ-LEUCOXENE CONCENTRATE CHLORINATION MECHANISM

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The process of chlorination of  $\text{TiO}_2$  in the grains of leucoxene has been studied. The reaction was carried out in a fluidized bed reactor, calcined petroleum coke was used as a reducing agent.

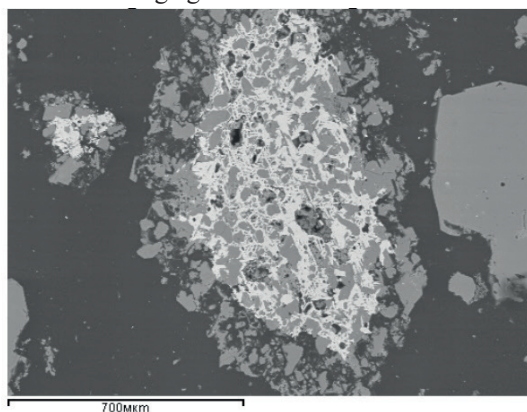


Figure 1. Polished grain of leucoxene after chlorination

The leucoxene of the Yarega deposit is a polymineral aggregate consisting of a reticulated matrix of rutile crystals (65.5%  $\text{TiO}_2$ ) whose voids are filled with quartz crystals (28.7%  $\text{SiO}_2$ ). The use of large fractions of leucoxene reduces the reaction rate. Reducing the size and increasing the content of carbon particles accelerates the reaction. The quartz matrix of the grains does not interact with chlorine; therefore, in the process of chlorination, the leucoxene grains do not change their size. The chlorination of  $\text{TiO}_2$  proceeds from the periphery to the center of the grain. As the  $\text{TiO}_2$  core compresses, the thickness of the quartz layer increases (Fig. 1). Quartz layer riddled with channels. The process proceeds quickly and at a constant speed, until the thickness of the quartz layer around the  $\text{TiO}_2$  core reaches  $60 \pm 10 \mu\text{m}$ . Then the reaction rate is significantly reduced. The chlorination reaction does not require the contact of carbon and  $\text{TiO}_2$  and flows through the formation of gaseous titanium oxychlorides acting as a carrier of titanium and oxygen from the surface of  $\text{TiO}_2$  through a quartz layer to the surface of carbon.

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## EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN THE U–Zr–Fe–O SYSTEM

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The data on phase equilibria in the U–Zr–Fe–O system are the fundamental basis for analyzing the behavior of the core melt at the In-Vessel stage of a severe accident at nuclear power reactors. Experimental study of this system, especially in the domain of liquid phase separation, is hampered by the high chemical activity of the forming two-phase melt. For this reason, the number of experimental studies of phase equilibria in it is very limited.

The main objective of this work is to fill the gap in the experimental data on the U–Zr–Fe–O system and, as a consequence, to increase the accuracy of its thermodynamic description. The investigations were carried out on the “Raspлав” experimental platform which are based on the method of induction melting in a cold crucible (IMCC). IMCC technology is a promising method for studying of high-temperature melts with separation in the liquid phase, since in this method there is no interaction with the crucible, there is no contamination of the melt with impurity components, the system can be in a steady state for a very long time. In the process of exposition it is possible to conduct multiple measurements and sampling.

In this work the liquidus/monotectic temperatures, as well as the composition and ratio of the coexisting liquid and crystallized solid phases of a number of compositions in the U–Zr–Fe–O system are determined. The obtained experimental results can be used to verify the databases of phase diagrams and severe accident codes.

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## HYDROWAVE TECHNOLOGY IN WASTEWATER TREATMENT OF ELECTROPLATING

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Efficiency of hydrowave technology in treatment of electroplating industry wastewater was studied. The treatment technology is based on its cavitation treatment in hydrowave generator and vacuum distillation<sup>1</sup>. Technology allows to decrease energy consumption compared to traditional wastewater treatment technologies. More than 95% of metal ions are removed from water as a result of treatment. An example of water treatment results are shown on table 1.

Table 1. Results of wastewater treatment in hydrowave unit

Parameter	Wastewater	Treated water
pH	6,6	9,7
TSS, mg/L	44	5
COD, mgO/L	36	20
P, mg/L	2,7	0,17
Cu, mg/L	8,0	0,004
Fe, mg/L	23	0,4
Ni, mg/L	5,5	0,02
Zn, mg/L	4,7	0,03
Al, mg/L	4,4	0,13

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## ELECTROFLOTATION EXTRACTION OF Cu, Ni IONS FROM AQUEOUS SOLUTIONS IN THE PRESENCE OF NH<sub>4</sub>OH LIGAND

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The wastewater from electroplating industry, the production of printed circuit boards, often contain ligand ions NH<sub>3</sub>, NH<sub>4</sub>OH, tartrate, and EDTA pyrophosphate. In this case, the extraction of ions from non-ferrous metals, Cu, Ni, Zn forming complexes with ligands is difficult. In the range of pH level between 8 and 10, the formation of the dispersed phase is also difficult. The size of the particles should not exceed 1-10 micrometer. The table presents the results of electroflotation and microfiltration extraction of the dispersed phase of Cu and Ni hydroxides dissolved in water from the joint presence.

Table 1. The effect of pH and the nature of the additive on the degree of extraction of Cu and Ni hydroxides the presence of the complexing agent NH<sub>4</sub>OH,  $\alpha$ , %.

Experimental conditions:  $c(\text{Cu}^{2+}) = 50 \text{ mg/l}$ ,  $c(\text{Ni}^{2+}) = 50 \text{ mg/l}$ ,  $c(\text{NH}_4\text{OH}) = 500 \text{ mg/l}$ ,  $\text{Org} = 5 \text{ mg/l}$ ,  $J_v = 0.4 \text{ A/l}$ .

Time, min 20 minutes	$\alpha$ %											
	pH=8		pH=9		pH=10		pH=11		pH=12		pH=13	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Without additives	16	11	8	7	19	18	20	33	19	31	28	45
With KataPAV	5	6	10	23	9	7	15	27	27	28	17	17
With SeptaPAV	90	31	15	28	8	28	6	9	8	10	7	14
With flocculant	28	15	80	37	34	35	80	73	59	59	77	78
Filtration with flocculant	65	63	93	76	99	98	98	99	99	99	98	98

The analysis shows that in the pH level 8, only Cu ( $\alpha = 90\%$ ) in the presence of cationic surfactant is efficiently extracted from a mixture of Cu and Ni, at pH = 9 ( $\alpha = 80\%$ ) in the presence of a cationic flocculant. At pH = 10-13, copper and nickel float precipitates, the percentage of the dispersed phase is 98-99%. At the same time, electroflotation extraction remains hard to proceed. The highest values of  $\alpha$  - 70-80% are observed in the presence of a cationic flocculant. Adding cationic surfactant does not increase the degree of extraction.

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## ELECTROMAGNETIC INSTALLATION FOR NEUTRALIZATION OF WASTEWATER PRODUCTION OF OLIVE OILS

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The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation, flotation, absorbtion, and also methods of biological clearing. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil	—	100 ÷ 1 mg/L
Final concentration of mineral oil	—	0,5 ÷ 0,05 mg/L
Productivity on initial water	—	Up to 100 m <sup>3</sup> /h
Working temperature	—	0 ÷ 50°C
Working pressure	—	0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres. The general distinctive characteristics of installation:

- 1) High efficiency and stability to a high level of pollution of communications (a rust, sand)
- 2) Standartization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth)
- 3) Absence of a problem of deterioration in case of use the plastic reactor

Installation has passed industrial tests in a zone: 1) Caspian pool: Russia, Republic Dagestan, 2006-2010; 2) Germany, Wesendorf and Hanover in 2015; 3) Greece, the Coast of the Ionian sea (Ligyra) and the island of Corfu, 2015

## STUDY OF THE EFFICIENCY OF THE MINI-RING PACKINGS

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For heat transfer processes, the complex of heat-hydravradic efficiency – ET can be estimated by the formula of A. G. Laptev:

$$E_T = \frac{K_T SH_{app}}{\Delta P G}$$

The industry uses ring packings of the following types: Raschig rings, Pall rings, Bialecki rings, GIAP - N3, mini-ring CMR-304 packings. The specified bulk nozzles with a standard size of 25 - 80 mm are made of metal, ceramics and polymeric materials. The analysis of the geometric characteristics of the annular packings of various shapes and sizes shows that mini-ring packings of the CMR - 304 type have the highest porosity values. Their porosity size ranges from 0.97 to 0.99 m<sup>3</sup>/m<sup>3</sup>. The porosity of the packing layer, as is known, has a significant impact on the efficiency and throughput of the technological process. The MKM type mini-ring head developed by us is designed in the form of Mobius rings and has the following geometric characteristics.

Table 1. The main geometrical characteristics of bulk attachments of the type MKM.

Packings size, mm	Geometric surface area of packing per unit volume, $\alpha$ , m <sup>2</sup> /m <sup>3</sup>	Relative void fraction of any type of packing, $\varepsilon$ , m <sup>3</sup> /m <sup>3</sup>	Nominal packing diameter, d, m	Amount of elements, N, pcs/m <sup>3</sup>
50× 5×0,2	179	0,9848	0,022	123000
50×10×0,2	170	0,9863	0,023	59400
50×15×0,2	160	0,9878	0,025	37700

Conducted by us experiments showed that the packings type MKM has the properties of self-orientation when loading it into a pile, which makes it competitive in comparison with the existing designs of industrial ring and mini-ring packings. In this paper, we studied the effect of the height of the elements of the MKM packing on its hydrodynamic and heat and mass transfer characteristics. The use of packings such as MKM instead of Pall rings allows you to increase the geometric surface area –  $\alpha$ , m<sup>2</sup>/m<sup>3</sup> by 1.7 times, and thus the process energy efficiency –  $E_T$ .



## MONITORING OF THE CATALYTIC DEWAXING PROCESS USING COMPUTER MODELING SYSTEM

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The relevance of developments in new technologies field for the production of low-freezing diesel fuels is due to the growth in consumption of winter and arctic types of this fuel not only in Russia but also abroad.

One of the main processes improving low-temperature characteristics is the catalytic dewaxing process. The goal of this process is the hydrocracking of long chain paraffins that enter into the feedstock composition. Evaluation of the process effectiveness is estimated by such a parameter as the cold filter plugging point.

The developed computer modeling system includes a mathematical model of the catalytic dewaxing process and an expert diagnostic system.

The expert system for diagnosing the causes of deviations in the operation of an industrial catalytic dewaxing unit consists of the principal block diagram of the unit, a database containing basic information about deviations and their causes, as well as an actions algorithm for engineering and technical personnel in emergency situations.

The mathematical model that includes a simultaneous equations of material and heat balance allows in the event of an emergency situation at the unit, after issuing recommendations to eliminate it, to quantify how much the technological parameters (temperature, pressure, flow rate, consumption of hydrogen-containing gas) need to be changed so that it is optimal for obtaining a product of a given quality with the highest yield for the current feedstock composition and catalyst activity.

Thus, the computer modeling system of the catalytic dewaxing process allows to monitor the change of the process parameters in real time and, if the unit fails, to make recommendations for their elimination. In addition, this development can be used as a simulator for the personnel of the industrial unit according to the scenarios of actions in case of an emergency situation.

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## SYSTEMS OF INFORMATION SUPPORT IN TECHNOLOGY OF HIGH PURE SUBSTANCES

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The analysis of information support systems for technology of chemical reagents and high pure substances obtained in FGUP “IREA” and R&D Centre «Fine Chemicals» is carried out<sup>1</sup>. Questions of modernization of systems and transfer of the existing information complexes, starting with the platforms dBase, FoxBase, FoxPro, Visual FoxPro etc. are considered. Over the last years the researches were carried out on the basis of information CALS technology (Continuous Acquisition and Life cycle Support)<sup>2</sup> by means of the PDM STEP Suite Enterprise Edition program (PSS-EE) for which we took up a license (APL-3451631-01).

Application of the concept of CALS in the considered subject domain allows to reduce significantly time and to increase quality of the performed works. By means of PSS-EE the information system containing all the necessary information for generation of technical specifications and application protocols for high pure substances production is developed<sup>3</sup>. In the system such important indicators as quality indications for products, examples of normative documentation, drawings and schemes of production, etc. are entered. Dictionaries of characteristics on high pure substances production and also the reference books of the processing equipment used in production structured by types of devices are created. It allows to carry out an integrated approach to the choice of hardware registration of each stage of production taking into account a possibility of replacement of units.

One of the latest CALS projects is connected with the integrated system of water management of low-tonnage chemistry enterprises<sup>4</sup>. The system allows to increase resource-and energy efficiency of production and to reduce negative impact of the enterprise on the environment.

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## SYSTEM ANALYSIS OF WASTE UTILIZATION OF CHEMICAL PRODUCTIONS

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The lack of theoretical generalizations resulted in need of development of methodology of the system analysis on the example of the phosphoric industry wastes utilization<sup>1</sup>. Researches are structured on three categories: analysis of the market of raw materials and processing, analysis of technology of waste recycling, analysis of the markets of waste utilization products.

In the first category for each of the considered countries (Russia, Kazakhstan and Greece) the following four main subcategories are entered: enterprises that manufacture phosphorus-containing substances; total number of wastes accumulated in relevant country and the state support of the enterprises in the field of utilization<sup>1</sup>.

In a subcategory «Enterprises» the leading enterprises of the phosphoric industry over the respective countries are entered<sup>2</sup>. On each enterprise the following information blocks are given: types of products; formation of waste (types of waste, accumulated volumes of waste, waste of the operating productions and the prospect of formation of new waste); ecological programs of the enterprise; licenses and certificates which are available at this enterprise.

Data on the applied technologies of secondary processing of phosphoric slime, phosphite and phosphoric slag are provided in the second category «Analysis of technology of waste recycling». In each subcategory four types of utilization are considered: burial, burning, recycling and outsourcing.

The analysis of the market of products of waste utilization (the 3rd category) showed three most perspective products of phosphoric slime recycling: sodium phosphite, bibasic lead phosphite and sodium hypophosphite<sup>2</sup>. This category contains information: about chemical and physical properties of these substances; the main manufacturers and economic profitability of production of the chosen products on technology of «secondary processing».

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EFFICIENCY IMPROVEMENT  
OF TITANIUM TETRACHLORIDE PRODUCTION TECHNOLOGYBurmakina O.V.<sup>a</sup>, Zanaevskii K.L.<sup>b,c</sup>, Cherezova L.A.<sup>a</sup><sup>a</sup> «AVISMA» Branch of PSC « VSMPO-AVISMA Corporation»,  
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Chlorination of titanium slag in AVISMA is carried out in melt chlorinator by passing of the anode chlorine gas through NaCl melt where titanium slag and hard coal are dosed continuously. With the impurities accumulation, the melt is periodically poured out. As a result, an insoluble residue of titanium chlorinators spent melt is obtained. Losses of titanium dioxide are about 7% that significantly reduces production technical and economic indices. The efficiency improvement of  $\text{TiCl}_4$  production technology could be achieved by returning of titanium dioxide from the insoluble residue into the production cycle.

Samples of insoluble residue taken in 2016-2018 were investigated. Investigations were carried out using complex, mutually complementary methods of analysis, including: Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Scanning Electronic Microscope (SEM), Electron Microprobe Analysis (EMPA), X-ray phase analysis (XRF). It is established that insoluble residues consist of three types of grains: carbon, quartz and chlorinated slag (CS). Table 1 shows the typical chemical composition of CS. Depending on the date of sampling, the output of CS grains ranges from 53 to 80%.

Table.1 Chemical Composition of Chlorinated Slag

$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	Other
87,58	5,87	3,23	0,83	0,67	1,82

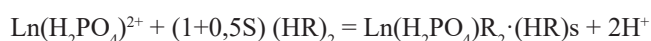
Various methods of physical separation were tested to isolate the CS from the insoluble residue. Gravity preparation on the screw sluice and the table concentrator allows to split off carbon, while, due to the insufficient difference in densities, the separation of quartz and CS does not occur. The most promising method for insoluble residue processing is the electrostatic separation. It has been established that to conduct it, it is necessary to first remove  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  films from the surface of the CS particles.

## EXTRACTION SEPARATION OF RARE-EARTH ELEMENTS HEAVY GROUPS

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Extraction of rare earth elements (REE) is important aim for government strategy. During processing of apatite valuable heavy part of REE concentrates in phosphate solutions. High extraction rates of REE from acidic media were obtained applying the organic extractant based on di-2-ethylhexylphosphoric acid (D2EHPA)<sup>1</sup>. Increasing concentration of D2EHPA in kerosene solution, could reach extraction rate of Dy about 60% and Y, Yb, Er about 100%. The increasing of effective charge of the complexing ion leads to additional solvation of organic acid molecules according equation:



Reextraction of REE provided by the applying of mineral acids. We can observe antagonistic effect applying tributyl phosphate.

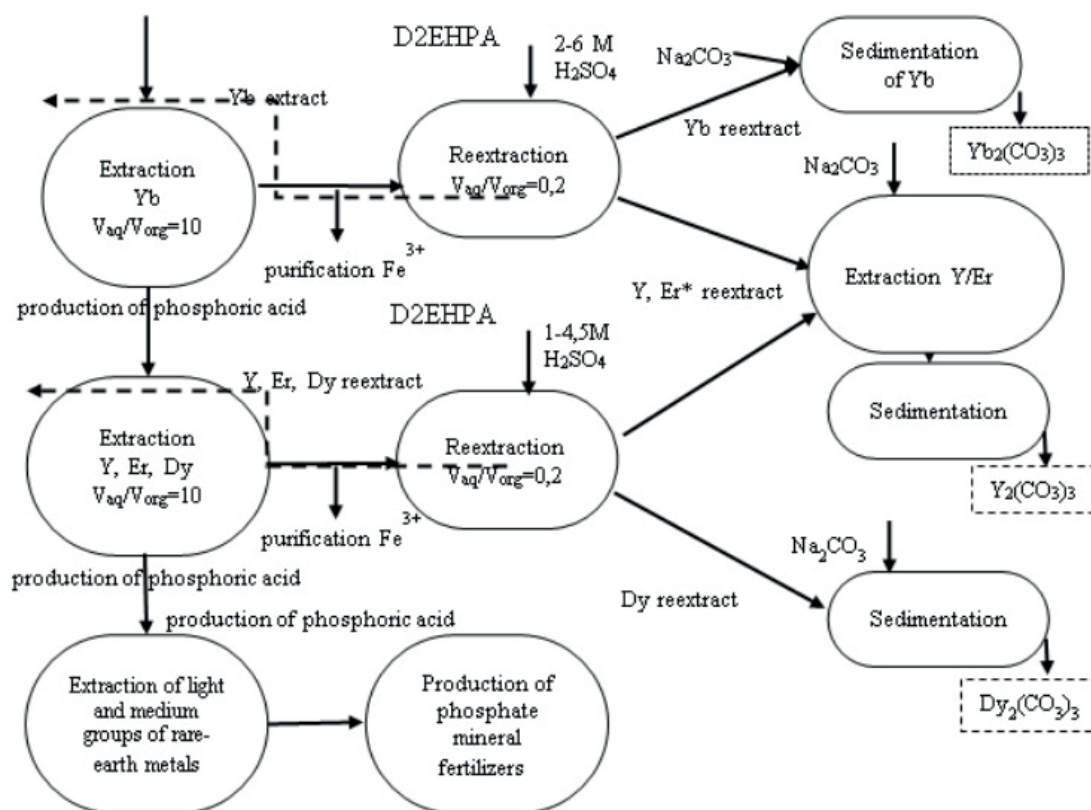


Figure 1. Separation of REE

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## ENZYMATIC HYDRATION OF VEGETABLE OILS

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Vegetable oils with a high content of phospholipids are characterized by a cloudy color, a specific smell, have a short expiry date. The phospholipids contained in the composition of vegetable oils are, mainly, glycerophospholipids that interact with water, prolonged storage in contact with oxygen and cooling to form a sludge that degrades the quality of the oils and makes it difficult to further stages of their processing<sup>1</sup>. One of the stages of vegetable oils purification is hydration - the process of purification from phospholipids and various hydrophilic substances. Enzymatic hydration has advantages over chemical – reducing processing time, simplifying the process technology, obtaining an environmentally and biologically more valuable product. The phospholipases used in this case contribute to the hydration of non-hydrated phosphatides into fully hydrated lysolecitine, which in turn facilitates the separation of phosphatides. The study of sunflower, rapeseed and camelina oils enzymatic hydration using the enzyme preparation Lecitaza A1 (Novozymes) was shown. The influence of the buffer pH on the process flow is analyzed. In the process of enzymatic hydration, the acidity of vegetable oils is reduced: sunflower oil by 55.3 %, rapeseed oil - 54.6 %, camelina oil – 19 %. A decrease in the amount of phosphorus in rapeseed oil from 0.22 % to 0.06 % was shown. Immobilization of the enzyme preparation in agar gel also shown in this work. Acidity reduction of rapeseed and camelina oil occurs at the same level as when using non-immobilized enzyme preparation. One of the indicators of effective hydration of vegetable oil is to reduce its color. The maximum value of oil color reduction was obtained in the experiment with sunflower oil. The colouration decreased by three units of iodine. The optical density measurement showed a decrease in colouration in all oils.

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## SELECTIVE SYNTHESIS OF CYCLIC ORGANOIODINE(III) WITHOUT CONTAMINATION OF HAZARDOUS PENTAVALENT COMPOUND

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The first report of hypervalent iodine compound in history was 1886, where iodobenzene dichloride ( $\text{PhICl}_2$ , Willgerodt reagent) was accidentally obtained during the attempt of chlorination of iodobenzene by chlorine gas.<sup>1</sup> A century later, hypervalent iodine reagents showing a variety of unique reactivities have received attention as useful oxidant due to their characteristics meeting green chemistry, such as low toxicity, ready availability, and easy handling. Particular noteworthy, they have replaced highly toxic heavy metal oxidants, *i.e.*, lead(IV), mercury(II), and thallium(III) reagents, in modern organic synthesis. The details of their synthetic versatility are well documented in several review articles by key contributors in the fields.<sup>2</sup>

Five-membered hypervalent iodine(III) compounds, such as 2-iodosylbenzoic acids (IBAs), have recently emerged as reagents for developing new synthetic transformations and photo-catalyzed reactions.<sup>3</sup> For the preparation of pure IBAs, we now suggest an improved method not causing formation and contamination of hazardous pentavalent IBXs. The reaction system consisting of the suitable oxidant<sup>4</sup> smoothly produces IBAs under mild conditions,<sup>5</sup> and co-existing catalyst suppresses undesired IBX formations<sup>6</sup> derived from disproportionation of IBA compounds.

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## PERFOMANCE OF ECO-POLYMERS

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At the present moment the most acute global problem is the degradation of the environment. In this case attention is being paid to extension of more eco-friendly equivalents of already existing products. In chemical area the development of biodegradable and non-toxic raw materials based on natural ingredients is extremely relevant.

The purpose of this project is to determine physical and chemical properties of ecological types of polymers, which has been provided by company BASF (Germany). Amphoteric polymer Polyquart Ecoclean Max (modified starch), anionic polymer Polyquart Ecoclean (starch acrylic copolymer), surfactant Glucopon 215 UP (aqueous solution of alkyl polyglucosides based on natural fatty alcohol C8 – C10) have been used in the present study. These products are anaerobically biodegradable, non-toxic and appropriate for realization of different eco-conceptions<sup>1</sup>.

The influence of polymers on such surfaces as tempered glass, glossy tile, stainless steel, PVC and fiberglass has been established. The adsorption modification of these surfaces has been evaluated by counting the surface free energy. Values of its components have been determined by using Owens, Wendt, Rabel and Kaelble method for original and modified surfaces<sup>2</sup>.

The impact of polymers on physical and chemical properties of surfactant solutions has been examined. For this aim isotherms of surface tension of surfactant solutions and its mixtures with polymers have been built within a wide range of concentrations.

The study of eco-friendly polymers helps to predict its behavior in solution and on the surfaces, which in turn contributes to the development of eco-conceptions.

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## INTEGRATED TREATMENT WASTEWATER OF COMPLEX COMPOSITION

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When cleaning waters of complex composition, it is often advisable to carry out a set of pre-treatment measures, including the stage of reagent purification, which allows the transfer of most of the main pollutants into solid-phase sediment.

The technology of complex treatment of highly concentrated effluents and waters of complex composition, including filtration water of solid waste landfills, consists of a stage of preliminary mechanical purification of contaminated water from coarse impurities, followed by a stage of reagent treatment by extracting most of the contaminants using both traditional iron- and aluminum-containing coagulants and hybrid reagents with increased flocculation and sorption<sup>1</sup>. In the mixing chamber of reagents with treated water, if necessary, it is possible to implement the hydrodynamic cavitation regime and additional aeration using ejectors, which ensures the use of lower doses of reagents with a high degree of purification<sup>2</sup>. Further, provided the level of filtration on the tangential filters with the withdrawal of the concentrate to the processing of sludge for dewatering. The final stage of purification includes the stage of post-treatment by demineralization with reverse osmosis (nanofiltration) together with UV disinfection of purified water.

This technology is also characterized by the fact that a special place is given to the collection of sludge of coagulated contaminants and concentrates from all stages, followed by their transfer to the solid phase, providing a comprehensive solution to the problem of water treatment of complex composition and improving the environmental situation by reducing the load on the environment<sup>3</sup>.

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## PASSIVATION OF MAGNESIUM SURFACES IN TITAN- AND ZIRCONIUM-CONTAINING SOLUTIONS

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The disadvantage of magnesium materials is their low corrosion resistance due to high electronegativity. One of the most effective methods to improve the corrosion resistance of magnesium alloys is to form a conversion adhesive coating on their surface, followed by applying paintwork materials.

Chromatic coatings are widely used as adhesion layers under the paintwork before staining magnesium and its alloys.

In recent years, in world practice, as an alternative to chromate layers on magnesium and its alloys, nanoscale conversion titan- and / or zirconium-containing adhesive coatings, obtained from solutions based on hexafluorozirconic and hexafluorotitanic acids, are used.

A solution containing hexafluorozirconic  $\text{H}_2\text{ZrF}_6$  and hexafluorotitanic acid  $\text{H}_2\text{TiF}_6$ , ammonium paramolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  and tartaric acid  $\text{HOOCH}(\text{OH})\text{CH}(\text{OH})\text{COOH}$  was developed.

Studies have shown that the permissible pH values of solutions are in the range of 4.5-5.5 units, and the working temperature range is 18-25 °C.

Using the ellipsometric method, the thickness of the coatings, which depends on the duration of their deposition was determined. The thickness of the coatings increases in the first 5 min and stabilizes at values of ~ 60-70 nm.

Conducted corrosion tests showed that the developed coatings on protective ability meet the requirements for adhesion layers under paintwork, since the penetration depth of corrosion from the incision site in these cases does not exceed 2.0 mm after 240 hours of testing.

It has been established that paintwork with the developed adhesive sublayer have a higher adhesion strength to the substrate compared to phosphate and chromate coatings.

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## THE EFFECT OF FLOCCULANTS AND PAV ON THE ELECTROFLOTATION PROCESS OF EXTRACTION OF A MIXTURE OF NON-FERROUS METALS FROM WASTEWATER GALVANO-CHEMICAL PRODUCTIONS

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The influence of the nature of Flocculants and PAV on the efficiency of electroflotation extraction of the dispersed phase of the mixture of non-ferrous metal hydroxides at the concentration of cation, anion and nonionic nature of 100 mg/L at Ph 10 was Studied.

Table 1. The Degree of electroflotation extraction of nonferrous metals from a multi-component solution at Ph = 10 and  $\tau = 30$  min.

System	$\alpha$ %,					
	Fe <sup>+2</sup>	Ni <sup>+2</sup>	Zn <sup>+2</sup>	Co <sup>+2</sup>	Cu <sup>+2</sup>	B.B $\Sigma$ Me(OH) <sub>2</sub>
Without Additives (Flocculant and PAV)	81 96	99 99	95 96	100 99	98 88	96
(Flocculant) PRAESTOL 859 (A)	89	99	97	99	99	97
(Flocculant) PRAESTOL 2503 (A)	87	99	92	99	98	95
(Flocculant) FERROCUYL 8737 (H)	74	99	95	99	93	92
(Flocculant) PRAESTOL 2500 (H)	36	63	78	64	69	62
(PAV) XЭВ (K)	69	99	98	99	90	91
(PAV) ALM-10 (H)	88	99	94	100	50	86
(PAV) PREPARATION OC-205 (H)	78	97	86	91	61	83
(PAV) NaDDS II (A)	72	85	81	84	65	77

Experimental Conditions: Fe<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>, Co<sup>+2</sup>, Cu<sup>+2</sup> 20 mg/L,  $\Sigma$ Me 100 mg/l; Na<sub>2</sub>SO<sub>4</sub> 1 g/l;  $J_v = 0.4$  A/L.

The Analysis showed that all the present ITM are extracted in optimal conditions up to 96-97%. Some difficulties arise when using the PAV NaDDS (A) and flocculant PRAESTOL 2500 (H).

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## MODIFIED METAL OXIDE ELECTRODES FOR HYDROGEN GENERATION AND STORAGE

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The capability of intermetallic compounds of a number of metals for reversible absorption of significant volumes of hydrogen ( up to 1.5 ... 7% of the mass) at relatively low pressures and temperatures , represents the most important scientific and practical interest for domain of development of new hydrogen-accumulating materials. Hydrogen is sorbed by 48 such as Ti, Al , Mo metals and their alloys of composition  $A_n B_m$ , ( $n=1-2$ ,  $m=2-17$ ). Titanium alloys can provide satisfactory capacitance and cycleability values. There should be a considerable change in the microrelief of their surface during cathodic polarization in aqueous solutions of molybdates as a result of the absorption of the releasing hydrogen as of the participation of molybdate-ions in the cathodic process. The state of molybdate ions in an aqueous solution also play an important role, This is related with the ability of molybdenum to form intermediary oxides of the homologous series  $Mo_n O_{3n-1}$  and accordingly, the anions of isopoly acids  $H_6 Mo_7 O_{24}$  .

The purpose of this work is to establish regularity of electrochemical formation of matrix structures from heteronuclear polymolybdate and polyphosphate-molybdate complexes as double salt  $Na_6 Ti_n Mo_{7-n} O_{24}$  и  $Na_{1-y} Ti_2 (MoO_4)_y (PO_4)_{3-y}$  at the surface of copper, aluminum, and titanium at time the cathodic treatment in acidic phosphate-molybdate solutions. The potential of the Cu electrode at the moment of immersion in 0.01M  $Na_2 MoO_4$  is +0.012 V, but suddenly shifted to a negative value -0.160 V and further, according to a logarithmic law, to -0.240 V. A similar effect it was when titanium and aluminum electrodes were immersed in the  $Na_2 MoO_4$  solution. The change of the currentless potential at time of cathode polarization is associated with the adsorption of molybdate ions, accompanied by the reduction of Mo (VI) with the formation of molybdenum oxides of incorporation valence and the oxidation of the base metal:



At high negative cathode implementation of cations leads to the formation of compounds of  $Na_x Me$  ,  $H_x Me$  and hydrides  $TiH_{2x}$  ,  $AlH_x$  ,  $MoTi_{0.5}$  ,  $Al_{0.5} H_{2.0}$  and the accumulation of hydrogen in the volume of the electrode metal.

## **SOLUTION PROCESSABLE POLYANILINE COMPLEXES AS A HOLE TRANSPORT LAYER IN PEROVSKITE SOLAR CELLS**

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Present developments in organic photoelectronics are aimed to increase of the efficiency of converting solar energy into electricity by creating new chemical compounds and optimizing the composition of known materials. Organometallic compounds forming perovskite structure (halides of methyl ammonium or formamidium of lead or tin) have shown to be promising photoconductors for photovoltaic solar cells (SC). Charge transport layers that improve the collection of electrons and holes at the corresponding electrodes play an important role in the SC devices.

Here, a comparative study of SCs with a photoactive layer made of lead methyl ammonium iodide of perovskite structure and a hole transport layer (HTL) based on a polyaniline complex with polymeric acid was carried out. HTL was deposited on the substrate using various methods: drop casting, electrochemical deposition, 2D inkjet printing. The conditions for successful deposition of the HTL layer by inkjet printing, resulting in the device with efficiency exceeding 12%, were found. The method allows forming a layer of uniform thickness over the entire area of a SC sample providing a high reproducibility of the parameters of individual pixels.

The effect of the perovskite layer thickness in the range of 350–500 nm on the SC efficiency was found to be negligible. This is in a good agreement with the weak dependence of the exciton generation rate in the photoactive layer on its thickness resulted from modeling the optical parameters of a polymer semiconductor in the framework of the Maxwell-Garnet model.

*The research was carried out with the financial support of the Russian Foundation for Basic Research (Scientific project No. 18-29-23045).*

## HYDROGEL COMPOSITIONS BASED ON LIGNOSULFONATES FOR WATERPROOFING INJECTION AND PRODUCTION WELLS

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Hydrogels based on polyacrylamide are widely used in water insulation technologies in the oil industry<sup>1</sup>. The advantage of this technology is selective isolation of water filtration in cracks and super-reservoirs<sup>2</sup>. The only drawback of polyacrylamide-based hydrogels is their high cost.

We have developed a composition based on the waste products of the pulp and paper industry – lignosulfonates, which allows to form hydrogel screens in pore and fractured reservoirs. The advantage of this composition, in addition to cheapness, is the ease of preparation and manufacturability of application. It becomes possible to regulate the time of gelation, variation of viscous and plastic properties of hydrogel, depending on the geological and fishing problem. Increasing the time of gel fluidity loss up to 40 hours or more allows to pump large volumes of gelant before its transformation into a «strong gel»<sup>3</sup>.

Concentration and temperature limits of the composition applicability are substantiated, its rheological and filtration properties are studied.

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## INTERPHASE DISTRIBUTION OF $\text{Ce}^{3+}$ AND $\text{La}^{3+}$ IONS IN A HETEROGENEOUS SYSTEM WITH POLYETHYLENE GLYCOL 1500

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Spheres of rare-earth metal use are extensive enough - from the oil industry to instrument engineering. Because of their rarity, they are an expensive resource<sup>1</sup>.

Potentially spent industrial waste can be considered as a highly concentrated source of raw materials for the extraction and further use of rare earth metals in various industries.

At present, the direction of extraction chemistry, involving the use of heterogeneous systems based on water-soluble polymers for the extraction and separation of metal ions, is actively developed<sup>2-4</sup>. The use of such systems is economical, eco-friendly and safe<sup>5</sup>.

The work is aimed to study the interfacial distribution of  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  ions in the aqueous two-phase system of polyethylene glycol 1500 -  $\text{NaNO}_3$  -  $\text{H}_2\text{O}$ . The kinetic dependences of the extraction of  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  ions in the polyethylene glycol 1500 -  $\text{NaNO}_3$  -  $\text{H}_2\text{O}$  system were obtained and the effect of complexing agents on the degree of their extraction was shown.

The experiment results showed that the interphase distribution regularities of  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  ions make it possible to carry out the extraction process of the studied metals more efficiently.

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## BINDING MATERIALS WITH HIGH FROST RESISTANCE AND THEIR STRUCTURE

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Frost resistance is one of the key characteristics of cement-based binder materials which are used in construction in the different regions of Russia and other Northern countries. However, the conception of the frost resistance is so wide, that it is not enough to determine the compressive strength of the samples only, to predict their frost resistance (according to the standard<sup>1</sup>). There are a viewpoints<sup>2,3</sup> that the current standards in different countries are based on the same principle and do not reflect the real frost resistance of the materials. Moreover, it is necessary to consider different cut-off-layers of sample surfaces (lower, upper, inner and wall sides, all of them have different durability), but not the average frost resistance of the whole sample. This could be a golden opportunity to evaluate the porosity of the test layer, the pore size distribution and to predict its properties. As a matter a fact, these parameters are the key when considering such properties as frost resistance.

In connection with this, the pore structure of cements which modified by chemical additives was studied. It is established that the additives of poly-carboxylate nature caused a decrease in the total pore volume while the pore distribution by volume were nearly the same (in comparison with Ordinary Portland Cement. At the same time, there is an increase in the specific surface of the hydrate phases of hydrated cement by 25 % (it is confirmed by the electronic-scanning microscopy). Thus, the possibility of the cement structure regulating was indicated. It can be not only by reducing the water requirements, but also by controlling the phase composition with chemical modifiers. It is shown that the reasons of the destruction of the cement by exposure to alternating freezing and thawing are phase transformation of ettringite to calcium monosulfoaluminate and back. The cement is destroyed in the reason of the internal volume changes.

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## CAST-STONE MATRICES FOR STORAGE OF RADIOACTIVE WASTE

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Molten cast-stone matrices containing radioactive waste (RAW) imitators and their collectors at different weight ratios were studied.

The work showed that RAW collectors based on silica gel, perlite, and aluminum oxide allowed obtaining matrices containing the following main phases: glass, quartz, and spinel for silica gel; glass and spinel for aluminum oxide; glass and Fe-Cu-Ti silicates for perlite.

The possibility of uranium localization in different collectors based on silica gel, perlite, and aluminum oxide was studied. Data on uranium wash-out into water from the collectors after their thermal treatment, as well as from the silica gel matrix after microwave irradiation (MWI) were obtained. The wash-out of U(VI) into H<sub>2</sub>O and 0.5 mol/l NaCl, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> solutions from Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and perlite of brand M150, which contained 30 mass % UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> and were preheated at 700°C during 5 h in air, was as follows after 24 h: for Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and M150, respectively, mg/l·g: 2.53, 14.25, and 38.40 for H<sub>2</sub>O; 11.73, 5.15, and 17.85 for 0.5 mol/l NaCl; 33.75, 7.00, and 25.00 for 0.5 mol/l NaNO<sub>3</sub>; and 65.00, 19.25, and 62.50 for 0.5 mol/l Na<sub>2</sub>SO<sub>4</sub>. After 24-hour contact with 1.0 mol/l HClO<sub>4</sub>, the SiO<sub>2</sub>-10 mass % UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> matrix preheated under MWI (800W, 10 min) retained 12 % of the initial U(VI) taken for the experiment.

The physicochemical properties of the matrices based on aluminum oxide, containing uranyl nitrate, were studied after their thermal treatment at different temperatures. After thermal treatment of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and perlite M150 containing 30 mass % UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> at 300, 700, and 1000°C, U(VI) was present in the composites only as UO<sub>3</sub>.

*The work was financially supported by the Presidium of the Russian Academy of Sciences (program for fundamental research № 14P «Actual problems of surface physicochemistry and creation of new composite materials» /Academician A. Yu. Tsivaddze/).*

## REGULARITIES OF ETHANOL TRANSFORMATIONS ON ZEOLITE-CONTAINING CATALYSTS

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The growing consumption of motor fuels, the reduction of world oil reserves and the tightening of environmental protection requirements lead to the need of finding alternative fuels. In this regard, an urgent task of chemistry is the design of catalytic systems for the processing of light hydrocarbons obtained as a result of biomass fermentation product conversion, into environmental-friendly high-octane components of motor fuels and valuable raw materials of the petrochemical industry. For this purpose, systematic studies were made of the activity and selectivity of high-silica ZSM-5 zeolites in the conversion of  $C_2$ - $C_5$  lower alcohols, and it was found that modifying the zeolite with zirconium (IV) led to an increased activity of the 1% Zr-ZSM-5 heterogeneous system in the secondary isomerization reactions of intermediate  $C_4$ - $C_{14}$  hydrocarbons.

It was shown that during ethanol conversion, the zeolite modified with zirconium (IV) sulfate reduced the content of aromatic hydrocarbons in the catalysate (from 17.5 wt.% to 11.8 wt.%) and increased the content of iso-alkanes (from 17.4 wt.% up to 24.8 wt.%) at a process temperature of 350°C and a bulk feed rate of 1 h<sup>-1</sup>. The conversion degree of  $C_2$ - $C_5$  alcohols reaches 99.9%, n-paraffin isomerization reactions predominate in the temperature range 300–400°C (the selectivity for isomerization reactions reaches 40%), while within 400–500°C the contribution of aromatization reactions increases (the selectivity for aromatization reactions is 33%).

Our studies of the physicochemical properties and the state of the active surface centers of the ZSM-5 zeolite systems have shown that modifying the ZSM-5 zeolite with zirconium (IV) sulfate can increase the acidity of Lewis centers (from 35.6 to 61.3  $\mu\text{mol/g}$ ) and Brønsted centers (up to 199.4  $\mu\text{mol/g}$ ), leading to a redistribution of the contribution of the isomerization, cracking and aromatization reactions of hydrocarbons. Regularities of transformations of hexene-1, ethylene, *n*-hexane as ethyl alcohol conversion intermediates were established.

Thermodynamic analysis of reactions involving carbocations has shown that tertiary carbocations are formed on the surface of our zirconium-modified pentasil 1% Zr-ZSM-5, and this process intensifies at temperatures of 300–350°C, which leads to an increased content of iso-paraffins and, as a result, an increased octane number of the components of motor fuels. The octane number at 350°C for all alcohols is above 100 points.

## CATALYTIC OXIDATION OF CARBON FUEL

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Our analysis of the state and development of the energy sector has shown that the main trends are more efficient use of fuels and improvement of the environmental characteristics of the combustion processes of traditional natural fuels. Therefore, we need innovative technologies with a high level of environmental safety when using energy raw materials.

Our study of the chemical reactions of solid fuel combustion has shown that carbon oxidation produces a number of intermediates, including CO, H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, which can generate hydrocarbons and oxygen-containing compounds of various classes as a result of their heterogeneous catalytic conversion.

A study was made of the effect of a liquid catalyst on the combustion process of solid fuels. Our solid fuel combustion modifier, including a combustion catalyst and an organic solvent, contained 5–20 wt. % manganese dicyclopentadienyltricarbonyl, and methylbenzene served as the organic solvent.

Manganese dicyclopentadienyltricarbonyl is a “sandwich” molecule with an atom of a transition metal (manganese) between two cyclopentadienyl rings, which decomposes under fuel burning conditions in the presence of oxygen to form manganese oxide.

The use of this modifier made it possible to raise the temperature in the coal combustion zone up to 1670°C. The proposed catalyst provides high heat emission of fuel, reduces the booster (natural gas) amount by 2 times, and allows for efficient flue gas cleaning from nitrogen oxides and carbon (II) oxide.

Chromatographic analysis of the composition of the flue gases of coal combustion has shown that the contents of hydrocarbons, nitrogen oxides and carbon oxides meet the requirements of maximum allowable concentrations.

Thus, our manganese-containing organic catalyst allows one to increase the burnout of solid fuels and to reduce the consumption of natural gas for boosting, as well as to reduce the content of toxic nitrogen and carbon oxides in the exhaust gases, thus ensuring the environmental purity of the fuel combustion process.

## ON THE PROSPECTS OF WASTE APPLICATION FROM WOOD INDUSTRY AS COMPONENTS OF SOLID FUEL FOR STEAM AND HOT WATER BOILERS

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Wood processing is carried out on the territory of the Russian Federation, which leads to formation of large amounts of waste (mainly in the form of sawdust) that can be used in the energy sector. Decrease of calorific value of coal-wood mixtures compared to homogeneous coals is compensated by a large-scale reduction of  $\text{SO}_x$  and  $\text{NO}_x$  emissions into the atmosphere. The aim of the work is an experimental study of the dependence of the main anthropogenic oxides concentrations in the products of thermal decomposition and combustion of coal-wood mixtures on the type of coal and wood concentration.

Experimental studies were performed for a large group of typical coals and a wide range of wood biomass concentrations in the mixture. It has been established (typical results are shown in Figure 1) that not all coals in a mixture with wood achieve synergistic effect of significant reduction in the yield of  $\text{SO}_x$  and  $\text{NO}_x$ . According to the results of the analysis and generalization of the experimental studies, a hypothesis was formulated on the mechanism of physical and chemical processes occurring during thermal decomposition of coal-wood mixtures and chemical reactions between intermediate products of this process, leading to a significant decrease of the concentrations of the main anthropogenic oxides in combustion products.

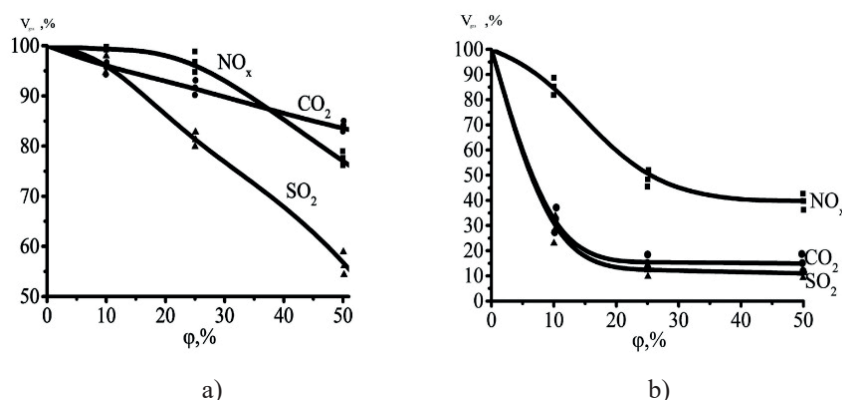


Figure 1. Concentrations of the main released oxides during thermal decomposition of mixed fuels based on coal of grades a) D, b) T; ( $\phi$  – proportion of wood in the fuel).

*Work was executed with financial support of RFBR, the project 18-29-24099.*

## THE EFFECT OF LIGAND ON THE MECHANISM OF CO OXIDATION ON CYCLIC THYOLATE GOLD COMPLEX

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Carbon monoxide is one of well-known pollutant gases. Therefore, the development of a catalyst for CO oxidation into CO<sub>2</sub> is an important task. Also, CO oxidation reaction is considered to be a model for studying the mechanism of heterogeneous-catalytic processes. Fundamental new catalytic systems are gold clusters stabilized by ligands (phosphine, thiolate). Oxidation of CO on gold nanoparticles can proceed at low temperatures. The problem lays in an unidentified mechanism of CO oxidation reaction<sup>1</sup>. Therefore, the aim of this work is to establish how the effect of stabilization with organic ligands affect the reaction mechanism of CO oxidation.

In this work, the catalysts based on (AuSCH<sub>3</sub>)<sub>4</sub>, (AuSCH<sub>2</sub>CHSCH<sub>3</sub>)<sub>4</sub> complexes protected by thiolate and dithiolate ligands were considered. The DFT/PBE method and SBKJC basis set were used in PRIRODA program on the Lomonosov Moscow State University supercomputer<sup>2</sup>.

