Experimental Modeling of the Immobilization of Heavy Metals at the Carbonate Adsorption—Precipitation Geochemical Barrier

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Abstract—Experimental data obtained on the adsorption—precipitation immobilization of heavy metals (Cu, Zn, Pb, Cd, Co, and Ni) from acidic and neutral solutions by calcite and dolomite demonstrate that interaction of solutions of heavy metals with these minerals at pH > 7.8-8.1 leads to a significant decrease in the concentrations of the metals because of the crystallization of carbonates of these metals. Except Pb, which is equally removed from solutions by both minerals, the immobilization efficiency of the metals on dolomite is greater than on calculate at the same pH. Residual Zn, Cd, Co, and Ni concentrations are immobilized by chemosorption, which is the most efficient for Cd and less significant for Co, Ni, and Zn. It is proved that artificial geochemical barriers on the basis of carbonate rocks can be efficiently applied to protect environment from contamination with heavy metals.

Keywords: heavy metals, immobilization, carbonate rocks, artificial geochemical barriers, experimental modeling

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INTRODUCTION

Anthropogenic environmental contamination nowadays becomes a global process and is one of the main negative environmental impacts. The propagation of contaminations can be fought by means of artificial geochemical barriers able to immobilize the contaminants. A good example of such geochemical barriers is trenches filled with carbonate rocks to localize soil contamination with Cu (from agricultural chemicals) via strongly decreasing the migration mobility of this metal (Perel'man et al., 1990). Artificial geochemical barriers can also be utilized to concentrate valuable components and thus form their secondary deposits, for example, from ore material disseminated in mining tailings at mining and processing complexes (Trubetskoi and Vorob'ev, 1998).

In the context of this problem, it is interesting to engineer new artificial geochemical barriers to immobilize heavy metals (Me)¹ contained in the most hazardous toxicants. Significant concentrations of heavy metals are contained in acidic mining and other industrial waste waters, whereas these waters of neutral and alkaline composition contain much less of these metals, because such compositions are favorable for the origin of low-solubility oxyhydroxides and carbonates,. The solubility of heavy-metal carbonates is usually much lower than that of calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$, the two most widely spread carbonates of crustal rocks. The ability of carbonates to neutralize acidic solutions makes carbonate rocks (limestone and dolomite) promising for utilizing in artificial geochemical barriers intended to immobilize heavy metals.

Our research was undertaken to obtain quantitative characteristics of the adsorption—precipitation immobilization of heavy metals from acidic and neutral solutions on artificial carbonate geochemical barriers.

EXPERIMENTAL

To experimentally model the neutralization of acidic solutions of heavy metals by carbonate minerals, we used chemically pure reactants $CaCO_3$ (calcite) and $CaMg(CO_3)_2$ (dolomite) that had specific surface areas of 0.45 and 2.35 m²/g, respectively. Cylindrical glass vessels were loaded with variable amounts (0.2–0.6 g) of calcite or dolomite and 100 mL of solution of various heavy-metal nitrates: (1) 0.05 M HNO₃ and 0.5 M NaNO₃; (2) 0.05 M HNO₃ 0.5 M NaNO₃, and 0.05 M Na₂SO₄; and (3) 0.05 M HNO₃ 0.5 M NaNO₃, and 0.01 M NaCl. The starting Cu, Zn, Pb, Cd, Co,

¹ In these experiments, immobilization was referred to as adsorption immobilization provisionally, because the starting solutions were in equilibrium with the sold phases of heavy-metal carbonates, but the equilibrium could be shifted when the solutions occurred in contact with CaCO₃, and new phases could be formed, such as basic carbonates and oxihydrocarbonates of metals of lower solubility.

and Ni concentrations in the solutions were, respectively, 89, 94, 27, 42, 63, and $93 \,\mu M$.

To evaluate the adsorption immobilization² of heavy metals on calculate, we prepared $Me(NO_3)_2$ – $Ca(NO_3)_2$ solutions in 0.01 M HNO₃ in equilibrium with solid MeCO₃ phases. To do this, minor CaCO₃ amounts (2 g/L) were added to the solutions, and they were held for two weeks. Preparatorily to starting the experiments, the solutions were filtered, and immediately after this, 70 mL of the solutions were poured into cylindrical glass vessels with variable amounts (0.1–0.22 g) of CaCO₃. The Zn, Cd, Co, and Ni concentrations in the starting solutions of the first (second) experimental series were, respectively, 36 (113), 760 (820), 176 (176), and 190 (175) μ M, and the Ca concentrations were 10 (50) μ M.