According to results, (AuSCH<sub>3</sub>)<sub>4</sub> thiolate complex is inert with respect to O<sub>2</sub> and CO due to the strong bond of Au-S. O<sub>2</sub> and CO are weakly activated on (AuSCH<sub>3</sub>)<sub>4</sub>. Replacing thiolate with dithiolate ligands significantly changed the structure (AuSR)<sub>4</sub>. The dithiolate complex is not flat and Au-S distance increased by 0.08 Å in contrast to the thiolate complex. The nature of the electron density distribution along the Au – S bond also differs. HOMO is localized on Au and S atoms in the dithiolate complex, in thiolate complex - on Au-S bond. This indirectly indicates increase in activity of (AuSCH<sub>2</sub>CHSCH<sub>3</sub>)<sub>4</sub>. O<sub>2</sub> and CO are activated on (AuSCH<sub>2</sub>CHSCH<sub>3</sub>)<sub>4</sub> dithiolate gold complex and CO oxidation proceeds with low activation energies. It can be concluded that stabilization with ligands change the reaction mechanism of CO oxidation.

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*This work was supported by the Russian Science Foundation, grant 17-03-00962.*

*The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.*



## CRITERIAL CHOISE OF ENERGY EFFICIENT SCHEME FOR DISTILLATION SEPARATION OF ZEOTROPIC MIXTURE

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Criterial equations are proposed that allow, on the basis of a simple calculation, without enumerating all the options, select the least energy consuming sequence of a clear separation of the zeotropic mixture<sup>1,2</sup> (direct separation, indirect separation and symmetric separation sequence).

$$\frac{A \cdot \Delta H_A \cdot (R_{\min}^I - R_{\min}^{I*} - R_{\min}^{II*} - 1)}{B \cdot \Delta H_B \cdot (R_{\min}^{I*} - R_{\min}^{II})} = 1$$

$$\frac{A \cdot \Delta H_A \cdot (R_{mn}^I - R_{mn}^{I**} - R_{mn}^{II**} - 1)}{B \cdot \Delta H_B \cdot \left( \frac{R_{mn}^{I**} \cdot b + R_{mn}^{III**}}{1 + b} - R_{mn}^{II} \right)} = 1$$

$$\frac{A \cdot \Delta H_A \cdot (R_{mn}^{I*} - R_{mn}^{I**} - R_{mn}^{II**} - R_{mn}^{II*})}{B \cdot \Delta H_B \cdot \left( \frac{R_{mn}^{I**} \cdot b + R_{mn}^{III**}}{1 + b} - R_{mn}^{I*} \right)} = 1$$

The efficiency of the criterial equations was tested on various mixtures formed by hydrocarbons, aromatics, alcohols, ketones, organochlorine compounds. The calculation error is less than  $\pm 2.5\%$  (in terms of total energy consumption) in comparison with the results of strictly calculating the distillation separation for a complex of columns.

The efficiency of the method is confirmed for any topologically equivalent column complexes, including columns with an internal separating wall.

State registration was obtained for the calculation program<sup>3</sup>.

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## CALS-TECHNOLOGY OF THE DEVELOPMENT OF HIGHLY EFFICIENT ROAD PROTECTIVE IMPREGNATIONS

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One of the key objective of the technology of maintenance of roads is the preservation of the quality of asphalt concrete pavement. This problem is solved with the help of artificial chemical compositions – impregnation of asphalt concrete pavement<sup>1</sup>.

For computer quality management of road impregnations based on the concept of CALS (Continuous Acquisition and Life cycle Support - continuous information support for the product life cycle)<sup>2</sup> an information system has been developed for two target classes: restoring and protective. The databases contain the impregnations of the respective chemical compounds, each of them is characterized by a set of quality indicators. A grouping of 32 quality indicators was carried out according to the 6 information clusters proposed by us: organoleptic, physico-chemical, physicommechanical; technological; environmental and operational. For each indicator, the most promising analysis method and analytical equipment is introduced into the system architecture. Based on the conducted multi-criteria analysis of the effectiveness of road impregnation, a new composition has been developed and protected by a patent<sup>1</sup>.

The development of modular production of protective impregnating compositions was carried out using the most modern and promising computer support system – CALS-technology<sup>2</sup>. The informational CALS-project of the technological regulation contains general drawings of the whole experimental-industrial production, drawings of individual modules (nodes), as well as the most important elements of the modules.

The developed impregnating composition has proven itself to protect the road surface from various negative impacts.

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## SYSTEM ANALYSIS OF ENVIRONMENTAL RISKS FROM THE APPLICATION OF ANTI-ICING MATERIALS

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The use of chemical anti-icing materials (AIM) reduces the cost of winter road maintenance, prevents the destruction of coatings and improves road safety<sup>1</sup>. However, the use of AIM leads to negative environmental consequences. Therefore, there is a need for a detailed and systematic approach in assessing the potential impact of AIM on humans and natural objects, as well as identifying risks and restrictions associated with the handling of these products. To solve these problems, a complex of system studies was carried out, as well as the development of a computerized environmental monitoring system for AIM<sup>2</sup>.

Based on the CALS-technology, an analytical system was developed for assessing environmental risks to the environment.<sup>2</sup> The following objects were selected as the top-level categories: snow cover and water bodies; soil cover; green spaces and atmospheric air. The impact on the environment of a large volume of the main components of AIM and their impurities (associated as potentially most dangerous) are separately considered. According to this, at the 2nd level of the developed system, the main groups of chemical AIMS are considered: chlorides, acetates, carbamides and nitrates. For each compound, 6 quality indicators are listed in the system, characterizing the level of risk from exposure of the AIM to a selected environmental object: mass fraction of soluble salts, mass fraction of water-insoluble substances, pH value, mass fraction of impurities, specific activity of natural radionuclides and corrosion activity on the metal.

The results of environmental monitoring included recommendations into reports on scientific agreements with the Moscow Department of Environmental Management and Environmental Protection.

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## IMPLEMENTATION OF HIGH-VOLTAGE ELECTROHYDRAULIC DISCHARGE BY THE YUTKIN METHOD

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The disadvantage of most electrohydraulic mixers (EHM) is the impossibility of their use, due to the complexity of the design and limited conditions in high-pressure petrochemical devices. We have developed a utility model, resulted in the simplicity of execution and the possibility of using it in petrochemical production apparatus without introducing additional elements into the apparatus cavity.

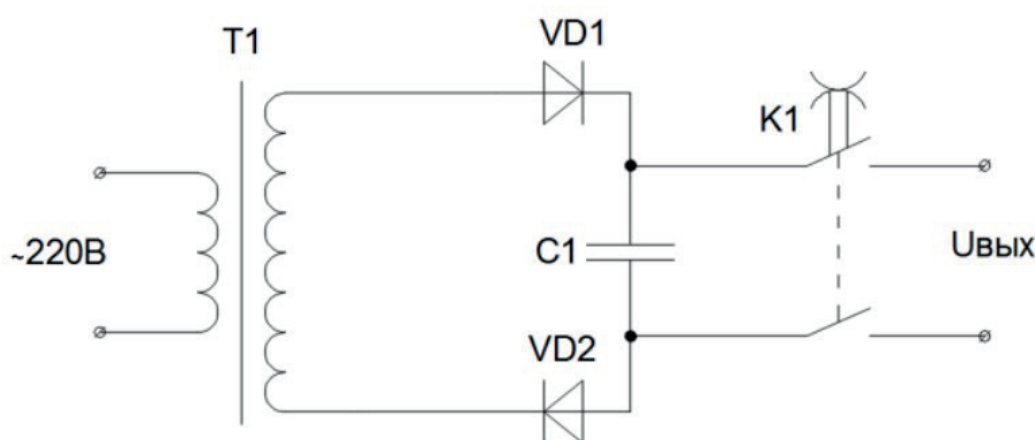


Figure 1. The electrical circuit of the electro-hydraulic mixer

The main difference from the standard EHM is - the introduction of the tube, which houses the electrodes and is connected to the casing of the apparatus through a threaded connection<sup>1</sup>. EHM according to the Yutkin method makes it possible to use a high-voltage electro-hydraulic discharge as a device for mixing coolant and during maintenance or repair of shell-type capacitive devices (as a cleaning of cavities from scale and sediment).

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## DETERMINATION OF GAS MIXTURES BY A SINGLE SEMICONDUCTOR SENSOR

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The main advantages of semiconductor sensors are usually considered to be their high sensitivity, low cost and long-term stability, and their main disadvantage is low selectivity. In this work, we increased the sensor selectivity based on nanodispersed tin dioxide with palladium additive using the pulsed heating mode and solved the problem of determining the composition of the “hydrogen – carbon monoxide” gas mixture.

Each of the repeated measuring cycles involved heating to 723 K for 2 s and cooling to 373 K for 13 s. Changing the temperature of the sensor allows us to distribute in time the following processes: sorption of the analyte gas, its chemical interaction with chemisorbed oxygen and the desorption of interaction products. As a result, the dependence of the sensor resistance on the measurement cycle time for different analyte gases differs from each other, which allows us to analyze gas mixtures qualitatively. Since the sample size of each measurement cycle exceeded 500, we used the principal component analysis (PCA) for reducing the dimension of sample data and polynomial regression models for qualitative analysis of gas mixtures. This method allowed us to use a relatively small set of analyte gas concentrations for instrument calibration at arbitrary test concentrations.

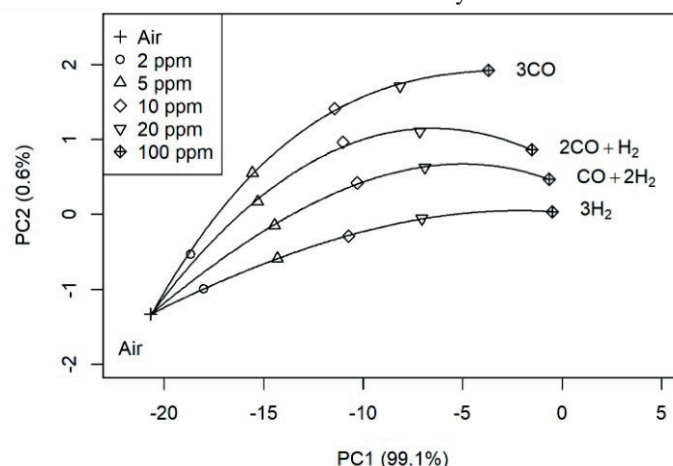


Figure 1. Training sample for the CO+H<sub>2</sub> gas mixture on the (PC1, PC2) plane

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## BLACK GALVANIC COATINGS BASED ON NICKEL

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There are several disadvantages of employed so-called black nickel plating processes such as: low corrosion resistance, low wear resistance of the resulting coatings, and their weak adhesion to the base metal, especially when applied to steel.

Despite the fact that there are some data on the effect of concentration of primary components on the composition and properties of the resulting coatings in the literature, the mechanism of black nickel deposition has not been studied in detail.

This research work is devoted to the study of the process of obtaining black coatings based on nickel.

In this research work the possibility of step-by-step deposition of black nickel-containing coatings was studied. This method of coating is based on the deposition of the first layer of light nickel and the next layer of "black" layer in the same electrolyte at different current densities. At the first stage, which is realized at sufficiently low current densities, light nickel is deposited, providing adhesion to the substrate, and then the current density increases stepwise a black coating is formed.

It is shown that black nickel coatings precipitated by this method contain metallic nickel, nickel and zinc sulfides, the nickel content is 28%, zinc - 59%, and sulfur - 13%.

It is revealed that protective ability, corrosion resistance and abrasion resistance of black «nickel» coatings obtained by this method are comparable to similar characteristics of black chromium coatings.

## **HIGHLY-EFFICIENT CATALYSTS BASED ON HIGHLY-POROUS CELLULAR METAL MATERIALS FOR AEROSPACE INDUSTRY**

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Before supplying the respiratory air mixture in aviation, the mixture is cleaned of ozone in order to prevent it from entering the human respiratory tract. The catalysts for the decomposition of ozone are oxides of transition metals - nickel, cobalt, manganese, etc.

These catalysts must meet the following requirements: high degree of ozone conversion, high strength, developed surface, low aerodynamic resistance. Currently used granular and ceramic catalysts do not fully meet the requirements due to their inherent drawbacks.

This paper is devoted to the development of the technological process of electrochemical nickel plating of highly porous polyurethane foam. Before electrodeposition of the metal, polyurethane foam samples were treated with a conductive composition, then the samples were dried with hot air, and then processed galvanically. Optimal electrolyte compositions and parameters of nickel plating processes based on nickel chlorides and nickel sulphates were selected, allowing to obtain high-quality coatings on flat polyurethane samples.

The possibility of creating a framework of the desired thickness in one stage in one electrolyte, and in two stages in different electrolytes and under different conditions was investigated.

The first nickel layer is deposited in a chloride electrolyte having a high covering ability, and then the coating grows to the desired thickness in a sulphate electrolyte having a higher current output. When using a two-stage process, the total duration of the deposition of the coating of the required thickness is reduced.



## SOLID-STATE SOLUTION (Nd,Pr)BaMn<sub>2</sub>O<sub>6</sub> AS NOVEL MAGNETOCALORIC MATERIAL

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Double manganites of Nd and Pr are novel magnetocaloric materials due to a demonstration of two magnetic phase transitions with field cooling (paramagnetic-ferromagnetic PM→FM and ferromagnetic-antiferromagnetic FM→AFM) near room temperature (Fig.1.)

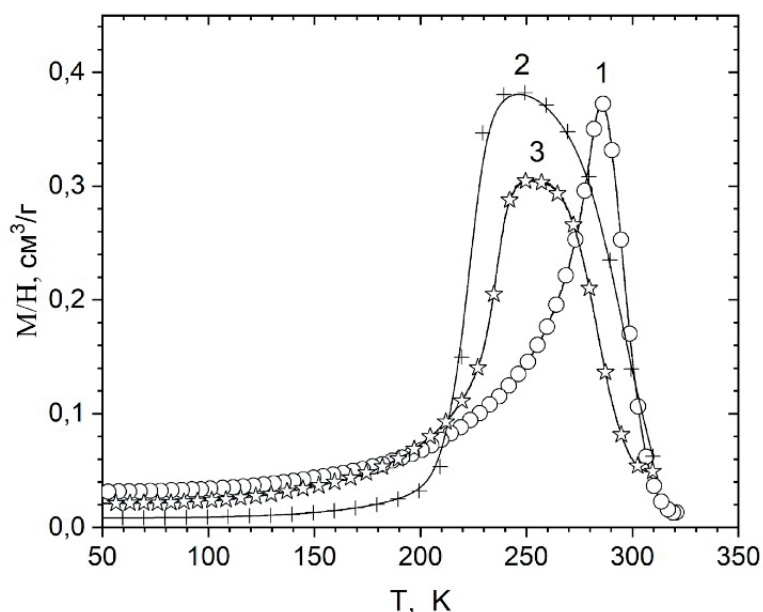


Figure 1. Temperature-dependent magnetization of double manganites:  
1 - NdBaMn<sub>2</sub>O<sub>6</sub>, 2 - PrBaMn<sub>2</sub>O<sub>6</sub>, 3 - Nd<sub>0.5</sub>Pr<sub>0.5</sub>BaMn<sub>2</sub>O<sub>6</sub>.

Nd-based double oxide undergoes a magnetic phase transition FM→AFM with a jump of the unit cell volume, this phenomenon leads to destruction of the material during thermocycling. For PrBaMn<sub>2</sub>O<sub>6</sub> that phenomenon is not found, however, the difference of temperatures between two magnetic phase transitions is about ΔT=48 K, while NdBaMn<sub>2</sub>O<sub>6</sub> oxide demonstrates ΔT=17 K. Hence, Pr-based compound requires a wider temperature range for the application. Such drawbacks are absent for an equimolar solid solution Nd<sub>0.5</sub>Pr<sub>0.5</sub>BaMn<sub>2</sub>O<sub>6</sub>: the temperatures of magnetic transitions are close (ΔT=29 K) and the jump of unit cell volume is not noticeable.

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## THE INFLUENCE OF CALCIUM AND MAGNESIUM IONS ON THE EFFICIENCY OF ELECTROFLOTATION EXTRACTION OF INSOLUBLE COMPOUNDS OF IRON (III)

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Electroflotation is an effective method of purifying industrial wastewater from heavy and non-ferrous metal ions. In water treatment processes for separation of metal hydroxides (Fe, Al, Cu, Zn, etc.), wastewater is treated with alkaline reagents: NaOH,  $\text{Ca(OH)}_2$ ,  $\text{Mg(OH)}_2$ ,  $\text{Ba(OH)}_2$ ,  $\text{Na}_2\text{CO}_3$  in order to form a precipitate. For the subsequent separation of the dispersed phase, are used sedimentation, filtration and flotation.

Table 1. Comparison of the degree of electroflotation extraction of  $\text{Fe(OH)}_3$  depending on the concentration of hardness salts. Experimental Conditions:  $\text{Fe}^{3+} = 100 \text{ mg/l}$ ,  $\text{NaCl} = 1 \text{ g/l}$ ,  $\text{pH} = 7$ ,  $J_v - 0,4 \text{ A/l}$ .

Electroflotation time, min	$\alpha, \% \text{ Fe(OH)}_3$				
	$\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ 0 g/l	$\text{Ca}^{2+}$		$\text{Mg}^{2+}$	
		0.5 g/l	1 g/l	0.5 g/l	1 g/l
5	73	24	11	30	28
10	82	36	26	47	37
20	94	49	40	58	50

It is established that the process of electroflotation extraction of insoluble iron hydroxides in the presence of hardness salts is suppressed. The decrease in the efficiency of the  $\text{Fe(OH)}_3$  extraction process is associated with the adsorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on the precipitation  $\text{Fe(OH)}_3$ , changes in the  $\zeta$ -potential of the particles and a decrease in their size. Similar effects are observed for barium ions.

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## POLLUTION BY PLASTICS: EXTENT OF THE PROBLEM AND KEY APPROACHES TO ITS EVALUATION

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Recently, due to the rapid development of the chemical and petro-chemical industry, and the growth in consumption of plastic products, the pollution of the World Ocean, as well as land, has become threatening to the ecosystem and human health<sup>1</sup>. UN experts rightly call such pollution “Global by scale and intergenerational by degree of impact.” Moreover, plastics are a significant problem not only for the marine environment, but also for coastal and inland areas, where plastic waste propagates by rivers and air currents.

There are recent works devoted to the analysis of the chemical reaction pathways of polymer decomposition in seawater<sup>2</sup>, which makes it possible to model the condition of the anthropogenic marine litter.

In the present work, will be analyzed literature sources on modeling the fate of plastic waste in the environment - including propagation and accumulation on land, in water basins and other environmental objects. As a result, the main elements of the potential model will be revealed: sources of pollution, objects of accumulation, chains of decay products along the propagation paths, criteria for assessing the state of objects and regions. The objectives and principles of the model will be formulated, which will help assess the situation at the levels of regions, countries and the World, in order to support political and technical decision-making.

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## APPLICATION OF MACHINE LEARNING FOR PREDICTION OF THE EQUILIBRIUM PROPERTIES OF TWO OR MORE COMPONENT SYSTEMS

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Using results of the experimental studies<sup>1</sup> on vapor-liquid equilibrium of the two component systems which includes organic compounds and water, as well as critical properties of individual components<sup>2</sup>, artificial neural network (ANN) models were developed for prediction of vapor-liquid equilibrium data in two or more component systems. For training the ANN models a set of 87169 equilibrium data points for 2859 binary systems consisting of 397 individual components was used. Models were developed using high-level neural networks API named Keras<sup>3</sup> with TensorFlow<sup>4</sup> as a backend.

The validity of the models was evaluated through a test data set, which were not employed in the training case of the network. Also comparison of predicting capabilities between conventional equations of state such as SRK and PR with developed models was conducted.

The trained models can be applied for prediction of vapor-liquid equilibrium properties, such as mole fractions of components in liquid and vapor (gaseous) states, temperatures and pressures in a wide range of values (from 40 to 600 K and from 3e-5 to 65 bar) of binary mixtures. Also models can be used for generation of pseudo-experimental data for further application in the modeling of absorption, distillation and rectification processes along with conventional equations of state.

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## INVESTIGATION OF THE CHEMICAL COMPOSITION OF POWER PLANTS ASH AND SLAG FOR APPLICATIONS AS SOIL COMPONENTS

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Recycling and safe use of wastes of power plants, in particular, coal, is a worldwide relevant problem. Russia has huge coal reserves and a developed industry that consumes them. Nevertheless, despite the worldwide and domestic practice of using ash and slag waste as soil components, there are almost no research on the actual environment impact of ash and slag waste in this country. Also scientifically proven standards for their use as well as chemical and biological methods for safety assessment have not yet been developed. The situation is complicated by the fact that the chemical and physical properties of a material such as coal ash substantially depend on both the feedstock and the combustion technology.

This paper compares the chemical composition of ash and slag waste from three large power plants in the Central Russia. Alkaline fusion was used to determine the total element composition. Trace elements were determined by treatment with nitric acid and a mixture of nitric and hydrofluoric acids under pressure in PTFE autoclaves. The mobile element species were measured using various extracts used for similar purposes in soil science (water, hot water, HCl, ammonium acetate buffer). The fractional composition of the samples was determined by the method of dry dispersion (8 fractions) and obtained preparative amounts of fractions, which were further analyzed. To simulate the conditions of actual interaction with the soil, ash and slag ash waste samples were mixed with sod-podzolic soil and chernozem in different ratios and incubated for two months at 20–22 °C and 60% of full water capacity.

As a result, we obtained that the studied ash and slag waste consisted mainly of Al, Ca, Si, Fe, K, Mg, Na, P, and S. We found that the total content of trace elements including hazardous As, Pb, Cd, etc. were in the typical ranges for the soil and do not significantly exceed the natural content.

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## EXTRACTION IN THE PROCESSES OF RECYCLING OF Ni-MH BATTERIES

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At present, one of the important problems is the waste volume growth of electronic, electrical equipment, as well as the associated accumulation of batteries (accumulators). It contains a number of valuable metals, including rare earth elements<sup>1,2</sup>. To date, there is no an eco-friendly and cost-effective technology that allows you to recycle spent batteries, in order to produce products of good quality. Therefore, it is important to create new eco-friendly technological processes for the separation of valuable components from aqueous solutions, their processing and pure substance production<sup>3-6</sup>.

The work presents the extraction experimental results of a number of metal ions ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  etc.) from chloride solutions using an environmentally safe extraction system based on polypropylene glycol 425. The values of the distribution coefficients and the degree of extraction of metal ions in the system under study are established. The effect of kinetic parameters on the extraction efficiency of metal ions in a system with polypropylene glycol 425 was investigated. The advantage of the extraction system with polypropylene glycol 425 for the selective extraction of metals from dilute chloride solutions is shown.

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## EXTRACTION $\text{Ni}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Co}^{2+}$ AND $\text{Mn}^{2+}$ IONS FROM NITRATE SOLUTIONS IN A SYSTEM WITH POLYETHYLENE GLYCOL 1500

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Recycling of electronic waste is a cost-effective opportunity to extract a number of valuable metals for further use. Liquid-liquid extraction in the classical system with organic extractants is an effective method for the separation of metals and provides a high percentage of extraction<sup>1</sup>. However, such systems include organic solvents that can be toxic, carcinogenic, and flammable<sup>2</sup>.

Recently, special attention has been paid to study aqueous two-phase systems based on water-soluble polymers (polyethylene glycol, polyvinylpyrrolidone) in the extraction of various organic and inorganic substances<sup>3-5</sup>. Therefore, the use of aqueous two-phase systems for the problems of metal extraction from solutions is of great interest both from a scientific and practical points of view.

In the present work, the study of  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  ion extraction in an aqueous two-phase system based on polyethylene glycol 1500 and sodium nitrate was conducted. The effect of phase contact time on the extraction efficiency of selected objects was studied. The dependences of the distribution coefficient and the degree of extraction of metal ions on various parameters (acidity of the medium, initial metal concentration, etc.) were established. Based on the results obtained, it can be concluded that the extraction system based on polyethylene glycol 1500 is effective for the complex extraction of a number of metals from nitrate solutions.

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## BLACK SILICATE-BASED COATINGS ON GALVANIZED ZINC

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Black conversation coatings on zinc, which possess anticorrosion and decorative properties, are widely used in car- and engineering industries as protective decorative coatings and in solar technology for increasing solar absorption by solar batteries surface.

It is known, that chromate solutions are highly toxic due to presence of hexavalent chromium ions.

The possible alternative to chromate treatment is the process of passivation in silicate-based solutions<sup>1,2</sup>.

The solution was developed, containing  $\text{Na}_2\text{SiO}_3$  10 g/l,  $\text{H}_2\text{SO}_4$  5 ml/l,  $\text{H}_2\text{O}_2$  7,5 ml/l,  $\text{FeSO}_4$  1 g/l,  $\text{NiSO}_4$  1 g/l,  $\text{CH}_3\text{COONa}$  3 g/l,  $\text{CuSO}_4$  12 g/l.

The performed experiments allowed determining the concentration range of solution components, where it is possible to obtain the coatings with high protective quality.

The research showed, that the optimal pH range is 2,0-2,4 and temperature is about 20-25°C.

It is found, that black silicate based coatings can keep 55 hours to first white rust spots. It should be noted that, time to zinc corrosion products of black chromate coatings is 50 hours.

The technology of producing black protective-decorative silicate-based coatings, which are comparable to black chromate coatings and might be used as an alternative, is developed.

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## METHODS OF WATER PURIFICATION FROM FLUORINE-CONTAINING INORGANIC IMPURITIES

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According to the existing norms in drinking water bodies, the concentration of fluorine should not exceed 1.5, and in fishery water bodies 0.75 mg/l. Fluorine can be present in effluents in the form of:  $F^-$ ,  $SiF_6^{2-}$ ,  $AlF_6^{3-}$ ,  $FeF_6^{3-}$ ,  $TiF_6^{2-}$ . Different cationic composition of fluorine-containing water for purification from fluorine require different approaches. When cleaning wastewater from fluorine in the form of  $F^-$  ( $C_F=10$  mg/l) with  $Ti^{IV}$  compounds, a high degree of purification (up to  $C_F=0.5$  mg/l) was achieved, the pH of the process was 4-4.5. Hydrolytic stability of complex anions ( $SiF_6^{2-}$ ,  $FeF_6^{3-}$ ,  $TiF_6^{2-}$ ,  $ZrF_6^{2-}$ ,  $AlF_6^{3-}$ ) varies<sup>2</sup>, their hydrolysis ends at pH: 4.35; 5.02; 5.25; 7.20; 7.70. It has allowed to assume, the suitability of titanium compounds to purify water not only from  $F^-$  but also from  $SiF_6^{2-}$  to 0.75 mg/l. the effluent from the fluorine in the form  $FeF_6^{3-}$ ,  $TiF_6^{2-}$ ,  $AlF_6^{3-}$ , carried out with the compounds of lanthanum or церия<sup>3</sup>. The optimal pH of the process is 5.5-6.0. Выявлено that the sulfates of the lanthanides more efficiently than chlorides, and compounds of cerium, more effective compounds of lanthanum. The residual content of fluorine in the purified solution was 1.3 mg/l. Water purification from  $F^-$  - have cheaper reagent - compound-tions of Fe and  $Al^{III}$ . A high degree of purification (0.5 mg/l) was achieved using  $AlCl_3$ , the pH of the process was 6.0-6.5.

Secondary pollution with  $SO_4^{2-}$  and  $Cl^-$  ions does not exceed the standards.

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## HYDROLYSIS OF THE FLUORIDES OF RARE EARTH ELEMENTS (Y, La, Ce, Pr, Nd) AND FLUORINATED COMPOUNDS OF TA AND NB

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Processing of fluoride extracts of niobium and tantalum (Nb and Ta) into oxides is associated with hydrolysis of fluorine and fluoro-tantalic acids, which has been studied, but deep purification of the resulting hydroxides from fluorine has not yet been achieved<sup>1</sup>. It is proposed to use the lanthanide (Tr) for sorption and precipitation of wastewater from fluorine<sup>2</sup>. This and not only determines the interest in the study of hydrolytic behavior of fluorides Tr and fluorinated compounds Nb and Ta.

A study of the hydrolytic behavior of suspensions  $\text{LaF}_3$ ,  $\text{CeF}_3$ ,  $\text{YF}_3$ ,  $\text{NdF}_3$ ,  $\text{PrF}_3$ ,  $\text{K}_2\text{TaF}_7$  and  $\text{K}_2\text{NbF}_7$  with an initial concentration of fluorine  $C_{\text{F(initial)}} = 10 \text{ mg/l}$ . The data obtained are shown in the figure 1.

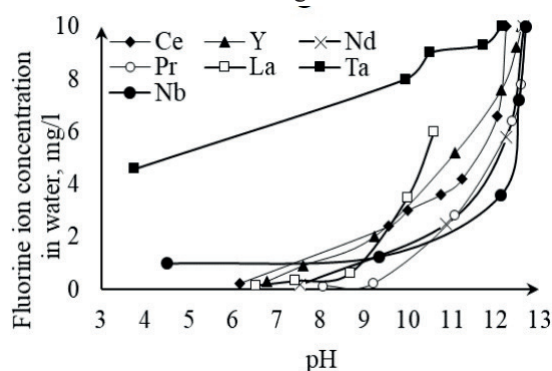


Figure 1. Dependence of the degree of complete hydrolysis of  $\text{LaF}_3$ ,  $\text{CeF}_3$ ,  $\text{PrF}_3$ ,  $\text{NdF}_3$ ,  $\text{YF}_3$ ,  $\text{K}_2\text{TaF}_7$  и  $\text{K}_2\text{NbF}_7$  and  $\text{K}_2\text{NbF}_7$  on the pH of the solution.

Hydrolytic stability increases in the series of fluorides  $\text{La} < \text{Ta} < \text{Ce} < \text{Y} < \text{Nd} < \text{Pr} < \text{Nb}$ . The stability of the fluorides of lanthanum and cerium is noticeably less than other fluorides, the stability of which is approximately the same. Stability of  $\text{K}_2\text{TaF}_7$  and  $\text{K}_2\text{NbF}_7$  differs significantly (hydrolysis of  $\text{K}_2\text{TaF}_7$  is completed at  $\text{pH}=12.15$ , and  $\text{K}_2\text{NbF}_7$  at  $\text{pH}=12.7$ ).

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**SCIENTIFIC BASES OF ENERGY RESOURCE EFFICIENT  
ENVIRONMENTAL AND SAFE PROCESSING  
OF TECHNOGENIC RAW MATERIALS  
OF PHOSPHOROUS CONTAINING APATITE-NEPHELINE ORE DEPOSITS**

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The mining complex of the Murmansk region is one of the most developed mining regions in Russia, and the depletion of the raw material base of phosphorus-containing minerals and the environmental problems of storing technogenic raw materials necessitate the involvement of apatite-nepheline ore production wastes in complex recycling and disposal. Unused dumps are not only huge damage to the natural environment, but also mineral raw materials irretrievably lost as a result of wind and water erosion. A special place among the technogenic deposits of the Kola Peninsula is occupied by waste dumps of enrichment, in which fine material is stored, which increases their susceptibility to wind and water erosion.

The purpose of the proposed scientific work is the creation of fundamental physicochemical, technological and organizational-technical foundations of energy efficient and environmentally safe resource-saving processing of waste from mining and processing enterprises, which will allow to utilize crushed raw material into competitive products with high added value - pellets and reduce the amount of waste sent to the burial of these wastes, to increase the degree of conversion of technogenic raw materials into final useful products, to ensure the elimination of landfills, to reduce the negative impact on the environment<sup>1</sup>.

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**POTENTIAL ENERGY SAVING IN CHEMICAL AND POWER-PROCESS  
SYSTEM OF PRODUCTION OF YELLOW PHOSPHORUS**Bobkov V.I.<sup>a,b</sup>

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The complex chemical and power-process system for the production of phosphorus includes the stages of thermal preparation and electrothermal sublimation. Lump phosphorite is subjected to roasting, fines can be agglomerated or burned in the form of pellets. Thermal preparation allows to save electricity, using fuel directly for decarbonization processes, rather than more expensive electric energy. All aggregates implement highly efficient technologies with intensive heat and mass transfer and internal regeneration of thermal energy, but their complex use requires further improvement<sup>1</sup>. Most even high-potential flows in this flowchart are not closed. From practice it is known that about 20 kg.w.t./t of natural gas and 110 kg.t.t./t of coke, 25 - 55 kWh / t of electric power are consumed per ton of suitable agglomerate of phosphate ore. For the production of agglomerate in the metallurgical industry, specific fuel consumption is in the range of 90 - 110 kg.t.t / t. The loss with heat of sinter is 33%. For firing machines that perform the same functions, unit costs are in the range of 25–50 kg.wt./t. The scheme of the firing machine involves the use of air heat from the cooling zone in the sintering zone with the displacement of used fuel. Specific electricity consumption for ore recovery electrothermal phosphorus furnaces lies in the range of 13–15 MWh / t of phosphorus. For ideal aggregates, this value is 9–11 MWh / t phosphorus. Thus, in separate units of the system there are unused resources.

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## THE EQUILIBRIUM CHARACTERISTICS OF THE CONCENTRATION OF ANIONIC SURFACTANTS ON POLAR AND NONPOLAR ADSORBENTS

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Anionic surfactants will adversely affect human health and aquatic ecosystems, and their removal from water is very difficult. In this regard, the aim of this work is to establish the optimal conditions of extraction and concentration from aqueous solutions of anionic surfactants on various adsorbents.

As anionic surfactants selected sodium oleate and sodium dodecyl sulfate, as sorbents selected activated carbons UBF and SV-50, «Polisorb», industrial sorbents Shungite and Kremen, ion-exchange resins CB-4, Purolite A-430 and S-930. Determination of the concentration of anionic surfactants in aqueous solutions was carried out extraction-photometric and potentiometric methods. With the aim of selecting the most effective sorbent obtained isostere sorption of sodium oleate on all selected sorbents. It is established that mesoporous SV-50, Shungite, POLYSORB and Kremen have the highest values of adsorption of anionic surfactants. On four selected sorbents, obtained sorption isotherms, determined its equilibrium characteristics. The isotherms have the form, close to linear, which allowed us to calculate Henry's law constant corresponding to the coefficients of the interphase distribution of the sodium oleate. According to the Langmuir equation, the maximum adsorption and constant adsorption-desorption equilibrium. The calculation is made on the assumption that adsorption at low concentrations of anionic surfactants occurs at the monomolecular mechanism.

The results of the study sorption of anionic surfactants, the most effective sorbent is activated carbon SV-50. The values of maximum adsorption and distribution coefficient on this sorbent is much higher than other objects of study. The efficiency of coal SV-50 for the adsorption of anionic surfactants probably due to a developed network of mesopores commensurate with the size of the surfactant molecules, the combination of the particular high-energy active sites.

To create the sorption layer based on activated carbon SV-50 for the concentration and subsequent determination of anionic surfactants in aqueous solutions in selected indifferent filler column fiber FIBAN AK-22-1. The peak of the curve of desorption has an asymmetric shape with a shift to the right. This peak shape is due to the large size of ions of sodium dodecyl sulfate, which leads to their slow movement in the sorption layer compared to the total flow. Based on the curve spent calculating the characteristics of concentration, namely the degree of extraction (93%) and coefficient of concentration (2,3).

## ION EXCHANGE DEMINERALIZATION OF AMINO-ACID WATER SOLUTIONS

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For a long time, ion-exchange sorption remains a promising method for the separation of both inorganic and organic substances, in particular amino acids. Rational technology for the extraction of biologically active substances should be based on the laws of ion exchange and molecular sorption of substances. The traditional method for the isolation of amino acids is ligand exchange chromatography; sulfonated polystyrene charged with copper is most often used as an ion exchange. In the general case, when aliphatic amino acids interact with metal forms of complexing ion exchangers, both the ionite complex can be destroyed with cation elution into the solution, and the formation of mixed ligand complexes in the phase of sorbents.

A significant difference in the effect of the pH of the solution on the interaction of amino acids with metal forms of complex-forming ion exchangers was found. In the system with carboxyl mono- and bifunctional ion exchangers in acidic and neutral solutions, amine acids destroy ion-exchange complexes, and copper (II) cations are eluted into solution. In alkaline solutions, mixed-nigand amino acid complexes are formed in the phase of sorbents: KB-2 and KB-4 at low concentrations of amino acids, ANKB-35 – in a wide concentration range. The opposite situation is observed in systems with phosphoric acid ion exchangers KRF-5p and KF-7. Mixed-ligand ionite complexes of amino acids are formed in acidic and neutral solutions, in alkaline solutions of amino acids they destroy copper complexes in the phase of the ion exchange and the metal (II) is eluted into the solution. Capacities of phosphoric acid sorbents in copper form are lower in amino acid anion than in cation or bipolar ion.

The influence of the pH of the medium affects, first of all, the change in the nature of the resulting complex compounds in the phase of the sorbent and the equilibrium solution and the ratio of their stability constants. If the stability stability of the ionite complex is higher than the stability constant of the compound with the low molecular weight ligand, then the sorbed copper cations interact with the incoming methionine ions without breaking the metal – functional coordination bond of the ion exchange. If the ratio of the constants is reversed, then predominant elution of cations occurs with the formation of complex compounds with methionine in an aqueous solution.



## THE INFLUENCE OF THE SURFACE PROPERTIES OF HYDROXIDES OF THE METALS ON THE EFFICIENCY OF THEIR FLOTATION EXTRACTION FROM AQUEOUS SOLUTIONS IN MULTICOMPONENT SYSTEMS

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Influence of solubility, disperse characteristics and charge ( $\zeta$ -potential) of low-soluble heavy metals compounds particles on an example of zinc (II), lead (II), cerium (III), iron (III), aluminium (III) compounds on efficiency of their extraction from water solutions as a multicomponent system dispersed phase by electroflotation is studied.

It is shown, that low-soluble lead connections are capable to be taken from water solutions only together with low-soluble connections of accompanying metals. Thus high flotation activity Pb (II) in all range pH is caused by sorption Pb(II) ions and disperse phase on Zn (II), Fe (III), Al (III), and Ce (III) disperse phase.

It is noticed, that in process of extraction of disperse phase low-soluble iron-containing connections (Fe (III)-Zn (II)-Pb (II), Fe (III)-Zn (II) and Fe (III)-Pb (II)) synergistic effect is observed - joint extraction of metals occurs more full and effectively. This fact can be connected with suppression of a negative charge. Considerable decrease of particles size in comparison with individual connections of iron and zinc (from 30 - 60 to 20 - 30 microns) is observed. Similar effects are observed for all investigated systems. The carried out researches have allowed will reveal pH environments, at which probably fullest removal of ions of metals from water as a part of multicomponent systems: for system Fe (III)-Zn (II)-Pb (II) - 9,0; for system Al (III)-Zn (II)-Pb (II) - 8,0; for system Ce (III)-Zn (II)-Pb (II) - 10,0. In this range pH degree of extraction by electroflotation method on all components reaches 93 - 98 %.

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## OBTAINING N(S)- AND NK(S)- FERTILIZER FROM THE SPENT ACID MIXTURE CELLULOSE NITRATE PRODUCTION

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In the existing technology for the production of cellulose nitrates, the spent acid mixture ( $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ) is regenerated and returned to the cycle. However, this process is very expensive (the costs are many times higher than the cost of production acid). In addition, in the process of regeneration, the amount of toxic gas emissions into the atmosphere ( $\text{NO}_x$ , mist  $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ) significantly increases. The need for acid regeneration is preserved due to the impossibility of safe storage of the spent acid mixture, which leads to an increase in the cost of the target products.

We have proposed a simple and inexpensive method of processing spent acid mixture to ammonium sulfate nitrate, which is an N(S) fertilizer with the ratio  $\text{N}:\text{S} \approx 30\%:7\% \approx 1:(0,25-0,45)$  wt. (meets the requirements of TU 2181-036-00205311-08 "Ammonium sulfur-containing nitrate") [1].

The main advantage of ammonium sulfate nitrate is the high content of two basic forms of nitrogen ( $\text{NO}_3$ ,  $\text{NH}_4$ ). The disadvantage of the proposed method of obtaining N(S) fertilizer is the need for additional equipment costs for catching ammonia vapors.

In view of the foregoing, the use of ammonia water with a certain amount of KOH was proposed as a neutralizer for the spent acid mixture. In the resulting complex NK(S)- fertilizer, the ratio of main elements is the optimal  $\text{N}:\text{K}_2\text{O}:\text{S} = 1:(0,7-2):(0,5-1)$  wt. (for most cultures the optimum is  $\text{N}:\text{K}_2\text{O} \approx 1:0,7$  wt.). In addition, the amount of sulfur relative to the main elements ( $\text{N}+\text{K}_2\text{O}):\text{S} \approx 1:(0,25-0,35)$  wt. (since an excess of sulfur leads to inhibition of plant nutrition by the main elements).

The introduction of the proposed method of processing into production will reduce the cost of cleaning gaseous wastes.

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## LABORATORY STUDIES THE CATALYTIC REDUCTION OF THE TEMPERATURE OF IGNITION OF METHANE

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The results of the dynamics of technogenic risks in the oil and gas industry analysis shows that only in the last ten years the economic damage from them has increased more than 2 times<sup>1</sup>. Fires in openly flowing gas and gas and oil wells are complex emergency situations of a technogenic character.

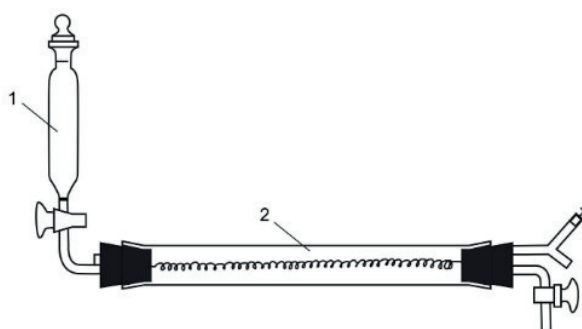


Figure 1. Laboratory setup for methane production. 1 - dropping funnel with acetic acid,  
2 - reactor with nichrome spiral and catalyst.

The phenomenon of catalysis is common in nature. It is likely that the catalysis phenomenon may contribute to the technogenic ignition of natural gas, the main component of which is methane. Thus, contact with the solid surface of some substances is the most important factor in the ignition of the methane-air mixture.

To study the catalytic reduction of the activation energy of the methane ignition reaction, an installation for obtaining constant quality methane from acetic acid was prepared. When methane was passed through the studied catalyst, the ignition temperature of methane was determined. Soil samples, as well as oxides, salts, hydrolysis salts and organic components, modeling the composition of possible deposits on pipes, were used as a catalyst. In particular, it was noted that the clay soil reduces the ignition temperature by more than 100 ° C.

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## APPLICATION OF SORBENTS BASED ON NATURAL ALUMINOSILICATES FOR CLEANING WASTEWATER FROM ANTIBIOTICS

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Antibiotics are biologically active substances used as drugs in medicine and veterinary for the prevention and treatment of diseases, as well as to stimulate the growth of cattle. Ways of their getting into agroecosystems are different:

- discharge with sewage of various enterprises;
- application in agriculture;
- with wastes of people and animals taking antibiotics.

Getting into the environment, and then into the organisms of animals and humans, drugs can accumulate, causing allergic reactions and resistance to antibiotics.

The aim of the work is to study the possibility of using sorbent based on vermiculite modified with hydrochloric acid for the treatment of wastewater from residual amounts of antibiotics of various classes. As the object of the study, domestic wastewater of Vladivostok with medicinal preparations introduced into them (chloramphenicol, tetracycline, cefazolin, ciprofloxacin) were selected.

It was shown that tetracycline, cefazolin and ciprofloxacin are sorbed completely, as evidenced by the absence in the absorption spectra of the eluate of the absorption maxima associated with the main absorption maxima of these antibiotics. A significant decrease in the turbidity of the studied water was established, which indicates additional purification.

The degree of absorption of chloramphenicol with low concentrations of the studied antibiotics in the solution reaches 40%, but with increasing of the sorbent load, the amount of absorbed antibiotic decreases. With a total mass of injected drugs of 4 mg, the degree of absorption of chloramphenicol drops to 2%. This indicates a lower, compared to other antibiotics, sorption removal capacity.

Thus, a sorbent based on vermiculite modified with hydrochloric acid is promising for the treatment of wastewater from antibiotics tetracycline, cefazolin and ciprofloxacin.

## APPLICATION OF ELECTROFLOTATION TECHNOLOGY IN THE PROCESS OF SEPARATION OF $\text{Sc}^{2+}$ AND $\text{Ti}^{4+}$ IONS

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Most of the rare earth metals do not form independent minerals in nature and are natural satellites of other metals. For example, among the numerous potential sources of scandium in Russia, of great interest are the ilmenite concentrates from titanium deposits, the waste of titanium magnetite production, complex rare metal ores from the promising Tomtor deposit with a unique content of  $\text{Sc}_2\text{O}_3$ . Obtaining individual rare earth elements is a very time consuming task. Electroflotation technology is increasingly being used not only in wastewater treatment and water treatment processes, but also as a method for separating metal ions based on differences in the pH of hydrate formation of the metals under study (Table 1).

Table 1. The dependence of the degree of extraction of metal compounds from the pH of the solution,  $\tau = 20$  min;  $i = 0,4 \text{ A}\cdot\text{L}^{-1}$ ,  $c(\text{NaCl}) = 1 \text{ g}\cdot\text{L}^{-1}$

pH Metal	Extraction rate, $\alpha$ (%)									
	2	3	4	6	7	8	9	10	11	12
Sc	-	-	-	65	98	93	90	22	7	-
Ti	60	98	25	15	30	92	67	60	61	46

It was established that the maximum degree of extraction of compounds during chanting is observed at  $\text{pH} = 7$ , which corresponds to the literature data. The dependence of the degree of extraction of titanium compounds on the pH of the solution showed two peaks (at  $\text{pH} = 3$  and 8). In the range of pH values 4 – 7, a low extraction efficiency was observed, which is apparently due to a change in the structure of the dispersed phase. Thus, to extract titanium from aqueous solutions containing a mixture of elements, the electroflotation process should be carried out with a solution pH of 3 for 20 minutes. After the necessary adjustment of the pH of the solution to 7 in order to extract compounds of scandium.

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## EXTRACTION OF CARBON MATERIAL IN THE PRESENCE OF ORGANIC COMPONENTS BY ELECTROFLOTATION METHOD

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Powdered activated carbon (AC) is widely used as a sorbent in industrial wastewater purification from organic and inorganic impurities. It has been proposed that activated carbons can be introduced directly into the aqueous phase. The effectiveness of this purification process is higher than one during adsorption in a stationary layer on the filters. Since particles of powdered coal (10 – 15  $\mu\text{m}$ ) are small, thus their extraction using classical methods (sedimentation, flotation, and filtration) is less effective. Efficient extraction of particles of about 1 to 30 microns sized can be achieved by use of the technique of the electroflotation. Wastewater may contain various components used in technological solutions of production. It is noted that the presence of washing liquids (GARDOSTRIP Q7940, VIGON SC-200 или ZESTRON FA+) used in the production of printed circuit boards in water suppresses the process of electrofloating extraction of OU-B brand coal (the degree of extraction decreases from 56 to 30%). However, with the application of flocculants and coagulant  $\text{FeCl}_3$  ( $c(\text{Fe}^{3+}) = 10 \text{ mg/l}$ ) into the test system, the degree of coal extraction increases to 92% (Table 1).

Table 1. The dependence of the degree of extraction of AC OU-B in the presence of washing liquid GARDOSTRIP Q7940 and flocculants on the duration of the process,  $\text{pH} = 7$ ;  $i_v = 0,4 \text{ A/l}$ ;  $c(\text{Na}_2\text{SO}_4) = 1 \text{ g/l}$ ;  $c_{\text{floc.}} = 10 \text{ mg/l}$ ,  $\Delta m_{\text{OU-B}} = 100 \text{ mg}$

$\tau, \text{ min}$	The degree of extraction of activated carbon ОУ-Б $\alpha_{\text{EF}}, \%$			
	Without additives	FO 4190 (k)	FA 920 (n)	AN 905 (a)
5	31	82	79	36
10	55	91	88	53
20	56	92	92	51

## EXTRACTION OF RARE EARTH ELEMENTS AT THE VIBRATIONS IN THE INTERFACIAL LAYER

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Usually, the process of solvent extraction is carried out in an emulsion; various devices are used to obtain it. The disadvantage of such a process is the complexity of hardware design, increased energy, spent first on dispersion, and then on separation. Often stable emulsions are formed, causing delayed stratification, extragent entrainment, limiting equipment performance. Carrying out the extraction in the pre-emulsion regime allows to get rid of these difficulties, but at the same time, due to the smaller interface, the extraction rate is lower. It is possible to increase the rate of extraction by local mechanical action on the interfacial layer, while maintaining the interface is inseparable.

The aim of the work was to establish the influence of local mechanical vibration in the interfacial layer of the extraction system on the rate of the process.

The impact is carried out by a vibroelement placed on the interface and driven by an electromagnetic vibrator.

The existence of a resonant frequency is established, at which a local effect on the interfacial layer leads to an increase in the rate of extraction of rare earth elements by a factor of 3-4. The effect of the influence depends on the nature of the REE, the extragent and the diluent. For a static system, the effect is higher than for a flow system. Moving fluid flows contribute to the interfacial formation entrainment in the organic phase, which leads to an increase in the renewal of the interface and a smaller value of the intensification effect.

Over time, the dependence of the intensification effect on time passes through a minimum. The appearance of an extreme point is due to the accumulation of REE salts in the interfacial layer. The effect of initial concentrations of REE and extragent on the value of the intensification effect achieved is studied.

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## INFLUENCE OF THE NATURE OF FLOCCULANTS AND SURFACTANTS ON THE EFFICIENCY OF ELECTROFLOTATION EXTRACTION OF IRON (III) HYDROXIDE FROM A TECHNOLOGICAL SOLUTION OF CALCIUM CHLORIDE

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The research was conducted on the effect of flocculants and surfactants on natural resources on the efficiency of electroflotation extraction of iron (III) hydroxide from calcium chloride solution. The addition of flocculants and SAS in the technological solution of calcium chloride increases the efficiency of precipitation of the dispersed phase<sup>1</sup>. It has been established, that the most effective electroflotation process takes place in the presence of amphoteric surfactants (БераПАВ 12.14.30) and anionic flocculant (Praestol 2530), fig. 1.

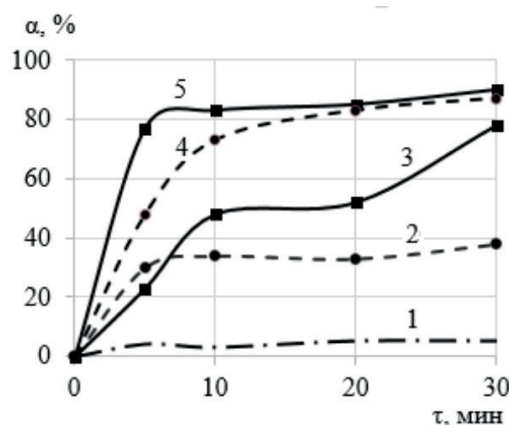


Figure 1. Dependence of the degree of extraction of iron (III) hydroxide on the duration of electroflotation and the nature of the additives (5 mg/l): 1 – without additives, 2 – nonionic SAS (ПЭО-1500), 3 – nonionic flocculant (Praestol 2500), 4 – amphoteric SAS (БераПАВ 12.14.30), 5 – anionic flocculant (Praestol 2530)

The use of filtration after the electroflotation process allows to increase the degree of extraction of iron (III) hydroxides up to 98% or more.

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## SYNTHESIS OF AMMONIUM NITRATE IN PLASMA

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Currently, ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is prepared by neutralizing nitric acid ( $\text{HNO}_3$ ) with ammonia ( $\text{NH}_3$ ). At the same time, modern methods for producing ammonia provide for the binding of air nitrogen to hydrogen contained in natural gas. five main stages are required to produce ammonium nitrate, three of which are complex high-temperature catalytic processes under high pressure. In addition, these methods of producing ammonia and nitric acid have serious environmental problems. Capital costs for the production of initial components account for more than 80% of the total capital costs for the production of ammonium nitrate itself, and the reduced costs account for up to 90% of the total costs<sup>1</sup>.

Experimental verification of the principal possibility of implementing the method was carried out at the pilot plant GIAP, in Vidnoye and was positive. A table steam generator was manufactured to produce water vapor. A mixture of air with water vapor in the above-mentioned ratio was fed into the tube of the working plasma torch through the mixer. After cooling the gas flow coming out of the plasma torch, a solid white plaque remained on the walls of the refrigerator, chemical analysis of which showed the presence of ammonium ( $\text{NH}_4^+$ ) and nitrate groups, and, consequently, the presence of ammonium nitrate. Thus, the principal possibility of direct synthesis of ammonium nitrate in plasma has been proved. Thus, it is advisable to work out the possibility of continuous production of ammonium nitrate from air and water vapor in plasma, as this opens up the possibility of organizing a scheme for obtaining nitrate not only at nitrogen plants, but also at other sources of water vapor and electricity, i.e., for example, at nuclear power plants.

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## METHOD OF EXTRACTING LANTHANIDES AND ACTINIDES IN THE URANIUM AND PLUTONIUM REFINING PROCESS

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One of the options for extracting lanthanides and actinides remaining in the electrolyte after electrochemical refining of uranium and plutonium can be an electrochemical method of preparing layers of lanthanide and actinide intermetallic compounds with nickel.

Alloys or intermetallic compounds formed as a result of the deposited metal and cathode material interaction can contain up to 85% by mass of an actinide and possess acceptable chemical resistance.

The method of lanthanide and actinide extraction does not entail processes other than the actual electrolysis used in uranium and plutonium refining, and thus, does not affect the electrolyte properties.

The extraction process under discussion can be performed in several successive stages. The operation sequence follows:

1. Extraction of uranium in the form of metal powder or dioxide, depending on its state in the melt.
2. Additional extraction of plutonium in the form of its intermetallic compound with nickel.
3. Extraction of americium in the form of its intermetallic compound with nickel.
4. Extraction of lanthanides and curium in the form of their intermetallic compounds with nickel.

The stages listed above can be combined into one process; in this case, its duration time will be about an hour.

The mechanism of the process and the composition of the resulting phases in their sequence were described in <sup>1</sup>. It is obvious that the possibility of practical application of the proposed electrolytic method directly depends on the scale of the technological output of the main process, i.e. electrodeposition in conjunction with alloy formation, against the background of possible side processes. The study of the role and degree of influence of the latter was reported in <sup>2</sup>. The optimal conditions for the electroplating process were also determined, ensuring the maximum product yield in the electrolyte.

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## STUDYING OF THE SORPTION PROPERTIES OF SILICA-GEL IN THE CONDITIONS OF CLEANING COMPRESSIBLE GAS FROM LIQUIDS

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To prevent contamination and erosion of equipment and pipelines at compressor stations, installations are used to clean compressed gas from liquids and mechanical impurities. Dust collectors, filter separators and silica gel adsorbers are used in gas treatment units for transportation (UGT). For the efficiency of the adsorbers during the entire lifetime, they must have constant high sorption properties. It is known that in UGPT oil may be carried away through the seals of blowers of a gas pumping unit operating on the oil-gas principle; therefore, adsorbents contain traces of fine oil that may affect the sorption properties of silica gel.

The presence of turbine oil on the adsorbent - silica gel used on the UGPT, installed chromatographically. Using thin-layer and high-performance chromatography methods, the components of the base oil and functional anti-corrosion and demulsifying additives have been identified. Our studies have shown that the applicable conditions for the regeneration of silica gel at high temperature is not enough for its complete purification from all components of the turbine oil.

In order to optimize the conditions for cleaning sorbents, kinetic studies of the sorption properties of silica gel were carried out in the presence of turbine oil components. The kinetics of water vapor sorption on pure silica gel samples with turbine oil and regenerated in an inert atmosphere for four hours was investigated. According to the kinetic curves, it was found that the sorption of water vapor on an uncontaminated silica gel adsorbent proceeds 2 times faster than on the regenerated one, which can be a confirmation of the fact of its incomplete regeneration.

*The studies were carried out in the framework of the project No. 4.2612.2017 / PC of the Ministry of Education and Science of the Russian Federation using the scientific equipment of the CEC "Environmental Analytical Center" of the Kuban State University, the unique identifier is RFMEFI59317X0008*

## HYDRODYNAMICS OF REGULAR CELLULAR NOZZLES

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An analysis of the results of research published to date, in particular<sup>1</sup>, shows that the operation of column apparatus with a nozzle in the phase inversion mode ensures the maximum possible intensification of the process. The concept of intensification of the processes of heat and mass transfer in column apparatus proposed by us is based on the use of successive layers of nozzles of various types located in the apparatus, contributing to the implementation of the pulsating mode<sup>2,3</sup>. As one of the possible elements of the nozzle, of practical interest is a cellular nozzle based on an equilateral 6 square, with sides of 6 mm.

Table 1. Geometric characteristics of the nozzle

Name and geometric dimensions of elements, mm	Specific surface, $a, \text{m}^2 / \text{m}^3$	Porosity, $\varepsilon, \text{m}^3 / \text{m}^3$	Equivalent channel diameter, $d_e = 4\varepsilon/a, \text{m}$
6-sided granite 6x10	387	0,96	0,0099

Using a layer of cellular packing allows to significantly increase the energy efficiency of the column apparatus, and in combination with other types of structures contributes to the appearance of pulsation.

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## ENERGY RESOURCE EFFICIENT PRODUCTION OF HIGH-QUALITY BINDING MATERIALS BASED ON PROCESSING OF WASTES OF HEAT AND ELECTRIC POWER PLANTS

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The main direction of development of the production of binders is the complex processing of raw materials, the saving of fuel and energy resources, the disposal of waste from other industries. Currently, the use of waste in the production of cements is carried out in the following areas:

- as a component of the raw mix, which saves natural raw materials, reduces the moisture of the raw mix, improves the chemical and mineralogical composition of the clinker;
- as an active mineral additive in cement, which contributes to fuel economy;
- as a mineralizer during clinker burning to intensify the technological process;
- as modifying components in the formation of clinker minerals, stabilizing high-temperature forms of clinker minerals, providing an increase in the hydration activity of the clinker minerals and, accordingly, cement.

Among technogenic materials, ash and slag wastes that are formed during the combustion of solid fuels represent particular interest. The chemical and mineralogical composition of these wastes predetermines the possibility of their use as a raw silica component in obtaining Portland cement clinker, and the presence of unburned fuel residues in the composition makes it possible to consider them as fuel additives that reduce the total heat consumption for clinker formation.

Studies of the properties of the ash and slag raw material mixtures, kinetics of mineral formation during roasting, composition and structure of cement clinker allowed to introduce the technology of cement production at Podolsk cement plant with complete replacement of the natural aluminosilicate component with ash and slag waste from the Lyubertsy heat and electric power plant.

## INCREASING THE ENERGY AND RESOURCE EFFICIENCY OF CHEMICAL TECHNOLOGY PROCESSES FOR FINISHING FIBROUS MATERIALS

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Extraction of technological contaminants is widely used in chemical technology of fibrous materials finishing. The disadvantage of the extraction (washing) process is its resource intensity and energy intensity, a significant duration.<sup>1</sup>

The efficiency of ultrasonic action on the kinetics of the process of washing cotton tissue after mercerization is evaluated. Comparison of mass transfer and mass conductivity coefficients without intensification and with ultrasound shows that the mass transfer coefficient almost doubled. As can be seen from the table 1, the mass conductivity coefficients increase significantly at the beginning of the kinetic curve.

Table 1. The coefficients of mass transfer coefficient when flushing with and without ultrasound

Concentration zones of the kinetic curve		1	2	3	4
$k_t \cdot 10^9, \text{m}^2/\text{s}$	With ultrasound	1,32	1,01	0,79	0,53
$k_t \cdot 10^9, \text{m}^2/\text{s}$	Without ultrasound	0,86	0,54	0,59	0,55

Table 2 shows the data on the reduction of the consumption of surface-active substances (surfactants) and their quantity in the wastewater in the improvement of technology periodic flushing of dense wool fabrics. The developed technological regime is protected by a patent.

Table 2. Indicators of the washing process of dense woolen fabric

Process parameter	Without ultrasound	With ultrasound
Amount of time in the area, $\tau$ , s	1807200	1048176
The concentration of the surfactant in the solution C, g/l	0,9	0,4
The amount of surfactants in wastewater, t/year	4,4	2,46

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## INTERPRETATION OF SYSTEM BEHAVIOR BY METHODS MATHEMATICAL CHEMISTRY

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Modern mathematical chemistry has a large set of tools for conducting studies of molecular systems and physicochemical processes, in particular, the phenomena we studied in petrochemical processes, using the equations of quantum mechanics and mathematical methods. The objects and subject of her research were molecular systems in the ground and excited states, substances in a condensed state, for which their geometric and electronic structure, mechanisms and dynamics of energy and charge transfer during chemical processes were established. Mathematical chemistry forming the basis of the modern theory of the structure of molecular systems and the dynamics of their transformations, the structure and chemical transformations of molecules in the processes of extraction and processing of extracted hydrocarbons, is able to operate with more detailed and accurate information about the structure of a chemical compound, allowing it to predict and explain molecular properties systems and their manifestations, including those that are not at times subject to the classical theory. To obtain the results, a solution to the multielectronic problem was presented, which was possible only with the use of simplified approaches. Mathematical chemistry based on the use of computer methods and discrete mathematics, first of all, methods of molecular mechanics and molecular dynamics, methods of linear algebra, graph theory and also methods of nonlinear dynamics, solves problems of fundamental and applied nature in petrochemistry, which is quite promising today. On the basis of the concepts of mathematical chemistry and the methods of quantum mechanics, it became possible to create models of the structure and mechanisms of transformations of chemical compounds (the study of the mechanism of the effect of additives for fuels and lubricants for various purposes). Being an exact science, this section of chemistry provides a complete mathematical description and assessment of the direction of chemical reactions, calculating the charge distribution in the studied molecules, determining the equilibrium geometry of complex compounds and molecular complexes, calculating the energy of intermolecular interactions, which have a certain effect on the results of refining processes.

## STUDY OF THE DECARBONIZATION PROCESS IN AN EXPERIMENTAL ELECTRODIALIZER

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According to the rules and regulations for the technical operation of power plants and heating networks in the Russian Federation, the regimes of operation of water treatment plants must ensure the operation of power plants and heating networks without any damage and reduction energy of efficiency associated with corrosion of internal surfaces of pipelines, valves, water treatment, heat and power equipment, as well as without the formation of scale and deposits on the heat transfer surfaces, deposits in the flow part and turbines of power stations and thermal networks. In order a special physicochemical preparation is necessary to meet the diverse requirements for the quality of water consumed by thermal power plants. One of the tasks is decarbonization of natural waters before desalting or deionization for thermal power engineering.

In this work, the electrochemical method of decarbonization (electrodialysis) was used.<sup>1</sup> The tests were carried out on an experimental electrodialysis unit with a two-chamber unit cell with bipolar (MB-3, made in the Russian Federation) and cation-exchange membranes (Ralex CMH made in the Czech Republic).

Studies of the decarbonization process of softened carbonate class water (total carbon content – 6.0 mg-eq/l) of the Krasnodar Territory were carried out in a flow hydrodynamic mode, the flow rate varied from 10 to 30 l/h.

As a result, it was established that in the process of electrochemical decarbonization of natural solutions of softened carbonate class water of the Krasnodar tap water, the electrodialysis method provides a degree of decarbonization up to  $\leq 1.0$  mg-eq/l. (depending on current modes), which meets the requirements for water quality for power system.

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## INVESTIGATION OF THE EFFECT OF THE WIND AIR FLOW ON THE MECHANICAL STRENGTH OF THE FIXED ARAL SANDS

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At present, a great deal of attention has been paid to the study of the processes of removal and migration of salts by various natural factors (surface and groundwater, air flows). Protecting sand from wind erosion using water-soluble polymers, as well as mixtures with industrial non-toxic waste, is a solution to an important environmental problem. It should be take into account that the Aral Sea and the dried bottom of the Aral Sea are highly saline.

The work of a number of authors<sup>1</sup> proved that such soil properties as structure, water resistance of aggregates, humus content and humidity are the main factors determining their anti-erosion and anti-deflationary stability<sup>2</sup>.

We have used the method of preliminary liming of soil and soil to increase the effectiveness of surfactant additives and reduce their dosage when combined with calcium hydroxide or ash.

It is known that the liming of soil grounds contributes to a sharp increase in the pH of soil solutions, the replacement of monovalent ions with  $\text{Ca}^{2+}$  ions in the absorbing complex of soil particles and, as a result, the strengthening of the soil microstructure and the replenishment of organic soil.

However, the process of liming by itself does not lead to the improvement of the microstructural state (aggregates > 0.25 mm) in the soil and the production of water resistant macroaggregates. At the same time, the presence of soluble salts in certain limits up to 20-30% even contribute to the improvement of the properties of the soil strengthened with the help of lime.

As for the other components of complex additives, it follows from what has been said that they must be substances capable of forming with the salts any compositions (not necessarily chemical compounds) that must be localized in the structure formed in the «soil-salt- $\text{Ca}(\text{OH})_2$ -water addition».

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THERMAL DESTRUCTION OF ORIGINAL AND SUBSTITUTED  
POLYCHLORINATED BIPHENYLS

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The interaction of technical mixtures of polychlorinated biphenyls Sovol (1) and Trichlorobiphenyl (3) with sodium methoxide in dimethyl sulfoxide and methanol medium were synthesized mixtures of methoxy-, hydroxy-, and methoxyhydroxy derivatives (2) and (4), respectively. The thermal stability of the initial mixtures (1), (3) and the synthesized samples (2), (4) was investigated by the method of thermogravimetric analysis.

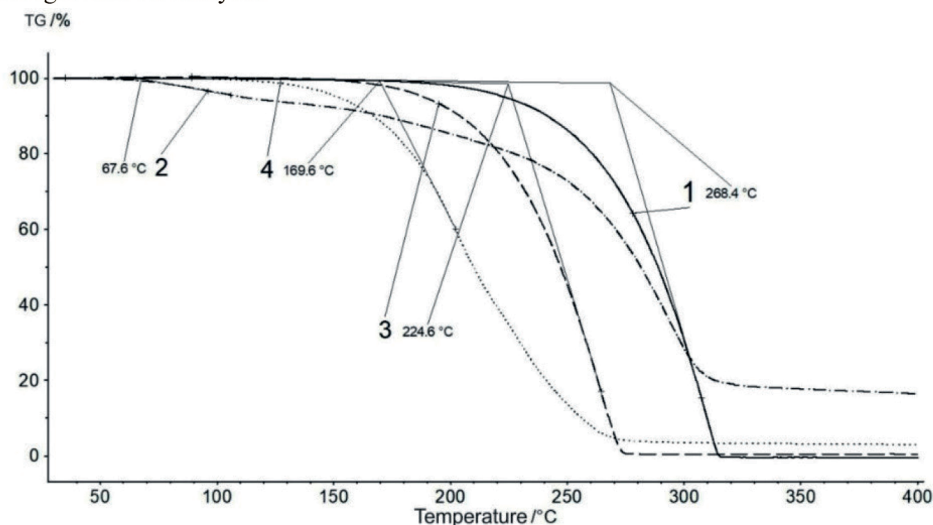


Figure 1. Temperature dependences of the mass change (TG) of the Sovol mixtures (1), Trichlorobiphenyl (3) and the synthesized samples (2), (4).

Mixtures of derivatives (2) and (4) are less thermostable compounds compared to the initial products (1) and (3), respectively, and undergo, after the evaporation stage, decomposition processes to the simplest volatile substances ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ).

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## CLEANING OF NATURAL WATER USING THE HYDRODYNAMIC METHOD

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The main consumers of installations for the purification of natural waters from the content of dissolved iron, manganese and partially hardness in it are residents who do not have a centralized water supply. In such cases, the main source of water supply is a well or a well, from where water is supplied to the consumer by a pump, therefore, the proposed method of water treatment is most likely to be of interest to individuals.

The relevance of the proposed method of purification of natural waters is that the most necessary for the private consumer of the stage of water treatment of natural waters can be made with just one special device, conventionally called hydrodynamic oscillator - GDGK, and most importantly without using any additional reagents.

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**SPECIFICS OF THE PROCESSES OF REMOVING CALCIUM SULPHATE FROM SOLID GALITE WASTE OF POTASSIUM PREPARING FACTORY**

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The physicochemical properties of solid halite wastes are largely determined by the properties and composition of the original ore, as well as the characteristics of the ore preparation and the enrichment method used<sup>1</sup>. The solid waste from the processing of sylvinitic ores is characterized by the following chemical composition: 94-96% NaCl; 1.0-3.5 KCl; 1.5-3% CaSO<sub>4</sub>; 1-1.5% insoluble residue and up to 0.15% MgCl<sub>2</sub>. The high content of calcium sulfate impurities complicates the further processing of halite wastes.

According to the results of the research it was established that there is a difference in the dislocation of calcium sulfate impurity in the waste of halurgic and flotation enrichment. In flotation wastes, calcium sulfate is mainly located on the surface of salt aggregates and is easily separated from it. In the process of halurgical enrichment, halite wastes recrystallize; therefore, a substantial part of the impurity is introduced into the surface layer of large crystals.

To remove impurity inclusions that are loosely fixed on the surface of large crystals, traditional methods of mechanical cleaning, such as hydro-mechanical treatment, are sufficient. To remove impurities embedded in the surface layer of crystals and remove impurities distributed in microcracks, as well as partial opening of aggregates and removal of impurities dislocated in the intercrystalline space, effectively apply the methods of directional acoustic effects.

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## DISPOSAL OF SOLID WASTES OF CHEMICAL INDUSTRIES - MINIMIZATION OF ENVIRONMENTAL RISKS

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Processing and use of solid waste products, consumption and saving on this basis of raw materials and material and energy resources are among the most important problems. In the chemical industry, as in a number of other industries, a large amount of solid waste is produced, which reduces the land fund and poisons the soil.

Solid waste in the production of phosphoric acid extraction is phosphogypsum, which is sent to the dumps<sup>1</sup>. The elimination of dumping, necessitates the use of full processing, which should be considered as the final stage of the production of phosphoric acid. By implementing the task, any technology for the integrated processing of phosphogypsum can be proposed, which allows to obtain: oxides and salts of rare-earth elements; sodium sulfate; calcium carbonate; carbonate strontium. Thus, phosphogypsum is a valuable material. The most promising areas for the disposal of phosphogypsum is its use in the production of gypsum binders.

One of the large-scale by-products in the production of nitroammofoski by the nitric-acid processing of apatite concentrate is conversion calcium carbonate, a significant part of which is not used and is also sent to dumps. Therefore, the problem of utilization of these wastes becomes very topical<sup>2</sup>. The solution to this problem is possible in obtaining new types of fertilizers by mixing them with calcium carbonate, while varying the method of its introduction into the melt of nitroammophoses of various brands, as well as the moisture content of the introduced component. Calcium carbonate purified from impurities allows its use in construction, paper, food and glass industries.

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## TECHNOLOGIES OF BUILDING COMPOSITES PRODUCTION FROM THE KMA TECHNOGENIC RAW STUFF

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Kursk Magnetic Anomaly is the largest iron-ore basin in the world.

At the exploitation of iron ore deposits, dozens of millions of cubic meters of rock materials, unconventional for construction industry, which differ from building industry raw materials in their mineral composition, texture and structure, were covered with mining operations areas<sup>1</sup>. To solve these problems the transdisciplinary approaches were used, which allowed developing the technologies of obtaining a wide range of building materials<sup>2,3</sup>.

The research findings were tested at dozens of enterprises in concrete, mortars, dry building mixes and break-stone production.

Thousands of kilometers of highways and millions of square kilometers of residential and industrial buildings and constructions were built, reconstructed or repaired.

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**INFLUENCE OF CHARGE AND SIZE OF DISPERSE PHASE  
ON INCREASE OF LEAD HYDROXIDE (II) ELECTROFLOTATION  
EXTRACTION FROM AQUEOUS SOLUTIONS  
IN THE PRESENCE OF IRON HYDROXIDE (III) AS COAGULANT**

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One of the ways to improve the quality of water purification from the ions Pb(II) is the use of coagulants, including low-soluble compounds Fe(III). The research of solubility of compounds Pb(II) and Fe(III) in a wide range of pH showed that the lowest solubility of Fe(III) compounds is observed in the interval  $\text{pH} = 6 - 9$ , compounds Pb(II) –  $7 - 11^1$ . Thus, the optimum pH value at which maximum removal of ions of both metals is possible by electroflotation method from aqueous solutions is  $8-9$ .

It was established that the use of Fe(III) as a coagulant in the selected pH range conduce to an increase in the degree of Pb(II) extraction by electroflotation with subsequent filtration from 90 to 97% and a decrease in its residual concentration in the filtrate from 4,9 mg/l to 0,81 mg/l. At the same time, the degree of extraction of Fe(III) exceeds 99%, the residual concentration is less than 0,3 mg/l.

High efficiency of water purification from Pb(II), is induced by sorption of its ions and hydroxides on the surface of Fe(III) hydroxides. As a result, the average hydrodynamic diameter of the disperse phase of the flotation complex is in the range of 24-32 microns, which exceeds the size of the Pb(II) hydroxide (9 – 13 microns) and match to the size of Fe(III) hydroxides in the selected pH interval. The absolute value of the  $\zeta$ -potential of the Fe(III)-Pb(II) flotation complex is -6 mV, which is lower than the values of electrokinetic potentials of Fe(III) and Pb(II) (-15 and -7 mV) hydroxides (respectively).

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## ENVIRONMENTALLY FRIENDLY MOLYBDATE-PHOSPHATE CONVERSION COATINGS ON THE ELECTROPLATED ZINC

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Protective decorative conversion coatings on the electroplated zinc are usually produced from solutions containing chromium compounds, which are environmentally very hazardous. An alternative to chromium compounds may be safer compounds of molybdenum, which is the closest analogue of chromium in the periodic system of elements. However, the molybdate conversion coatings have weaker protective properties in comparison with chromate ones<sup>1</sup>. To increase protective properties the phosphate ions are proposed<sup>2,3</sup> to introduce in the solution together with molybdate ions.

In this paper, the protective properties of conversion coatings produced from solutions  $(0,05-0,15) \text{ M Na}_2\text{MoO}_4 + 0,15 \text{ M H}_3\text{PO}_4$  are investigated using methods of drop and polarization curves. The obtained conversion coatings have good decorative properties: the color of coatings varies from light yellow to golden depending on the processing time and the content of molybdenum in the solution.

The results of the study of protective properties of coatings depending on the content of molybdenum in the solution showed that the best protective properties have coatings obtained from solutions with concentrations  $\text{Na}_2\text{MoO}_4$  0.05 and 0.1 mol/L. The molar ratio Mo/P in that solutions equal to 0.33 and 0.66. With a higher content  $\text{Na}_2\text{MoO}_4$  in solution the protective properties of conversion coatings were even worse than in the case of the total absence of sodium molybdate in the solution.

Thus, it is possible to produce good quality protective-decorative coverings on the electroplated zinc from solutions based on the environmentally friendly phosphates and molybdates.

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## LOW TEMPERATURE PHOSPHATING OF LOW-CARBON STEEL

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Phosphating is utilized most commonly before application of paint coatings in order to improve adhesion and corrosion resistance in car manufacturing<sup>1</sup>. One of the drawbacks of the existing phosphating technologies is that they employ relatively high temperatures required to obtain high-quality coatings within a technologically acceptable time. The majority of phosphating processes require temperatures of 50-90°C<sup>2</sup>. Studies in this field showed that addition of cerium (IV) sulfate to electrolytes allowed the phosphating temperature to be lowered to room temperature. The electrolyte had the following composition: ZnO – 10 g/l, H<sub>3</sub>PO<sub>4</sub>–19 g/l, HNO<sub>3</sub> – 8 g/l, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O – 0.3 g/l, FeCl<sub>3</sub>·6H<sub>2</sub>O– 0.3 g/l. We have found that if nickel nitrate contained in the base electrolyte is replaced with cerium (IV) sulfate, the phosphating process can be performed at 30 °C without deterioration of adhesion to the substrate and protective capability, whereas if the temperature is decreased below 60 °C and the original formulation is used, then the quality of the phosphate layer gets worse and it is formed more slowly. The role of cerium (IV) sulfate is to sufficient increase in the rate of phosphate layer formation at temperatures of 30 – 35 °C. Finer-crystalline, low-porous coatings are formed.

It has been determined that effect of cerium (IV) sulfate present in solution on the phase composition of phosphate layers is similar to the effect of Ni<sup>2+</sup> ions. X-ray diffraction analysis has shown that, like Ni<sup>2+</sup> ions, cerium (IV) sulfate considerably alter the phase composition of coatings by decreasing the percentage of hopeite in the coating and increasing the fraction of phosphophyllite. It is known that increasing the content of the phosphophyllite phase enhances the stability of phosphate coatings in alkaline solutions<sup>3</sup>, which allows such coatings to be utilized before application of cathophoretic primers.

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## USING GAS ANALYZERS IN DETERMINATION OF DEPARTING GASES COMPOSITION OF GAS COPPERS AND THE GAS PHASE AT METHANOL OXIDATION IN PRESENCE OF METAL OXIDE CATALYST

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Gas analyzers are more and more used in industry for technological processes control now. Depending on a design of the device the determination of a gas phase can be realized in continuous or periodic mode. The CO content was determined in the continuous mode by means of a gas analyzer "Test-200" both at input and output flow of the methanol oxidation reactors of "PAO Uralchimplast". Also for CO concentration determination at this enterprise the gas analyzer "Oksi 5M" was used. Gas analyzers were applied also to measure the concentration of O<sub>2</sub> and CO in departing gases of "PAO UralRTI". In technological processes of "PAO Uralhimplast" real concentration of CO as a rule exceeds the detection ranges of a gas analyzer of "Oksi 5M" (up to 0.6%), as well as of "Test-200" (up to 0.8 %). To fit the optimum conditions for the catalyst the content of CO in a gas phase is necessary to be within the specified range. Besides, to calculate the yield of formaldehyde based on a technological gas composition, the CO content in a gas phase also should be measured. The values of the CO concentrations collected both with gas analyzers "Test 200" and "Oksi 5M" are somewhat underestimated, because the gas stream from the reactor was diluted with the air from the pumps of gas analyzers to avoid a damage of CO sensor at high load on catalyst. The results of CO analysis were recalculated taking into account the dilution degree. The concentration of O<sub>2</sub> in a gas stream not diluted by air was performed by the gas analyzer "Test 200", and in addition with in-line paramagnetic sensors of O<sub>2</sub> as well as with chromatograph "Crystal 5000.2" using thermal conductivity detector. Thus, offered express control of concentration CO for real technological gas streams allows us to expand a scope of use of using gas analyzer "Oksi 5M" which is designed for measurement of CO and O<sub>2</sub> contents in departing gases of the coppers.

## GENETIC DAMAGE OF WHITE PHOSPHORUS

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Our previous studies have demonstrated the absence of white phosphorus toxicity for fungi<sup>1-3</sup>.

However, the toxic properties of the substances are of different nature. It is of great interest to study the genotoxicity - a possible source of mutations. We evaluated the genotoxicity of white phosphorus is evaluated using the Ames test, which demonstrated the absence of toxicity. However, with all the advantages of this method, the use of the Ames test only is not enough to reliably assess the genotoxicity.

For this purpose a whole battery of tests is used, and the SOS-lux test for DNA damaging activity is among them. In the present work SOS-lux test has demonstrated genotoxicity of white phosphorus. This result is obtained for the first time – all the available literature sources reported no genotoxic properties of white phosphorus. Since the genetic apparatus of prokaryotes is differently arranged than in eukaryotes (including humans), the results of the studies on *Salmonella* is not completely transferable to humans.

In addition to the gene mutations studied by the Ames test and the SOS-lux test, which have a common nature in all living organisms, there are genomic rearrangements that should be studied in eukaryotes. For this purpose, an *Allium* test is used on onion rootlets (*Allium cepa* L.). In this work, we present the first report on the negative effect of white phosphorus on the cell cycle of eukaryotes by the *Allium* test method. It turned out that white phosphorus, even at very low concentrations of 0.01%, exponentially increases the number of chromosomal aberrations.

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**STYRENE–BUTADIENE RUBBER PYROLYSIS  
IN A CARBON DIOXIDE ATMOSPHERE**

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The pyrolysis of styrene–butadiene rubber was investigated by a dynamic thermo gravimetric apparatus, where it is possible to treat samples in form of cylinders with a weight of about 27 g.

A preliminary mechanistic understanding has been developed to explain the formation and relationship of light hydrocarbons, substituted aromatics during the decomposition of styrene–butadiene rubber in a carbon dioxide atmosphere.

Various heating rates between 0.1 and 1 °C/s were investigated. A distributed parameter model able to describe heating inside the sample and its kinetics of decomposition was built. The pyrolysis enthalpy seems to be a very important parameter; its best fitting value was identified equal to 180 kJ/kg.

Light gases produced by pyrolysis were analyzed and the influence of heating rate and sample size on the pyrolysis products (gases, tar, and char) was studied. This investigation showed that for big samples (some tenths of grams) the influence of heating rate on the pyrolysis products is often less important than for few mg samples, as often reported in the literature. Different pyrolysis conditions lead to strong variation of light gas yield, but the molar fraction of most of the light gases is almost constant.



## EFFECT OF A HYDROTHERMAL TREATMENT OF AN AMORPHOUS ALUMINUM HYDROXIDE GEL ON THE PROPERTIES OF THE ALUMINA CATALYST PRECURSOR BASED ON IT

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Alumina catalysts are widely used in such acid processes as the dehydration of 1-phenylethanol and the skeletal isomerization of olefins. During the synthesis of their precursor by the method of precipitation by the ammonia-nitrate method amorphous compounds such as basic salts and amorphous aluminum hydroxide are formed, which negatively effect on the catalyst according to the literature. However, it is possible to modify these compounds in hydrothermal conditions to minimize that effect.

For the first time an aluminum hydroxide gel was obtained by the precipitation method from an aluminum nitrate solution by ammonia at pH = 6.00 and room temperature. The gel is a mixture of basic salt (66.0 wt%), amorphous aluminum hydroxide (20.2 wt%) and pseudoboehmite (13.8 wt%), which has no pores (specific surface area <1 m<sup>2</sup>/g) and the impurities of 0.41 and 4.57 wt% of carbon and nitrogen respectively. After its calcination at 550 °C / 3 h number of acid sites on the surface of the obtained alumina reaches 200.2 μmol NH<sub>3</sub>/g. After hydrothermal treatment (HTT) at T=110-150 °C during 3 h of the aluminum hydroxide gel in an aqueous suspension pseudoboehmite and boehmite are formed. The basic aluminum salt in the gel is hydrolyzed to amorphous aluminum hydroxide under hydrothermal conditions, replacing -NO<sub>3</sub> to -OH groups. Then, the amorphous hydroxide forms pseudoboehmite up to 72 wt% at temperatures of hydrothermal treatment of 110-130 °C/ 0-3 h, 140 °C/ 0-2 h and at 150 °C / 0-2.5 h. In other cases the pseudoboehmite forms its more crystallized form - boehmite in an amount up to 97 wt%, i.e. a complete phase transformation of amorphous compounds into boehmite is observed. However, the porous system of the HTT products is inherited from their starting compound, that is, it is also absent. Acidity is increased almost 2 times.

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## CLEANING OF WASTE WATER POLLUTED BY OIL AND PETROLEUM PRODUCTS WITH ENERGY WALKING WATER SUPPLY

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According to the BP Statistical Review of World Energy, Kazakhstan ranks 9th in the world in proven oil reserves<sup>1</sup>. Sorbents based on plant wastes with hydrophobic properties were studied (Table 1)

Table 1. The main parameters of sorbents on the basis of waste plant materials

Sorbents	Water absorption, g water / g. sorbent	Oil absorption, g. of oil / g. of a sorbent	Cleaning degree, %
Sunflower cake	3,3	4,4	72
Corn Cobs	3,1	7,2	89
Activated carbon	1,4	2,1	60
Birch coal	2,1	2,4	46
Cereal waste	5,3	10,8	78
Walnut shells	1,3	2,6	70

Amangeldy oil refinery North-West Conys was used as a model system (Table 2).

Table 2. Physical and chemical indicators of oil «North Western Conys»

Specifications	Indicators
Density at 20 ° C, kg / m <sup>3</sup>	845
Pour point, °C	-3
Saturated vapor pressure, kPa (mm Hg)	45
Bulk Sulfur Content, % / / mechanical impurities, %	0,37 / 3,04 / 0,07

New technical solutions have been proposed with the aim of improving sorption methods using natural sorbents, which are currently the most effective for in-depth treatment of wastewater from oil and oil products.

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## **ADSORPTION CLEANING OF REVERSE OSMOSIS CONCENTRATE PRODUCED ON INDUSTRIAL ENTERPRISES BY GRANULATED CARBONATE SLUDGE**

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A number of industrial enterprises face the problem of salt effluent cleaning after chemical desalting process and reverse osmosis. The existing purification technologies are very cumbersome, with high capital, energy and operating costs.

The paper proposes the adsorption technology for the purification of saline wastewater and the concentrate of reverse osmosis plants from sulphates and chlorides with a large-tonnage waste of energy - sludge from water treatment that is formed at the stage of preliminary purification of raw water. Chemical water treatment sludge is a waste that is formed during liming and coagulation at water treatment plants from thermal power plants (TPP). Experimental studies were carried out with carbonate sludge at Kazan TPP-1 (humidity - 3%). The technological and physicochemical characteristics of the sludge as a sorption material have been studied. Based on it, a granulated sorption material for the purification of reverse osmosis concentrate under dynamic conditions has been developed. Optimal conditions for the manufacture of granules were determined: fine slurry with a particle size of from 0.01 to 0.09 mm is mixed with liquid sodium glass at a mass volume ratio of 2: 1, respectively, then the mixture is brought to a homogeneous mass, pelleting of granules with a diameter of 0.5 to 2.5 mm occurs manually, heat treatment is carried out at a temperature of 400 °C for 3 hours.

The adsorption process of sulfate and chloride anions was studied under dynamic and static conditions. Adsorption isotherms of sulfate and chloride ions were obtained, and the effect of pH on the process was also studied. The high values of the enthalpy of adsorption and the activation energy can be interpreted by the formation of a strong bond between sulfate, chloride ions and the functional groups of the granular sorption material. The output curves of the adsorption of sulfate and chloride ions by the developed material are obtained under dynamic conditions.

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## DEVELOPMENT OF AUTONOMOUS STATIONS AND SYSTEMS FOR CONTROL OF ATMOSPHERIC AIR POLLUTION

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The problem of clean air in a city with increased technogenic stress is a complex problem. To develop effective measures to reduce emissions, careful monitoring of all sources of emissions to the atmosphere in a given territory, taking into account meteorological conditions and landscape features is required. It is obvious that in modern conditions for the implementation of monitoring and analysis of its results, it is most expedient to use an automated system that allows you to instantly receive and analyze data from posts taking measurements. Developed complex «ECOMONITOR». The software part of the ECOMONITOR complex allows collecting, analyzing, storing and displaying environmental information on a map. The system was developed using modern technologies (.NET platform). The system uses two types of Microsoft SQL Server or Oracle DBMS for data storage. Sensors included in the hardware of this system allow measurement of the concentration of various substances with a high degree of accuracy<sup>1</sup>.

The system is equipped with modern hardware and software for performing the whole complex of necessary operations, including primary measurements, collecting, transferring, accumulating and processing measurement data, analyzing the environmental situation, supporting decision-making on environmental management, distribution of control results among users<sup>2</sup>.

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## DEVELOPMENT OF CATALYTIC COATING ON INNER SURFACE OF MICROCAPILLARY REACTOR FOR SELECTIVE HYDROGENATION OF ACETYLENIC ALCOHOL.

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Microreactor technology for catalytic reactions in fine organic synthesis directed to solve the problems of environmental safety and control of selectivity in sequential reactions. Recently, the use of mixed metal oxide systems has been highlighted to improve the stability or/and texture of catalytic coatings.<sup>1,2</sup> With the aim to create catalytic coatings on inner surface of microcapillary reactor for selective hydrogenation of 2-methyl-3-buten-2-ol, modification of titania nanomaterials  $\text{Ti}_x\text{M}_{1-x}\text{O}_2$  ( $\text{M} = \text{Ce}, \text{Zr}$ ) with  $\text{Ce}^{3+}$  and  $\text{Zr}^{4+}$  were performed by means of self-assembly.

The productivity of the microcapillary reactor after 88 hours of continuous stream increases in the series  $\text{PdZn}/\text{TiO}_2 < \text{PdZn}/\text{Ti}_{0.95}\text{Ce}_{0.05}\text{O}_2 < \text{PdZn}/\text{Ti}_{0.8}\text{Zr}_{0.2}\text{O}_2$ .  $\text{PdZn}/\text{TiO}_2$  was the most selective to 2-methyl-3-buten-2-ol (more than 96%), stable during long-term test up to 88 hours and reduction treatment. The effect of the support on the stability and reactivity of the PdZn nanoparticles can be explained by charge transfer to or from the nanoparticles.

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## EFFECT OF THE COMPOSITION OF THE ENVIRONMENT AND PARAMETERS OF ELECTRO-FLOTATION TREATMENT ON THE EFFICIENCY OF THE TREATMENT OF DISPERSED CHROME (III) PHASE FROM AQUEOUS SOLUTIONS

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Improving the efficiency of electroflotation treatment of wastewater containing poorly soluble chromium (III) compounds from solutions of complex composition is an important scientific task.

On the basis of experimental studies, the main directions for increasing the efficiency of the process of electroflotation extraction of particles of poorly soluble chromium (III) compounds from aqueous solutions were established.

It was shown that the most complete extraction of particles of poorly soluble chromium (III) compounds is possible in the range of pH 7 - 8. The degree of extraction reaches 81–83%. In this pH range, an isoelectric point is observed ( $z = 0$ ) for poorly soluble chromium compounds, the size of the dispersed phase passes through an extremum ( $d_{av} = 13.5 \mu\text{m}$ ), the dispersed phase is characterized by minimal solubility.

It has been established that the use of anionic flocculants (M-10 and LT-30), an increase in the ambient temperature to  $45^\circ\text{C}$  and the effect of a constant magnetic field increase the average particle size of the dispersed phase of poorly soluble chromium (III) compounds from  $13.5$  to  $90 \mu\text{m}$ . This leads to an increase in the degree of extraction to 99% and an increase in the productivity of the electroflotation process by 2–3 times, and the residual concentration decreases to  $0.04\text{--}0.06 \text{ mg/l}$ , which is lower than the permissible MAC values for household needs ( $0, 5 \text{ mg/l}$ ) and fishing reservoirs ( $0.07 \text{ mg/l}$ )<sup>1</sup>.

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## APPROACH TO SYSTEM ANALYSIS OF MULTI-STAGE PRODUCTION OF SHEET GLASS

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In article an approach to the system analysis of multi-stage production of sheet glass is proposed, which includes the steps of:

Let a production system be set in which there are problem situations  $O=\{o_1, o_2\}$ , that limit the effectiveness of its functioning, understood as <sup>1</sup>. In this system we will set a variety of reasons for problem situations  $R=\{r_1, r_2\}$ . The relationship  $\alpha \subset O \times R$  establishes a link between problem situations and their causes. Each problem situation,  $o_i \in O$  corresponds to many causes of  $R_{o_i} \subset R$

It is necessary to define the objectives of the management of the  $G=\{g_1, g_2\}$  and the set of control criteria of the  $C=\{c_1, c_2\}$  for the management of the production system. Objectives are determined based on the decomposition of management periods. It is established a relationship  $\beta \subset G \times C \times R(o_i)$  between control objectives, criteria, and control algorithm. Each control goal,  $g_k \in G$  understood as in <sup>2</sup>, corresponds to a set of control criteria  $C(g_k) \subset C$ .

On the basis of goals  $g_k \in G$ , control tasks  $S=\{s_1, s_2\}$  and control algorithms  $A=\{a_1, a_2\}$  are defined, which are determined on the basis of the decomposition of the functions of the control object. Let's set the relationship  $\gamma \subset S \times A \times C(g_i)$  between management tasks, control algorithms and causes of a problem situation. Each control problem  $s_j \in S$ , understood as in <sup>3</sup>, corresponds to a set of control algorithms  $A(s_j) \subset A$ .

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## REDUCTION OF ENERGY CONSUMPTION TO THE CHEMOSORBENT REGENERATION DURING GAS CLEANING

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To purify gases from carbon dioxide in large-scale production of basic chemistry, as a rule, when heated circulating absorption-desorption units are used with the regeneration of a solution of chemisorbent. Aqueous solutions of amines or similar aqueous-organic mixtures are used as the absorbent. The main energy consumption of the gas purifying process is associated with the regeneration stage; therefore, cut energy down at the regeneration stage significantly affects the cost of the process as a whole.

The mixed water-organic absorbent on the basis of the monoethanolamine (MEA) with different water concentrations was studied on a single-flow circulating unit operating in a closed circuit<sup>1</sup>. The regeneration temperature was varied from 90 to 106 °C. The energy consumption for the process was determined by the amount of heating steam condensate. As a result of processing the experimental data, the function of energy consumption from the regeneration temperature while using this mixed water-organic absorbent was obtained, the concentration of chemisorbent – MEA – was 21 %. The experiments were necessarily duplicated and experiments were taken for processing with an imbalance of no more than 10 %.

The minimum energy consumption was achieved at a temperature of about 98 °C, which is 17 degrees less than for a known solution of 20 % MEA + water<sup>2,3</sup>.

Thus, the obtained results allow us to conclude that it is expedient to use a particular solution in industrial installations, which will reduce the energy consumption for the process of absorption and desorption purification of industrial gases from carbon dioxide.

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## APPLICATION OF SCHUNGITE FOR NEUTRALIZATION OF TOXIC 1,1-DIMETHYLHYDRAZINE

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Asymmetric dimethylhydrazine (ADMH), or 1,1-dimethylhydrazine, which is a component of widely used rocket fuel, is a physiologically active toxic compound, even small amounts of which can poison air, water, and soil. The high reactivity of ADMH gives rise to the formation of numerous toxic products of its oxidative transformation. Some of these substances are rather stable and may be retained for a long time and accumulated in places of accidental spillages and areas of the environment, thereby creating potential danger for people, flora, and fauna. Numerous products of ADMH transformation in air have not yet been identified, and the consequences of their physiological action are unknown. Efficient methods for neutralizing objects contaminated with ADMH that would meet the contemporary requirements of environmental safety have not yet been developed. Therefore, the search for new methods of ADMH neutralization in environmental objects using available, cheap, and environmentally safe materials remains to be an urgent problem. Schungite has been proposed to be applied for purification of spillages of technological liquids containing ADMH, because this mineral is most suitable for using in large amounts and in large lands.

Chromatography and mass spectrometry have been employed to study the interaction of mineral schungite with wastewater containing ADMH and products of its oxidation, cyclization, and oligomerization. The products of transformation and resinification of ADMH contained in solutions that were in contact with schungite and the products desorbed from the surfaces of schungite and model sorbents (silica, iron and aluminum oxides, clay) have been identified. It has been found that schungite efficiently sorbs ADMH and products of its transformation. The absence of these toxic compounds on its surface one day after the onset of the sorption contact suggests their rapid catalytic oxidation to low-molecular-mass volatile nontoxic substances. It has revealed the efficiency of schungite as a low-cost and environmentally friendly sorbent. Environmentally safe methods have been proposed for the regeneration of used schungite.

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## FORECASTING THE KINETICS OF CLINKER FORMATION PROCESSES WITH A POSITION OF ELEMENTS IN A PERIODIC SYSTEM D.I. MENDELEEV

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2019 has been declared the year of the Periodic Table of Chemical Elements in Russia. The periodic system of D.I. Mendeleev systematizes not only the elements, but also the most diverse of their properties, which was confirmed when studying the processes of mineral and clinker formation during the production of cement.

Clinker formation is a aggregate of acid-base interactions occurring in oxide-salt melts at various stages of the process. The mechanism and kinetics of these processes largely depends on the composition and properties of the clinker melt.

To identify patterns of influence of elements on the structure and properties of the melt, the effect of various combinations of compounds formed by s-, p- and d-elements was studied. The influence of their acid-base properties on viscosity, surface tension, density, ion mobility, and segregation phenomena in clinker melt, the kinetics of dissolution and crystallization of minerals is determined.

It is shown that, depending on the nature and concentration of the modifiers, oxide or oxide-salt melts are formed in the clinker grain. The appearance of the salt component is due to liquation phenomena, and the tendency of the melt to liquation increases with increasing acidity of the p-element ions ( $\text{SO}_4^{2-} \rightarrow \text{Cl}^- \rightarrow \text{F}^-$ ) and increasing the basicity of s-elements ( $\text{Mg}^{2+} \rightarrow \text{Ca}^{2+} \rightarrow \text{Na}^+ \rightarrow \text{K}^+$ ).

It is found that the surface activity of ions in the clinker melt is determined by the energy of their interaction with the oxygen anion, and as it increases in a number of s-elements, the surface tension increases, and in the presence of p- and d-elements decreases with increasing oxidation state and anion size.

On the basis of the models obtained, scientifically-based recommendations have been developed on the efficient use of industrial waste in the technology of various clinkers. The use of technogenic materials allows to intensify the processes of clinker formation and hydration of cements, which helps to reduce fuel and energy costs, and solves an important environmental problem.

## **SOME ASPECTS OF THE DISPOSAL AND USE OF BY-PRODUCT –DUST REFRACTORY PRODUCTION**

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The problem of nature protection is particularly acute in areas of concentration of industrial enterprises that pollute the environment with production waste - emissions of large amounts of dust and gases into the atmosphere. The involvement of these wastes in the technological process solves environmental, technological and economic problems.

Refractory materials are made on the basis of mineral raw materials. The pollutants in the manufacture of refractories include dust formed in a number of technological operations.

This paper shows some results of studies of the properties of dust – waste refractory production and the possibility of involving it in commercial products, which reduces the negative impact of anthropogenic factors on nature and improves the environmental situation. For a comprehensive study of the chemical composition of dust x-ray spectral, x-ray, methods of analysis were used.

After analyzing the properties of the captured dust, we can say that the powder contains about 80% of magnesium oxide in an easily soluble form, with a small amount of impurities, which allows it to be used as a fertilizer, both basic and in combination with other elements in complex fertilizers. As a result, the caught dust from the waste of production turns into a commodity product, making the production waste-free, which is extremely important.

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## SOLUBILITY OF TRANSITION METALS OXIDES IN CRYOLITE MELTS

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The behavior of transition metal oxides in the molten mixtures of sodium and potassium cryolites is necessary to know when studying the issues of corrosion of the metallic, cermet and ceramic materials that can be used as non-consumable (low-consumable) anodes during aluminum production by electrolysis of cryolite-alumina electrolytes, when developing refining salt flux compositions for obtaining a high-purity aluminum, as well as upon synthesizing complex aluminum alloys.

The solubility of the transition metal oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$  and  $\text{MnO}$  in the low-melting cryolite melts  $\text{KF-AlF}_3$  and  $\text{KF-NaF}(10 \text{ wt}\%)\text{-AlF}_3$  was studied by isothermal saturation. The exposure temperature was 30, 60, 90 °C higher than the liquidus temperature. The melt samples were analyzed for the content of the Fe, Ni or Mn elements.

It was found that the solubility of transition metal oxides in the  $\text{KF-AlF}_3$  melts with  $\text{CR} = 1.3\text{-}1.5$  ( $\text{CR} = (x\text{NaF} + x\text{KF}) / x\text{AlF}_3$ , mol/mol) decreases in the series  $\text{MnO-Fe}_2\text{O}_3\text{-NiO}$  at temperatures of 30-90 degrees above the corresponding liquidus temperature.

The  $\text{MnO}$  solubility in potassium cryolite increases with an increase in CR and temperature and reaches 0.65 wt% at 850 °C. In the presence of NaF in the mixture of  $\text{KF-NaF-AlF}_3$ , the  $\text{MnO}$  solubility decreases. The  $\text{Fe}_2\text{O}_3$  solubility in the  $\text{KF-AlF}_3$  melts with  $\text{CR}=1.3$  in the temperature range of 700-760 °C has the same order as in the  $\text{KF-NaF}(10 \text{ wt}\%)\text{-AlF}_3$  melt with  $\text{CR}=1.4\text{-}1.5$  at 830-880 °C. The  $\text{NiO}$  solubility in the low-melting cryolite melts is an order of magnitude lower than the solubility of the  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$ , and the dissolved  $\text{NiO}$  is in the melt in the form of potassium ferronickelate.

The  $\text{KF-NaF}(10 \text{ wt}\%)\text{-AlF}_3$  electrolyte with  $\text{CR}=1.3$  has the lowest  $\text{Fe}_2\text{O}_3$  solubility among all the melts studied, and is recommended for the low-temperature aluminum electrolysis at about 800 °C in an electrolytic cell with inert anodes containing Fe.

## CONVERSION CEMENT SUSPENSION AFTER RECYCLING CONCRETE MIXTURES

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Presently the green technologies develop intensively. They provide for the development, production and introduction of promising economically beneficial technologies, materials and products. Green technologies are based on the principles of saving energy and natural resources. They minimize the negative impact on the environment and human health throughout the entire life cycle of the created material or product. Currently, green technologies attach great importance to the creation of environmentally friendly building materials. Their progress contributes to the development of scientific bases of production and the introduction of energy and resource saving technologies.

Green technologies of building materials provide for a minimum degree of impact on the environment and humans, both during maintenance and in the manufacture of products and the disposal of the generated waste. For some wastes it is difficult to choose a method of processing and scope. Such waste must be disposed of. Waste disposal leads to environmental degradation. One of these problems is the disposal of concrete mixes waste that remain on the working bodies and the walls of the tanks of concrete mixers.

Existing recycling technologies involve the removal of fine and coarse aggregate from concrete mixes waste. This is accomplished by flushing the waste from the working bodies and tanks of concrete mixers into a screening and washing system for separating coarse and fine aggregates. The remaining cement slurry does not find proper use and is often drained to the ground. Such an impact leads to cementation and a change in the pH of the soil, destruction of the fertile layer, water pollution, etc. occur.

A green technology of the full recycling of concrete mixes is proposed when the cement slurry is returned to the concrete mixing unit. Reuse the concrete mix cement suspension should be without loss of product quality. The return of the cement slurry is proposed by the creation of hydraulically active additive based on it. Cement suspension is activated and stabilized by the introduction of surface-active additives. The use of such stabilized suspensions allows to get the finished product without loss at quality characteristics and to apply green technology in the concrete industry.

## IMPROVEMENT OF TECHNOLOGY FOR STYRENE PRODUCTION BY DEHYDRATATION OF METHYL-PHENYL-CARBINOL

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Styrene is one of the monomers in the plastics production and copolymer rubbers. Currently, in Russia, styrene is produced in industry, mainly in two ways. The first way is ethyl benzene dehydrogenation, the other is the only one in our country that is based on the dehydration of methyl-phenyl-carbinol (MPHC).

The MPHC dehydration process is carried out in the vapor phase in the presence of a diluent — steam with a  $\gamma\text{-Al}_2\text{O}_3$  catalyst. The process execution in the presence of a significant amount of water vapor leads to the ample quantity of saturated hydrocarbon wastewater formation.

One of the ways to solve the current situation is necessary to consider the search for new catalytic systems that would reduce or completely eliminate the necessity of using the steam dilution for the MPHC dehydration process, without changing the production technology. This direction of solving the problem was taken in this laboratory study, the results of which are presented in the table.

Table 1 - Catalyst  $\text{Al}_2\text{O}_3$ . Temperature 290 °C. Volume velocity 0.6 h<sup>-1</sup>. Experiment duration - 300 min.

The ratio of MPHC:H <sub>2</sub> O	Conversion, %	Selectivity, % mol
1:0,25	99,6	98,3
1:0,5	99,8	99,8.
1:1	99,75	101,8

It is shown that an increase in the molar ratio of IFC: H<sub>2</sub>O entails a slight decrease in the styrene formation and practically does not affect the MPHC conversion.

Herewith, there is a considerably high styrene formation selectivity (94-102 mol%). This value of selectivity is explained by the fact that at this temperature there pass the hydrogenation acetophenone and the heavy products decomposition by forming more styrene.



## CERIUM-BASED COATINGS ON STAINLESS STEEL

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A known disadvantage of stainless steels is their tendency to local types of corrosion (pitting, intergranular, etc.). In order to increase the corrosion resistance, they are passivated in toxic aggressive solutions containing chromate ions (up to 250 g/l). In recent years, the literature discusses the perceptiveness of using as an alternative to chromate passivating layers of ceramic-oxide-cerium coatings<sup>1-3</sup>.

A solution containing cerium (III) nitrate salt and hydrogen peroxide (37% H<sub>2</sub>O<sub>2</sub>) was chosen as an object of study.

The working parameters of the process were determined the range of permissible values for pH is 2-3, the temperature of the working solution is 50-60°C, the process duration is 10-20 minutes, the drying temperature is 60-100°C.

Studies showed that stainless steel treated with this cerium-containing solution has an average relative pitting rate of 0.91 g/(m<sup>2</sup>·h), which is significantly lower than the value of the same parameter for untreated stainless steel (3.76 g/(m<sup>2</sup>·h)). Using the ellipsometric method, it was found that the thickness of these coatings is 85-90 nm. Thus, it is shown that passivation of stainless steel in a cerium-containing solution can significantly increase its corrosion resistance to pitting corrosion.

It is revealed that protective coating on alloy steel consists of cerium oxides Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, iron oxide Fe<sub>2</sub>O<sub>3</sub> and chromium oxide Cr<sub>2</sub>O<sub>3</sub>.

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## HYDROPHOBIZATION OF ALUMINIUM ALLOY AMg6 SURFACE

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Recently one of the most in-demand methods for protection of metallic surfaces against aggressive ambience is producing continuous films with water-repellent properties and ability to self-healing on their surfaces which provide hydrophobicity and also protect them from abrasion<sup>1</sup>.

The hydrophobization ability of the aluminium alloy AMg6 surface in a solution, containing stearic acid (SA) 0,01 M, dimethyl sulfoxide (DMSO) and water in the ration 7:1, was studied.

It is found that the coating produced in this solution has a wetting angle  $\theta=130^\circ$ . The protective coating ability, defined by an express drop method, as time to corrosion products under the drop of Akimov's reagent is 125 s.

The effect of SA concentration in this solution on the quality of produced coatings is studied. It is found that coatings with maximum wetting angle and protective coating ability of 140 s are formed in the concentration range of SA 2-3 g/l.

The neutral salt spray tests of alluminium alloy AMg6 with water-repellent surface in produced solution were performed. The research showed that the produced coating can keep 82 h to first spots of the base, while untreated aluminium alloy starts corroding in 24 h. It is found that the produced water-repellent coating thickness about 270-300 nm.

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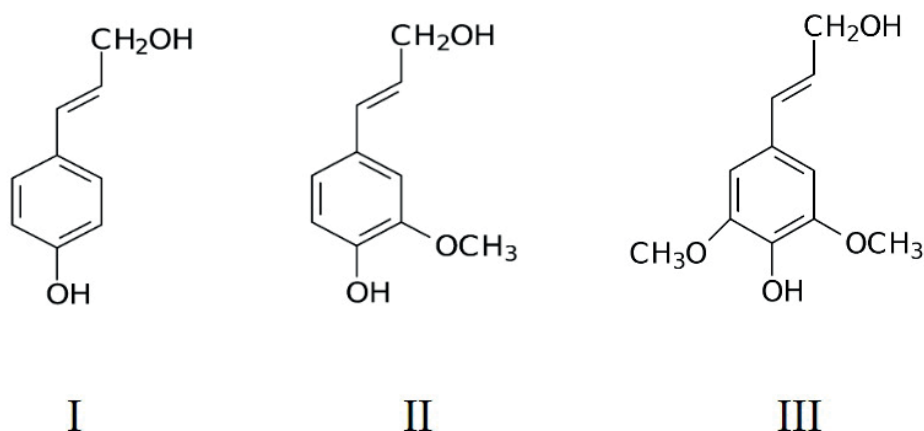
## THE MODIFIED WASTE OF RECEIVING CELLULOSE AS REAGENTS FOR INCREASE IN OIL PRODUCTION

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Cellulose is the integral satellite of lignin – the inlaying wood substance. Delignification of wood in the environment of cooking solution leads to office of cellulose with the subsequent receiving a by-product of the difficult chemical composition which main substance is sulfoderivative lignin-lignosulphonate (LST), monomeric links - which-it derivatives of a fenilpropan (FPE), mainly the coniferyl, coumaric and sinaproic alcohols connected by various connections:



Picture 1. I-coumaric, II-coniferyl, III-sinapic alcohols

LST has a number of the important physical and chemical properties promoting receiving on its basis of the water-soluble kompleksonat that gives to its modified forms unique ability to reduce risks of complications when drilling oil and gas wells, due to regulation of rheological properties of boring washing fluids at the dosed additive of reagent in them<sup>1</sup>. Carrying out additional innovative modification of the neutral lignosulphonate having for today low reactionary and technological properties and small, in this regard demand allowed to improve LST properties and to receive quality boring FHLS-2M reagent (the Stalemate. The Russian Federation), exported to the CIS countries and promoting increase efficiency of oil production in general.

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## A STUDY OF THE INFLUENCE OF PHYSICAL FACTORS ON THE CONCENTRATION OF TROPOSPHERIC OZONE IN THE MEGAPOLIS

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Ozone (according to who) is a transformable atmospheric gas that affects the environmental safety of the human environment in the metropolis, its life expectancy and active longevity.

Using scientific and technical publications in this field and on the basis of their own research conducted by the authors since 2010<sup>1-3</sup>, it was found that the concentration of tropospheric ozone, due to the simultaneous physical and chemical reactions of formation and decomposition, are a complex oscillatory process with an uncertain frequency and amplitude. Photo-catalytic reactions of ozone formation Dominance over the territory of the metropolis (due to the comparability of day and night values of O<sub>3</sub>) is not observed. Mathematical modeling, as a consequence of the multifactorial process is difficult, and, at this stage of the study, the statistical collection of information is preferable.

In 2018-2019, the influence of a number of physical indicators of the atmosphere (temperature, K-index and UV-index) on the tropospheric ozone concentration in the Moscow region was assessed. It was found that the concentration of tropospheric ozone depends on seasonal and daily temperatures, which confirms the previously obtained patterns.

No significant effect of the magnetic field and ultraviolet radiation on the concentration of tropospheric ozone was found.

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## HIGHLY-EFFICIENT CATALYSTS BASED ON HIGHLY-POROUS CELLULAR METAL MATERIALS FOR AEROSPACE INDUSTRY

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Before supplying the respiratory air mixture in aviation, the mixture is cleaned of ozone in order to prevent it from entering the human respiratory tract. The catalysts for the decomposition of ozone are oxides of transition metals - nickel, cobalt, manganese, etc.

These catalysts must meet the following requirements: high degree of ozone conversion, high strength, developed surface, low aerodynamic resistance. Currently used granular and ceramic catalysts do not fully meet the requirements due to their inherent drawbacks.

This paper is devoted to the development of the technological process of electrochemical nickel plating of highly porous polyurethane foam. Before electrodeposition of the metal, polyurethane foam samples were treated with a conductive composition, then the samples were dried with hot air, and then processed galvanically. Optimal electrolyte compositions and parameters of nickel plating processes based on nickel chlorides and nickel sulphates were selected, allowing to obtain high-quality coatings on flat polyurethane samples.

The possibility of creating a framework of the desired thickness in one stage in one electrolyte, and in two stages in different electrolytes and under different conditions was investigated.

The first nickel layer is deposited in a chloride electrolyte having a high covering ability, and then the coating grows to the desired thickness in a sulphate electrolyte having a higher current output. When using a two-stage process, the total duration of the deposition of the coating of the required thickness is reduced.

## DOMINATION AND DEVELOPMENT OF CHEMICAL INDUSTRY IN THE TULA AREA

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The gross regional product (GRP) in the whole country is quite low - 17.4%. Industry gives the country one sixth of its national wealth. Under socialism, this figure exceeded 40% <sup>1</sup>. Nevertheless, the Tula region at the end of 2017 ranked 1 in the scale of the whole of Russia - more than 41% of the GRP. The maximum contribution to the GRP comes from the chemical and defense industries. The chemical industry is one of the main branches of the scientific and technological revolution, the most dynamic branch of the modern industry. It provides the national economy with a huge amount of products, without which the life of modern society would be impossible.

The main giants of the chemical industry in the Tula region are: JSC Novomoskovsk AK Azot (ammonia, nitrogen fertilizers, methanol) <sup>2</sup>; Procter and Gamble - Novomoskovsk LLC (production of detergents and cleaning products); Novomoskovsk AK «Polyplast» (chemical additives for various industries, lubricants, binder); LLC Orgsintez (production of products of organic chemistry); JSC Shchekinoazot - leading manufacturers of industrial chemicals (methanol, caprolactam, cyclohexane, urea-formaldehyde concentrate, highly concentrated low-methanol formalin, phenol-formaldehyde resins, sulfuric acid, technical ammonia) and other.

In 2016, the construction of a special economic zone of the industrial type "Uzlovaya" began, where chemical industry enterprises will also be concentrated.

There are few such regions with preserved dominance and development of the chemical industry in Russia. The development of the chemical industry brings human life to a completely new quality level.

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## STUDY OF CHEMICAL PROCESSING METHODS WASTE HYDROMETALLURGICAL PRODUCTION OF VANADIUM PENTOXIDE

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Wastes of hydrometallurgical production of vanadium pentoxide are sludge materials – dump sludge formed after leaching of vanadium from the calcined vanadium slag, and sludge neutralization of draining waters<sup>1</sup>. The sediment of neutralization of the drain water is obtained by processing with lime milk or by ozonation of solutions of hydrometallurgical production of vanadium pentoxide containing sulfuric acid, followed by filtration<sup>2</sup>. Currently, sludge and lime sediment is used in small volumes-sludge is added to the charge at the firing stage, lime sediment is used in the cement industry. The bulk of them is stored in dumps, which because of the content of soluble forms of vanadium and chromium are an environmental threat. Recycling of these wastes will solve not only environmental problems, but also to obtain marketable products.

Studies of leaching of waste sludge production of vanadium pentoxide by sulfuric acid have been carried out. The optimal conditions for the extraction of vanadium compounds to obtain vanadium concentrate were determined.

Sulfuric acid and hydrochloric acid methods of leaching sludge neutralization of drainage water are studied. Concentrates suitable for smelting ferrovanadium and other vanadium alloys were obtained.

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## THE STUDY OF FORMS OF VANADIUM COMPOUNDS IN THE PROCESSING CHAIN OF HYDROMETALLURGICAL PRODUCTION OF $V_2O_5$

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Converter vanadium slag is the main raw material for the production of vanadium pentoxide, which is mainly used in the production of ferrovanadium. Hydrometallurgical production of technical vanadium pentoxide is characterized by a significant amount of vanadium containing waste. Previously, we studied the mobile forms of elements in samples of annealed vanadium slag and sludge using chromatography and selective dissolution<sup>1,2</sup>. It is shown that sludge can pose a serious environmental threat due to soluble compounds of vanadium and chromium.

Methods of processing of vanadium sludge can be divided into two types – hydrometallurgical to obtain vanadium concentrate and pyrometallurgical to obtain iron, ligature, steel billet. For the development of physical and chemical bases of complex technology of sludge processing it is necessary to know in the form of what compounds vanadium is in the dump sludge and at what stage of processing they were formed. The present work studies the behavior of vanadium in the existing technological chain (with the investigation of industrial and synthetic products of technological processing) using a set of modern analytical methods (XPS, XRF, SEM, PXRD). Basing on the studies of slag, cinder, cake and sludge several mechanisms were proposed for the insoluble compounds of vanadium formation depending on the technological conditions of processing of slag.

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## ANALYSIS OF RISKS WHEN BUILDING TREATMENT PLANTS

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The organization of a solid waste processing system is necessary and appropriate for an urban area with a high population density and the use of indecomposable or very slowly decompose products. For the organization of complex process-sing and disposal of solid waste<sup>1</sup>, the types of risk assessments were made during the implementation of this project:

1) indicators of the degree of risk of emergency situations for the facility personnel and the resident population near the facility are determined;

2) the possibilities for the occurrence of emergency situations and their consequences at a given facility and in neighboring territories (facilities) are determined;

3) the work on the prevention of emergency situations and readiness for emergency response at the facility was assessed;

4) a list of measures to reduce the risk and mitigate the consequences of emergency situations at the facility has been developed.

When conducting a risk analysis all sources of information are involved, the criteria for acceptable risk are defined, all sources of hazards and ways of their application are considered. As a result of the identification of hazards, a list of undesirable events was created, the sources of hazards, risk factors, conditions for the occurrence and development of undesirable events were described, and hazard and risk assessments were made. Then the consequences of these undesirable events were evaluated, as well as a summary of risk assessments was made.

The results of calculations for the inventories (capacity of 400 tons/year) show that the value of individual fire risk as a result of exposure to hazardous factors in emergency scenarios<sup>2</sup> does not exceed the criterion of acceptable risk at production facilities. Recommendations for risk reduction based on the results of risk assessments are presented.

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## ENERGY RESOURCE-EFFICIENT METHOD OF PURIFICATION OF WASTE WATER CONTAINING WATER-SOLUBLE DYES

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In the finishing technology of textile materials, a significant part of TVV and dyes are removed under washing conditions and fall into the waste water of textile finishing production <sup>1</sup>. Shungite sorbent for wastewater treatment containing water-soluble dyes is proposed. In non-crystalline forms of carbon in shungite substance traces of its crystalline varieties - graphite and fullerene and fullerene-like structures were found <sup>2</sup>. The efficiency of extraction of dyes from aqueous solutions is shown by the example of the kinetics of the sorption of dyes from model solutions of dyes by shungite fraction-1-5 mm.

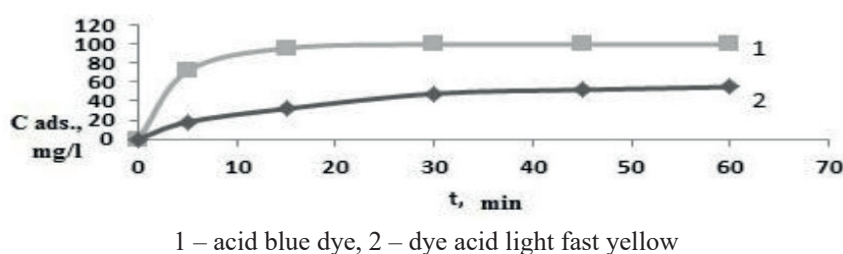


Figure 1. Change in the concentration of the dye model solution of acid blue and acid yellow light-strong after sorption with shungite fraction of 1-5 mm

The studied equilibrium adsorption isotherms showed that the mechanism of sorption by shungite and activated carbon is different. Sorbent shungite due to its globular pore structure exhibits sorption from aqueous solutions of substances having a large molecular weight.

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## THE MAIN PROBLEMS OF THE DEVELOPMENT OF THE FEC OF RUSSIA AND THE WAYS OF THEIR SOLUTION

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In the fuel and energy complex of Russia, factors restraining the development of the industry and negatively affecting its competitiveness remain. To increase competitiveness, the fuel and energy complex of Russia needs to minimize the impact of the problems presented in Table 1.

Table 1. The main problems of the development of the fuel and energy complex of Russia and their solutions

Identified problem	Ways to solve
insufficiently effective use and processing of resources	To improve the technology of processing and transportation of resources. The increase in the share of renewable sources in the fuel and energy complex.
insufficient level of education and special training	Close cooperation between leading industry players and universities. Systematic staff development and the creation of a personnel reserve. Internship abroad.
Inefficient technology for the extraction and processing of resources	Approximation of the domestic technological structure to the West European level.
High degree of depreciation of fixed assets	Increase awareness of new technologies through participation in international forums. Support the development of domestic equipment production.
Low innovation activity	Strengthen financing and support of innovative projects by attracting private business and developing public-private partnerships.
Degree of export orientation	Output of domestic products to new international and regional markets.
Degree of import dependence	Support the development of the production of domestic equipment, the replacement of foreign equipment with domestic counterparts.

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# **SECTION 5**

## **CHEMICAL ASPECTS OF MODERN ENERGETICS AND ALTERNATIVE ENERGY RESOURCES**

## ALKALI AND TRANSITION METAL FLUORIDE-PHOSPHATES AS PERSPECTIVE CATHODE MATERIALS FOR METAL-ION BATTERIES

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The ever-growing demand for portable energy in various fields puts forward new challenges to rechargeable battery technologies in improving specific energy and power, life and safety. The battery performance is critically governed by the properties of the cathode material. Fluoride-phosphates of transition metals with  $A_xMPO_4F$  ( $A = \text{Li, Na, K}$ ;  $M = \text{V, Fe, Co}$ ) formula take several advantages over existing oxide cathode materials: a substantial increase of operating voltages due to the inductive effect and much faster kinetics.

A distinctive structural feature of these materials is a presence of dangling oxygen atoms (bonded to P and alkaline cations, but not included into the octahedral coordination of transition metals). These oxygen atoms can determine the mechanism of the structure transformation during charging and even trigger the undesirable cation intermixing. Different activities of the alkali positions surrounded by a distinct number of the dangling oxygen atom can explain the striking difference between desodiation mechanisms in Na-ion and Li-ion cells of a layered  $\text{Na}_2\text{FePO}_4\text{F}$  cathode material.

Recently we proposed a novel series of vanadium-based  $\text{AVPO}_4\text{F}$  ( $A = \text{Li, Na, K, Rb}$ ) cathode materials crystallizing in a  $\text{KTiOPO}_4$  (KTP)-type structure. The KTP-type “ $\text{VPO}_4\text{F}$ ” framework featured outstanding rate capability and capacity retention especially in Li cells: the material maintained more than 75% of the initial specific capacity at the 40C rate with an average potential of 4.0 V vs.  $\text{Li/Li}^+$ . Another quality of this framework is supporting reversible  $\text{Na}^+$ ,  $\text{K}^+$  and even  $\text{Rb}^+$  ions de/insertion sustaining the host structure. The electrochemical performance and ion transport properties were different for various alkali ions. The ion diffusion coefficients obtained by PITT were the lowest for  $\text{Li}^+$  ( $10^{-12} - 10^{-14} \text{ cm}^2/\text{s}$ ) and the highest for  $\text{K}^+$  ( $10^{-11} - 10^{-12} \text{ cm}^2/\text{s}$ ), with the latter anticipating high-power applications of  $\text{KVPO}_4\text{F}$  in K-ion batteries.

Our current activities on transition metal fluoride-phosphate based cathode materials for metal-ion batteries will be reported with a particular focus on the interrelation between crystal structure peculiarities and electrochemical properties.

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## TRENDS IN PHOTOVOLTAICS BASED ON ORGANIC AND HYBRID MATERIALS

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The key functional layers in organic and hybrid solar cells (SCs) are photoactive and charge-transport layers. The former may consist of a single material (e.g. organic-inorganic lead halides of the perovskite structure), a donor-acceptor blend forming a bulk heterojunction (e.g. polymer photoconductor (donor) and fullerene (acceptor)), and a ternary mixture, where the third component is to increase light absorption and charge carrier generation. Charge-transport layers provide the transfer of electrons and holes from the photoactive layer to the cathode (electron transport layer) and anode (hole transport layer), respectively.

In the report, (1) approaches to creating new materials, (2) electronic processes in the layers of SCs, defining requirements for the materials, and (3) trends in the development of the new generation SCs are discussed. In particular, SCs based on perovskite structures<sup>1,2</sup>, small organic molecules<sup>3,4</sup>, quantum dots<sup>5</sup>, and conducting polymers<sup>6</sup> are considered.

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## MATERIALS SCIENCE AS A BASIS FOR THE DEVELOPMENT OF NUCLEAR INDUSTRY

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In the course of its development, civilization, widely using the objects of the environment and mechanizing industry, forms a technological structure as a set of related industries with a single technical level.

The change of production technologies dominating today in the economy creates the contours of a new, sixth technological structure characterized by the development of knowledge-intensive cognitive technologies, genetic engineering, Photonics and micromechanics with the transition of hydrocarbon energy to nuclear energy.

In this regard, the basis of the scientific breakthrough in Russia today - the individualization of production and consumption of new products in nanobionics, communications, personalized medicine and pharmaceuticals for a decent increase in the life expectancy and quality of human life is the development of new nuclear technologies based on the use of key materials underlying them.

Among the mentioned materials are heterogeneous metallized catalysts acting in the processes of redox reactions involving actinides at the stages of processing spent nuclear fuel, the release of high-energy radionuclides, the disposal of organic-inorganic radioactive waste containing complexing compounds.

The transition to two-component nuclear power requires high-density, nanodispersed, modified uranium oxide and mixed nuclear fuel compositions with controlled grain size and volumetric porosity.

They are obtained by means of mechanochemical pressing and pulse plasma sintering. The report will provide data on re-establishment of domestic lithium industry through the introduction of technologies of processing of dumps Zavitinsk lithium-beryllium deposit and obtaining a lithium-containing materials for the defense in Russia.

Materials necessary for the atomic sphere for the production of selective sorbents and extractants, radioluminescent light elements, adsorbents for the purpose of localization of gaseous and matrices for the immobilization of liquid high-level waste were also obtained. The introduced materials with improved characteristics will ensure the development of nuclear power, the defense capability of the Russian Federation, nuclear medicine and isotope products.

## MEMBRANE MATERIALS FOR ALTERNATIVE ENERGY

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Ion exchange is widely used in chemical power sources, including fuel cells, redox batteries, reverse dialysis devices and lithium-ion batteries. High ionic conductivity and selectivity of transfer processes are general requirements for them. Homogeneous perfluorinated membranes have a significant advantage over heterogeneous ones, since the latter contain large pores which determine a decrease in their selectivity. However, their use is limited by high cost. The use of grafted membranes is very promising. The composition of such membranes is almost identical to heterogeneous one. But the lack of secondary porosity makes them much more selective<sup>1</sup>. Their high efficiency in the energy generation with the use of reverse electrodialysis has been shown.

The properties of ion-exchange membranes can be improved by their modification, for example, by the nanoparticles incorporation. First of all, it is worth noting the possibility of ionic conductivity increase. To explain this phenomenon, a model of "limited elasticity of the membrane pore walls" has been proposed. The formation of nanoparticles in the pores leads primarily to the displacement of the «electrically neutral» solution from the center of the pores of the membranes and an increase in their selectivity. Therefore, a number of hybrid membranes are characterized by a decrease in the transfer of methanol and gas molecules show a reduced transfer of methanol and gas molecules. The membrane selectivity can be enhanced by doping with nanoparticles with acidic surface. In addition, an important advantage is the increase in conductivity of hybrid membranes at low humidity, which is a significant advantage for their use in fuel cells. In addition, the increase in conductivity of hybrid membranes at low humidity is an important advantage for their use in fuel cells.

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## PRODUCTION OF HYDROGEN VIA TRANSITION METAL CATALYZED DEHYDROGENATION

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As it is generally accepted, the development of a mature and diffuse “hydrogen economy” is based on the overcoming of two severe drawbacks which ask for (i) a “sustainable” production of hydrogen using therefore not coal or natural gas but especially renewable energies, and (ii) to solve the great problem of achieving an effective development of a reliable and cheap hydrogen transportation system. This second issue needs that an efficient and safe hydrogen storage system capable of positively competing with liquid hydrocarbons is developed.

Among the materials most promising for hydrogen storage a special role is taken by tetrahydroborate salts ( $\text{BH}_4^-$ ) and ammonia-borane ( $\text{NH}_3\text{BH}_3$ ). Indeed, the homogeneously-catalyzed dehydrogenation/hydrolysis of these compounds is the effective chemical path to exploit them as hydrogen storage materials. Coordination compounds containing  $\text{BH}_4^-$  ligands possess many other practically valuable properties and may be used as selective reducing agents, as precursors for the production of molecular or nanostructured borides, hydrides and other inorganic materials, and also as discrete catalysts for carrying out important industrial process. In this talk we present our recent results<sup>1-3</sup> on the amineboranes dehydrogenation to produce  $\text{H}_2$ . Variable temperature spectroscopic and computational studies were used to investigate the mechanisms of amine boranes dehydrogenation catalyzed by various transition metal hydrido complexes. These studies showed the importance of relatively weak metal-ligand interactions for keeping active conformation of catalyst or for its activation as well as the role of  $\text{Cl}\cdots\text{H-N}$  and  $\text{H}\cdots\text{H-N}$  hydrogen bonds in amine boranes dehydrogenation.

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# SYNTHETIC MODELS OF HYDROGENASES AS MOLECULAR ELECTROCATALYSTS FOR HYDROGEN ENERGY - FROM MOLECULES TO MATERIALS

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Replacing platinum in hydrogen fuel cells with earth abundant metals will be a crucial step toward the viable use of H<sub>2</sub> as a solar fuel. Understanding the factors that control the binding and heterolysis of H<sub>2</sub> to these metals can play a key role in improving H<sub>2</sub> activation/production. The [FeFe]- and [NiFe]-hydrogenases easily catalyze reversible interconversion between dihydrogen gas and protons and electrons at mild conditions. The structures of hydrogenase active sites have provided attractive targets for synthetic chemists to advance our understanding of the electronic structure and reactivity of these unique enzyme active sites. These efforts contribute to the synthesis of new Fe, Co and Ni catalysts for hydrogen oxidation or production that could have significant impacts on alternative and renewable energy solutions. The development of new biomimetic catalytic systems mimicking the action of metalloenzymes and biological nanoreactors is based on cage structures, which contain P, N and S donor atoms coordinated to metal atoms and form cavities composed of macrocycles. The maximum TOFs of hydrogen evolution from the best Ni catalysts reach 15200 s<sup>-1</sup>, which exceeds the values for most synthetic electrocatalysts known in the literature and is comparable with the activity of natural hydrogenases. In recent years new materials have been created for fuel cells based on organometallic hydrogenase models, which have shown their effectiveness. So, the diaza-diphosphacyclooctane nickel(II) complex [Ni(P<sup>Py</sup><sub>2</sub>N<sup>p-Tol</sup><sub>2</sub>)]<sup>2+</sup><sub>2</sub> on Vulcan XC-72(C) functions as both the cathode and anode catalysts in polymer electrolyte membrane fuel cell with the cathode the power density of 14.66 mWcm<sup>-2</sup>, which is the highest power density of the none-noble organometallic analogs. Membrane-electrode assemblies with a cathode catalyst made of a nickel sodium pectate complex PG-NaNi with maximum current density of 59 mAcm<sup>-2</sup> and power density of 5.9 mWcm<sup>-2</sup> have been successfully created. These results permit the development of environmentally friendly and stable catalysts for PEMFCs made of a available biological raw material. The main advances and trends in the development of synthetic analogues of natural metal-containing hydrogenases and materials based on them are analyzed and summarized.

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## **HYDROGEN ELECTROCHEMICAL SYSTEMS BASED ON POLYMER ELECTROLYTE MEMBRANE: FROM NANOSTRUCTURED ELEMENT BASE TO CREATION OF INSTALLATIONS OF INDUSTRIAL SCALE**

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Hydrogen electrochemical systems based on polymer electrolyte membrane allow for the transformation of the kinds of energy with high efficiency and without environmental damage. The systems are implemented for transport and decentralized power supply application more and more widely. Recent years, integration of low-temperature hydrogen electrochemical systems with power plants on the basis of renewable and nuclear energy sources, including the so-called Power-to-X technologies, is actively worked out. Hydrogen electrochemical systems are rather promising for power supply of robotics and some other applications.

In this report, the aspects of application of nanomaterials and nanotechnologies in the course of research and development of element base (electrocatalysts, active layers, membranes and gas diffusion electrodes) of low-temperature electrochemical systems is considered, experience of development of pilot power plants of industrial scale is generalized, and possibilities of their practical application are shown.

## NANOSTRUCTURED CATALYSTS, PREPARED ON THE BASE OF BIMETALLIC CLUSTERS, FOR LOW-TEMPERATURE FUEL CELLS

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Studies of the catalytic activity of highly dispersed platinum alloys for obtaining efficient cathode catalysts of oxygen reduction are widely reported in the literature [1,2]. In the present work we continue to develop an approach to the preparation of bimetallic electrocatalysts, based on organometallic clusters of platinum with other metals synthesized and then subjected to thermal decomposition on highly dispersed carbon carriers at a temperature of 450°C in a hydrogen atmosphere. It has been shown previously that a distinctive feature of such catalysts is a high reproducibility in composition and uniform distribution over the carbon support, which ensures stability and reproducibility of their characteristics [3].

Bimetallic clusters of the following gross formula were synthesized:

$\text{PtCo}(\text{CH}_3\text{CO}_2)_4(\text{CH}_3\text{COOH})$ ,  $\text{PtNi}(\text{CH}_3\text{CO}_2)_4(\text{CH}_3\text{COOH})$ ,  $\text{PtMn}(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})$ , and  $\text{PtZn}(\text{CH}_3\text{CO}_2)_4(\text{CH}_3\text{COOH})$ , their structure having been confirmed by X-ray diffraction, IR and NMR spectroscopy. The prepared supported catalysts PtCo/C, PtNi/C, PtMn/C, and PtZn/C were characterized by XRD, EDAX, TEM, EXAFS and XANES methods. It has been shown both in model experiments and while testing MEAs with PtCo/C, PtMn/C, and PtZn/C, in particular, that catalysts prepared from bimetallic clusters of the corresponding metals have advantages over a commercial platinum catalyst (Pt(20%)/C) in terms of their high specific activity and are therefore promising for use in hydrogen-air fuel cells.

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## OXYGEN REACTION IN AQUEOUS AND APROTIC MEDIA IN DEVICES OF ELECTROCHEMICAL ENERGETICS

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The oxygen reaction, including the processes of cathodic O<sub>2</sub> reduction and its anodic evolution, plays a key role in energy conversion in many devices of electrochemical energetics.<sup>1-3</sup> The current-voltage characteristics and the operation stability of the low-temperature hydrogen-air fuel cell (FC) are determined primarily by cathode catalyst properties. The study of kinetics and mechanism of the oxygen reduction reaction in aqueous media is the theoretical basis for the development of catalysts for FC.

Active R&D of primary and rechargeable power sources based on O<sub>2</sub> and metallic Li, Na, K in the last decade has led to an increase in the number of studies on the oxygen reaction features in aprotic electrolytes.<sup>2,3</sup> The Li-O<sub>2</sub> system has the highest theoretical specific energy and, as in the case of hydrogen-air fuel cells, the processes on the oxygen electrode are critical here. The specific requirement for materials of the positive electrode of a lithium-oxygen battery (LOB) is not only the acceleration of the cathodic reaction during the LOB discharge, but also of the anodic reaction that occurs at the LOB charging.

This work considers the features of oxygen reaction in aqueous solutions and Li<sup>+</sup>-containing aprotic media, features of the processes on oxygen electrodes of fuel cells and LOB, as well as the possibility of using the experience of hydrogen-air fuel cells R&D to develop scaled-up LOB batteries.

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## HIGH-CAPACITY FUNCTIONAL MATERIALS FOR SODIUM-ION BATTERIES

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Sodium-ion batteries are promising energy storage and conversion systems due to the wide availability and low cost of sodium resources. It is assumed that sodium-ion batteries will be widely used for large-scale energy storage devices in the future. The lecture will provide an overview of the study of high-capacity functional materials (cathode and anode) for sodium-ion batteries. Promising high-capacity functional materials for sodium-ion batteries are considered taking into account their multi-electron reaction with sodium ions. The lecture will highlight the problems of high-capacity functional materials, including their low electron and ion conductivity, adverse interactions with the electrolyte, significant changes in the volume at sodium introduction, poor cyclability. Ways to improve high-capacity functional materials, such as the using of carbon coatings, architectural design, doping, modification of the electrolyte will be pointed.

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## HYBRID PHOTOCATALYSTS BASED ON TETRAPYRROLIC MACROCYCLES AND INORGANIC NANODISPERSED SUPPORTS

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The tetrapyrrole (TP) complexes with  $d^0$ - and  $d^{10}$ -metals are promising photocatalysts due to the intense absorption of light in the red region of the spectrum and the ability to form long-lived triplet states with high quantum yield. However, their application in practice is difficult due to the low solubility and tendency to form aggregates. One of the ways to control the aggregation state and photophysical properties of these compounds is their immobilization on the surface of particles of an inert solid carrier, which prevents aggregation of macrocycles<sup>1,2</sup>. The report discusses the production of heterogeneous photocatalysts based on Zn<sup>II</sup>, Al<sup>III</sup> and Si<sup>IV</sup> phthalocyanines adsorbed on the surface of nanodispersed mineral particles (silica, montmorillonite, modified cationic surfactants, *etc.*). The aggregation behavior and photophysical properties of adsorbed TPs are discussed, and their photocatalytic activity is compared in oxidation reactions of various substrates in the composition of hybrid materials, including those containing mixtures of various metal complexes of phthalocyanine and porphyrins. The role of substituents and axial ligands in regulating the aggregation behavior of TP and, as a consequence, their photocatalytic activity is considered.

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## THE SELF-ASSEMBLY OF METAL NANOPARTICLES IN REVERSE MICELLAR SOLUTIONS

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The self-organization of nanoparticles has been identified as an important process where the building blocks spontaneously organize into ordered structures by thermodynamic and other current restriction<sup>1</sup>. However, in order to successfully exploit nanoparticle self-assembly (SA) in technological application and to ensure the efficiency of processes, a high level of investigation is required. Recent advances in this area have to focused, allowed to reveal the features of formation of metal nanoparticles (NP<sub>s</sub>) at various stages of chemical and radiation-chemical reduction of metal ions in the reverse micelles as microreactors<sup>2</sup>, including *spontaneous* («Self-Assembly» SA) nanostructures in the post-radiation period<sup>3</sup>.

The report will present the results of a comparison of the optical properties of the NP Re and NP Fe obtained by *molecular assembly* «bottom-up» in reverse micellar solutions (OMR). The processes of NP formation are based on reactions: *chemical reduction* of metal ions by quercetin, *radiation-chemical* – the interaction of metal ion with particles of water radiolysis -  $e^-_{aq}$  and H radicals with reducing properties, and *due to direct* self-assembly of NPs. Additional information on the evolutionary processes in colloidal systems that do not contain metal ions was confirmed by data on the electrical conductivity and luminescence of OMR. One of the most important conclusions about the properties of water in the water pool of OM is that it is *polarized*. The presence of reducing components in such water in the form of negative charges allowed to explain the role of SA at the same concentration of metal ions as with both RadChem and Chem methods. Formation nanoparticles due to the reducing properties of «polarized» water in the water pool and subsequent self-organization of NPs confirmed by the results of TEM, AFM and UV-VIS spectrophotometry.

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## LOW-TEMPERATURE DOUBLE LAYER SUPERCAPACITOR

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In order to expand the temperature range of performance of double-layer supercapacitors, for the first time, a 1 M solution of an ionic liquid in freon-22 was used as an electrolyte. 1-Butyl-3-methylimidazolium tetrafluoroborate was used as the ionic liquid. The electrodes were made of activated carbon fabric CH-900 (Kuraray, Japan) with a specific surface area of 1500 m<sup>2</sup>/g. Cyclic voltammetric measurements were carried out at temperatures from –140 to +90 °C. The results obtained at a voltage scan rate of 0.01 V/s are shown in Figs. 1 and 2.

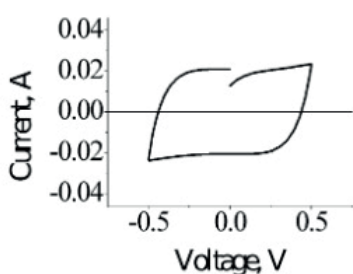


Fig. 1. Voltammogram at the temperature +90 °C

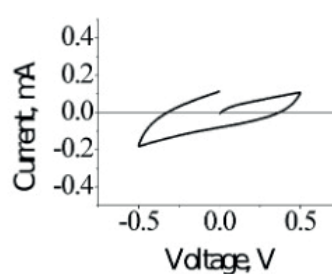


Fig. 2. Voltammogram at the temperature –140 °C

At a temperature of +90 °C, the voltammogram reflects the almost purely capacitive behavior of the supercapacitor. The shape of voltammogram at a temperature of –140 °C is typical for a device with a noticeable contribution of ohmic resistance. An analytical solution for cyclic voltammograms for systems with a series connection of capacitance and resistance has been obtained. The solution adequately describes the curves of Figs. 1 and 2.

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## COMPOSITES BASED ON LITHIUM TITANATE AND MESOPOROUS CARBON AS ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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Lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) seems to be a promising anode material for lithium-ion batteries. Long cycling life and safety are the main advantages of batteries with anodes on its base. In some cases, the electrochemical properties of electrode materials can be significantly improved by formation of composite materials with carbon.

In this work, composite materials  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  were prepared by the hydrothermal method. Both commercial mesoporous carbon, carbon replicas obtained using mesoporous silica SBA-15 as template, and carbon black Timcal were used for the synthesis. The obtained materials were characterized using XRD, SEM, TEM, BET method, Raman spectroscopy. The influence of surfactants (CTABr, Triton X), the nature and content of carbon material on the formation of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  composites and their electrochemical properties was studied. The use of CTABr leads to a slight improvement in the cycling performance of the samples, including cycling at high current densities. A decrease of the discharge capacity and cycling performance of the composites obtained using more than 20% of the carbon material was shown. At low charge/discharge rates, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  samples with commercial mesoporous carbon exhibit the highest electrochemical capacity. At high current densities (3200 mA/g), the discharge capacities of samples with commercial mesoporous carbon and carbon black Timcal are 70 and 84 mAh/g, respectively. The degradation of the studied materials during cycling does not exceed 4-7%.

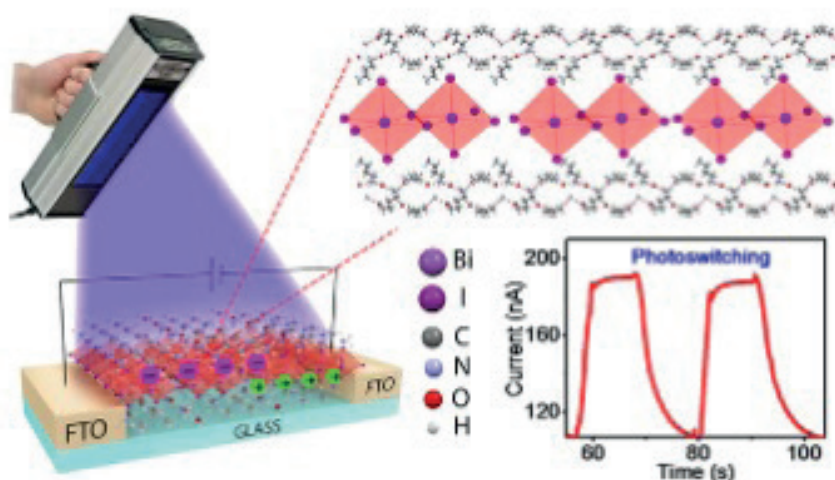
*This work was supported by the Russian Foundation for Basic Research, project 16-29-05241.*

## ZERO-DIMENSIONAL LEAD-FREE HYBRID PEROVSKITE WITH QUANTUM-WELL STRUCTURE: SYNTHESIS, OPTOELECTRONIC PROPERTIES AND APPLICATIONS

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Low-dimensional hybrid perovskites are an emerging class of materials with high stability and excellent optoelectronic properties.<sup>1,2</sup> Recently, we have designed and synthesized a novel, lead-free, zero-dimensional perovskite, (1,3-propanediammonium)- $\text{Bi}_2\text{I}_{10}\cdot 2\text{H}_2\text{O}$ , for optoelectronic applications.<sup>2</sup> This material exhibited good moisture and thermal stability under ambient conditions. Single crystal X-ray diffraction analysis revealed a quantum-well structure having the inorganic  $\text{Bi}_2\text{I}_{10}^{4-}$  clusters are periodically arranged in the crystallographic 'c' axis separated by a distance of 5.36 Å, sandwiched by independent layers of organic cations. The density functional theory calculations showed that the oxygen in water molecules have a significant contribution to the band edges of the material. Emission and Raman spectroscopy analysis revealed the presence of trap states in the material formed due to the strong excited electron-phonon coupling. Photodetector device fabricated using this material showed an efficient charge separation at low voltage (1V) due to the good electronic conduction between the  $\text{Bi}_2\text{I}_{10}^{4-}$  dimer units. Use of this material for neuromorphic computing is currently under progressing. Details will be presented.



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## BROMATE ANION REDUCTION IN ACIDIC MEDIUM: THEORETICAL ANALYSIS AND EXPERIMENTAL STUDY

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Use of  $\text{BrO}_3^-$ -to- $\text{Br}$  reduction process inside the cathodic section of flow cells corresponds to enormous redox-charge densities in view of the 6-electron character of the process and high solubilities of both lithium salts (over 8V at room temperature)<sup>1</sup>. However,  $\text{BrO}_3^-$  does not possess any electroactivity within the needed range of electrode potentials.

Our theoretical analysis<sup>1,2</sup> has shown that this transformation can take place owing to a redox-mediator cycle composed of  $\text{Br}_2$ -to- $\text{Br}$  reduction at electrode and  $\text{BrO}_3^- + 5\text{Br} + 6\text{H}^+ = 3\text{Br}_2 + 3\text{H}_2\text{O}$  reaction inside solution. Because of the autocatalytic character of the cycle the components of the  $\text{Br}_2/\text{Br}$  redox couple are accumulated near the electrode surface, thus leading to enormous currents limited by the  $\text{BrO}_3^-$  transport.

Experimental data for this process at rotating disk electrode (RDE)<sup>3</sup> have turned out to be in quantitative agreement with these theoretical predictions (Fig. 1).

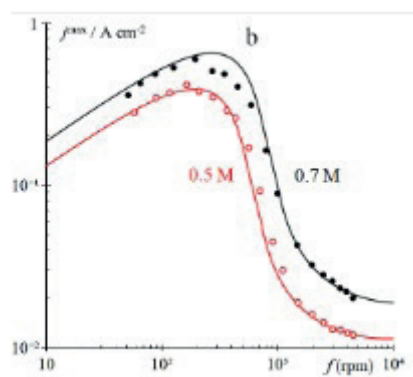


Figure 1. Dependence of the maximal current density for RDE on the electrode rotation frequency for solution:  $x \text{ M BrO}_3^- + 2 \text{ M H}_2\text{SO}_4$ ;  $x = 0.5 \text{ M}$  или  $0.7 \text{ M}$ . Experimental points vs. theoretical lines for each bromate concentration.

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## A STUDY OF THE STRUCTURE AND ELECTROCONDUCTIVITY OF LITHIUM-ION POLYMER ELECTROLYTES BASED ON POLYETHYLENE GLYCOL AND POLYPROPYLENE GLYCOL

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In recent years, increased the amount of research in the field of lithium (Li)- ions polymer electrolytes. This interest is due to the fact that the Li-ion polymer electrolytes can create solid secure device of any shape and size with high specific energy in the production process of lithium batteries<sup>1,2</sup>.

The objectives of this work were to study the structure of the structure, complexation processes, solvation, the degree of amorphization and crystallinity of solid electrolytes of the “lithium salt - polymer” type using vibrational spectroscopy, differential scanning calorimetry, electrometry and X-ray diffraction. The objects of research are polymeric electrolytes based on matrices of polyethylene glycol (PEG-400, PEG-1500) and polypropylene glycol PPG-2000 doped with salts  $\text{LiNO}_3$ ,  $\text{LiSCN}$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . Based on the analysis of vibrational bands form loops molecular anions vibrational modes of the functional groups of the polymer matrix calculated parameters characterizing their vibrational relaxation. Based on a comprehensive analysis of the spectroscopic results, X-ray diffraction and electrometric measurements determined the most probable mechanisms of ion transfer respective PE. The phase composition was refined and the analysis of structural changes, as well as structural features and regularities in the obtained lithium polymer electrolytes with changes in salt concentration.

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## ACTIVITY OF PtCuAu/C CATALYSTS WITH DIFFERENT CONTENT OF GOLD IN THE REACTION OF ALCOHOL ELECTROOXIDATION

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Alcohol fuel cells (FC) are promising power sources that can be used in various portable devices. Special requirements are imposed on catalysts for alcoholic fuel cells - resistance to poisoning by intermediate oxidation products of alcohols. The main directions of improvement of these catalysts are: doping of Pt with various metals (Cu, Co, Ni, Ru, etc.); the use of non-carbon carriers, for example, SnO<sub>2</sub>, TiO<sub>2</sub>.

The purpose of this work was to obtain trimetallic Pt<sub>x</sub>Cu<sub>y</sub>Au<sub>z</sub>/C catalysts with different gold content deposited on a highly dispersed carbon carrier, as well as to study their activity and stability in the reaction of electrooxidation of alcohols. Synthesis of PtCuAu/C catalysts with different nanoparticle architecture (from homogeneous solid solutions to nanoparticles with core-shell and "gradient" structures) was carried out using the methods of simultaneous and sequential reduction of metals developed earlier in our laboratory [1-2].

The obtained PtCuAu/C materials demonstrated a higher corrosion-morphological stability and activity in the oxygen reduction reaction (ORR) and the methanol electrooxidation (MOR) as compared with Pt/C material. This fact may be associated with a high concentration of Au in the surface layers of the nanoparticles. Thus, according to the results of the study, it was found that the optimal amount of gold additive is 5% of the atomic fractions of the metal component and the catalysts based on PtCuAu nanoparticles are of fundamental and applied interest, and they are promising for further study.

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## GRAPHITIZATION OF CARBON SUPPORT FOR RUTHENIUM CATALYSTS FOR AMMONIA SYNTHESIS

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Low-temperature synthesis of ammonia is very important for energy saving technologies and hydrogen energy. Industrial KAAP-plus-process is carried out on a double-promoted ruthenium catalyst on a carbon support. However, the carbon supports at high temperatures is gasified in hydrogen environment, therefore, requires methods to improve their stability. One of the most effective methods to improve the stability of carbon supports is graphitization, so we graphitized Sibunit at 1400, 1600, 1800, 2000 and 2200 °C. To quickly determine the degree of graphitization, a series of physical and chemical methods can be used: XRD, Raman spectroscopy and thermogravimetric analysis (TGA) in air. The aim of the work was to determine the effect of Sibunit graphitization on its stability according to TGA data.

According to TGA data, all characteristic temperatures of the burnout Sibunit - based increases with increasing temperature of graphitization, which correlates with the XRD data. So the interplanar distance  $d_{002}$  decreases from 3.49 Å for the original Sibunit to 3.44 Å for Sibunit calcined at 2200 °C. However, according to Raman spectroscopy, the  $I_D/I_G$  ratio changes little, and becomes noticeable only at 2200 °C – 1.59 and 1.18 for the initial and calcined at 2200 °C, respectively.

It can be concluded that the graphitization leads to the ordering of the structure of the original carbon support of Sibunit, but the specific surface area is reduced by 10 times. Graphitization increases the thermal stability of supports, but may adversely affect the ability to prepare a ruthenium catalyst with a sufficient content of ruthenium. The data of XRD, Raman spectroscopy and TGA correlate well with each other.

*The work was supported by RSF, project № 18-73-00255.*

## COMPOSITES BASED ON ELECTROCONDUCTIVE POLYMER AND 2D MATERIALS FOR OPTOELECTRONICS

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The creation of hybrid composites combining the advantages of both organic and inorganic materials is of great interest for modern optoelectronics. In the report, the effect of 2D materials on optical, electrical properties and frontier electron levels of composites based on a water-soluble polyaniline complex (PANI) with polymeric sulfonic acid is considered. Graphene of various oxidation states and graphene-like molybdenum disulfide ( $\text{MoS}_2$ ) and tungsten disulfide ( $\text{WS}_2$ ) were used as 2D materials. The created composites were investigated by electron spectroscopy and X-ray analysis. The results of measurements of electrical conductivity, mobility and concentration of charge carriers (4-probe method, Hall Effect) showed the influence of the 2D materials on the flow of electric current in layers of the composites. The increase of the  $\text{MoS}_2$  and  $\text{WS}_2$  nanophase concentration was found to change the type of major charge carriers in the nanocomposites. By using Kelvin-probe microscopy the work function distribution on the composite layers was investigated. It was shown that the work function of graphene is higher than that of PANI, and therefore, the former can create relatively deep electronic states in the composite. The composites used as a charge-transport layer in organic solar cells increased the extraction of holes from photoactive layer and, as a result, the performance of the devices. Since the work function of 2D  $\text{MoS}_2$  and  $\text{WS}_2$  is lower than that of PANI, the composites exhibit ambipolar conductivity above the threshold concentration of the 2D materials. Such composites are of interest for use as a connecting interlayer in tandem solar cells.

*The research was carried out with the financial support of the Russian Foundation for Basic Research (Scientific project No. 16-29-06423).*

## MOLECULAR DYNAMICS STUDY OF THE SILICENE ON Cu (111) AND Al (111) SUBSTRATES SUITABILITY AS ANODE MATERIAL FOR LITHIUM-ION BATTERIES

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Silicene is a two-dimensional material, similar to graphene, has a honeycomb structure with silicon atoms in the nodes of the hexagonal unit cell. The ability of silicon to hold a large amount of lithium makes silicene a promising anode material for lithium-ion batteries (LIB)<sup>1</sup>.

In this work by the molecular dynamics method the intercalation and deintercalation of  $\text{Li}^+$  ions in the two-layered silicene on Cu(111) and Al(111) substrates is simulated. Self-diffusion coefficients of lithium, internal energy of systems, mechanical strength are estimated. The detailed structure of silicene is investigated by the method of constructing Voronoi polyhedra. The stresses  $\sigma_{zz}$  arising in silicene for none of the systems exceed of its ultimate tensile stress ( $\sim 15 \text{ GPa}^2$ ).

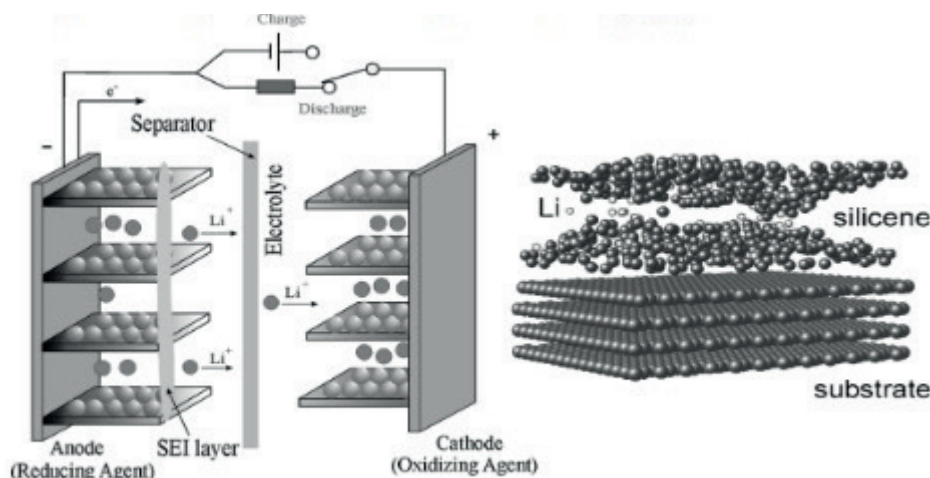


Figure 1. Schematic representation of the LIB operating principle (left), simulated system: part of the LIB anode (right).

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## INFLUENCE OF THE STRUCTURE OF AROMATIC SUBSTRATES ON HYDROGEN ABSORPTION AND RELEASE EFFICIENCY IN HETEROGENEOUS CATALYTIC HYDROGEN STORAGE SYSTEMS

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Hydrogen fuel cell engines are one of the few environmental technologies that can make a real alternative to petroleum fuels in transportation. But traditional hydrogen storage methods for transport are expensive (liquid hydrogen) or have a low capacity (compressed hydrogen, metal hydrides). A fundamentally different way of storing hydrogen is implemented in chemical systems based on aromatic hydrocarbons (> 7 wt. % H<sub>2</sub>) which capable of reversible hydrogenation-dehydrogenation reactions<sup>1</sup>.

The activity of polycyclic aromatic hydrocarbons with different degrees of condensation (benzene, naphthalene, anthracene and biphenyl, *ortho*-, *meta*- and *para*-terphenyl) and the related polycyclic naphthenes (cyclohexane, decalin, perhydroanthracene, bicyclohexyl, and *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl) was compared in reversible hydrogenation-dehydrogenation reactions on a catalyst a Pt/C (Sibunite). Hydrogenation was carried out in an autoclave: benzene, biphenyl and isomers of terphenyl at  $T=180^{\circ}\text{C}$  and  $P=70$  atm; naphthalene and anthracene – at  $T=280^{\circ}\text{C}$  and  $P=90$  atm. Dehydrogenation was carried out in a flow reactor in the temperature range  $T=280\text{--}340^{\circ}\text{C}$  at a flow rate of  $1\text{ h}^{-1}$  and atmospheric pressure.

The report compares the kinetic parameters of catalytic hydrogenation-dehydrogenation reactions with the structure of aromatic substrates.

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## Ho-, Yb-DOPED BISMUTH TITANATES: SYNTHESIS, STRUCTURE, ELECTRICAL PROPERTIES

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The study of compounds with the pyrochlore structure doped by rare-earth elements attracts attention both dielectric and photoluminescent properties. In this work, Ho- and Yb-containing bismuth titanates  $\text{Bi}_{1.5-x}\text{M}_x\text{Ti}_2\text{O}_{7-8}$  ( $x = 0.25; 0.50$ ) and  $\text{Bi}_{1.3}\text{M}_{0.5}\text{Ti}_2\text{O}_{7-8}$  (M – Ho, Yb) were obtained by the method of organic-inorganic precursors combustion. The phase composition and structure of compounds were studied by X-ray method on a SHIMADZU XRD-6000 diffractometer and by SEM on a TESCAN VEGA 3 SBU microscope (X-ACT (EDS) microanalyzer). It has been shown that  $\text{Bi}_{1.5}\text{M}_{0.25}\text{Ti}_2\text{O}_{7-8}$  and  $\text{Bi}_{1.3}\text{M}_{0.5}\text{Ti}_2\text{O}_{7-8}$  (M – Ho, Yb) are single-phase and exhibit the pyrochlore-type structure ( $Fd-3m$ ). Distribution of dopants over the pyrochlore sites was determined by fitting of X-ray diffraction pattern with Rietveld analysis. It has been established that the Ho and Yb atoms are distributed in the Bi sites predominantly. This fact also follows from the values of the ionic radii of the atoms ( $r(\text{Bi}^{3+}) = 1.17 \text{ \AA}$ ,  $r(\text{Ho}^{3+}) = 1.015 \text{ \AA}$ ,  $r(\text{Yb}^{3+}) = 0.985 \text{ \AA}$  with CN = 8;  $r(\text{Ti}^{4+}) = 0.605 \text{ \AA}$  with CN = 6)<sup>1</sup>. Electrical properties of the samples were investigated by impedance spectroscopy (immittance analyzer E7-28) in the air, oxygen and “wet” atmospheres ( $25\text{-}10^7 \text{ Hz}$ ,  $25\text{-}750 \text{ }^\circ\text{C}$ ). The temperature dependence of the conductivity of the samples obeys the Arrhenius law with  $E_a$  of  $0.1\text{-}0.2 \text{ eV}$  ( $T < 350 \text{ }^\circ\text{C}$ ) and of  $1.3\text{-}1.5 \text{ eV}$  ( $400 \leq T \text{ (}^\circ\text{C)} \leq 750$ ) in the air. Thus, the conductivity of the compounds is caused by different charge carriers. According to data of temperature programmed isotope exchange (TPIE) with  $\text{C}^{18}\text{O}_2$  for doped bismuth titanates the oxygen transport is activated up to  $300\text{-}350 \text{ }^\circ\text{C}$ <sup>2</sup>. The dielectric characteristics of the samples are close to each other and vary in the  $90 \leq \epsilon' \leq 105$  ( $25\text{-}750 \text{ }^\circ\text{C}$ );  $0.002 \leq \tan\delta \leq 0.003$  ( $25\text{-}200 \text{ }^\circ\text{C}$ ); TCC =  $-100\text{-}(-200) \text{ ppm/}^\circ\text{C}$  ( $25\text{-}400 \text{ }^\circ\text{C}$ ) ranges at  $1 \text{ MHz}$ .

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**SOLUBILITY OF ACTINIDES FLUORIDES IN CANDIDATE FUEL SALT  
LiF-NaF-KF (FLINAK) FOR MOLTEN SALT NUCLEAR REACTOR**

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The choice of the carrier salt for the molten salt reactor (MSR) is discussed. The special attention is paid for the solubility of  $\text{PuF}_3$ ,  $\text{UF}_4$  и  $\text{AmF}_3$  in the eutectic salt system 46.5LiF-11.5NaF-42KF (FLiNaK) which is necessary for the fast molten salt reactor operation with U-Pu fuel cycle<sup>1,2</sup> or reactor for minor actinides afterburning<sup>3</sup>.

The solubility of individual actinide fluorides, as well as the joint solubility of  $\text{PuF}_3$  and  $\text{UF}_4$  at 550-700 °C were experimentally established by the method of isothermal saturation of the FLiNaK molten salt. The obtained values are presented in table 1.

Таблица 1. Solubility of actinide fluorides in the FLiNaK salt system

Temperature, °C	Individual solubility, mol. %			Joint solubility, mol. %		
	$\text{AmF}_3$	$\text{PuF}_3$	$\text{UF}_4$	$\text{PuF}_3$	$\text{UF}_4$	$\Sigma(\text{PuF}_3 + \text{UF}_4)$
550	24,5±1,2	6,1±0,6	15,3±0,8	1,2±0,1	1,8±0,1	3,0
600	34,7±1,7	11,1±1,1	24,6±1,2	2,9±0,3	3,5±0,5	6,4
650	44,8±2,2	21,3±2,1	34,8±1,7	13,2±1,6	11,0±1,6	24,2
700	24,5±1,2	32,8±3,3	44,7±2,2	19,1±2,3	17,3±2,6	36,4

The high solubility of the fluorides of actinides in this molten salt in combination with other physical and chemical characteristics makes a FLiNaK as one of the promising for the molten salt reactor.

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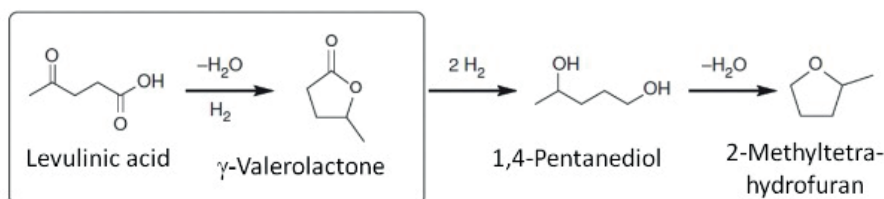
*This work was supported by the State Atomic Energy Corporation ROSATOM.*

## HYDROGENATION LEVULINIC ACID USING RUTHENIUM CATALYSTS ON THE BASIS OF HYPER-CROSSLINKED POLYSTYRENE AND ZEOLITES

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Catalytic hydrogenation of levulinic acid (LA) with the formation of gamma-valerolactone (GVL) is one of the most promising reactions for the transformation of lignocellulose biomass into products of fine organic synthesis and liquid transportation fuels. LA can be transformed into 2-methyltetrahydrofuran (2-MTHF). 2-MTHF is allowed to mix up to 70% with gasoline without harming internal combustion engines, and thus a similar mileage is achieved. There is the possibility of direct conversion of LA to 2-MTHF, but improved product yields can be achieved by indirect routes, which proceed via the production of GVL as an intermediate.



At present, different catalysts based on noble metals deposited on organic and inorganic supports are used for hydrogenation of LA. The highest GVL yields can be achieved using Ru-containing catalysts, e.g. 5%-Ru/C.

Series of catalysts based on Ru and  $RuO_2$  nanoparticles impregnated into the matrix of hyper-crosslinked polystyrene (HPS) and also zeolite ZSM-5 were synthesized in the framework of this study at variation of metal content and reduction method. Obtained catalysts were tested in the reaction of selective hydrogenation of LA. It was found that the catalysts 5%-Ru/HPS and 3%-Ru/ZSM-5 allow the hydrogenation of LA in an aqueous medium with the achievement of high GVL yields (more than 99%) and can compete with the catalyst 5%-Ru/C.

*The work was supported by the Russian Foundation for Basic Research, project 18-58-80008.*

# **RADIATION DESTRUCTION OF EXTRACTANTS BASED ON CROWN ETHERS: THE ROLE OF MECHANISM OF METAL CATION EXTRACTION**

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Design of efficient and radiation resistant extractants for the selective removal of radionuclides from liquid radioactive wastes is one of the challenges in modern nuclear technology<sup>1</sup>.

Basic scenarios of radiation destruction of the macrocyclic component forming part of the extractants based on crown ethers (CE) are considered in the present study. These scenarios depend on the mechanism of interphase transport of metal cations<sup>2</sup> ( $\text{Me}^{n+}$ ). In the first case, the radionuclides are extracted from nitric acid media by CE solutions in traditional diluents or hydrophobic ionic liquids (IL). This process results in accumulation and radiolysis of neutral  $\text{CE} \times \text{Me}^{n+} (\text{NO}_3^-)_n$  complex. In the second case, when using hydrophilic IL as a diluent, the transfer of  $\text{Me}^{n+}$  into extractant occurs by a cation exchange mechanism. Accordingly, macrocyclic  $\text{CE} \times \text{Me}^{n+}$  cations and anions originated from the IL ( $\text{PF}_6^-$ ,  $\text{NTf}_2^-$  and so forth) are irradiated in organic phase. In the third case, in metal-free conditions, the organic phase is saturated with  $\text{H}_3\text{O}^+ \text{K}^+ \text{A}^-$  complexes. The nature of anion  $\text{A}^-$  under these circumstances may be varied as a function of diluent nature. In all situations considered here, the mechanism of macrocyclic component radiolysis<sup>3</sup> is strongly different from currently accepted concepts based on irradiation of metal-free and unprotonated CE solutions, in which the actual chemical composition of the extractant composition were ignored.

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## PHYSICO-CHEMICAL APPROACHES FOR OPTIMIZATION THE PARAMETERS OF PEROVSKITE SOLAR CELLS

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In the last decades, numerous studies on renewable energy are focused on the development of perovskite solar cells (PSCs) based on hybrid organic-inorganic materials, such as  $\text{CH}_3\text{NH}_3\text{PbX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ), which allow to achieve high power conversion efficiency (PCE) using cheap manufacturing technology<sup>1,2</sup>. However, the behavior of PSCs under low levels of solar radiation has not been studied in detail yet, while it is of prime importance for operating of solar cells in real weather conditions especially in the European and northern parts of the Russian Federation. In this work, we developed physico-chemical approaches, which allowed to optimize the structure and parameters of the PSCs and to improve PCE values at low light intensities.

We have fabricated and investigated a series of PSCs with the structure glass/FTO/ $\text{TiO}_2$ / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-MeOTAD/Au, for which the photovoltaic parameters were obtained at different light intensities (10-1000  $\text{W/m}^2$ ) and impedance spectroscopy measurements were provided. The effect of the following factors on the PSC performance was studied: 1). The ratio of the rutile to anatase phases in mesoporous  $\text{TiO}_2$  layer; 2) The introduction of a buffer layer at the  $\text{TiO}_2$ /perovskite interface to passivate the recombination processes; 3). The doping of perovskite material with potassium ions.

The data obtained revealed a major impact of the above mentioned factors on the PCE of PSCs. It was found that the performance of PSCs under low illumination intensities was enhanced after the introduction of a buffer layer at the  $\text{TiO}_2$ /perovskite interface.

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## MESOPOROUS $\text{TiO}_2$ -B NANOTUBES DOPED WITH VANADIUM: SYNTHESIS AND ELECTROCHEMICAL PERFORMANCE

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The rapid progress in a number of high-technology areas, such as hybrid and electric vehicles, renewable energy sources, uninterrupted power supplies, etc. demands an acceleration of designing advanced lithium-ion batteries (LIBs). One of the major obstacles for large-scale usage of traditional LIBs with the carbonaceous anode in these applications is limited operating parameters (namely, low charge rate, narrow operating temperature range, and insufficient security). Recently, titanium-based compounds (mainly  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{TiO}_2$ -B) having a potential of about 1.5 V vs.  $\text{Li/Li}^+$  and increased structure stability during cycling are under intensive research as promising replacements for the carbon anode. However, lithium titanate possesses an insufficient specific capacity (175 mA·h/g). Hence, at present more attention is paid to bronze titanium dioxide ( $\beta$ -phase  $\text{TiO}_2$  or  $\text{TiO}_2$ -B), the theoretical capacity of which reaches 335 mA·h/g. An important factor distinguishing the  $\beta$ -phase of titania from other polymorphs is pseudo-capacitance character of guest ions incorporation, which is not limited by solid-state diffusion. Unfortunately,  $\text{TiO}_2$ -B has wide band gap (3.0–3.2 eV) and, hence, poor electrical conductivity ( $\sim 10^{-12}$  S/cm) hampering its application as LIBs anode. Newest studies have been devoted to improve the electronic properties of  $\text{TiO}_2$ -B. And, as expects, the combination of approaches based on morphology tailoring and doping is one of the most promising ways in this regard.

Within this study, the results of doping mesoporous  $\text{TiO}_2$ -B nanotubes with vanadium will be presented, the relationship between the dopant concentration and the electrochemical properties of obtained materials will be demonstrated, and the nuances of heterovalent cationic substitution in the structure of  $\text{TiO}_2$ -B will be discussed.

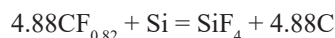
*This work was supported by the Russian Science Foundation, grant 19-73-10017.*

## FORMATION OF SILICON-CARBON NANOCOMPOSITES FOR NEGATIVE ELECTRODES OF LI-ION BATTERIES

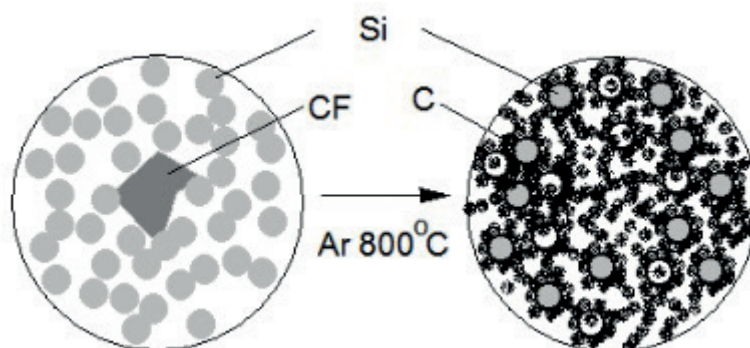
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A new simple method for carbonization of nanosilicon is proposed by interacting it with polymer carbon monofluoride (CF<sub>x</sub>)<sub>n</sub> [1]. The process involves the compression of a mixture of Si nanopowder with fluorocarbon and the subsequent annealing of the resulting tablet in an inert atmosphere. In the course of annealing, the fluorocarbon is disproportionated to form volatile carbon fluorides interacting with silicon particles. The total reaction can be written as



Heterogeneous reactions developing in the mixture are exothermic and lead to almost complete reduction of carbon from its fluorides. In this case, the reacted part of the silicon is removed in the form of gaseous SiF<sub>4</sub>, which increases the total porosity of the tablet. Since the reactions take place on the surface of the silicon particles, a carbon shell appears around each of them, and when a sufficient amount of carbon is emitted, a connected conductive network forms in the material.



The density, porosity, structure and resistivity of the obtained nanocomposite were determined depending on the composition of the initial mixture. The electrochemical characteristics of the negative electrodes of lithium-ion batteries made of this material have been studied.

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## THE HYDROGENATION-DEHYDROGENATION THERMODYNAMICS AND KINETICS OF THE POLYCYCLIC AROMATICS AND NITROGEN-CONTAINING HETEROCYCLES

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The rapid development of renewable energy supports for the gradual replacement of traditional energy sources with renewable energy (RE) ones. Perspectives for the use of alternative energy sources are directly related to the researches for effective ways of accumulation, storage and release of this energy. One of the solutions to this problem is the usage of a new energy carrier – hydrogen. The most perspective technology for storage, transportation and usage RE from hydrogen is the use of organic compounds that can accumulate hydrogen, forming chemical bonds with it. Liquid organic hydrogen carrier (LOHC) compounds suppose the cycle «accumulation – generation of hydrogen», could be repeated many times.

It was proved, that aromatic compounds and nitrogen-containing heterocycles are promising LOHC. Mostly, chemical reactions of hydrogenation-dehydrogenation (HYD-DEHYD) for these classes are reversible and occur in the presence of catalysts. It is obvious, that the choice of preferred LOHC should be based on the thermodynamic analysis of the system consisting of two forms of substrates – saturated and unsaturated.

This research summarizes the results of studies of the thermodynamics and kinetics of the HYD-DEHYD reactions of aromatic and nitrogen-containing compounds performed in the laboratory of advanced technologies in the Samara state technical university and available literature data. The chemical equilibrium of HYD-DEHYD reactions data was compared with reliable thermochemical data and theoretical calculations based on composite quantum chemical methods. Good consistency of the results was found. The reliable approaches were developed for predicting the thermodynamic characteristics of HYD-DEHYD reactions for new compounds of interest as a promising LOHC. The obtained results were discussed from the point of view of the «structure-property» concept.

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## THERMODYNAMICS OF THE VOLOXIDATION PROCESS OF NITRIDE SPENT NUCLEAR FUEL

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Currently, a new, nitride nuclear fuel is being developed, which in the future should replace the oxide fuel currently used. The likely composition of the nitride fuel may be, for example,  $0.85\text{UN} + 0.15\text{PuN}$  or  $0.8\text{UN} + 0.2\text{PuN}$ . At the same time, a technology is being developed to reprocess this spent nitride nuclear fuel (SNF). One of the likely first stages of processing may be voloxidation, i.e. oxidation of SNF by air, oxygen, ozone or other agents in order to transfer the SNF to the oxide form.

The purpose of this work is the thermodynamic simulation of nitride SNF voloxidation.

Using the HSC Chemistry 9.6 software package, thermodynamic modeling of the nitride SNF voloxidation process was performed depending on the temperature and oxidizer composition. The results are shown in Fig. 1.

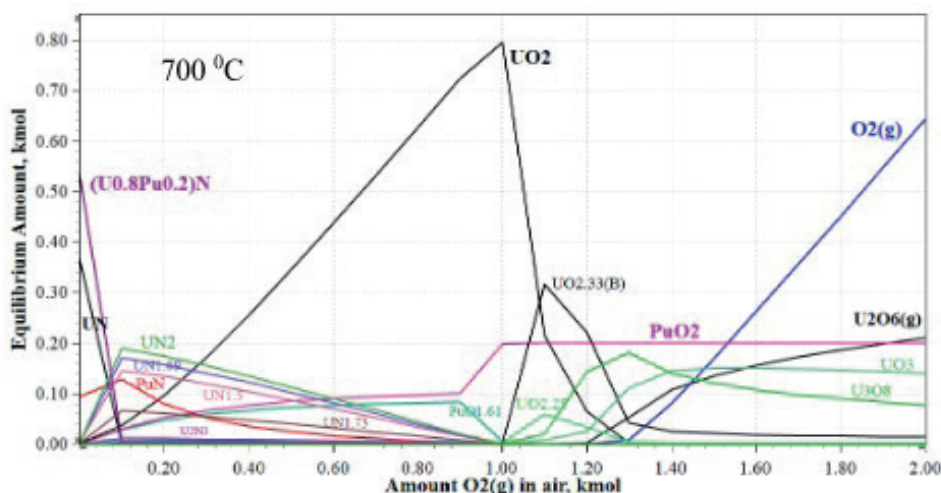


Figure 1. Equilibrium composition of nitride SNF during its oxidation by air

Simulation revealed that the voloxidation products have a complex composition, which depends on the amount of oxidizing agent. Simulation allows you to choose the optimal conditions (temperature, amount and composition of the oxidizer) of the process.

## STRUCTURED CATALYSTS FOR THE OXIDATIVE CONVERSION OF HYDROCARBONS INTO SYNTHESIS GAS

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Despite the growth in the production and consumption of energy from renewable resources (solar-wind energy, the use of biomass), the active distribution and introduction of various appropriate devices for generating and storing energy, it is predicted that for many decades more fossil resources (crude oil and natural gas) will form the basis of global energy consumption. Increasing the efficiency of using hydrocarbons while improving performance (an important factor for the end user) is associated with the use of fuel cells and hydrogen storage technologies for the needs of distributed energy.

One of the niches of using electrochemical generators based on kilowatt class fuel cells with a hydrocarbon fuel processor is the main or backup power supply of both stationary and mobile objects demanded in remote regions of the Russian Federation - the Arctic and the Far East. Compared to thermoelectric, gasoline and diesel power generation units, electrochemical devices, with comparable mass and dimensional characteristics, have significantly higher efficiency, low noise, longer period of maintenance cycle.

The work will consider the latest achievements in the development of catalytic processes of partial oxidation, steam, autothermal conversion of liquid and gaseous hydrocarbons, which are effective methods for producing syngas or hydrogen-containing gas for use in fuel cells. Catalysts deposited on composite supports (honeycomb structure from a FeCrAlloy wire mesh with an oxide surface layer) provide controlled reaction conditions throughout the reactor volume (Fig.1). Being its structural element, they provide effective heat and mass transfer, low gas-dynamic resistance and high performance, which allow reducing the amount of catalyst per unit volume of the reactor.



Fig.1 The overview of catalytic structured modules

*This work was conducted within the framework of the budget project # AAAA-A17-117041710088-0 for Boreskov Institute of Catalysis*

## TRANSMUTATION OF METAL TECHNETIUM AND PRODUCTION OF ARTIFICIAL STABLE RUTHENIUM

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A long-lived nuclide  $^{99}\text{Tc}$  is accumulated in a significant amount in the NPP fuel. The most promising way of isotope  $^{99}\text{Tc}$  de-activation is its irradiation-induced transmutation into short-lived and stable isotopes of ruthenium, rhodium and palladium. The transmutation of technetium will result in a valuable product that is artificial stable ruthenium.

Data are summarized on the development of production technology for the artificial stable ruthenium by neutron transmutation of technetium. The key production technology parameters were calculated: the required neutron flux density and spectrum, requirements to the preliminary purification of technetium from actinides and further purification of ruthenium from technetium, minimal admissible and optimal burnups. Metal technetium foil was irradiated at the thermal neutron flux of  $(0.68 \div 1.14) \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ . According to the emission spectra and spectrophotometric analysis, the irradiated samples of metal technetium had burnups 19%, 45% and 70%  $^{99}\text{Tc}$ . There have been developed two different charts of chemical treatment of irradiated technetium targets being Tc-Ru alloys. The charts consist of the dissolution of irradiated technetium targets, separation and refinement of technetium and ruthenium and production of artificial metal ruthenium. The first chart uses potassium periodate as an oxidizing agent. The second chart is based on the oxidizing dissolution of alloy Tc-Ru with ozone using cations-accelerants (Ag(II), Co(III)). The achieved total coefficient of ruthenium purification from technetium made up  $(3 \div 5) \times 10^{12}$ . Once the fission  $^{106}\text{Ru}$  decays in 8-10 years after irradiation, the produced artificial ruthenium will be suitable for use with no limitations.

## MODERN TECHNOLOGY REPROCESSING SNF

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Active development of nuclear technologies is a global trend related to the sustainable development of the world community. The concept of uranium and plutonium reuse in nuclear power engineering proposed in the Russian Federation is based on the developed technology of spent nuclear fuel (SNF) processing with subsequent disposal and final disposal of radioactive waste (RW).

The challenges of the XXI century are the search for new and optimization of modern technologies of SNF recycling of a wide range with an increase in the volume of its processing, the final disposal of accumulated RW with the extraction of valuable components from them.

Much attention is paid to the development of low-acid technology of SNF processing using Fe(III); CARBEX-process based on the dissolution of uranium oxide and MOX fuel processing in carbonate media.

There was a modernization of the PA «Mayak». Optimization of processes of processing of defective and non-reprocessed SNF of power, transport, research reactors, critical and subcritical stands, ground stands-prototypes of ship and space power plants is carried out.

Performed the removal and processing of spent fuel from RBMK and MOX-fuel. The storage reservoir for reception of long domestic and foreign assemblies has been reconstructed. For the first time in the world the stand on cutting and pedaling of assemblies of SNF from AMB is created.

New technologies for processing complex compositions (UZr, UN, UC) are being created. The nomenclature of target radionuclides from high-level waste (HLW) is being expanded with further sales in the markets.

Solve the environmental problems of the prohibition of emissions in the open waters. The technology of concentration and separation of noble radioactive gases is developed. The construction of a furnace for immobilization of current and accumulated RW from the “old” defense programs has been completed. Tested a technology of solidification of HLW in borosilicate glass. A variant of extraction of the cesium-strontium fraction of HLW, which does not require deep burial, has been worked out. Promising and alternative technologies of radioactive waste immobilization into advanced solid matrices, for example, “cold ceramics”  $\text{KMgPO}_4$  are considered.

## THE ALUMINUM-ION BATTERY – MATERIALS AND PERSPECTIVE

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The expansion of renewable energies and the growing number of electric vehicles and mobile devices demand for improved and low-price electrochemical energy storage with highest energy densities, readily available raw materials, and safety. Prospectively, lithium, cobalt and phosphorous may show substantial supply challenges. Therefore, the search for new chemistries will become increasingly important in order to diversify battery technologies.

Using a selection algorithm<sup>1</sup>, for evaluation of suitable materials, the concept of a rechargeable aluminum-ion and thus high-valent ion all-solid-state battery appears promising. Metallic aluminum is used as the negative mass. This offers the advantage of a four times higher volumetric capacity compared to the lithium analogue. So far, the technological potential has not been exploited, as suitable materials are still lacking<sup>2</sup>. With crystallochemical analyses<sup>2,3</sup>, we identify and present promising material candidates (e.g.  $\text{AlVO}_3$ ,  $\text{Al}_2\text{Se}_3$ , or  $\text{AlI}_3$ ), and discuss the current state of the aluminum-ion battery.

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## NOVEL MEMBRANES FOR ACID GASES SEPARATION

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Nowadays, the acid gases (like CO<sub>2</sub>, H<sub>2</sub>S, and others) are quite successfully separate from natural and synthesis gas, as well as exhaust gases from power plants by using a chemical amines absorption. Unfortunately, this commercial process has a number of environmental and economic disadvantages. An alternative to sorption methods could be “green” membrane methods.

In recent years, the ionic liquids which are has lower (or even close to zero) volatility with its low toxicity in a case of green ionic liquids becomes more and more interesting for the acid gases separation due to its higher sorption ability for these gases<sup>1</sup>. Moreover, its usage in membrane technologies has a high commercial potential due to ability of realizing of facilitated transport, which realization in membranes shows outstanding results on selectivity and permeability compared to traditional polymer membranes.

The purpose of this work was to examine and compare among themselves the various options for membrane evolution of acid gases separation by using novel membrane materials. Firstly, novel supported ionic liquids membranes (SILMs) were obtained by immobilizing ionic liquids into a polymer support<sup>2</sup>, but their low stability is the main limitation for commercialization. Also, membranes based on polymeric ionic liquids, which have a high selectivity and permeability compared with polymeric membranes, coupled with enhanced performance properties, have been studied. And also there were design a hybrid process for the acid gases separation – membrane-assisted gas absorption, in which new membranes were tested. The process showed a high separation capacity at larger values of a stage cut compared with the traditional membrane gas separation, not only for the case of separation of individual gases, but also for separation of binary and ternary gas mixtures.

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## ABOUT RESEARCHING POSSIBILITIES OF IMPROVING THE ENERGY CHARACTERISTICS OF SOLID PROPELLANTS

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For high-speed aircraft (FV), flying in the earth's atmosphere, the most promising engines are ramjet engines (Ramjet). At the same time, it is a great interest to use solid propellants in these engines, which has higher performance compared to liquid ones.

The report presents a comparative analysis of the possibilities of different propellants and fuels that can be used in FV with Ramjet. As a criterion of propellant efficiency, are considered not its separate characteristics, but the flight performance characteristics (FPC) of the FV on which the propellant is used. The best propellant is propellant that provides the achievement of the highest FPC for the FV performing a specific flight mission. A complex mathematical model including mathematical models of FV, its engine and propellant is used for the analysis of FPC. FPC calculation is made for the flight of FV on a typical trajectory for flight mission.

In order to increase the energy capabilities of solid propellant in its composition, as it is possible increases the path of combustible components and reduce the amount of oxidizer used in the propellant. As a result, such propellant burns in the conditions of deficiency of thermal energy. Therefore, it is desirable to use as oxidizer compounds that could be source of heat and oxygen in one time.

For these purposes, we consider the use of polyazide compounds with high enthalpy of formation. The report provides information about new types of poliazide compounds and their characteristic. The poliazide compounds are discussed as possible compounds for FV propellants.

On the basis of poliazide compounds, it is possible to create «green» propellants that have acceptable energy characteristics for use in FV and do not damage the environment.



# **THERMAL STABILITY OF CROWN ETHER COMPLEXES WITH ALKALINE EARTH METAL CHLORIDES: EFFECT OF METAL CATIONS**

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Macrocyclic complexes of crown ethers (L) with alkaline earth metal (AEM) salts are considered as precursors in the processes of vapor-phase deposition of organometallic species (MOCVD)<sup>1</sup>, promising solid electrolytes<sup>2</sup>, constituents of crowned ionic liquids<sup>3</sup> and electrolytes being an alternative to the lithium-based composition<sup>4</sup>. Functional characteristics of the macrocyclic complexes,  $\text{Me}^{n+} \cdot \text{L} \cdot n\text{A}^-$ , when using in these fields, are defined by their behavior and stability under heating. In turn, the thermal properties of  $\text{Me}^{n+} \cdot \text{L} \cdot n\text{A}^-$  compounds presumably depend on  $\text{Me}^{n+} \cdots \text{L}$  и  $[\text{Me} \cdot \text{L}]^{n+} \cdots n\text{A}^-$  interactions and the nature of these components. Nevertheless, the effects of these factors on thermal stability of the macrocyclic complexes in homologous series were not investigated systematically.

Stereoisomeric complexes of dicyclohexano-18-crown-6 with AEM chlorides were synthesized in this study, and their TGA/DSC analysis unexpectedly demonstrated an increase in melting points and thermal stability in the following order:  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ . Moreover, a change in destruction channels was revealed. These results in combination with FTIR data allowed us to find a correlation between the thermal stability of the macrocyclic complexes and increase in  $\text{Me}^{n+} \cdots \text{O}$  and  $[\text{Me} \cdot \text{L}]^{n+} \cdots \text{A}$  interactions and to propose a mechanism of the destruction.

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## THE ELECTRODE PROCESSES IN METHANESULFONIC ACID

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The study of electrode reactions in methanesulfonic acid solutions and methods for its preparation are of great practical importance in the process of obtaining various substances and modern materials<sup>1-4</sup>. In this work, we investigated the electrode processes in a solution of methanesulfonic acid on a smooth platinum (Pt) electrode in a wide range of anodic potentials and in the presence of organic substances: ethanol (Fig. 1), hexanol-1, and cellulose.

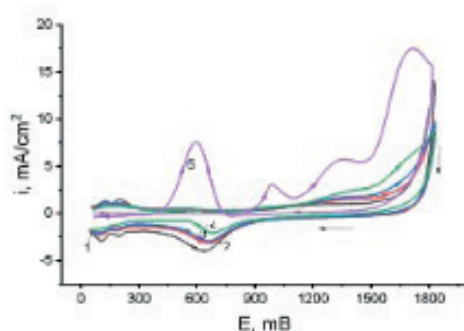


Figure 1. CVA of a smooth Pt-electrode in a 1.0 M solution of MSA (1) and in the presence of ethanol, M: 0.0001 (2); 0.001 (3); 0.01 (4); 0.1 (5).

It was found that ethanol oxidation in the cathode potential sweep range of 400–760 mV is associated with the discharge of oxygen-containing particles on platinum, and three oxidation waves in the anode potential sweep range are associated with  $C_2H_5OH$  oxidation to aldehyde -  $CH_3COH$  (0.8–1.1 V), acid- $CH_3COOH$  (1.15-1.4 V) and gases -  $CO_2$  and  $C_2H_6$  (1.45-1.8 V).

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## THE INFLUENCE OF THE QUASI-SOFTENING EFFECT ON THE FORMATION OF SCALE ON THE SURFACE OF HEAT EXCHANGERS

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When water is used in heat-and-power engineering, the formation of calcium carbonate sediments is the main one in the formation of scale, which has a negative effect on the operation of heat exchangers.

The purpose of this work was to study the processes of membrane and reagent water treatment, which allow practically without reducing the water hardness to reduce the formation of scale on the walls of heat exchangers<sup>1</sup>.

In the process, water treatment methods using microfiltration membranes and activating additives, such as ferric compounds and sodium bicarbonate, which promote the crystallization of hardness salts (calcite) in the form of aragonite and reduce the formation of scale, were investigated. Studies on the effects of microfiltration and activating additives on the formation of scale and on the shape of hardness salt crystals indicate that microfiltration and reagent treatment do not lead to a change in water hardness, but the subsequent heating of this water practically does not lead to the formation of scale. The discovered effect, called “quasi-softening”, was previously noted when filtering through a polymer with a spatial-globular structure<sup>2</sup> and is explained by the fact that as a result of microfiltration, as well as reagent treatment, conditions are created for the formation of needle-like aragonite having a bad adhesion to the substrate, weak adhesion among themselves and capable of being in solution for a long time<sup>3</sup>. In this case, the hardness salts in the water do not form dense deposits on the tubes of the heat exchangers.

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## PECULIARITIES OF PHYSICO-CHEMICAL PROPERTIES IN GALLIUM DOPED PEROVSKITE-LIKE COBALTITES

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Among the topical issues of modern energy, the problem of environmentally friendly generation and efficient accumulation of electricity remains steadily leading. One of the principal directions in the development of this subject is the creation of materials with optimal characteristics for the functional components of intermediate-temperature solid oxide fuel cells (IT SOFC).

Nowadays perovskite-like cobaltites based on  $\text{PrBaCo}_2\text{O}_{6-\delta}$  due to the exceptionally high values of both ionic and electronic conductivity are of great research interest as cathode materials. However, high values of thermal expansion coefficients, due to a wide range of oxygen nonstoichiometry, impose restrictions on the practical application of these compounds. An effective method to vary the functional properties of materials is the introduction of other cations into the crystal structure. The purpose of this research was to study the effect of small additions of gallium in the cobalt sublattice on thermal expansion, as well as the basic physicochemical properties of  $\text{PrBaCo}_2\text{O}_{6-\delta}$ .

It was shown that the formation of solid solutions in the system  $\text{PrBaCo}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$  occurs at a gallium concentrations not exceeding 12.5 at. % per cobalt sublattice. X-ray diffraction and EDX confirmed the introduction of gallium into the  $\text{PrBaCo}_2\text{O}_{6-\delta}$  lattice. It is worth mentioning, the density of oxide ceramics obtained increases significantly while the magnetic moment of the samples tends to decrease. Thermogravimetric measurements showed a decline in the oxygen content in  $\text{PrBaCo}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$  with increasing x. Dilatometric experiments did not reveal significant changes in the thermal expansion of oxides; however, their electrical conductivity increased significantly, which opens up prospects for further study of  $\text{PrBaCo}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$  materials as cathodes for IT SOFC.

## TRANSPORT PROPERTIES OF SOLID OXIDES



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Strontium ferrite based perovskites are promising materials that demonstrate high ionic and electronic conductivity in mixed oxides and therefore can be potentially used as cathode and anode materials in SOFC

However, the development of new electrode materials requires a deep understanding of the nature of charge transfer in materials and the mechanisms of action on their properties.

This paper is devoted to the study of structure, transport properties, thermal expansion and equilibrium of defects in solid solutions  $\text{Nd}_x\text{Sr}_{1-x}\text{Fe}_{0.8}\text{Mo}_{0.2}\text{O}_{3-\delta}$  ( $0 \leq x \leq 0.2$ ).

According to the results of X-ray diffraction,  $\text{Nd}_x\text{Sr}_{1-x}\text{Fe}_{0.8}\text{Mo}_{0.2}\text{O}_{3-\delta}$  ( $0 \leq x \leq 0.2$ ) form a series of solid solutions with a perovskite structure of rhombohedral symmetry (space group  $R\bar{3}c$ ).

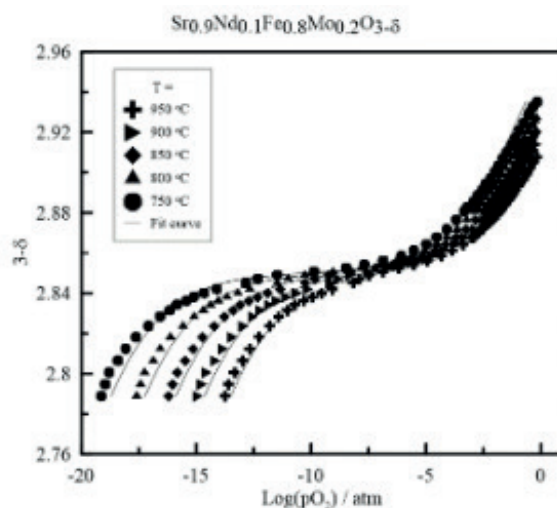


Figure 1. Dependence of oxygen nonstoichiometry on the partial pressure of oxygen

Oxygen nonstoichiometry of  $\text{Nd}_x\text{Sr}_{1-x}\text{Fe}_{0.8}\text{Mo}_{0.2}\text{O}_{3-\delta}$  oxides was determined by the methods of thermogravimetric analysis and coulometric titration.

## NANOSTRUCTURED CARBON FOR ADVANCED LEAD-ACID BATTERIES: PROPERTIES AND INFLUENCE ON ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF NEGATIVE ELECTRODE

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The use of valve-regulated lead-acid (VRLA) batteries in hybrid electric vehicles and as energy storage for renewable energy sources places high demands on the VRLA from the point of view of improving cycleability at high rate-partial state of charge (HRPSoC) conditions. The effect of carbon additions on reducing the sulfation of negative plates and significantly improving the cycleability and charge acceptance of VRLA was demonstrated<sup>1</sup>.

Two types of carbon materials were synthesized and characterized: multi-walled carbon nanotubes (“Art-nano” NSU “S” (TU BU 690654933.001.-2011)) and multilayer graphene (“Art-nano GT” (TU BU 691460594.004-2017)).

Table 1. Characteristics of carbon materials

“Art-nano” NSU “S”	“Art-nano GT”
Diameter nanotubes – 10-50 nm; Number of walls – 10-20; Specific surface – 65 m <sup>2</sup> ·g <sup>-1</sup>	Layer thickness – 20-30 nm; Number of layers – 20-30; Specific surface – 40 m <sup>2</sup> ·g <sup>-1</sup>

The investigated carbon additives were introduced in the amount of 0.5, 1.0, 1.5 wt.% into the active mass of the negative electrode. Testing of the electrodes was carried out in the model of a lead-acid battery. It was found that the introduction of carbon additives increases the discharge capacity and the utilization of the active mass of the negative electrode by 10-15%. The processes occurring at the border of the lead electrode / electrolyte were studied by the method of impedance spectroscopy, and the elements of the proposed equivalent circuit were calculated. The study of the structural characteristics of negative electrodes by the method of contact reference porosimetry showed that the introduction of carbon additives increases the total porosity, the specific surface of the electrodes and the proportion of the smallest pores.

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## A NEW HIGH-PERFORMANCE METAL-FREE ELECTROCATALYST FOR HYDROGEN-EVOLUTION REACTION ON BASE OF THE ACRIDINE DERIVATIVES IMMOBILIZED ON CARBON MATERIALS

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The report presents the data obtained in the study of the adsorption of acridine (I) and its derivatives 9-phenylacridine (II) and N-methyl-9-phenylacridium iodide (III) on carbon materials (Vulcan XC-72 (VU)) as well as the electrochemical properties of the resulting systems. Immobilization of compounds I, II or III on the surface of carbon materials will allow to obtain unique catalytic materials in which the catalysts will form a monolayer due to saturation of the surface, which will lead to an increase in the efficiency of the catalytic process as compared to homogeneous conditions. It has been shown that the adsorption of compounds I and II is a structurally dependent process that depends on the presence of functional substituents on the molecule, and the adsorption of compound III has a complex mechanism and partially flows through the stage of stabilization of the compound on the surface of the material due to the presence of functional groups. Using quantum chemical calculations, it has been shown that the adsorption of compounds I, II and III on graphite-like sections by the  $\pi$ - $\pi$  stacking mechanism is not realized, due to the discrepancy between the energy of the boundary orbitals and adsorbate. The electrochemical characteristics of organic compounds immobilized on a carbon material were determined by cyclic voltammetry. Electrochemical data have shown that for all immobilized compounds, a linear dependence  $\log I_p$  vs  $\log v$  with a slope close to 1, which is characteristic for systems in which the limiting stage is the transfer of an electron from the electrode surface to the catalyst, rather than the charge transport between the redox centers. The modified carbon electrodes with compounds I and II demonstrate a high electrocatalytic activity for production of molecular hydrogen from  $H^+$  ions and the chemical stability for a long time.

*The work was supported by the Russian Foundation for Basic Research, project 18-03-00211 .*



## «MOLECULAR PLATFORM» BASED ON ACRIDINE - NEW «METAL-FREE» CATALYTIC SYSTEMS FOR HYDROGEN EVOLUTION REACTION

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“Molecular platforms” based on organic derivatives of acridine can be easily transformed by point functionalization, which allows “tuning” the value of redox potentials, as well as the basicity of the catalyst. The report presents the data obtained in the study of electrocatalytic activity in a new class of catalysts for the hydrogen evolution reaction- organic compounds based on acridine derivatives. We have studied in detail the influence of the nature of the acid on the efficiency of the electrocatalytic process in the presence of N-methyl-9-phenylacridium iodide (1), 9-phenylacridine (2) and acridine (3) (Fig. 1).

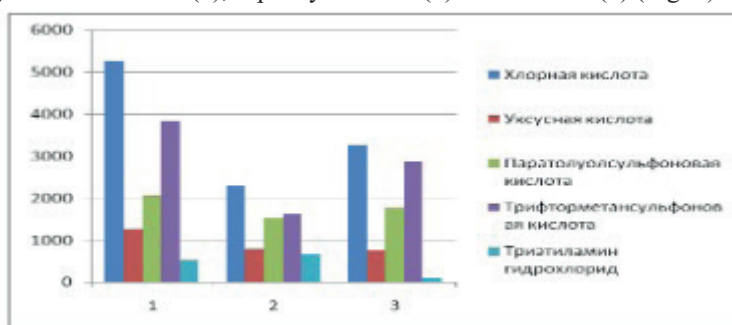


Fig.1 TOFmax values for PhAcrl (3), PhAcr (2) Acr (1) systems in the presence of acids

As can be seen from Fig.1 N-methyl-9-phenylacridium iodide has the highest electrocatalytic activity, and the efficiency of the catalytic process strongly depends on the pK of the acid used. The key stage of the catalytic process is the acid-base equilibrium between the electrochemically generated base (radical) and the corresponding acid. It can be assumed that by rational design of the molecular core of the acridinyl cation, the basicity of the nitrogen atom can be increased, which should lead to a decrease in the energy of formation of the radical cation and, as a consequence, to an increase in the rate of formation of molecular hydrogen.

*The work was supported by the Russian Foundation for Basic Research, project 18-03-00211 .*

# INFLUENCE OF THE STRUCTURE OF NICKEL POLYMER COMPLEXES WITH SCHIFF ON THE REDUCTION OF THE ELECTROACTIVITY OF POLYMER FILMS IN THE PRESENCE OF LEWIS BASES IN A BACKGROUND ELECTROLYTE SOLUTION

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Polymeric complexes of transition metals with Schiff-bases are promising materials for modification of nanoporous carbon supercapacitor electrodes [1] that have several strong advantages over non-modified electrodes: for example, reversible electrochemical oxidation in a wide range of potentials, unique thermal stability up to 350 °C and great redox and electric conductivity [2], which provides a high speed charge transfer

The mechanism of degradation was studied in electrolytes containing of additions of various Lewis acids. Besides pyridine was added to electrolyte, because the additive is an external ligand that does not oxidize at a given potential range. In this work the cyclic voltammetry (CVA) and electrochemical quartz microbalance (EQCM) were used. The degradation rate was calculated from the loss of useful capacitance of the polymer at the 50<sup>th</sup> discharge cycle.

In the result was determined by CVA method that the addition different Lewis bases to the background electrolyte solution, lead to a sharp increase in the oxidation charge on the anode branch of the current-voltage curve. The nature of such a change in the current-voltage response (the magnitude of the change in the peak and its shape) in all cases depends both on the structure of the complex and on the structure of the Lewis base added to the electrolyte. This suggests the possibility of practical use of polymer films of nickel from the Schiff base as amperometric sensors for various Lewis bases, such as, for example, biogenic amines.

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# PHYSICO-CHEMICAL PROPERTIES OF $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ AND DEVELOPMENT OF THE COMPOSITE ELECTRODES ON ITS BASIS WITH $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ ELECTROLYTE

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Synthesis and study of physical and chemical properties of new cathode materials with layered structure and electrodes development on their basis is a very promising direction of modern researches in the field of solid oxide fuel cells. As the object of this research layered misfit phase  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  (Ca349) was selected. This material is known for its thermoelectric properties. The Ca349 oxide has a low LCTE value ( $9\text{--}10 \times 10^{-6} \text{ K}^{-1}$ ), which makes it compatible with many SOFC electrolytes. The using of this material as cathodes was began to develop relatively recently[1].

In the present work, the structure and physico-chemical properties of Ca349 oxide were investigated. The study of electrochemical behavior of the composite electrodes on Ca349 basis with a proton-conducting electrolyte  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (BCZYYb) was performed.

Synthesis of materials Ca349 and BCZYYb was carried out by glycerol and citrate-nitrate methods. The phase composition and crystal structure of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  powders were investigated by XRD. Crystal structure parameters were refined by the Rietveld method.

According to X-Ray data data, the obtained materials were single-phase. Chemical interaction of materials in the temperature range 800 – 900°C (studied by contact annealing) was not found.

Electrochemical properties of the BCZYYb-Ca349 electrodes (in mass. percent's: 70:30, 60:40, 50:50, 40:60, 30:70, 0:100) was studied by electrochemical impedance. The optimum temperature of the functional layers heating is established, the influence of different collectors is investigated, the optimal electrode design for use in the SOFC is revealed.

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## **$\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$ : CORRELATION BETWEEN SYNTHESIS CONDITIONS AND PHYSICO-CHEMICAL PROPERTIES**

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To the present date, oxides with the double perovskite structure  $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$  have been successfully tested as anode materials for solid oxide fuel cells. The aim of this work is to study the effect of the composition of the redox mixture during the synthesis of  $\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$  on the pyrolysis course and physico-chemical characteristics of the target oxide.

The  $\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$  samples were obtained by pyrolysis of glycine- and glycerin-nitrate solutions by varying of the pyrolytic mixture composition (a set of R and  $\phi$  parameters). On the dried after pyrolysis films  $\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$  a study of the thermochemical generation process was performed. The resulting powders were annealed in air at temperature 1100°C, then pressed into compact samples, which were annealed at 1300°C.

X-ray studies of the samples were carried out in air at 298 K on the DRON-6 diffractometer in the angle range of  $20 \leq 2\theta \leq 90$  in Cu/K $\alpha$  radiation. Thermogravimetric studies of the samples were performed in air and in the reducing atmosphere using Netzsch STA 449F3.

The conductivity of the samples was measured by a four-probe method at a constant current in the air at temperature range of 300–850°C using an automatic system Zirconia-318. Linear expansion of the samples was studied by dilatometric method in air and in the reduction atmosphere using Netzsch DIL 402 PC in the temperature range 200–800°C.

According to the thermodynamic stability and electroconductivity and thermal expansion measurements data study, the optimal pyrolytic mixture composition at the  $\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$  synthesis was established. From the practical use as anode materials for SOFC point the  $\text{Sr}_2\text{Ni}_{0.7}\text{Mg}_{0.3}\text{MoO}_6$  samples were optimally synthesized via the glycerol-nitrate method, with pyrolytic parameters of the mixture R=0 and  $\phi=3$ .

*The work was partly financially supported by RFBR, projects №18-33-00544, 19-03-00230.*

## SYNTHESIS AND TRANSPORT PROPERTIES OF COMPLEX OXIDES $\text{BaLaM}_x\text{In}_{1-x}\text{O}_4$ WITH RUDDLESDEN-POPPER STRUCTURE

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Currently, as part of the development of the concept of hydrogen energy, the priority is given to the work of the creation of fuel cells (FC), which will allow the use of hydrogen for electricity production. The fuel cell consists of two electrodes and a membrane with electrolytic conductivity. There is an active search for ways to convert most energy-intensive industries, including transport, to hydrogen fuel and electrochemical generators based on the use of fuel cells.

Although in the second half of the twentieth century, scientists and technologists have advanced far enough towards the development of practical devices, but their widespread use is still not implemented. This is primarily due to the fact that the materials do not allow creating a long-term device. The main problem is the choice of technological and inexpensive solid electrolyte with high ionic conductivity, stable in both oxidizing and reducing atmosphere, reliably coupled with an extensive complex of physical, chemical, mechanical and functional characteristics with electrodes and connectors.

Currently, the global trend is the development of medium-temperature FC (500-700°C). Most of the known medium-temperature proton conductors are complex oxides with perovskite or perovskite-like structure. However, in recent years, the studies have been conducted showing the possibility of ion transport in complex oxides based on  $\text{BaNdInO}_4$ , characterized by the structure of Ruddlesden-Popper.

In the present work new complex oxides  $\text{BaLaIn}_{0.9}\text{M}_{0.1}\text{O}_{4.05}$  (M=Ti, Zr) were obtained. The structure and transport properties were examined.

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## STABILITY OF BOROHYDRIDE FUELS IN THE PRESENCE OF TRANSITION METAL IMPURITIES

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Alkaline solutions of some borohydrides ( $\text{LiBH}_4$ ,  $\text{NaBH}_4$  and  $\text{KBH}_4$ ) can be used as fuel in low-temperature fuel cells (direct borohydride fuel cells DBFC) and in hydrogen generators (HG). In such devices, the fuel is a suspension or concentrated alkaline solution, where hydroxide ions stabilize the system, preventing hydrolysis  $\text{BH}_4^-$ . Fuel stability is important both for the efficient operation of DBFC and for the development of hydrogen storage technologies.

Currently, a significant amount of work is devoted to the study of the properties of alkaline aqueous solutions of borohydrides. Special attention is paid to the study of hydrolysis kinetics of ions  $\text{BH}_4^-$  in solution and the influence of various factors (temperature, pH, impurities) on this process. Borohydride fuel is prepared on industrial equipment, while various contaminants are possible, the most likely of which are having catalytic activity of metal.

The influence of small amounts of the Fe, Co and Ni impurities on the spontaneous hydrolytic process of borohydride was studied in the temperature range of 60-100 °C. The object under study was a model solution containing 9.53 M of  $\text{OH}^-$  and 0.14 M of  $\text{BH}_4^-$  ions, used as fuel for borohydride fuel cells. The composition of the working solution during storage was determined by quantitative chemical analysis (acid-base and iodometric titration). Direct experimental data on the decomposition rate of solutions containing ions  $\text{BH}_4^-$  and  $\text{OH}^-$  with metal impurities measured at several temperatures, allowed us to estimate the values of the process rate constants, the activation energy and the maximum permissible concentration of impurities of each metal, which does not affect the self-decomposition rate of borohydride. The catalytic effect of Fe, Co and Ni impurities on the hydrolysis process is established, but the kinetic regularities of this process in the presence of Fe, Co and Ni impurities do not change. The catalytic activity of these metals increases in the order  $\text{Fe} < \text{Co} < \text{Ni}$ .

## DEVELOPMENTS OF PERSPECTIVE MONOLITH OXID CATALYSTS FOR AUTONOMOUS CATALYTIC AIR HEATERS

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Catalytic air heaters are an autonomous source of heat and an alternative solution to the conventional central heating. Those devices are using to provide heat to houses, industrial premises in the field, to agricultural enterprises (heating greenhouses, etc.).

The basis of the work is the use of energy released during the exothermic reaction of complete oxidation of hydrocarbon fuels on the catalyst. Used chromium catalysts do not meet sanitary safety requirements due to the content of Cr (VI). Modern studies in this field are directed to create highly active and environmentally friendly catalysts, with appliance of non-traditional preparation methods.

The aim of the work is to develop the efficient and stable catalysts based on  $Mn_xO_y$ ,  $La_2O_3$  and  $Ce_xO_y$  supported on ceramic honeycomb monoliths.

The specific task of the work is the investigation of influence of the preparation methods (impregnation method, "solution-combustion synthesis" method (SCS)) on the physicochemical properties of catalysts and the catalytic activity in the complete butane oxidation reaction.

The SCS catalysts exhibit significantly higher catalytic activity and stability of operation in comparison with the impregnation analogue, due to the formation of reduced forms of manganese oxides, the enrichment of the support pores with manganese component (up to 94% SCS method, no more than 55% impregnation method), a decrease of the aggregates size of active component particles (8-30 nm SCS method, 15-100 nm impregnation method) and its stabilization.

Developed La-Mn/AlSi-5gl, Ce-Mn/AlSi-5gl catalysts are superior in activity to Cu-Cr/ $Al_2O_3$ , used in catalytic air heaters ( $T_{50\%}$  is 308, 285 and 405 °C, respectively) and are environmentally safe due to the absence highly toxic Cr (VI) compounds.

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DEVELOPMENT OF FURFURAL AND LEVULINIC ACID  
HYDROCONVERSION OVER NICKEL PHOSPHIDEGolubeva M.A.,<sup>a</sup> Maximov A.L.<sup>a,b</sup><sup>a</sup>*A.V.Topchiev Institute of Petrochemical Synthesis RAS,  
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The search of alternative energy sources relates to the need of taking it from unlimited resources. Important factors in this search are environmental friendliness and economy. Biomass may be used as an alternative source for the production of fuels and chemicals. The main structural components of biomass are cellulose (38-50%), hemicellulose (23-32%) and lignin (15-30%). Cellulose is a linear polymer which consists of  $\beta$ -glucose residues. Hemicellulose is a branchy polymer which consists of residues of different hexoses and pentoses, principally xyloses. Lignin is an amorphous polymer, which structural units are coumaryl, coniferyl and sinapyl alcohols<sup>1</sup>.

One of the main products of hemicellulose acid-catalyzed processing are furfural and levulinic acid. In present work, hydrogenation processes of these substrates over *in situ* and *ex situ* generated unsupported nickel phosphide were developed.

Table 1. Results of furfural and levulinic acid hydroconversion over  $\text{Ni}_x\text{P}_y$  catalyst

Solvent	Furfural		Levulinic acid	
	Conversion, %	Products	Conversion, %	Products
Ethanol	98	ethyl levulinate	100	ethyl levulinate, $\gamma$ -valerolactone ethyl valerat
Toluene	93	tetrahydrofurfuryl alcohol, 2-methylfuran	97	$\gamma$ -valerolactone, valeric acid

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## PHOTOELECTROCATALYTIC ACTIVITY OF NEW GENERATION COATINGS FROM NANOSIZED TITANIUM DIOXIDE DOPED BY BISMUTH AND LEAD IN VISIBLE LIGHT REGION

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Fujisima and Honda were the first to use  $n$ -TiO<sub>2</sub> for photoelectrochemical decomposition of water upon irradiation with ultraviolet light [1]. An increase in the efficiency of photocatalytic and photoelectrocatalytic oxidation of various substrates on  $n$ -TiO<sub>2</sub> is associated primarily with an increase in the visible light absorption by photocatalyst ( $\lambda = 400\text{--}780$  nm) for a more complete use of solar radiation, as well as decrease in the rate of recombination of photogenerated electron-hole pairs.

A method for the preparation of film coatings of titania, doped with bismuth (Bi<sup>3+</sup>) and lead (Pb<sup>2+</sup>) ions, separately and simultaneously, has been developed based on sol-gel synthesis. These films represent a single-phase system of titanium dioxide in anatase modification. The film coatings have been studied as catalysts of photoelectrooxidation of methanol, formic acid, and phenol under visible light illumination. It should be noted that non-doped titania films didn't exhibit activity in this region of spectrum [2].

It has been assumed that photoelectrochemical oxidation of the mentioned model systems with visible light is due to a decrease in the band gap of doped titania to 2.7 eV.

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## SYNTHESIS AND STUDY OF CATALYTICALLY ACTIVE SOL-GEL-DERIVED $\text{SiO}_2\text{@Pt/Pd}$ COMPOSITES

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One of the promising ways of research is the synthesis of catalysts of metal nanoparticles of mixed composition, which include various noble metals, particularly Pt/Pd bimetallic nanoparticles. Different methods of synthesis allow one to acquire nanoparticles of different structures: «core-shell», alloy with intermetallic compound or cluster-in-cluster, mixture of individual crystallites<sup>1</sup>. The sol-gel synthesis is one of many methods used to generation of Pt/Pd bimetallic nanoparticles<sup>2</sup>. This method used to acquire platinum and palladium catalysts for gas sensors and electrochemical devices.

In this work presents the results of a study of the structure of xerogels and thin films prepared from silica sols containing platinum and palladium compounds by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was determined that nanoparticles consist of the crystallites with a common bimetallic Pt/Pd lattice. The size of crystallites formed in xerogels is 10-18 nm and of the ones formed in films is 5-6 nm. The possibility of the formation of colloidal crystals and mesocrystals is discussed.

Optimal ratios of platinum and palladium in  $\text{SiO}_2\text{@Pt/Pd@C}$  sol-gel-derived composites, which providing maximum catalytic activity as catalyst layers in hydrogen-air solid-polymer fuel cells were found.

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## RESEARCH OF COMPOSITE CATHODES OF LITHIUM CELLS FOR HIGH-POWER CONSUMERS

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Currently, in a number of areas of science and technology, there is an urgent need to create high-energy and powerful miniature chemical current sources. Such current sources can be widely used in medical equipment, such as endoscopic video capsules and cardioverter-defibrillators, as well as in various autonomous measuring instruments. In these devices in the period of shooting, discharging, polling sensors and transmitting information, the current source operates in a hard pulse mode. The main requirement for the current source in this mode is the minimum voltage drop at the output terminals when it generates a high-current pulse. Currently, for high-current pulsed modes, for example, cardioverter-defibrillators use lithium cells with cathodes based on  $\text{Ag}_2\text{V}_4\text{O}_{11}$ . The lithium-fluorinated carbon system has a high capacity, but due to low electrical conductivity it can not be discharged by high current densities.

In this work, in order to increase the cathode specific power, it is proposed to use the nanodispersed  $\text{Ag}_2\text{V}_4\text{O}_{11}$  compound, synthesized in NRU «MPEI» by the original method. The assembly of high-current lithium chemical current sources mockups was carried out in a three-electrode polypropylene cell, the ratio of the components of the active mass was varied in a wide range. A multichannel potentiostat-galvanostat Elins P-20X8 was used to simulate the discharge process. The discharge was carried out in a pulsed mode. It has been established that composite fluorocarbon electrodes containing the additive  $\text{Ag}_2\text{V}_4\text{O}_{11}$  have higher polarization characteristics and an advantage over traditional fluorocarbon electrodes in the initial stages of the pulsed mode. In turn, the specific capacity of the proposed cathodes is higher than that of industrial designs for cardioverter-defibrillators. The proposed electrodes can be used in various samples of autonomous medical devices, including cardiac pacemakers with advanced functionality, cardioverter-defibrillators and gastroscopic video caps.

## PHYSICAL-CHEMICAL PROPERTIES OF PARAFFIN EMULSIONS. PROMISING PHASE CHANGE MATERIALS

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Paraffin emulsions are promising substance for Phase Change Materials (PCM)<sup>1</sup> - a substance with a high heat of fusion which, melting and solidifying at a certain temperature, is capable of storing and releasing large amounts of energy. When such a material freezes, it releases large amounts of energy in the form of latent heat of fusion, or energy of crystallization. Conversely, when the material is melted, an equal amount of energy is absorbed from the immediate environment as it changes from solid to liquid.

By means of ultrasonic dispersion and subsequent filtration through filters with a pore size of 0.45  $\mu\text{m}$ , 0.2  $\mu\text{m}$  and 0.1  $\mu\text{m}$  the emulsions of pure n-alkanes (from  $\text{C}_{19}\text{H}_{40}$  to  $\text{C}_{28}\text{H}_{58}$ ) in water without the addition of surfactants were prepared. The radius of the emulsion droplets was measured by dynamic light scattering. The average hydrodynamic radius of the emulsions was from 45 to 150 nm, depending on the filter used in the preparation, and the zeta potential was from -20 to -50 mV. Using the previously proposed method<sup>2,3</sup> for determining the temperature of phase transitions of paraffins in emulsions, based on measuring the temperature dependence of the intensity of scattered light, the temperature of melting, crystallization and crystal-crystal transition temperatures (rotator phases) were determined for the emulsions under study. The phase transition temperatures thus determined for the n-alkanes under study coincide with the known literature data. For the emulsion with the smallest droplet size (radius 45 nm), there is a strong overcooling of paraffin droplets in the emulsion. Apparently, this is a «finite-size effect».

We showed that light scattering techniques could be able not only to measure the cluster size in the paraffin emulsions but even to determinate the phase transitions temperatures, actual task for scientific communities such as the one involved in the study of the Phase-change material (PCM) products.

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## STUDY THE DEPENDENCE OF THE ZETA-POTENTIAL ON pH OF THE SYSTEM FOR DISPERSION IN WATER OF PURE $C_{23}H_{48}$ (TRICOSANE) AND $C_{28}H_{58}$ (OCTACOSANE) n-ALKANES

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This work presents the results of studies of aqueous dispersions of pure n-alkanes  $C_{23}H_{48}$  and  $C_{28}H_{58}$  prepared without the use of surfactants. Samples were prepared by ultrasonic dispersion and remained stable throughout the year. The average radius of paraffin particles in the dispersion, measured by the method of dynamic light scattering (DLS), is about 100 nm.<sup>1,2</sup> Paraffin dispersions (emulsions) are promising substance for Phase Change Materials (PCM) - a substance with a high heat of fusion which, melting and solidifying at a certain temperature, is capable of storing and releasing large amounts of energy.<sup>3</sup> When such a material freezes, it releases large amounts of energy in the form of latent heat of fusion, or energy of crystallization. Conversely, when the material is melted, an equal amount of energy is absorbed from the immediate environment as it changes from solid to liquid. This property of PCMs can be used in a number of ways, such as thermal energy storage whereby heat or coolness can be stored from one process or period in time, and used at a later date or different location. PCMs are also very useful in providing thermal barriers or insulation, for example in temperature controlled transport.

To study the stability of the prepared samples the electrophoretic light scattering method was used, the zeta potential of dispersions was measured as a function of the system pH. Zeta-potential measurements were carried out with the Photocor Compact-Z (Russia) commercial setup. In a neutral media, the zeta potential of the studied dispersions is about -50 mV, which is a surprising result for an oil-water system without the addition of surfactants. After the conducted studies, it can be concluded that small changes in pH do not almost affect the zeta potential of paraffin particles. The decline to zero of the zeta potential occurs in strongly acidic and strongly alkaline environments. At the same time, it was not possible to observe changes in the sign of the charge of paraffin particles in a wide pH range.

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## CONDUCTIVITY AND TRANSPORT NUMBERS IN FILMS OF PROTON ELECTROLYTE $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$

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Development of efficient and environmentally friendly ways of energy generation which include energy production using solid oxide fuel cells (SOFCs) is one of the priority trends in the global energy sector.

One of the most important requirements to the electrolyte for SOFCs is high ionic conductivity and stability in operation conditions. From this viewpoint,  $\text{SrZrO}_3$ -based proton electrolytes are considered as promising materials.

Using of film electrolytes allows reducing SOFC operation temperature due to the ohmic losses reducing, that is why significant efforts are currently focused on the film cells development. In SOFCs, an electrolyte film is usually deposited on a supporting electrode that suggests a high temperature processing of the refractory solid oxide film on the electrode which is necessary for fabrication of the gas-tight film membrane. Obviously, that at high temperatures the interaction between the film and substrate is activated which can lead to degradation of the film electrolyte and SOFC. Therefore, study of the effect of interaction between the film electrolyte and the supporting electrode on charge transport in the electrolyte is an important task.

In this study, electrical conductivity and ionic transport numbers ( $t_i$ ) in  $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$  (SZY) film electrolyte deposited on Ni-YSZ supporting electrode (YSZ is  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ ) under SOFC operation condition were measured. 2.5- $\mu\text{m}$ -thick films were obtained by chemical solution deposition which allows obtaining of gas-tight films at relatively low temperatures ( $\leq 1000^\circ\text{C}$ ). Measurements were performed using a gas concentration cell fed with wet air and hydrogen. The ionic transport numbers in the film electrolyte were found to be slightly less than those in a massive ceramic electrolyte of the same composition: 0.96 и 0.99, respectively, at  $700^\circ\text{C}$  and  $p\text{H}_2\text{O}=2.3$  kPa in the gaseous fuel and oxidant. One of the reasons for  $t_i$  decreasing in the film electrolyte was supposed to be Ni diffusion from the substrate.



## FACTORS DETERMINING THE ELECTROCHEMICAL BEHAVIOR OF THE CALCIUM-DOPED LANTHANUM NICKELATE BASED ELECTRODES

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Lanthanum nickelate  $\text{La}_2\text{NiO}_{4+\delta}$  with a layered perovskite-like structure and solid solutions based on it in recent years are the subject of attention in connection with the possibility of their use as oxygen electrodes in electrochemical devices - solid oxide fuel cells and electrolyzers.

$\text{La}_2\text{NiO}_{4+\delta}$  is characterized by the values of the coefficient of surface oxygen exchange  $k$  and the diffusion coefficient  $D^*$ , which are close to the cobaltites of rare and/or alkaline-earth elements. The temperature coefficient of linear expansion  $\text{La}_2\text{NiO}_{4+\delta}$  allows you to successfully apply this material in combination with many well-known solid electrolytes.

Despite the advantages, the electronic conductivity of the layered lanthanum nickelate  $\text{La}_2\text{NiO}_{4+\delta}$  (60–80 S/cm at 700 °C) is insufficient for the cathode to work effectively. An increase in the electronic component of the conductivity of nickelates is possible by doping lanthanum with calcium,  $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ .

The purpose of this work is a systematic study of the effect of doping of lanthanum nickelate with calcium on the structural, thermomechanical and transport properties and the determination of factors affecting the electrochemical response of electrodes based on them.

It is established that the introduction of calcium stabilizes the crystal structure in the tetragonal syngony. Despite the increase in the electrical conductivity of the material with increasing calcium content, the electrochemical activity of the electrodes based on  $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$  decreases.

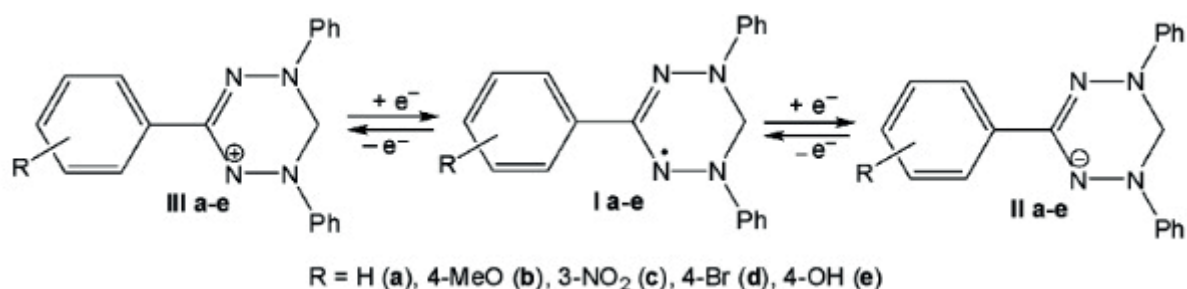
TRIPHENYLVERDAZIL RADICALS – REDOX-ACTIVE  
COMPONENTS OF ORGANIC RADICAL BATTERIES

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Stable radicals are of considerable interest as electroactive materials for organic radical batteries (ORB)<sup>1</sup>. Their main advantages are low cost and the possibility of changing the redox properties of the introduction of various substituents at the different positions.

We have synthesized a series of asymmetric verdazyl radicals<sup>2</sup> (I a-e) capable of multiple reversible redox-transformations:



Electrochemical properties were investigated using the method of cyclic voltammetry. All studied radicals are redox-active in both the cathode and anodic regions. It is shown that the substituents in the phenyl ring strongly influence the values of the reduction potentials: the donor substituents shifts the potential to the cathode region while the acceptor to the anodic region. In the anodic region, one-electron reversible waves are also observed for all compounds; however, unlike the reduction processes, the substituent's have weak effect on the value of the oxidation potentials.

Thus, it was shown that the studied verdazyl radicals are promising compounds for further use in ORB. Moreover, by varying the substituents in the benzene ring, the values of the electrochemical gap can be governed.

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## PERSPECTIVES OF $\text{Ln}_3\text{Mo}_5\text{O}_{16}$ ( $\text{Ln}=\text{Pr}, \text{Nd}$ ) FLUORITE-LIKE MOLYBDATES AS ELECTRODE MATERIALS FOR SOFC

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Complex oxides with perovskite structure are commonly used as electrode materials for solid oxide fuel cells (SOFCs). However,  $\text{Ln}_3\text{Mo}_5\text{O}_{16+\delta}$  ( $\text{Ln}=\text{Pr}, \text{Nd}$ ) oxides with fluorite structure may be considered as alternative electrode materials. The  $\text{Ln}_3\text{Mo}_5\text{O}_{16+\delta}$  phases are mixed conductors and have oxygen-ion conductivity which exceeds the electronic one in the range of high oxygen partial pressures and reaches 0.01 S/cm at 973–1073 K<sup>-3</sup>. Thermal expansion coefficient (TEC) of these compounds is similar to one for conventional solid electrolytes of SOFCs. Thereby, the purpose of this work was to study the availability of using  $\text{Ln}_3\text{Mo}_5\text{O}_{16+\delta}$  ( $\text{Ln}=\text{Pr}, \text{Nd}$ ) as electrode materials for SOFCs.

Investigation of high-temperature conductive and thermochemical properties of molybdates showed that conductivity enhances at change of ambient gas atmosphere from air to reducing conditions ( $\text{Ar-H}_2$ ) and reaches 1.2 S/cm at 1073K as well as chemical activity relative to  $\text{Pr}_6\text{O}_{11}$  and conventional solid electrolytes of SOFCs –  $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  under oxidizing and reducing conditions is absent. In order to evaluate the possibility of electrocatalytic activity increasing in oxygen reduction reaction, the electrochemical properties of molybdate–xGDC and molybdate– $\text{xPr}_6\text{O}_{11}$  composite electrodes were studied in air. It was shown for the first time that the composites based on praseodymium molybdate and  $\text{Pr}_6\text{O}_{11}$  exhibit the highest electrochemical performance among the investigated composite electrodes (the transition from the pure  $\text{Pr}_3\text{Mo}_5\text{O}_{16+\delta}$  electrode to the  $\text{Pr}_3\text{Mo}_5\text{O}_{16+\delta}$  – 50 wt. %  $\text{Pr}_6\text{O}_{11}$  composite reduces polarization resistance by one order of magnitude to 0.6  $\Omega\cdot\text{cm}^2$  at 1073K in air). The data obtained point out the perspective of the proposed fluorite-like molybdates as electrode materials of SOFCs.

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## ELECTROCHEMICAL INSERTION OF LITHIUM AND SODIUM INTO PHOSPHORUS SULFIDE

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The search for new functional materials for chemical power sources is an urgent task of electrochemical energy. In the present work, we have synthesized composites based on phosphorus sulfide and carbon ( $P_xS_y@C$ ). Synthesis of  $P_xS_y@C$  was carried out in an atmosphere of argon at a temperature of 470 °C for 2 hours. The stoichiometric mixtures of red phosphorus and sulfur were used as starting reagents. Two types of carbon black with different specific surface area: Ketjen Black-300 (KB-300) and Ketjen Black-600 (KB-600) were used as a carbon substrate.

For physico-chemical and electrochemical characterization of the synthesized samples scanning electron spectroscopy, Raman spectroscopy, electron dispersion analysis, cyclic chronopotentiometry were used.

As a result, the synthesized composites were found to have the composition  $P_4S_3@C$ , and the morphology of the synthesized samples is determined by the morphology of the carbon substrate.

Electrochemical tests showed that lithium and sodium are capable of being reversibly incorporated into the synthesized composites. The reversible capacity for lithium insertion at a current density of 250 mA/g was about 550 and 660 mAh/g for  $P_4S_3@KB-600$  and  $P_4S_3@KB-300$ , respectively. Reversible capacity when introducing sodium in  $P_4S_3@C$  was much lower and for both composites did not exceed 300 mAh/g.

### *Acknowledgments*

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## STUDY OF THE MICROSTRUCTURE OF SOLID ELECTROLYTES WITH HIGH LITHIUM ION CONDUCTIVITY

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The dependence of the ionic conductivity of solid electrolytes with the NASICON structure the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  composition (LATP) and with defect-perovskite structure the  $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$  composition (LLT) on their microstructure was studied in order to obtain samples with maximum Li-ion conductivity.

Scanning electron microscopy (SEM LEO-420) was used to study the microstructure of LATP and LLT ceramics formed during classical high-temperature sintering of powders synthesized by sol-gel method<sup>1,2</sup>. The grain size of LATP ceramics and the microstructure evolution are evaluated using the Scan Master program designed for mathematical processing of SEM images. During the analysis of the microstructure of LLT ceramics using the Scan Master program as the evaluation criterion was chosen pore area. Differential curves of pore area distribution are obtained.

The grain size of the ceramics with increasing sintering temperature in the 1100-1300°C range increases to more than 10 µm, which indicates a significant grain growth in the sintering process. As a result of high-temperature sintering, the formation of LLT ceramics with a homogeneous microstructure consisting of extended areas with weakly expressed grains, grain boundaries and few pores is shown. The influence of microstructure on reduction of grain boundary resistance and increase of ionic conductivity of LATP and LLT ceramics is established. These results correspond to the mechanism of ionic conductivity in polycrystalline solid electrolytes<sup>3</sup>.

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## GERMANIUM NANOFILAMENTS AS ANODIC MATERIAL FOR LITHIUM-ION BATTERIES

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As we know germanium - one of the promising material for negative electrode in lithium-ion batteries.<sup>1</sup>

In this study, the electrochemical deposition of germanium was carried out in a three-electrode cell. A titanium plate etched with indium nanoparticles was used as the working electrode; the counter electrode was a platinum plate, and the saturated calomel electrode served as a reference electrode. The pH of the solution was adjusted to 6.5 by the addition of  $\text{NH}_4\text{OH}$ . The current densities of the germanium deposition were about 0.1, 0.5 and 2  $\text{mA}/\text{cm}^2$ .

Electrochemical testing of electrodes was carried out in hermetically sealed three-electrode elements with a counter-electrode and a reference electrode made from metal lithium. The electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate – diethyl carbonate – dimethyl carbonate (1: 1: 1).

SEM data indicate that the synthesized samples are filamentous structures with a diameter of from 30 to 60 nm. An increase in current density leads to the formation of germanium filaments of a smaller diameter. Cyclic voltammograms (CVA) of the germanium electrode were recorded at different potential scanning rates in the potential range from 3 to 0.01 V ( $\text{Li}^+/\text{Li}$ ). The reversible capacitances calculated by the area under the anode branches of CVA for a potential scan rate of 0.05  $\text{mV}/\text{s}$  were 740, 650, and 1210  $\text{mAh}/\text{g}$  for samples obtained at current densities of 0.1, 0.5, and 2.0  $\text{mA}/\text{cm}^2$  respectively.

The above permitting to conclude that nanostructured germanium, obtained by electrochemical deposition from an aqueous solution, is a promising material for the anodic electrode of lithium-ion batteries.

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## SOLID SOLUTIONS WITH SCHEELITE STRUCTURE IN THE Ca(Sr)-La(Bi)-Nb(V)-Mo(W)-O SYSTEM

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This work is devoted to the synthesis and study of scheelite-like solid solutions based on alkaline earth metal molybdates (Ca or Sr) or lanthanum niobate.

Samples with the composition  $\text{La}_{1-x}\text{Bi}_x\text{NbO}_4$  ( $0.0 \leq x \leq 1.0$ ),  $\text{LaNb}_{1-y}\text{W}_y\text{O}_{4+\delta}$  ( $y \leq 0.3$ ),  $\text{La}_{1-x}\text{Bi}_x\text{Nb}_{1-y}\text{W}_y\text{O}_{4+\delta}$  ( $x \leq 0.5$ ,  $y \leq 0.2$ ),  $\text{Ca}(\text{Sr})_{1-x}\text{Bi}_x\text{MoO}_{4+\delta}$  ( $x \leq 0.5$ ),  $\text{Ca}(\text{Sr})_{1-1.5x}\text{Bi}_x\text{MoO}_4$  ( $x \leq 0.5$ ),  $\text{Ca}(\text{Sr})_{1-x}\text{Bi}_x\text{Mo}_{1-y}\text{V}_y\text{O}_{4+\delta}$  ( $x \leq 0.5$ ,  $y \leq 0.5$ ),  $\text{Sr}_{1-1.5x}\text{Bi}_x\text{Mo}_{1-y}\text{V}_y\text{O}_{4+\delta}$  ( $x \leq 0.4$ ,  $y \leq 0.2$ ) were prepared by multistep solid state synthesis method. The final products were controlled by XRD method. The concentration boundaries of the areas of single-phase products formation are determined and the x-ray structure characteristics of the samples are calculated. In a series of samples based on  $\text{LaNbO}_4$ , solid solutions have a scheelite-like distorted monoclinic structure at low temperatures ( $\sim 25$ – $500^\circ\text{C}$ ) and a tetragonal structure at higher temperatures. In the  $\text{Ca}(\text{Sr})_{1-x}\text{Bi}_x\text{MoO}_{4+\delta}$  series for all samples, along with the main phase  $\text{Ca}(\text{Sr})\text{MoO}_4$ , bismuth molybdenum compounds are present as impurities, for example,  $\text{Bi}_2\text{Mo}_2\text{O}_9$ ,  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ . For  $\text{Ca}(\text{Sr})_{1-1.5x}\text{Bi}_x\text{MoO}_4$  homogeneity region corresponds to  $x \leq 0.425$ . When two sublattices are replaced, solid solutions  $\text{Ca}(\text{Sr})_{1-x}\text{Bi}_x\text{Mo}_{1-y}\text{V}_y\text{O}_{4+\delta}$  in the entire  $x$  and  $y$  range are formed only for series with calcium molybdenum. In the strontium molybdate series  $\text{Sr}_{1-1.5x}\text{Bi}_x\text{Mo}_{1-y}\text{V}_y\text{O}_{4+\delta}$  solid solutions exist in the ratio  $x=0.2$  and  $y=0.05$ ,  $x=0.3$  and  $y=0.05$ – $0.1$ ,  $x=0.4$  and  $y=0.05$ – $0.2$ . For the  $\text{LaNb}_{1-y}\text{W}_y\text{O}_{4+\delta}$  ( $0.1 \leq y \leq 0.3$ ) and  $\text{Sr}_{1-1.5x}\text{Bi}_x\text{MoO}_4$  ( $0.2 \leq x \leq 0.4$ ) samples superstructural ordering was found. The morphology and surface composition of briquettes and powders were studied by scanning electron microscopy and laser light scattering. The electrical conductivity of complex oxides was investigated by impedance spectroscopy method using an impedance meter Z-3000 and LCR meter (LCR-819) at 1 kHz. With the increase in the concentration of dopants, the modification of the conductive properties of complex oxides, which has its own characteristics for a specific series of samples, is observed.

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## SYNTHESIS AND PROPERTIES OF $\text{Bi}_{26}\text{Mo}_{10}\text{O}_{69}$ SUBSTITUTED WITH NONMETALS

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The present work is devoted to the synthesis and investigation of properties and structure of S-,P- and Sb- substituted bismuth molybdate  $\text{Bi}_{26}\text{Mo}_{10}\text{O}_{69}$ . The  $\text{Bi}_{26}\text{Mo}_{10}\text{O}_{69}$  has unique structure what contains columns  $[\text{Bi}_{12}\text{O}_{14}]_n$ ,  $[\text{MoO}_6]$  polyhedra and isolated Bi ions and shows one-dimensional oxygen-ionic conductivity at mediate temperatures. The  $\text{Bi}_{26}\text{Mo}_{10}\text{O}_{69}$ -based solid solutions crystallizes in monoclinic symmetry at the temperatures above  $\sim 310^\circ\text{C}$ , or it has triclinic distortion below this temperature. Substitution in  $\text{Bi}_{26}\text{Mo}_{10}\text{O}_{69}$  can be realized by doping molybdenum or isolated bismuth positions resulting to the formula  $\text{Bi}_{26-2x}\text{Me}_{2x}\text{Mo}_{10}\text{O}_{69-d}$  or  $\text{Bi}_{26}\text{Mo}_{10-2y}\text{Me}_{2y}\text{O}_{69-d}$ . In this work the solid solutions  $\text{Bi}_{26}\text{Mo}_{10-2y}\text{S}_{2y}\text{O}_{34.5}$ ,  $\text{Bi}_{26}\text{Mo}_{10-2y}\text{P}_{2y}\text{O}_{34.5-d}$  and  $\text{Bi}_{26}\text{Mo}_{10-2y}\text{Sb}_{2y}\text{O}_{34.5-d}$  were investigated. The complex oxide samples have been synthesized using conventional solid state method from metal oxides, and  $(\text{NH}_4)_2\text{SO}_4$  /  $\text{Sb}_2\text{O}_3$  /  $(\text{NH}_4)_2\text{HPO}_4$ . The phase composition was defined by XRPD. The dopant concentration homogeneity ranges were determined to be  $y=0.6-0.7$  for all dopants. The ranges of stabilization of the monoclinic form is observed at  $y>0.4$ . The IR FT spectroscopy and Rietveld full profile structure refinement at XRPD data showed substitution of Mo by S, P and Sb and forming  $\text{SO}_4$  and  $\text{PO}_4$  groups. The laser diffraction and SEM were used for investigation of morphology of powder samples. The geometrical sizes of particles lie in the range of 1-10  $\mu\text{m}$  in powder samples and 50-100  $\mu\text{m}$  in dense ceramic samples. Porosity of samples was examined by hydrostatic weighting and was determined to be less than 5%. Electrical conductivity has been studied using impedance spectroscopy method. The impedance measurements were carrying out in the range of 523-1123 K over the respective frequency ranges 3 MHz to 10 Hz with two Pt electrodes. For analysis of impedance plots the equivalent electrical circuits method was used Zview. According to the results of the impedance measurements the temperature and concentration curves of electrical conductivity were plotted. The maximum of conductivity is  $\sim 10^{-2} \text{ S}\cdot\text{cm}^{-1}$  at 973K and  $\sim 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  at 623K. As a result  $\text{Bi}_{26}\text{Mo}_{10-2y}(\text{S/P/Sb})_{2y}\text{O}_{34.5}$  family can be recommended as a high ionic conductive material.

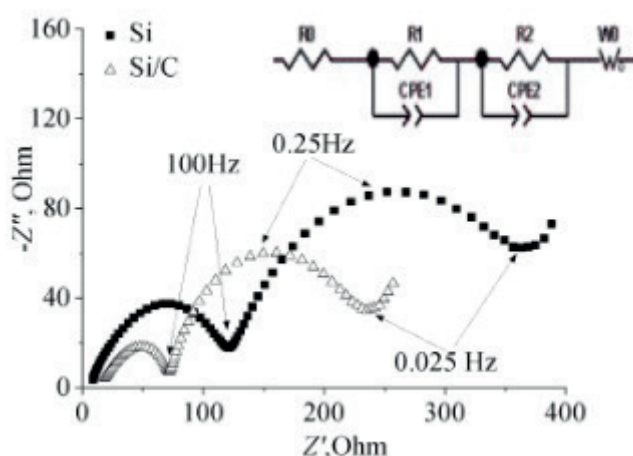
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## INFLUENCE OF CARBONIZATION OF SINTERED SILICON ANODES ON THEIR ELECTROCHEMICAL CHARACTERISTICS

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As was shown in [1], cold compression and high-temperature sintering of a Si nanopowder make it possible to obtain macroporous anodes for high-capacity lithium-ion batteries. This report reports on the properties of such anodes subjected to carbonization by sucrose pyrolysis. It is established that the impregnation of the sintered tablets with a water-alcohol solution of sucrose and the subsequent annealing in Ar allow to obtain a composite material containing 10-15% carbon. Carbonization leads to a decrease in the specific resistance of the tablets from hundreds to 30 Ohm·cm. Galvanostatic studies of the charge / discharge curves of the obtained electrodes in the two-electrode and electrochemical impedance in the three-electrode cells with respect to the lithium counter-electrode were carried out. The introduction of lithium was carried out in the mode of limiting the voltage on the electrode of 10 mV. In fig. impedance hodographs obtained after the first lithiation are shown. Here you can see the corresponding equivalent electrical circuit, where  $R_2 = 220$  and 140 Ohm for the source and carbonized electrodes, respectively. From the impedance spectra, it is concluded that carbonized Si electrodes have lower charge transfer resistance than non-carbonated ones.



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## HYDROTHERMAL SYNTHESIS AND ELECTROCHEMICAL INVESTIGATION OF $\text{KTiPO}_4\text{F}$ AS A CATHODE MATERIAL FOR RECHARGEABLE METAL-ION BATTERIES

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Recently, it has been shown that  $\text{KTiOPO}_4$ -(KTP)-type  $\text{KVPO}_4\text{F}$  can be used as a 4V cathode material for metal-ion batteries<sup>1,2</sup>. However, a significant part of its electrochemical activity related to the  $\text{V}^{+4}/\text{V}^{+3}$  redox couple occurs at 5 V, which is beyond the voltage stability window of conventional electrolytes. This fact frustrates a careful investigation of electrochemical behavior and structural evolution of  $\text{KVPO}_4\text{F}$  under cycling. An isostructural  $\text{KTiPO}_4\text{F}$  with a lower-potential  $\text{Ti}^{+4}/\text{Ti}^{+3}$  redox couple could be an object under investigation in commercial electrolytes avoiding electrolyte degradation processes and revealing all peculiarities of KTP-type electrode materials.

Thus, the goal of this work is to obtain  $\text{KTiPO}_4\text{F}$  and investigate its electrochemical properties as an electrode material for metal-ion rechargeable batteries.

Since  $\text{Ti}^{+3}$ -containing compounds are not easy to synthesize by standard solid-state techniques, a hydrothermal approach was developed for the synthesis of  $\text{KTiPO}_4\text{F}$ . The cell parameters and crystal structure of  $\text{KTiPO}_4\text{F}$  were refined based on XRD data using Rietveld method ( $a = 13.004(3)$  Å,  $b = 6.435(1)$  Å,  $c = 10.764(2)$  Å,  $V = 900.6(4)$  Å<sup>3</sup>):  $\text{KTiPO}_4\text{F}$  crystallize in the orthorhombic symmetry (space group  $Pna2_1$ ) and isostructural to  $\text{KTiOPO}_4$ . The morphology was studied by SEM:

The electrochemical measurements were carried out in potassium cell. It was demonstrated that  $\text{KTiPO}_4\text{F}$  exhibits a reversible electrochemical activity in the 0.6 to 4.5 V vs  $\text{K}/\text{K}^+$ . The cell parameters evolution and the mechanism of  $\text{K}^+$  de/intercalation were investigated by *Operando*-XRD in the potassium cell.

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## DEVELOPMENT AND STUDY OF A PROTON CONDUCTIVE MEMBRANE BASED ON CROSSLINKED POLYVINYL ALCOHOL DOPED $\text{NH}_2\text{SO}_3$ AND $\text{SiO}_2$

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Expensive perfluorinated sulfonic acid membrane is widely used in low-temperature proton-exchange membrane fuel cells (PEMFC). The membrane has a high proton conductivity ( $10^{-2}$  S/cm) in a narrow temperature range of 40-60°C. One of the alternative types of proton-conductive membranes for PEMFC are hybrid membranes<sup>1</sup> based on furfural cross-linked polyvinyl alcohol (PVA) and sulfonic acid.

In this work, proton conductive membranes molded from a material obtained by chemical synthesis in dimethylsulfoxide, including those using the sol-gel technology, were investigated. An analysis of the IR-spectra of the membranes confirmed the formation of water-insoluble, cross-linked of furfural (FUR) PVA doped with aminosulfonic acid (ASA) with and without  $\text{SiO}_2$ . The hybrid PVA/ASA/FUR/ $\text{SiO}_2$  membrane has the best conductivity values among the membranes investigated.

Table. Conductivity values of electrolytic membranes

Name sample	Conductivity of the membranes at 20°C, S/cm	Maximum specific conductivity of «dry» membranes when their heated, S/cm, (temperature, °C)	Maximum specific conductivity of membranes moistened with water when their heated, S/cm, (temperature, °C)
Nafion-115	$5,85 \cdot 10^{-4}$	$1,11 \cdot 10^{-3}$ (50)	$1,40 \cdot 10^{-2}$ (55)
PVA/ASA	$3,40 \cdot 10^{-4}$	$1,31 \cdot 10^{-3}$ (40)	$2,80 \cdot 10^{-2}$ (40)
PVA/ASA/FUR	$4,25 \cdot 10^{-4}$	$1,69 \cdot 10^{-3}$ (80)	$1,76 \cdot 10^{-2}$ (70)
PVA/ASA/FUR/ $\text{SiO}_2$	$5,34 \cdot 10^{-4}$	$2,88 \cdot 10^{-3}$ (90)	$2,35 \cdot 10^{-2}$ (75)

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## ELECTROCHEMICAL ACTIVITY ENHANCING OF $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4$ CATHODE MATERIAL BY MODIFICATION OF THE ELECTRODE/ELECTROLYTE INTERFACE

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Currently, the electrochemical activity enhancement of cathode materials for intermediate-temperature solid oxide fuel cells (SOFCs) is associated with both the application of technological approaches to the microstructure formation of the electrode/electrolyte interface and the employment of methods of its chemical modification. Among the technological approaches, the application of the laser processing technique to creation a given topology of a solid electrolyte surface seems to be very promising. However, the chemical modification of the electrode/electrolyte interface by infiltration of electrocatalytically active additive  $\text{Pr}_6\text{O}_{11}$  is also a very promising way to improve the electrochemical performance of the cathode material. In this work the possibilities of electrochemical activity enhancing in oxygen reduction reaction by employment of the above-mentioned methods on the example of  $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4$  (PLCO)<sup>1</sup> cathode material are considered. It was found that the transition from the initial surface of the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (GDC) solid electrolyte to the modified one by forming an ordered columnar structure with a profile depth of about 11-12  $\mu\text{m}$  provides a double decrease in the polarization resistance of the PLCO cathode (from 0.73  $\text{Ohm}\cdot\text{cm}^2$  (the initial sample) to 0.33  $\text{Ohm}\cdot\text{cm}^2$  (the modified sample) at 710 °C in air). Besides, it was shown in case of infiltration of the electrocatalytically active additive  $\text{Pr}_6\text{O}_{11}$  that the polarization resistance of the PLCO cathode reduces to 0.15  $\text{Ohm}\cdot\text{cm}^2$  at 650 °C in air.

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## OXYGEN PERMEABILITY AND STABILITY OF CERAMIC MEMBRANES BASED ON $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8-x}\text{Al}_x\text{Fe}_{0.2}\text{O}_{3-\delta}$

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High purity oxygen is highly required in different industrial processes. High temperature air separation by using of the dense ceramic membranes is considered as perspective way for obtaining high-purity oxygen. The key properties of these materials are high ambipolar conductivity and density, moderate thermal expansion coefficient and stability at reducing atmospheres.

Complex oxides  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8-x}\text{Al}_x\text{Fe}_{0.2}\text{O}_{3-\delta}$  was synthesized via glycerol-nitric technique with further temperature treatment. The phase attestation and crystal structure parameters were determined by X-ray powder diffraction technique. It was observed that a light substitution of cobalt by aluminum is favorable for gas-tight membranes formation. Oxygen permeability was measured by application of air/Ar and air/water gas gradient atmospheres. Values of oxygen flow about 2.76 ml/(min×cm<sup>2</sup>) was achieved with the use of 1 mm thickness membrane and sweep gas flow 1.6 l/min at 950°C. After water gas treatment thin layer formation of cobalt hydroxide was observed at sweep gas side.

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## DECALIN DEHYDROGENATION OVER SUPPORTED PLATINUM CATALYSTS

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Hydrogen storage by chemical binding in a suitable organic compound, called liquid organic hydrogen carrier (LOHC) – is a perspective not expensive and safe technology providing long-term and lossless energy accumulation, as well as facilitates its transport<sup>1</sup>.

Decalin/naphthalene pair can be considered as an efficient hydrogen carrier, as it meets the requirements of LOHC. Naphthalene hydrogenation to decalin has been studied quite well, while the reverse reaction of dehydrogenation is still actively studied. The development of effective and stable catalysts is one of the most important aspects of technology.

In the present research, the decalin dehydrogenation over Pt-catalysts (2 %wt. platinum) supported on different carriers: Pt/Sup, where Sup – SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SBA-15, MCM-41, and MCM-48. Catalytic tests were carried out on the laboratory catalytic flow type unit with the fixed-bed catalyst at temperatures of 300-335°C, hydrogen pressure of 0.5 MPa, liquid hour speed velocity (LHSV) 12-120 h<sup>-1</sup> and hydrogen to feed ratio of 500 nm<sup>3</sup>/m<sup>3</sup>. The concentration of decalin in the feedstock was 1 %wt.

It was found that the dehydrogenation activity of the synthesized catalysts decreases in the following order Pt/MCM-48 > Pt/SBA-15 > Pt/SiO<sub>2</sub> > Pt/MCM-41 > Pt/Al<sub>2</sub>O<sub>3</sub>. The influence of temperature, pressure, and LHSV on the reaction rate constants was studied.

Presented research shows that Pt-catalysts supported on mesostructured silicates such as SBA-15, MCM-41, MCM-48, exhibit high activity in the decalin dehydrogenation. Obtained results could be used for the development of new technologies for energy accumulation and transportation on the basis of LOHC.

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## APPLICATION FEATURES OF HIGH-TEMPERATURE PROTON-CONDUCTING ELECTROLYTES IN REVERSIBLE SOLID OXIDE CELLS

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Reversible solid oxide cells (rSOCs) based on proton-conducting electrolytes ( $H^+$ ) represent a relatively new and cost-effective possibility for carrying out chemical-to-electrical energy conversion in direct and reverse directions (figure 1) with very high efficiency and low environmental impact. Here we report our findings regarding a modernised approach of rSOC- $H^+$  testing, which differs from the traditional characterisation of electrochemical cells, consisting in volt-ampere measurements and impedance spectroscopy analysis under open circuit (OCV) conditions. Expanding the range of voltage bias from 0.4 to 1.6 V, the designed rSOC- $H^+$  was studied in different (fuel cell, OCV, electrolysis) modes and its performance successfully correlated with ohmic and electrode electrochemical responses depending on the measurement temperature, water vapour partial pressure in oxidant gas and applied bias voltage. This approach allows the main external factors affecting the performance of the rSOC- $H^+$  to be disclosed along with proposed means for its future optimisation in the applied direction.

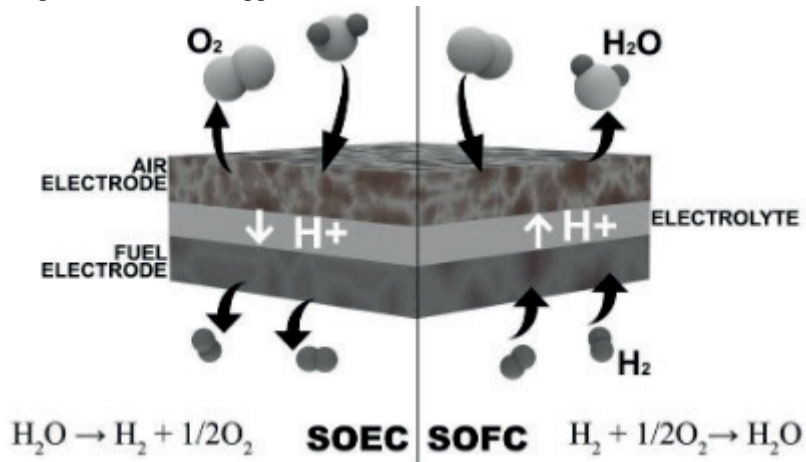


Figure 1. Principal scheme of rSOC- $H^+$  operation: fuel cell and electrolysis cell modes.

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## CONVERSION OF WASTE INTO ELECTRICAL ENERGY THROUGH MICROBIAL ELECTROCHEMICAL TECHNOLOGIES

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The wastewater is potential processing facilities, from which you can receive bioenergy and biochemicals. Wastewater treatment using microbial fuel cells (MFC) is one of the strategies of biological treatment of industrial and agricultural wastewater. Recovery of energy and valuable products can partially compensate for the cost of wastewater treatment and reduce some of the dependence on fossil fuels. The purpose of this work is modeling of process of wastewater treatment by means of mediator microbic fuel elements and also assessment of efficiency of microorganisms (*Escherichia coli*, *Enterobacter cloacae* and *Shewanella xiamenensis*) used as the biocatalyst in the course of bioelectrochemical oxidation of various substrates (glucose, sucrose and citric acid) in neutral environments.

It is shown that methylene blue is reversible redox mediator and can be used in the implementation of a microbial mediator anode based on the studied substrates and cells *Escherichia coli* and *Enterobacter cloacae*. It is shown that the size of its coefficient of diffusion through a cellular membrane of microorganisms of *Escherichia coli* makes  $(4.5 \pm 0.2) \cdot 10^{-7} \text{ cm}^2/\text{s}$  with that diffusion coefficient sizes through a cellular membrane of microorganisms of *Enterobacter cloacae*  $(1.3 \pm 0.3) \cdot 10^{-7}$  of  $\text{cm}^2/\text{s}$  are 3.5 times higher with and, therefore, cell of *Escherichia coli* are more effective biocatalyst the process of oxidation of glucose.

Thus, researches have shown that the model system of the mediator - glucose - cells of *Escherichia coli* is efficient, allows you to reduce the concentration of glucose in the working solution to the background current value, which indicates almost complete purification. The system substrate – cells of *Shewanella xiamenensis* with the addition of a mediator and without is analyzed. When solving practical problems to improve the efficiency of wastewater treatment from organic substances using mediator microbial fuel cells, it is necessary to optimize the bioelectrochemical system both in the concentration of the mediator and in the concentration of bacterial cells, or the concentration of cells should be in excess.

## TRANSPORT AND THERMOMECHANICAL PROPERTIES OF $\text{BaSn}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ PROTON CONDUCTING ELECTROLYTES

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$\text{BaSnO}_3$ -based materials can be applied in a variety of technical fields, such as solar cells, gas sensors and other electrochemical devices. Such materials can demonstrate proton transfer. It makes possible to utilize stannate-based materials in intermediate-temperature solid oxide devices, including fuel cells and electrolyzers. However, information on proton conductivity of stannates is fragmentary.

The aim of this work is revealing the correlations between composition of materials based on Sc-doped  $\text{BaSnO}_3$ , their structure, microstructure, conductivity and thermomechanical properties.

To achieve this aim the following tasks were resolved: synthesis of powder samples, fabricating the ceramic samples and calculating their relative densities, conductivity measurements depending on temperature and water vapour partial pressure, carrying out dilatometric analysis.

The required materials were synthesized via solid state method (calcination temperature - 1100°C, sintering temperature - 1500°C). The phase composition of sintered samples was studied by XRD (X-Ray diffraction).

Electrical properties of the ceramic samples were investigated via 4-probe DC method in oxydizing (air) and reducing (hydrogen) atmospheres in wide ranges of temperatures (500–900 °C) and water vapour partial pressures ( $p_{\text{H}_2\text{O}} = 0.001\text{--}0.30$  atm). It is found that the Sc-doped stannates are characterized by predominant proton transfer in wet hydrogen, proton-hole transfer in wet air at low temperatures, and, finally, ionic( $\text{H}^+/\text{O}^{2-}$ )-hole transfer in oxydizing conditions at higher temperatures.

The dilatometric measurements show that the presence of water vapour in air has an appreciable influence on thermal extension of the samples.

On the base of the obtained results, the conclusions regarding the most perspective representatives of  $\text{BaSn}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$  were made.

## MOLECULAR LAYERING OF NICKEL(II) OXIDE FOR THIN-FILM LITHIUM-ION BATTERIES

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Recently, a large number of studies indicate the promising use of nickel oxide as electrocatalysts, active components of solar cells, chemical sensors, etc. Also, nickel oxide is promising as an anode material for a lithium-ion battery electrode. Nickel oxide has the value of the theoretical electrochemical capacity of 718 mAh / g, which is close to the values for such promising anode materials as  $\text{SnO}_2$  (790 mAh/g),  $\text{CoO}$  (715 mAh/g),  $\text{MnO}$  (650 mAh/g). The capacity of these oxide materials is more than twice the capacity of graphite (372 mAh/g) used in the industry of lithium-ion batteries.

Molecular layering (ML), also known as atomic layer deposition (ALD), is one of the most promising directions for producing homogeneous thin-film electrodes for lithium-ion batteries. In this work, bis(methylcyclopentadienyl)nickel (II) ( $\text{Ni}(\text{MeCp})_2$ ) and bis(cyclopentadienyl)nickel (II) ( $\text{Ni}(\text{Cp})_2$ ) were used as reagents for the synthesis of  $\text{NiO}$  thin films by the ALD method. Oxygen plasma was used as a counter-reactant. The synthesis was carried out in a Picosun R-150 reactor. It was found that the optimal conditions for precipitation for  $\text{Ni}(\text{Cp})_2$  are 200-300°C and for  $\text{Ni}(\text{MeCp})_2$  250-300°C. The obtained electrodes were studied by spectral ellipsometry, scanning electron microscopy, atomic force microscopy, X-ray diffraction, X-ray reflectometry, and X-ray photoelectron spectroscopy. The growth per ALD cycle was 0.011–0.012 nm for both reagents. Films, using  $\text{Ni}(\text{Cp})_2$  and oxygen plasma at 300°C, are polycrystalline with high density (6.9 g/cm<sup>3</sup>) and low roughness.

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## SYNTHESIS AND STUDY NANOCERAMICS FOR MEDIUMTEMPERATURE SOLID OXIDE FUEL CELLS

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An urgent task for alternative energy is the development of ceramic materials for mediumtemperature solid oxide fuel cells (SOFC).

Nanocrystalline powders (8–10 nm) in the systems  $\text{ZrO}_2\text{--HfO}_2\text{--Y}_2\text{O}_3\text{--CeO}_2$  (solid electrolyte),  $\text{NiO--Nd}_2\text{O}_3$  (cathode),  $\text{In}_2\text{O}_3\text{--ZrO}_2$  (interconnector) were obtained by liquidphase synthesis methods and sintered in the temperature range 1200–1400°C (air).

Table 1. Properties of sintered ceramic compositions

Chemical the composition of the ceramics	$P_{\text{open}},$ %	$d_k, \text{ nm}$	$\text{CTE} \cdot 10^6,$ $\text{K}^{-1}$	$\sigma, \text{ Sm} \cdot \text{cm}^{-1}$	
				600°C	800°C
$80\text{ZrO}_2\text{--}8\text{HfO}_2\text{--}7\text{Y}_2\text{O}_3\text{--}5\text{CeO}_2$	~1	70–80	11	$2.34 \cdot 10^{-1}$	1.27
$92\text{In}_2\text{O}_3\text{--}8\text{ZrO}_2$	2–3	70–80	10	$1.07 \cdot 10^2$	$6.75 \cdot 10^2$
$50\text{NiO--}50\text{Nd}_2\text{O}_3$	30–32	50–60	13	$5.03 \cdot 10^2$	$5.03 \cdot 10^2$

Designations:  $P_{\text{open}}$  –open porosity,  $d_k$  –average size of crystallites,  
CTE –coef-ficient of thermal expansion,  
 $\sigma$  – specific electrical conductivity.

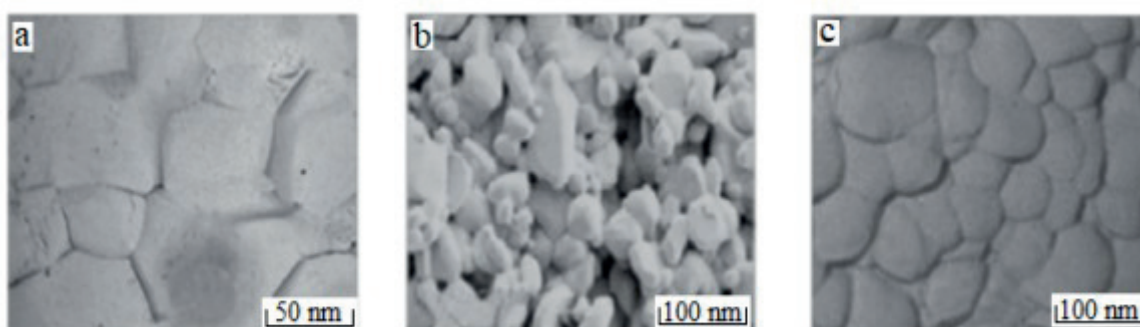


Fig.1. Microstructure of sintered ceramics: a–solid solution composition  $80\text{ZrO}_2\text{--}8\text{HfO}_2\text{--}7\text{Y}_2\text{O}_3\text{--}5\text{CeO}_2$  (1400°C, 2 h),  
b–connection  $\text{Nd}_2\text{NiO}_4$  (1200°C, 3 h),  
c–solid solution composition  $92\text{In}_2\text{O}_3\text{--}8\text{ZrO}_2$  (1400°C, 2 h).

THE SYNTHESIS AND INVESTIGATION OF NEW POLYMER SYSTEMS  
FOR LITHIUM-SULFUR BATTERIES

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The need for reliable and powerful batteries is growing every year, and the most important parameters when choosing them are: high energy intensity, stability in operation and lifetime<sup>1</sup>. The resource of lithium-ion batteries has almost been exhausted due to the limited range of operating temperatures (from -10 to +60 °C), as well as the inability to increase the power density<sup>2</sup>. The most promising in this regard are lithium-sulfur (Li-S) batteries, the specific energy of the cathode material itself can be up to 2550 W/kg. However, one of the obstacles in the development of the Li-S battery industry is their short lifespan and the low window of electrochemical stability of existing electrolytic cells<sup>3</sup>.

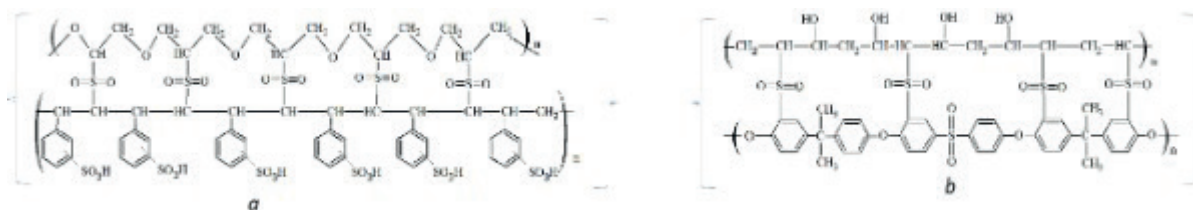


Figure 1. Copolymer structure: PVA-co-PSS (a) and PEO-co-PS (b)

Therefore in the present work to improve lithium-sulfur battery were synthesized and investigated copolymer matrix (Figure 1) polyvinyl alcohol - polysulfonic acid (PVA-co-PSS-LiX) and polyethyleneoxide-polysulfone (PE-co-PS-LiX) in the presence of lithium salts: LiClO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>SO<sub>3</sub>Li, LiNO<sub>3</sub>. The specific ionic conductivity of the systems obtained was  $> 10^{-4} \text{ Cm} \cdot \text{cm}^{-1}$  (T = 20 °C), the L<sup>+</sup> number was 0.9, the anodic resistance was up to 6.0 V.

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## INFLUENCE OF THE COMPOSITION OF OXIDE-CARBON SUPPORT ON THE FUNCTIONAL CHARACTERISTICS OF PLATINUM-CONTAINING ELECTROCATALYSTS

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Recently dioxide of tin ( $\text{SnO}_2$ ) is widely being researched. The presence of platinum-containing electrocatalyst nanoparticles  $\text{SnO}_2$  can increased the activity material in the reactions of oxygen reduction and electro-oxidation of alcohols with an increase in the durability of materials<sup>1</sup>.

The basis of the present study is the hypothesis that the use of composite  $\text{SnO}_2/\text{media}$  obtained by the original method of electrodeposition<sup>2</sup>, and containing tin dioxide in the form of nanoparticles of small size, for the subsequent application of platinum nanoparticles, will provide a three-phase  $\text{Pt}/(\text{SnO}_2/\text{C})$  electrocatalysts, in which, on the one hand, supply is provided and the removal of electrons to/from the platinum nanoparticles, and on the other direct contact a considerable part of platinum nanoparticles with nanoparticles of tin dioxide.

The resulting  $\text{Pt}/(\text{SnO}_2/\text{C})$  materials have a mass activity close to the commercial sample  $\text{Pt}/\text{C}$  (HiSPEC 3000). The addition of tin dioxide contributes to a significant increase in the durability of the material. In addition, a comparison of activity in the reaction of electro-oxidation of methanol showed that the introduction of tin oxide into the system allows to increase the activity. The potential to start the reaction of electro-oxidation of methanol by 30-50 mV is shifted to lower potentials.

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# NEW OXYGEN-AND PROTON CONDUCTING MATERIALS $\text{La}_4\text{Zn}_2\text{Al}_2\text{O}_{11}$ AND $\text{La}_4\text{Zn}_2\text{In}_2\text{O}_{11}$ WITH PEROVSKITES-TYPE STRUCTURE

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The search for new functional materials that can be used in various electrochemical devices currently remains relevant. Among such materials, the most widely used are complex oxides with the perovskite structure<sup>1-3</sup>.

This paper is devoted to the complex investigation of physicochemical properties of new compounds obtained by substitution a half of position B-cations in perovskites  $\text{LaAlO}_3$ <sup>4</sup> and  $\text{LaInO}_3$ <sup>5</sup> with zinc. Zinc oxide has been used for several reasons: as an acceptor dopant, that ensures the appearance of oxygen deficiency; as an element not belonging to the group of alkaline earth metals, that allows to increase the chemical resistance; as an additive that lowers the melting point and, accordingly, allows to improve the quality of ceramics.

Solid state synthesis of the samples  $\text{La}_4\text{Zn}_2\text{Al}_2\text{O}_{11}$  and  $\text{La}_4\text{Zn}_2\text{In}_2\text{O}_{11}$  was realized. The synthesis was performed by stepwise with increasing temperature in the range 700°C–1400°C. After each annealing step, the samples were ground in a ball mill. Sequence of phase transformations and structure of compounds was determined by X-ray analysis.  $\text{La}_4\text{Zn}_2\text{Al}_2\text{O}_{11}$  was crystallized in cubic symmetry with space group  $Pm\bar{3}m$ ,  $a = 3.78\text{Å}$ ,  $\text{La}_4\text{Zn}_2\text{In}_2\text{O}_{11}$  – space group  $Pnma$   $a = 5.72\text{Å}$ ,  $b = 5.93\text{Å}$ ,  $c = 8.20\text{Å}$ .

The conductivity of samples was studied by varying thermodynamic parameters ( $T$ ,  $p\text{H}_2\text{O}$ ,  $p\text{O}_2$ ). It was determined, that the sample  $\text{La}_4\text{Zn}_2\text{In}_2\text{O}_{11}$  exhibited proton transport as a result of the dissociative dissolution of water from the gas phase and the formation of proton defects. Significant proton transport in  $\text{La}_4\text{Zn}_2\text{Al}_2\text{O}_{11}$  was not realized. Specimens exhibits mixed ionic and p-type electronic conductivity, increasing which increase in temperature.

The chemical stability of the samples with respect to carbon dioxide and water vapor was investigated.

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## MANGANASE-DOPED $\text{TiO}_2$ -ANATASE MICROTUBES WITH IMPROVED ELECTROCHEMICAL CHARACTERISTICS

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Anatase titanium dioxide polymorph is a promising alternative to the conventional carbonaceous anode of lithium-ion batteries operated at high current densities and temperatures below  $-5\text{ }^{\circ}\text{C}$ . Moreover, theoretical capacity of  $\text{TiO}_2$  ( $335\text{ mA}\cdot\text{h/g}$ ) is almost twice higher as compared to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  ( $175\text{ mA}\cdot\text{h/g}$ ), which widely studied for similar reasons. Unfortunately,  $\text{TiO}_2$ -anatase has poor conductivity ( $\sim 10^{-12}\text{ S/cm}$ ) and slow  $\text{Li}^+$  diffusivity ( $\sim 10^{-15}\text{ cm}^2/\text{s}$ ). In this regard, designing the methods for improve the properties of  $\text{TiO}_2$ -anatase is topical issue, and one of the perspective way is doping with metals and/or non-metals.

Herein, the manganese-doped ( $\text{Mn/Ti} = 0.05; 0.1; 0.2$ ) titanium dioxide was synthesized by a template sol-gel route. The scanning electron microscopy investigation show that as-prepared materials consist of hollow tubes  $50\text{ }\mu\text{m}$  in length with the inner diameter from  $2$  to  $4\text{ }\mu\text{m}$  and outer – up to  $5\text{ }\mu\text{m}$ . The samples are identifying as mixtures of phases including anatase and rutile  $\text{TiO}_2$ , pirophanite  $\text{MnTiO}_3$ , hausmannite  $\text{Mn}_3\text{O}_4$ . It is interesting that when the Mn to Ti atomic ratio did not exceeds  $0.05$ , the formation of manganese compounds was not detected. On the other hand, the anatase peaks shift was registered due to the lattice distortion after the partial substitution of tetravalent titanium with manganese cations. Furthermore, the incorporation of manganese into the crystal structure of titanium dioxide leads to conductivity enhancement up to two orders in magnitude. During 30-fold cycling within the electrochemical half-cell with lithium metal counter electrode the  $\text{Ti}_{0.95}\text{Mn}_{0.05}\text{O}_2$  demonstrate a largest specific capacity of  $186\text{ mA}\cdot\text{h/g}$  at  $0.1\text{C}$ -rate in the range of  $1\text{--}3\text{ V}$  among the all studied samples. Even at current density of  $2\text{C}$ , the  $\text{Ti}_{0.95}\text{Mn}_{0.05}\text{O}_2$  still maintains about  $121\text{ mA}\cdot\text{h/g}$ , that is three times higher as compared to undoped  $\text{TiO}_2$  ( $39\text{ mA}\cdot\text{h/g}$ ).

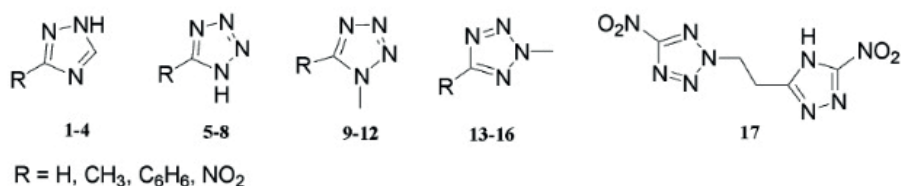
## PYROLYSIS AND MASS-SPECTROMETRIC FRAGMENTATION OF HIGH-NITROGEN HETEROCYCLIC COMPOUNDS - 1,2,4-TRIAZOLES AND TETRAZOLES

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High-nitrogen heterocyclic compounds – 1,2,4-triazoles 1-4, tetrazoles 5-16, and a compound belonging to hybrid system (5-nitrotetrazol and 3-nitro-1,2,4- triazole bounded by a linker group) 17, are considered as promising components of the energetic materials.



General correlations between the routes of fragmentation in electron impact mass spectra (70 eV) and thermal decomposition of these compounds have been discovered previously<sup>1-3</sup>.

We obtained the electrospray ionization mass spectra of high-nitrogen compounds using different fragmentation modes. Both common and distinct features of mass spectrometry fragmentation were found, which allow predicting general patterns of the thermal decomposition of the studied compounds.

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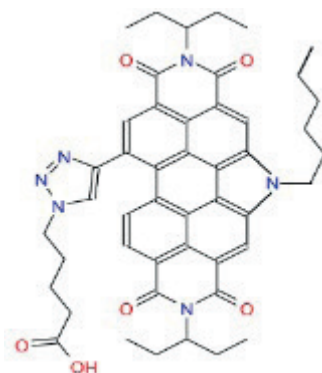
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## OPTICAL PROPERTIES OF SURFACE MOLECULAR-IMPRINTED TITANIUM DIOXIDE NANOPARTICLES

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Perylenediimide (PDI) dyes - acceptors of well-known organic semiconductor systems<sup>1</sup>. They are often used in organic photo-voltaic cells in which low values of the band gap are achieved, but PDI have a tendency to self-aggregate.



PDI-Taz-C<sub>5</sub>OOH

The method of surface molecular imprinting<sup>2</sup> to create films on the surface of TiO<sub>2</sub> nanoparticles with 1-H-pyrrol-N, N'-bis (3-pentyl) perylene-3,4,9,10-bis (dicarboximide)-5-hexyl-11-1H-1,2,3-triazol-1-yl-pentanoic acid (PDI-Taz-C<sub>5</sub>OOH) imprints with acceptor properties was used. The band gap of the obtained material has reduced by 0.1–0.5 eV (Table 1), and the sorption capacity after template removal with ethanol has reached 0.75 μmol/g. At the same time, molecular imprinted (MIP) material can re-bind 2 times more PDI-Taz-C<sub>5</sub>OOH than unimprinted (NIP).

Table 1. Band gap (E<sub>g</sub>) of NIP and MIP samples

Sample	Precursor : template	$E_g \pm \delta$ (P=0.95, n=3), eV	$\Delta\lambda$ , nm
TiO <sub>2</sub>	-	$3.09 \pm 0.01$	-
MIP	1:81	$2.62 \pm 0.10$	72
NIP		$2.98 \pm 0.05$	16

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**SYNTHESIS OF SOLID ELECTROLYTES BASED ON CLOSO-DODECABORATE AND SODIUM AMID**

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In recent years the renewable energy sector is dynamically develop, thereby additional storage capacity is constantly are required: cheap and capacious, withstanding repeated cycling and capable of efficiently transmitting energy. Lithium reserves in the crust are limited: it will be enough for no more than the next 120 years, given the increasing demand for energy (hybrid and electric vehicles production, underwater robotics, powerwalls, etc.). In Russia, there are no significant stocks of lithium raw materials, and meanwhile, lithium and cobalt, used in the manufacture of batteries, went up in 2015–2018 by 150% and 260%. Today, the most promising alternatives to the lithium-ion battery (LIB) are sodium ion technology<sup>1</sup>. According to experts, a sodium-ion battery (SIB) with similar characteristics can cost up to 80% cheaper than the lithium analog. The relevance of the choice of sodium-ion technology in the field of electricity storage is emphasized that sodium is a constituent chemical element of common salt, is contained in large quantities at the bottom of oceans and salt lakes in particular in Russia.

Due to high chemical and thermal stability, cluster nature of structures, susceptibility to chemical modification polyhedral boron hydride compounds are very promising candidates as solid electrolytes for SIB. The report presents data on the development of solid electrolytes based on closo-dodecaborate and sodium amid for sodium-ion batteries. The electrophysical properties, structural and morphological features of the synthesized materials are described.

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## FIRST-PRINCIPLES CALCULATIONS OF PEROVSKITE-LIKE MOLYBDATES

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Today, complex oxide compounds with a perovskite-like structure containing d-metals, in particular, perovskite-like molybdates  $\text{Sr}_2\text{MMoO}_6$ , where M – Mg, Fe, Ni, Mn are of great interest for theoretical studies. This oxide type possesses interesting properties that opens up prospects for the use of such materials as fuel cell anodes, functional components of spintronics devices, etc. It should be noted that, compared with the large amount of experimental research, theoretical picture considering oxides' properties are not sufficiently developed. Thus, questions about the nature of charge carriers, defect formation processes, ionic conductivity, electronic and magnetic structure remain the subject of active discussions. In the framework of this work, the perovskite-like molybdates  $\text{Sr}_2\text{MgMoO}_6$  were investigated using the electron density functional theory. The densities of electronic states and the energy of formation of various defects (Fig. 1), as well as the migration barriers of oxygen ions, were calculated. The results obtained are compared with experimental data.

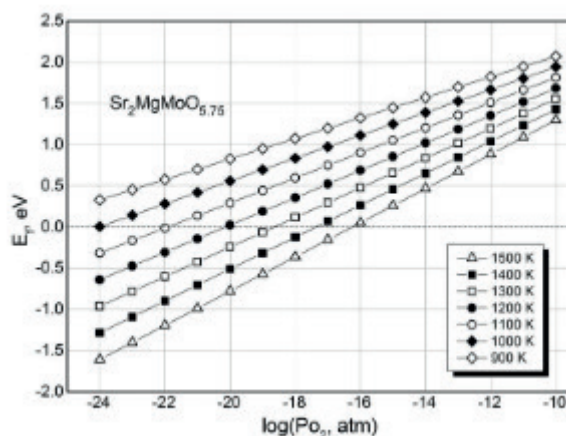


Figure 1. Oxygen vacancy formation energy for  $\text{Sr}_2\text{MgMoO}_6$

## ELECTROCATALYSTS SUPPORTED ON $\text{SnO}_2$ MODIFIED CARBON MATERIALS FOR SOLID POLYMER ELECTROLYTE FUEL CELL

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Platinum-based electrocatalysts are commonly used for solid polymer electrolyte (SPE) fuel cells. Corrosion resistance is a very important characteristic of suitable catalyst support together with high electrical conductivity, high surface area, hydrophobicity, morphology, porosity etc. The promising strategy aimed to mitigate carbon supports degradation is the usage of carbon-based hybrid supports. One of the most attractive materials is a tin oxide ( $\text{SnO}_2$ ) owing to its availability, cost-effectiveness, and non-toxicity<sup>1</sup>

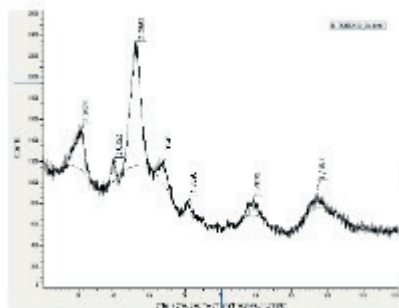


Fig. 1. XRD spectra of  
 $\text{Pt}^{20}\text{SnO}_2^{10}/\text{C}$

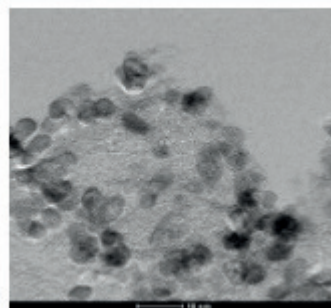


Fig. 2. TEM image of the  
 $\text{Pt}^{20}\text{SnO}_2^{10}/\text{C}$  catalyst particles.

In presented study several Pt-electrocatalysts with tin dioxide coating to protect the carbon support was synthesized and evaluated (Fig. 1,2). Their cyclic voltammetry behavior, oxygen reduction reaction activity and durability were studied. The use of tin oxide as a coating for carbon carriers improves the durability of electrocatalysts in oxygen reduction reaction but slightly decrease the catalyst active surface.

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## THEORETICAL STUDY OF THE UNITIZED REGENERATIVE FUEL CELL MEMBRANE ELECTRODE ASSEMBLY AND ITS COMPONENTS: THE OPTIMIZATION OF COMPOSITION AND STRUCTURE

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In present work we consider the challenge of the catalytic layer (CL) optimal structure of the unitized regenerative fuel cell (URFC) oxygen electrode. The development of a modified transport model in the CL of the URFC oxygen electrode is based on the approach used previously<sup>1</sup>. Series of calculations using the developed transport model was carried out. The results of the calculations are presented as the dependences of URFC voltages (in both FC-mode and E-mode) and URFC efficiency on the specific weight of Pt and Ir in the CL. The calculations were carried out at various values of the polymer electrolyte volume content in the CL, the CL porosity, as well as the operating conditions (temperature, humidity, current density).

The results of calculations showed:

1. Under the most favorable conditions for high URFC efficiency optimal oxygen electrode noble metal loadings are  $m_{Pt}=0,8$  mg/cm<sup>2</sup> and  $m_{Ir}=0,7$  mg/cm<sup>2</sup>. The maximum value of the URFC efficiency is  $\eta_0 = 0,41$ .
2. The optimal value of the polymer volume fraction in relation to the volume of the entire layer considering the porosity is 0.18 - 0.2.

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## TUNGSTEN CARBIDE NANOPOWDER SYNTHESIS UNDER THE EXPOSURE OF 24 GHz GYROTRON RADIATION ON THE NANOCOMPOSITE OF THE W-C SYSTEM OBTAINED IN A THERMAL PLASMA

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The aim of the work was an experimental study of the formation of tungsten carbide nanopowder WC when processing a multi-component powder nanocomposite system W-C, produced by plasma-chemical synthesis, in an electromagnetic field with a frequency of 24 GHz. A multipurpose gyrotron system with a nominal power of 7 kW with at a frequency of 24 GHz was used for the experiments. The microwave application system described in [2]. The powders were treated in an argon flow. The experiments were carried varying exposure time and microwave power. The samples of nanopowders obtained in the experiments were analyzed using the following methods: XRD, TEM, SEM, BET, LDA, CEA.

It was established that microwave radiation with a frequency of 24 GHz allows heating samples of powders to a temperature of 1100-1200 C almost immediately (after 1-2 s) after switching on. The tungsten carbide WC is formed in a few minutes under the exposure to microwave radiation of the original W-C nanocomposite system. There is only a slight increase in the average particle size from 20 to 30 nm. The investigations showed that the synthesis of tungsten carbide WC under the microwave heating as compared to conventional heating in an electric furnace may be carried out for significantly less time while maintaining the particles in the nanometer range.

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## ENERGETICS OF HOMOLYTIC DISSOCIATION OF WATER

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The water molecule is capable of dissociating heterolytically with the formation of  $H^+$  and  $OH^-$  ions and homolytically with the formation of  $\bullet H$  and  $\bullet OH$  radicals. As shown by our calculations of the electronic structure and mobility of water molecules, performed by ab initio molecular dynamics, heterolytic dissociation is promoted by a high dielectric constant of the medium ( $\epsilon=78$ ), and its decrease is favour to homolytic dissociation.

Therefore, the most likely homolytic dissociation of water will be in a vapor state due to its finely dispersed state, contact with air ( $\epsilon=1.0$ ), and also due to the extreme dynamism of its single hydrogen bond network. Reducing the dielectric constant in micro- and nanodroplets contributes to the processes of aquaclaration [1]. In the aquaclarated (AC) state  $[H_2O(H_2O)_{m+n}]$ , a single  $H_2O$  molecule will dissociate homolytically into aqua radicals in the AC state  $[\bullet H(H_2O)_m]$ ,  $[\bullet OH(H_2O)_n]$  and, naturally, with energy absorption  $Q_1$ .

It is the presence of water vapor in the air or gas, their endothermic homolytic dissociation caused by the unexplained fact of the still lowering of the temperature to minus ( $40^\circ\div 200^\circ$ ) C, while passing air or gas through direct-flow vortex tubes. In Ranque-Hilsch vortex tube, the central air flow is cooled to  $-40^\circ\text{C}$ , and its peripheral part is heated to a temperature of  $50^\circ\div 70^\circ\text{C}$ . The proposed approach allows us to explain the observed temperature effects.

The cooling of the air in the central part of the stream has already been explained. Heating of the peripheral part of the flow is caused by the release of centrifugal forces to the periphery of a small part of the AC radicals. At the same time, they are released from the aquaclaratic shells  $Q_2 \leq 0$  and actively interact in the free state, emitting  $Q_3 = 550 \text{ kJ/mol}$ , warm the air flow. The separation of conditions and the different mechanism of direct and reverse reactions of the homolytic dissociation of water and the release of energy equal to  $550 - |Q_1| - |Q_2|$  during its vortex motion was unknown until now. So, the vortex motion water is an alternative source of energy.

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IONIC CONDUCTIVITY IN COMPLEX OXIDES BASED ON  $\text{BaLaInO}_4$ 

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Complex oxide materials that exhibit high ionic conductivity have attracted considerable attention owing to the wide range of applications, such as fuel cells. Perspective ionic conductors for medium-temperature SOFC are proton electrolytes based on the complex oxides. The most studied proton conductors are complex oxides with perovskites or perovskite-related structure. Further development of proton conductors involves investigations of materials with new types of structures. Recently, the new data about oxide ionic transport in the complex oxides based on  $\text{BaNdInO}_4$  with Ruddlesden-Popper structure are appeared, and afterwards the possibility of proton transfer in such phases has been investigated. The structure of  $\text{BaNdInO}_4$  is represented by two alternating layers. First of them consists of connected by vertices octahedra  $[\text{InO}_6]$  and Ba atoms located between the octahedra. Second layer is represented by the Nd atoms.

As it was proved, the acceptor doping of  $\text{BaNdInO}_4$  leads to the increase in the electrical conductivity values up to one order of magnitude. At the same time, the presence of oxygen disordering can lead to the appearance of proton conductivity in atmospheres with high partial pressure of water vapor. Moreover, an alternative process, this is a possible hydration of salt blocks, creates prerequisites for high concentrations of proton carriers and fast  $\text{H}^+$  – transport.

Thus, new class of proton conductors with Ruddlesden-Popper structure based on  $\text{BaNdInO}_4$  is promising for the creating new proton conductors with high efficiency.

In the present work new complex oxides  $\text{BaLa}_{0.9}\text{M}_{0.1}\text{InO}_{3.95}$  ( $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$ ) with Ruddlesden-Popper structure were obtained via solid state method. The structure, possibility of water uptake and proton transport were examined.

*The research was supported by grant of the President of the Russian Federation, project MK-24.2019.3*

## THE INFLUENCE OF ANIONIC DOPING ( $F^-$ , $Cl^-$ ) ON CHEMICAL STABILITY OF PROTON CONDUCTORS WITH PEROVSKITE-RELATED STRUCTURE

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One of the most important trends in modern materials science is the development and research of materials that can be used in various electrochemical devices, such as solid oxide fuel cells (SOFC). Perspective ionic conductors for medium-temperature SOFC are proton electrolytes based on the complex oxides.

The most studied proton conductors are the acceptor doped cerates and zirconates of alkaline earth metals. However, doped cerates exhibiting the best conductivity are degraded in the atmosphere of carbon dioxide and water. The problem of competition between high proton conductivity and chemical stability does not allow creating long-term working electrochemical devices based on solid oxide protonic conductors.

The novel strategy permitting both to increase proton conductivity and to improve chemical stability is the anionic doping of perovskite-related matrix. This work describes the study of new types of proton electrolytes – halogen-doped oxygen-deficient complex oxides based on  $Ba_2In_2O_5$ ,  $Ba_4In_2Zr_2O_{11}$  and  $Ba_4Ca_2Nb_2O_{11}$  with perovskite or perovskite-related structure. The transport properties, state of oxygen-hydrogen groups, the relationship between concentration and mobility of protons were examined earlier. It was shown that anionic doping ( $F^-$ ,  $Cl^-$ ) allows to increase the oxygen-ion and proton conductivity in the region of low dopant concentrations. The determining factor is not the change in the concentration of the current carrier, but the increase in its mobility.

In the present work, the influence of anionic doping on chemical stability was investigated. It was proved that  $F^-$ - and  $Cl^-$ -containing samples are more chemically stable compared to undoped compositions. The method of halide doping can be used as a promising technique of obtaining new perovskite-related materials with high level of ionic conductivity ( $O^{2-}$ ,  $H^+$ ) and chemical stability.

*The research was supported by grant of the Russian Science Foundation, project 18-73-00006*

## PROTON CONDUCTIVITY OF SOLID ELECTROLYTE FILMS: EFFECT OF DRY-CHARGE BATTERY

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Materials with proton conductivity are widely used in various devices: fuel cells, electrochemical sensors, electrochemical reactors, electrochromic devices, etc. Dried graphene oxide (GO) is an insulator, while in a humid atmosphere, GO exhibits proton conductivity. Graphene oxide as a proton-conducting material is used in humidity sensors, supercapacitors, and in a field-effect transistor circuit. Nafion membranes are widely used in fuel cells. Nafion is a polymer with high proton conductivity and adjustable swelling in a humid environment. In this study, the possibility of accumulation and storage of electric charge in proton-conducting films based on Nafion and GO (Fig. 1) was experimentally demonstrated for the first time.

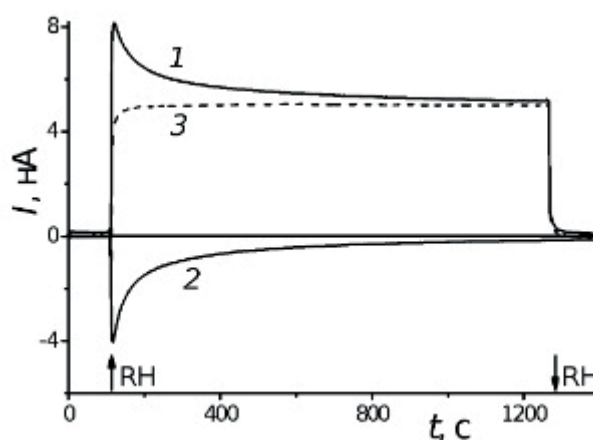


Figure 1. 1 - Kinetics of charge accumulation in graphene oxide films at RH = 75%, U = 0.4 V.  
2 - The process of discharge of the GO film at RH = 75%, U = 0 V. 3 – The sum of curves 1 and 2.

The amount of accumulated charge is tuned by the humidity of the environment. In a dry atmosphere, the accumulated charge can be stored for a long time. The charge is stored directly in the film without any chemical conversion.

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*The work has been performed using the equipment of the MUAC of IPCP RAS.*

## SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF LITHIUM-VANADIUM PHOSPHATE

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Based on lithium-polymer batteries, a combined power plant for energy and transport can be created. In addition, these devices can be used in laptop computers, analog and digital communication systems, in consumer electronics. One of the main problems with their creation is the development of efficient cathode materials. The structure of cathode materials based on polyanion phosphate in recent years has attracted much attention. In particular, monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  is considered to be one of the promising candidates for the role of cathode material for high power lithium polymer batteries, due to its high theoretical power, high operating potential and good ion mobility.

An original method has been developed for the synthesis of lithium-vanadium phosphate, which includes two stages: 1st — synthesis of vanadium-phosphate from a mixture of ammonium dihydrogen phosphate and metal oxide; The second is the synthesis of lithium-vanadium phosphate by thermal lithiation of the product obtained at the 1st stage, which includes the mechanical activation of the precursor during plastic deformation. It was found that plastic deformation of the precursor effectively acts in the second stage of synthesis: the greatest amount of lithium-vanadium phosphate is observed in the sample, upon receipt of which plastic deformation was used only before the 2nd stage of heat treatment at a temperature of 750 °C. The cyclic voltammograms of the electrode, taken at a potential sweep rate of  $0.1 \text{ mV}\cdot\text{s}^{-1}$  in the range from 3.0 to 4.3 V, show three peaks of oxidation current and three peaks of recovery current, which is consistent with galvanostatic charge – discharge curves. The satisfactory coincidence of cyclic voltammograms and the symmetry of the peaks of oxidation and reduction on them indicates the good reversibility of the reactions of the introduction – extraction of lithium. The life tests of the material electrodes showed that they stably cycled at current densities of  $0.01\text{--}0.15 \text{ mA}\cdot\text{cm}^{-2}$ : the loss of capacity during 150 charge – discharge cycles was 0.04–0.07% per cycle.



## MODIFIED CARBON NANOTUBES – HIGHACTIVE AND STABLE MATERIALS FOR OXYGEN REDUCTION/EVOLUTION

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The reactions with oxygen participation are related to widely used and important ones in practical attitude. Herewith, the significant attention is paid to questions connected with the degradation of electrode materials at carrying out anodic evolution and cathodic reduction of oxygen. In this respect, the creation of catalysts for oxygen reaction as in aqueous and aprotic solvents is actual problem.

The investigations are in progress in both directions, namely, the enhancement of activity and stability of metallic phase and development of disperse corrosion-resistant support. The significant progress was reached at development of multi-component bi- and three-metallic catalysts having the structure of core-shell. It was shown that the properties of platinum which is contained in shell owing to ligand influence of core are differed by enhanced activity and stability in comparison to monoplatinum<sup>1</sup>.

The second direction is connected with the creation of corrosion-resistant support. The most popular supports are disperse carbon materials (CM), namely, carbon nanotubes (CNT), graphenes, carbon blacks and others. The stability of CM to degradation can be enhanced by modification with oxygen-contained groups, doping them by adatoms of N, S, P. Moreover, the functionalization results in the creation of active centers on the surface for fixation of metallic phase at catalyst synthesis. In Li-O<sub>2</sub> power sources CM play role not only as support but as the catalyst. Herewith, the material of active layer of positive electrode of Li-O<sub>2</sub> power source should possess by bifunctional properties, namely, to accelerate electroreduction and evolution of oxygen<sup>2</sup>. The introduction of N and P results in enhancement of electrochemically active surface area and activity in cathodic reduction of oxygen in aqueous and non-aqueous electrolytes.

The aim of this investigation is the development of effective methods of modification of CNT for enhancement of their corrosion stability, estimating relationships of structure, surface composition and stability to degradation of different CNT in aqueous and non-aqueous electrolytes.

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## SEDIMENTATION AND DEHYDRATION OF PHYTOPLANKTON UNDER THE ACTION OF ACCELERATED ELECTRONS

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Phytoplankton is widely distributed in freshwater bodies of almost all continents of the planet. It is important in the biological balance of aquatic ecosystems. Due to its unpretentiousness phytoplankton can multiply in a variety of conditions. On the one hand, microalgae impede the preparation of drinking water and the efficiency of open water recycling systems, where it is necessary to fight microalgae. On the other hand, microalgae are considered as a source of raw materials for the production of biofuels of the third and fourth generations. To solve these problems, effective methods of phytoplankton removal, concentrating and dehydration are required.

In the present work, the effects of irradiation on the sedimentation of *Chlorella vulgaris* microalgae were studied. *Chlorella* was grown in the Bioflo 110 bioreactor using Tamiya nutrient medium. The samples were irradiated using a linear electron accelerator UELV-10-10-C-70 (electron energy 8 MeV, pulse duration 6  $\mu$ s, pulse repetition rate 300 Hz, average beam current  $\gg$  800  $\mu$ A, scan width 245 mm, scan frequency 1 Hz). The degree of sedimentation was determined using turbidimetry and spectrophotometry.

Non-irradiated microalgae are fairly resistant to sedimentation. Their precipitation from the water is slow and can take several days. The original chlorella cells have the properties of micelles and remain in a separate state in the aquatic environment. Irradiation causes the destruction of microalgae cells. Electrons and water radiolysis products, apparently, can change the charge and electrostatic repulsion forces between the cells. In parallel, there is a radical cross-linking of macromolecules. As a result, chlorella cells aggregate and their precipitation is accelerated. Cell aggregation also accelerates the filtration and drying of sediments.

Thus, it was shown that irradiation with a dose of 6–8 kGy almost doubles the precipitation of microalgae from water, which affects the efficiency of their concentrating. In this case, the irradiated and concentrated substrate is filtered twice as easily.

PHYSICO-CHEMICAL PROPERTIES OF IONIC LIQUID  
ON THE BASIS OF 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE

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The investigation of physico-chemical properties such as specific electrical conductivity, density and viscosity of a liquid is an important step in choosing the most efficient electrolyte for chemical power sources. Analysis of the literature demonstrated the absence of systematic researches of the physicochemical properties of the ionic liquid consisting of 1-ethyl-3-methylimidazolium chloride organic salt ([EMIM]Cl) and aluminum trichloride in a wide concentration range. This paper presents the results of measurements of specific electrical conductivity by the method of impedance spectroscopy, density by the bottle method and dynamic viscosity by the capillary method of the [EMIM]Cl / AlCl<sub>3</sub> system at different molar ratios of electrolyte components at a temperature of 303 K. The measurements were carried out in the glovebox MBRAUN UNILab in an argon atmosphere with an oxygen and water content of less than 0.1 ppm.

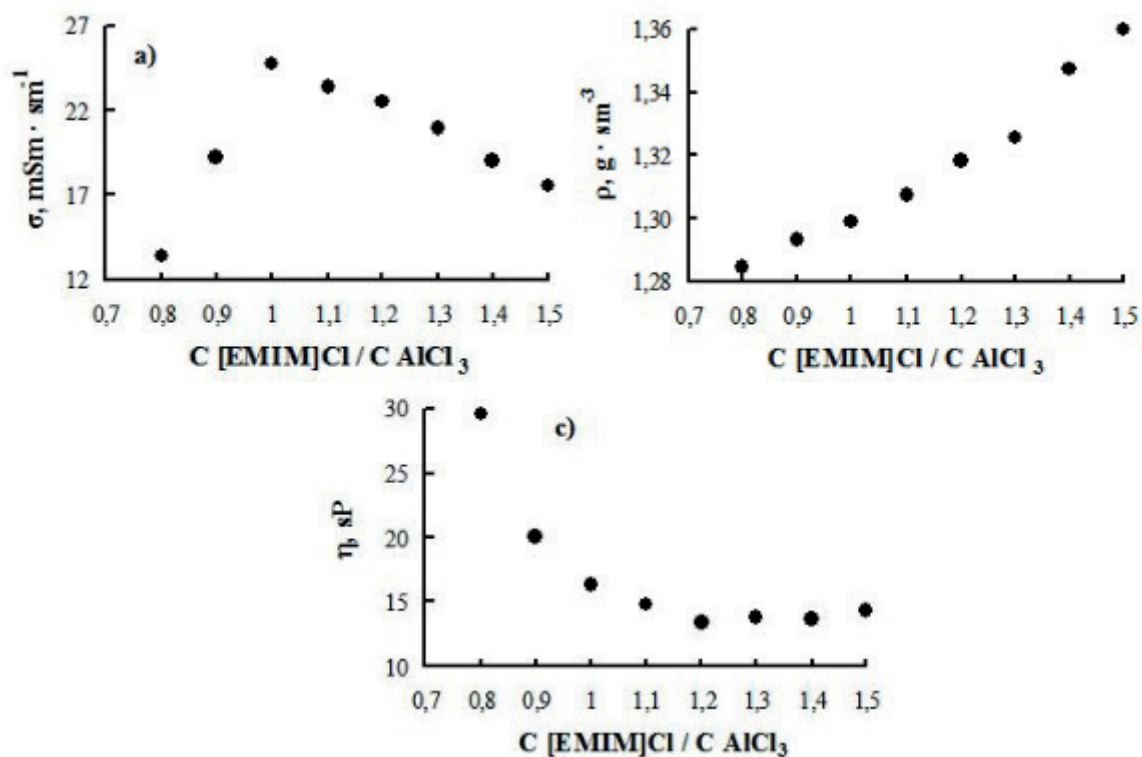


Figure 1. Dependences a) specific electrical conductivity, b) density, c) dynamic viscosity of the investigated electrolyte on the molar ratio of 1-ethyl-3-methylimidazole chloride to aluminum trichloride

## METHANE SORPTION ON NANOSTRUCTURED CARBON BEARERS BY CONSTRUCTING AN OPTIMAL QUANTUM-CHEMICAL MODEL

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The main task is to develop carbon nanostructured materials capable to sorb methane. In the future, the materials under consideration will be able to store natural gas without ultra-low temperatures, heavy metal cylinders and high pressures<sup>1</sup>.

In this task we considered a graphene monolayer with a potentially very small volume of the structure-forming matrix. Using the model Hamiltonian and the PRIRODA<sup>2</sup> software package, the interaction potentials of the methane molecule with the graphene layer were calculated for 18 different mutual orientations. With sufficient accuracy, these potentials can be approximated by the effective Lennard-Jones potentials.

With the help of the constructed potentials, it is possible to analyze analytically the dependence of energy on the location of methane in a system of several graphene layers with arbitrary mutual orientations. Based on this, thermodynamic functions of methane were calculated and the dependence of the degree of filling on temperature and pressure for different interplanar distances was calculated.

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**DEFECT STRUCTURE AND ELECTROPHYSICAL PROPERTIES OF  
ELECTRON-DOPED MANGANITES  $\text{Sr}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{V}_y\text{O}_{3-\delta}$** 

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Transition metal oxides belong to promising thermoelectric materials due to their chemical stability and environmental safety. The perovskite-type manganites  $\text{AMnO}_{3-\delta}$  ( $A = \text{Sr}^{2+}, \text{Ca}^{2+}$ ) have large values of thermoelectric power and, therefore, can be applied in thermoelectric generators operating in air at elevated temperatures. The increase of the strontium content reduces the thermal conductivity and, in turn, promotes thermoelectric efficiency of these compounds<sup>1</sup>.

The present report is focused on the study of physicochemical properties for  $\text{Sr}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{V}_y\text{O}_{3-\delta}$  manganites. Doping  $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  with vanadium ions has been shown to stabilize of the perovskite-type crystal structure with a high content of strontium. Powder X-ray diffraction confirms that the solid solution  $\text{Sr}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{V}_y\text{O}_{3-\delta}$  synthesized by citrate-nitrate combustion route crystallizes with unit cells of different space groups that is limited by the dopant concentration. Measurements of electrical conductivity ( $\sigma$ ) and thermoelectric power ( $S$ ) reveal that the formation of  $\text{Mn}^{3+}$  ions, caused by doping with  $\text{V}^{5+}$  ions and oxygen non-stoichiometry  $\delta$ , significantly increases the values of  $\sigma$  while maintaining high values of  $S$ . An electron transfer hopping mechanism has been proposed. The absolute values of  $S$  and  $\sigma T$  increase simultaneously with temperature. This dependence is consistent with model<sup>2</sup> of the activation character of electron motion when the decrease in  $\text{Mn}^{3+}$  concentration is considered, as a result of the reaction:  $2\text{Mn}^{3+} = \text{Mn}^{2+} + \text{Mn}^{4+}$ . Thermodynamic analysis which includes determination of the equilibrium constants and values of standard enthalpies and entropies of the defect formation reactions have been performed to calculate the concentration of manganese ions and electron mobility.

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## PREPARATION OF CERTAIN HIGH-PURITY ISOTOPICALLY ENRICHED ELEMENTS FROM THEIR VOLATILE HALOGENIDES IN PLASMA SUSTAINED BY DIFFERENT DISCHARGES

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Silicon, germanium, boron, molybdenum and sulfur, as well as their compounds with the given parameters for chemical and isotopic purity, are of interest both for basic research and for solving various applied problems. To obtain these substances, the plasma-chemical methods are promising, in which the reducing processes of chemically and isotopically pure silicon halides, germanium, molybdenum boron and sulfur boron in hydrogen are realized.

The paper reports the results of a study of the processes of plasma-chemical hydrogen reduction of the  $\text{SiF}_4$ ,  $\text{GeF}_4$ ,  $\text{BF}_3$ ,  $\text{MoF}_6$ ,  $\text{SF}_6$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$  and  $\text{BCl}_3$  in various types of gas discharges – RFCCD (RF capacitive-coupled discharge), RF-IC (RF inductively coupled), RFAD (radio frequency arc discharge) and MW. The main chemical reactions responsible for the reduction processes of the indicated halides are established, and the regularities of their occurrence are investigated depending on the main external parameters of the reduction process (pressure, reagent ratio and energy input). Investigated halides can be recovered both to elementary Si, Ge, B, Mo and S and up fluoro and chlorosilanes, hexachlorodisilane, dihlorborane, polifluorogermanes  $(\text{GeF}_2)_n(\text{GeF})_m$  and polychlorosilanes  $(\text{Si}_2\text{Cl}_2)_n$  as well as to molybdenum trifluoride.

A numerical simulation of gas-dynamic and thermal processes has been carried out and the heat balance in RFAD, RF-IC and MW plasmatron has been investigated. The power required for heating gas in discharges at elevated pressure, the gas temperature and the residence time of the reactants in the plasma zone are determined. The presence of temperature zones with special conditions for reduction reactions has been established.

The chemical, isotopic and phase composition of elemental Si, Ge, B, Mo and S obtained in plasma-chemical hydrogen reduction processes is investigated. The effect of the type of discharge on the form of formation of elements is established.

Single-step plasma-chemical methods have been developed for the preparation of high-purity isotopically modified  $^{28}\text{Si}$ ,  $^{72}\text{Ge}$ ,  $^{10}\text{B}$ ,  $^{98}\text{Mo}$  и  $^{32}\text{S}$  with different structures.

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## PROTON CONDUCTIVITY OF POLYANTIMONIC ACID, DOPED WITH VANADIUM IONS

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Polyantimonic acid (PAA) is one of the perspective compounds, on the basis of which composite ion conducting membranes can be obtained. It is known that PAA crystallizes within the pyrochlore-type structure (sp.gr. Fd3m). One of the methods, which increases the sorption selectivity, is the composition change plane by means of iso- and heterovalent doping<sup>1</sup>.

In this respect the goal of the present study is the research of the PAA doping  $V^{+3}$  proton conductivity.

Samples of PAA, doped with vanadium ions, have been synthesized, using the co-precipitation method. RFA data show that the sample is a single-phase and has pyrochlore-type structure. According to the of XRF-spectrometry and thermogravimetric analysis data, doped samples had the following composition  $H_{2+2x}[SbO_3]_{2-x}[VO_3]_x \cdot nH_2O$ , the samples, containing  $x = 0; 0,28; 0,38; 0,48$ , the number of molecules of hydrated water  $2 < n < 3$ . The proton conducting and dielectric characteristics of the compound were investigated with the help an Elins Z-1500J impedance in frequency range of 1Hz-2MHz, temperature of 25°C and relative humidity of RH = 58%.

The impedance' hodographs of the samples present a semicircle and a straight line at a small angle to the abscissa axis in the low-frequency region. This indicates the presence of charge relaxation processes occurring near the electrodes (low-frequency region) and in the sample particles (high-frequency region). An increase in the dopant  $V^{+3}$  leads to a shift of the semicircle into the high-frequency region and a decrease in the radius.

Proton conductivity values were found by the impedance curves of the cut-off to the axis of active resistances. At room temperature, the proton conductivity of the PAA is  $8 \cdot 10^{-3}$  S/m and sample with  $x = 0,48$  is  $7 \cdot 10^{-2}$  S/m. The increase in proton mobility in the doped sample is probably due to the presence of  $[VO_3]^{3-}$  - octahedra in the pyrochlore type structure, for the compensate of charge these ions are requires a greater number of protons than  $[SbO_3]^-$  - octahedra.

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## THE FIRST UNIQUE DATA ABOUT A NEW MAGNETIC BASED ON A CARBON NANOFORM COMPOSITED WITH COBALT(II) PORPHYRIN WITH BOTH A PET AND A ROOM-TEMPERATURE MAGNETOCALORIC EFFECT

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1'-N-methyl-2'-(pyridin-4-yl)pyrrolidino[3',4':1,2][60]fullerene - cobalt(II) 5,10,15,20-(tetra-4-tert-butylphenyl)porphyrin triad,  $(\text{PyC}_{60})_2\text{Co}^{\text{II}}\text{TBPP}$  have been synthesized using axial coordination of  $\text{N} \rightarrow \text{Co}$  to investigate the presence of a room-temperature magnetocaloric effect in it and if it is present, for doing a comparative analysis of the triad magnetocaloric parameters and those of the precursors. Direct determination of MCE/magnetization thermodynamic parameters and specific heat capacity for the donor-acceptor triad in comparison with  $\text{C}_{60}$  and precursors by the microcalorimetric method developed by us [1-4] and DSC, respectively, shows that the carbon nanomaterials  $\text{C}_{60}$ ,  $\text{PyC}_{60}$ , the porphyrin complex and the triad display positive MCE of 0.004, 0.016, 0.028 and 0.0075 K at 278 K and magnetic induction of 1.0 T.

MCE in both  $\text{PyC}_{60}$  and  $\text{Co}^{\text{II}}\text{TBPP}$  is a little reduced by the donor-acceptor triad formation but it also leads to the appearance of new interesting properties, namely the photoinduced electron transfer (PET). Using the temperature dependences of the magnetization thermodynamic parameter (specific heat,  $Q_{\text{MCE}}$ , enthalpy,  $\Delta H$ , entropy,  $\Delta S$ , and specific heat capacity) the MCE increase via fullerene substitution (transition of  $\text{C}_{60} \rightarrow \text{PyC}_{60}$ ) may be explained by the presence of aromaticity and antiaromaticity areas state in fullerene. The MCE decrease in the triad,  $(\text{PyC}_{60})_2\text{Co}^{\text{II}}\text{TBPP}$ , compared with the precursors,  $\text{PyC}_{60}$  and  $\text{Co}^{\text{II}}\text{TBPP}$ , is caused by the triad higher specific heat capacity. This fact indicates the need to move from tetracoordinated  $\text{Co}^{\text{II}}\text{TBPP}$  to pentacoordinated porphyrin complexes of metals with a non-zero spin, in which there is only one axial coordination place for the substituted fullerene bonding.

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**SOLID ELECTROLYTE  $\text{Li}_{8-x}\text{Zr}_{1-x}\text{Ta}_x\text{O}_6$   $x = 0 - 0.5$   
FOR LITHIUM BATTERIES**

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Lithium-conducting solid electrolytes are interesting objects most of all because of the possibility of creating on their basis completely solid-phase chemical current sources (CCS). The advantages of solid-phase CCS [1, 2] are fire and explosion safety, a wide range of operating temperatures and an increase of the possibility of manufacturing varied designs of CCS.

In the work lithium zirconate  $\text{Li}_8\text{ZrO}_6$  was doped by isostructural phase  $\text{Li}_7\text{TaO}_6$  [3], which has unipolar lithium ion conductivity. The crystal lattice of these phases consists of octahedral layers, between which there are tetrahedral layers of lithium. One lithium position of the eight positions is vacant in tantalate lithium in contrast of  $\text{Li}_8\text{ZrO}_6$  [3]. It is located in both octa- and tetra-positions of lithium, i.e. it is delocalized in all eight positions. Therefore, lithium tantalate  $\text{Li}_7\text{TaO}_6$  can be considered as a structurally disordered phase.

It is shown that the conductivity of solid solutions  $\text{Li}_{8-x}\text{Zr}_{1-x}\text{Ta}_x\text{O}_6$  increases by 1-2 orders of magnitude in comparison with the undoping zirconate  $\text{Li}_8\text{ZrO}_6$  due to the formation of lithium vacancies. In addition, electrochemical cycling was carried out on full solid-state electrochemical cells with electrolyte  $\text{Li}_{7.85}\text{Zr}_{0.85}\text{Ta}_{0.15}\text{O}_6$ , ceramic anode  $0.75\text{Li}_2\text{SnMo}_3\text{O}_{12} \cdot 0.25\text{B}_2\text{O}_3$  and the cathode  $0.2\text{Li}_2\text{O} \cdot 0.2\text{LiF} \cdot 0.45\text{V}_2\text{O}_5 \cdot 0.25\text{B}_2\text{O}_3$  at 300°C. It is shown that the resistance of cell  $0.75\text{Li}_2\text{SnMo}_3\text{O}_{12} \cdot 0.25\text{B}_2\text{O}_3 \mid \text{Li}_{7.85}\text{Zr}_{0.85}\text{Ta}_{0.15}\text{O}_6 \mid 0.2\text{Li}_2\text{O} \cdot 0.2\text{LiF} \cdot 0.45\text{V}_2\text{O}_5 \cdot 0.25\text{B}_2\text{O}_3$  decreases after charge / discharge cycles.

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## ELECTRICAL CONDUCTIVITY OF AQUEOUS SUSPENSIONS OF $\text{VO}_2 \cdot x\text{H}_2\text{O}$

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Nowadays modern techniques require the materials having a long period of service with multi-adjustable properties. In this aspect vanadium oxide compounds in the intermediate oxidation state can be attractive.  $\text{VO}_2$  has many crystalline phases which are known for their unique properties.  $\text{VO}_2$  is known to undergo a reversible semiconductor-metal phase transition from the monoclinic (M) to rutile tetragonal phase (R) at 68 °C, that was first reported in [1].

Materials and composites on vanadium dioxide are used in various technical devices based on its electrochromic, thermochromic and other properties [2]. Hydrated forms of  $\text{VO}_2$  and its suspensions can be used in electrochemical devices with proton conductivity and for low-temperature fuel cells.

Aqueous suspension of bidisperse vanadium dioxide in two crystalline modifications (tetragonal and monoclinic) was obtained by hydrothermal synthesis. Impedance measurements were performed by potentiostat-galvanostat Biological SP-200 with Impedance Meter in a two-electrode cell with stainless electrodes. The electrical conductivity of  $\text{VO}_2$  suspension containing 10 wt. %  $\text{VO}_2$ , was  $3 \cdot 10^{-2} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$  at room temperature. It was found that synthesized vanadium dioxide contains impurity of vanadium pent-oxide by chemical analysis. It is also shown that the conductivity of the aqueous suspension  $\text{VO}_2 \cdot x\text{H}_2\text{O}$  does not increase additive with decreasing water content.

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## THE UTILISATION TECHNOLOGY OF THE FAT-CONTAINING WASTES WITH THE FREE FATTY ACID IMPURITIES

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Fat-containing waste (FW) is one of the newest raw materials for the production of fatty acid esters. However, there is the problem in the FW conversion by traditional technology, which is related to presence of free fatty acids. In this work, a new variant of the utilization technology of the fat-containing wastes is proposed. This variant of technology includes the extraction of free fatty acids from the oil phase in the emulsification mode by using low molecular weight alcohols (methanol and ethanol). After extraction, the purified oil proceeds to alkaline-catalyzed transesterification, and the acid-catalyzed esterification is used for conversion of free fatty acids concentrate. The final product of esterification and transesterification reactions is a mixture of fatty acid esters.

During the FW conversion according to present technology the methanol or ethanol (extractants) were used as reagents for the esterification and transesterification reactions. It allows to save the component composition of the alcohol phase, which passes on esterification procedure. It also allows to use the purified oil and residual alcohol (after its content correction in the oil phase) as reagents in transesterification procedure.

It is possible to maximally increase the degree of FW conversion into esters, increase the purity of final product and reduce the waste production by using the principle of the extracted fatty acids and purified oil separation.

A new variant of the technology was tested in the conversion of a real FW, derived from rapeseed oil. The content of free fatty acids in FW was 3.3% wt. Methanol was used as the extractant. The total yield of esters was 0.93 kg of esters per 1 kg of processed FW. The resulting product was obtained, the content of the main component in product was 96.9%. The alcohol consumption was 0.15 kg per 1kg LW considering its regeneration and technological losses.

The results confirm, that the used variant of technology allows to utilize of FW with the free fatty acids impurities and to achieve the raw materials high conversion degree and to get the small amount of impurities in esters as a technology product.

## SYNTHESIS AND STUDY OF THE PHYSICO-CHEMICAL PROPERTIES OF LANTHANUM NICKELATE DOPED BY GADOLINIUM.

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Lanthanum nickelate  $\text{La}_2\text{NiO}_{4+\delta}$  possesses the  $\text{K}_2\text{NiF}_4$  type structure and belongs to the first-order Ruddlesden-Popper phases. At present, the crystal structure and physico-chemical properties of  $\text{La}_2\text{NiO}_{4+\delta}$  are well studied, and this material is used as air electrodes of electrochemical devices and membranes for oxygen production.

However, the electronic conductivity of the layered lanthanum nickelate  $\text{La}_2\text{NiO}_{4+\delta}$  is insufficient for the cathode to work effectively. In a number of studies, it has been shown that doping of  $\text{La}_2\text{NiO}_{4+\delta}$  with isovalent impurities (Pr, Nd) increases the electrical conductivity and the total amount of interstitial oxygen in lanthanum nickelate, which contributes to faster oxygen-ion transport [1, 2].

The purpose of this work is the synthesis of the materials of the  $\text{La}_{2-x}\text{Gd}_x\text{NiO}_{4+\delta}$  series and investigation of their physico-chemical properties in order to determine the prospects for their use as materials of the air electrodes of SOFCs. For the synthesis of the series pyrolysis of formates was chosen, which, in turn, is based on the Pechini method. As a result of the synthesis it has been found that the composition of  $\text{La}_{1.5}\text{Gd}_{0.5}\text{NiO}_4$  is the boundary of the formation of a solid solution. Conductivity was studied by the four-probe method with direct current in the temperature range from 450-1250 °C. Dilatometric studies were carried out on ceramic bar-shaped samples in the temperature range of 30-900 °C with heating / cooling at a constant speed of 2 °C / min in a controlled atmosphere of zeolite-dried air ( $p\text{H}_2\text{O} = 0.04$  kPa) and moist air ( $p\text{H}_2\text{O} = 3.35$  kPa)

At temperatures up to 600 °C, there is a tendency to decrease the thermal expansion coefficient of doped compositions. The total conductivity increases with Gd-doping and reaches the maximum value at 20% of Gd-substitution.

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## THE PROBLEM OF HYDROCARBON RAW MATERIALS IN THE CONDITIONS OF ISOLATION OF NATURAL RESOURCES

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The most valuable raw materials for the petrochemical industry are hydrocarbon minerals: natural gas, coal and oil. These minerals are also the primary sources of energy. The main source of motor fuels is oil. More than 4 billion tons of oil are processed in the world, of which motor fuels account for up to 70% in different countries<sup>1</sup>.

Currently, many oil and gas fields have been significantly depleted and consumed, so a very relevant question arises: how will the future of humanity be ensured? After all, the increase in energy resources is mainly due to the increase in the share of oil and gas in the energy balance.

In the near future, two main directions for solving this problem can be identified: deeper processing of oil and gas and the involvement of coal and natural gas in the production of alternative energy sources. This will require significant material investments, improvement of the technological process in order to reduce heavy fractions: fuel oil, tar.

Automobile transport, the main consumer of hydrocarbons, should switch to alternative motor fuels: compressed and liquefied natural gas, methanol, biogas. Electric vehicles deserve special attention, which can significantly reduce the environmental burden on the environment in megacities, however, the electricity they consume is the product of refining of oil products as well<sup>2</sup>.

Russia, being one of the leaders in oil production, is far from the leading place in its refining. This is due to the traditional policy of exporting hydrocarbons. In the coming years, it is necessary to develop more economical vehicles, introduce alternative types of fuel, achieve greater environmental cleanliness in the production of electricity. Thus, we will come to the conclusion that oil will constitute a smaller share in the overall distribution of energy consumption.

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## BIOBUTANOL AS AN ALTERNATIVE FUEL

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Russia has not only significant reserves of hydrocarbons, but also has a strong potential of renewable natural resources and various sources of energy (solar, wind, geothermal, biomass energy, etc.). The technical potential of renewable energy sources many times exceeds the volume of consumption of all fuel and energy resources of Russia, and the economic potential is about 25% of the annual domestic consumption of energy resources in the country<sup>1</sup>.

The use of alternative energy sources is a contribution to the future and is dictated by concern for the environment. Thanks to the widespread introduction of alternative energy sources, it is possible to achieve the solution of many strategic tasks of modernity - diversification of the economy, development of promising areas of energy, rational use of fuel and energy resources, reduction of dependence on centralized energy supply<sup>2</sup>.

In the USSR at the end of the 70s of the last century biobutanol was produced on an industrial scale from potatoes. In terms of performance, this gas is closer to unleaded gasoline. Older technologies for producing this gas are currently not profitable due to high energy intensity. The raw material for its production can also serve as cellulose, and straw, vegetable and agricultural raw materials.

Biobutanol has a low vapor pressure, its mixture with gasoline is not hygroscopic, which contributes to its use without the need to modify vehicles. At the same time, significant fuel savings are ensured, and environmental advantages are ensured in comparison with petroleum-based fuels, including lower greenhouse gas emissions.

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SYNTHESIS OF THE FUEL OXYGENATES UNDER THE CONDITIONS  
OF SUPERCRITICAL FLUIDS

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The development of methods of substance exposure to intensive action is of particular interest. It enables practically important transformations not available under normal conditions. Thus, the esterification of lower fatty acids (LFA) in the formation of supercritical fluids (SCF) of alcohols leads to a mixture of carboxylates containing higher homologs formed as a result of alkylation of acidic and alkoxyl fragments of carboxylates by alcohol in addition to the derivatives of the initial LFA. Possible intermediates in this process are dialkyl-ortho-carboxylates. Diethyl-ortho-butyrate was registered by chromatography-mass spectrometry in case of SCF-etherification of butyric acid by ethanol. The formation of ortho-ether is a specific SCF-process and is not observed under normal conditions.<sup>1</sup>

Application of SCF-technique to esterification of a set of LFA (acetic, propionic, and butyric) produced in biocatalytic processing of carbohydrate materials allows obtaining a synthetic analog of biodiesel. A similar set of carboxylates complemented by hydroxy- and keto-acids, hydroxyaromatic compounds, and derivatives of glycerol is observed in the transformations of glucose in ethanol and water under SCF-conditions. The transesterification of vegetable triglycerides in ethanol-acetone mixed media under SCF-conditions allows obtaining biodiesel without free glycerine undergoing in situ conversion to alkyl- and alkylidene-glycerines.<sup>2</sup>

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# **PARTNERS AND SPONSORS**



# ART SCIENCE AND SPORT

## **Alisher Usmanov's Charity Foundation "Art, Science and Sport"**

The Art, Science and Sport Charity Foundation was founded by Russian businessman and philanthropist Alisher Usmanov in 2006 with the goal of assisting in organizing socially significant events in the field of art, culture and sport, as well as implementing scientific, educational and social projects.

**The mission of the Foundation** is to preserve and enhance the cultural heritage of Russia, support the country's scientific and sports potential, and create an inclusive socio-cultural environment.

**The Art, Science and Sport Foundation** is a dynamic non-profit institution actively integrated into the professional charity community. For several years, the Foundation has been a full member of the Donors Forum, an association of the largest grant-giving organizations working in Russia. Moreover, the Foundation with its own projects and programs participates in all major economic and cultural forums in Russia and abroad.

**Patronage activities** are carried out in the following areas:

- **Culture and art:** support for the leading cultural institutions of Russia. Many of the projects implemented with the assistance of the Art, Science and Sport Foundation and the personal participation of Alisher Usmanov have become iconic in the cultural life of the country.
- **Science and education:** support for projects on the exchange of experience and opinions between specialists from various fields of science and education, assistance to educational institutions at all levels, including higher education institutions.
- **Sport:** promotion of a healthy lifestyle and physical culture, popularization of sports in Russia.

**The Foundation is actively developing its own projects and programs:**

- **The Special Vision support program for people with visual impairment** has been implemented by the Foundation since 2013 with the goal of creating an accessible sociocultural environment in Russia and solving problems of social integration of blind and visually impaired people.
- In 2017, the Art, Science and Sport Foundation established the **ART-WINDOW arts festival**, which was created with the aim of ensuring free creative dialogue between the regions and cultural centers of Russia. In 2019, the project changed the vector of activity and turned into the ART-WINDOW cultural platform, promoting the development of the urban cultural environment.
- **The "With Confidence in the Future" project** has been implemented by the Art, Science and Sport Foundation since 2013. During its existence, the project has been transformed from providing targeted assistance into a comprehensive program that provides assistance in developing potential and acquiring knowledge and skills necessary for confident entry into adulthood and the choice of profession.



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# №1

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**in Europe** by capacities of carbamide and mineral fertilizers at one industrial complex (Apatit, Cherepovets); <sup>1</sup>

**as a supplier** of phosphate-based fertilizers to the Russian and CIS markets. <sup>2</sup>

**A major taxpayer** in the Murmansk and Vologda regions.

**Russia's only and Europe's** leading producer of feed phosphate (MCP) and liquid complex fertilizers. <sup>2</sup>

**Russia's only** producer of nepheline concentrate.

<sup>1</sup> Source: IFA, Fertecon, CRU

<sup>2</sup> Source: CRU, RAFF

The PhosAgro Group includes the Russia only specialized Research institute on fertilizers and insectofungicides, which de facto created the mineral fertilizer industry in Russia. NIUIF JSC, celebrating its 100th anniversary in 2019, continues to generate innovative solutions for the development of the mineral fertilizer industry. The Institute is the core of the company's research and development department, which gives PhosAgro the ability to respond flexibly to customer needs and launch production of new fertilizer grades. At the same time, the company actively cooperates with the Russian Academy of Sciences and leading agricultural universities. PhosAgro's development strategy was elaborated with direct involvement of the management of Saint-Petersburg Mining University.

In March 2013, PhosAgro, UNESCO and the International Union of Pure and Applied Chemistry (IUPAC) signed a partnership agreement on the establishment of a grant program for young scientists as part of the joint project "Green Chemistry for Life". The agreement provides financial and scientific support to researchers involved in the development of new advanced technologies based on the green chemistry principles to solve the problems of environmental protection and healthcare, nutrition, energy efficiency and the rational use of natural resources.

The uniqueness of the program lies in the fact that for the first time in the long history of UNESCO and the entire UN

system, such an initiative is being implemented on an extra-budgetary basis at the expense of Russian business funds. Over the first five years of the program's existence, the jury reviewed more than 600 applications, and 34 young scientists from 26 countries became grantees. Given the success of the project, it has been extended till the end of 2022.

Furthermore, PhosAgro is the general partner of the IUPAC Postgraduate Summer Schools on Green Chemistry. In 2019, a record number of delegates attended the event in Dar es Salaam (Tanzania) - more than 100 young professionals and 30 world-class teachers from 43 countries.

The summer school curriculum focuses on the 17 United Nations Sustainable Development Goals. The main topics of the training session concerned the exploitation of natural resources, green methodologies, material synthesis, green technologies and waste management. 35 Of the 50 winners of the Summer School receiving financial support represented the African nations.

PhosAgro is aware that without innovation it is impossible to ensure competitiveness and high growth rates of a company: science in industry is not noticeable, but its absence is immediately apparent. In total, investments in expanding production using the best available technologies, increasing its efficiency and R&D exceeded 180 billion rubles over the past 5 years.



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A man with dark, wavy hair and glasses, wearing a white lab coat over a light blue shirt, is holding a black tablet. He is looking towards the camera with a slight smile. In the background, a woman with blonde hair in a ponytail, also in a white lab coat, is seen from behind, working in a laboratory setting with shelves and equipment.

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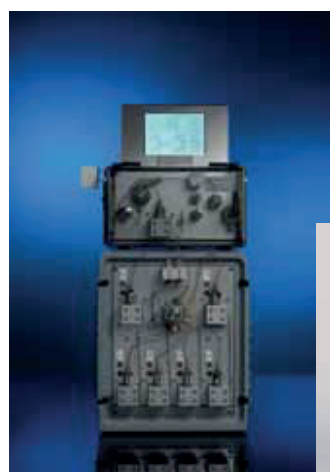
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