The closed samples were daily stirred by a magnetic stirrer for three weeks, the pH of the solutions was measured, and the time needed to reach equilibrium (when pH ceased to change) was recorded. Before their analysis, the samples were filtered through 0.45 μ m membrane filters, and the pH of the filtrate was potentiometrically measured accurate to ± 0.005 pH units; the residual heavy-metal concentrations were analyzed by atomic absorption accurate to $\pm 2\%$.

RESULTS AND DISCUSSION

When carbonate rocks interact with acidic solutions, heavy metals are immobilized by precipitation as a result of replacement reactions

$$Me^{2^{+}} + Ca_{1-x}Mg_{x}CO_{3}$$

= MeCO_{3} + (1 - x)Ca²⁺ + xMg²⁺ (1)

and neutralization (hydrolysis)

$$Me^{2^{+}} + 2H_2O + Ca_{1-x}Mg_xCO_3$$

= Me(OH)₂ + (1 - x)Ca²⁺
+ xMg²⁺ + 2H⁺ + CO₃²⁻. (2)

The thermodynamic equilibrium constants of these reactions $K_{(1)}^0$ and $K_{(2)}^0$ can be derived from the corresponding ionic products L^0 of carbonates of Ca, Mg, and heavy metals

$$K_{(1)}^{0} = \frac{L_{Ca_{1-x}Mg_{x}CO_{3}}^{0}}{L_{MeCO_{3}}^{0}} = \frac{a_{Ca^{2+}}^{1-x}a_{Mg^{2+}}^{x}}{a_{Me^{2+}}^{2}},$$
 (3)

$$K_{(2)}^{0} = \frac{L_{\text{Ca}_{1-x}\text{Mg}_{x}\text{CO}_{3}}^{0}(K_{w}^{0})^{2}}{L_{\text{Me}(\text{OH})_{2}}^{0}} = \frac{a_{\text{Ca}^{2+}}^{1-x}a_{\text{Mg}^{2+}}^{x}a_{\text{H}^{+}}^{2}a_{\text{CO}_{3}^{2-}}}{a_{\text{Me}^{2+}}}, \quad (4)$$

where K_w^0 is the dissociation constant of water, and *a* is the activity of the solute components.

The activity of solute component *i* is related to its concentration [*i*] through the expression

$$a_i = \alpha_i f_i[i], \tag{5}$$

where α_i and f_i are the fraction and activity coefficient of free ion *i*, from which it follows that the efficiency of precipitation immobilization of heavy metals depends on the degree of their complexation: the higher the mole fractions of the free ions, the higher the complexation degree and the equilibrium concentration of the metal.

It is known that heavy metals can form complexes with several inorganic ligands, including major anions of natural and waste waters: Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} (Volkov and Solomin, 1983; Lur'e, 1989; Martell et al., 1997). Because nitrate complexes are among the weakest, the background electrolyte we used in experiments on neutralizing acidic solutions by calcite and dolomite was 0.5 M NaNO₃, and the effect of complexation on the efficiency of the precipitation immobilization of heavy metals was quantified by comparing experimental series with NaNO₃ solutions and mix solutions of 0.5 M NaNO₃ + 0.005 M Na₂SO₄ and 0.5 M NaNO₃ + 0.01 M NaCl.

The experimental results presented in Table 1 indicate that, at certain differences in the precipitation of metals on calcite and dolomite, the process always depends on the pH of the solution and is not specifically affected by sulfates and chlorides. A principal decrease in the concentrations of all of the examined heavy metals occurs at pH > 7.8–8.1, with all heavy metals, except only Pb (which is equally efficiently removed by calcite and dolomite), more efficiently immobilized by dolomite than calcite at any given pH

(Fig. 1). This is explained by that the CO_3^{2-} -normalized activity product of dolomite is approximately fivefold higher than that of calcite (Naumov et al., 1971; Lur'e, 1989).

Additionally to the precipitation of low-solubility phases, heavy metals can be immobilized by carbonate rocks by means of chemosorption

$$\frac{Me^{2+} + Ca_{1-x}Mg_x}{(1-x)Ca^{2+} + xMg^{2+} + Me},$$
(6)

where overlined symbols denote components adsorbed on the surface of the solid phase. The great majority of the constants of adsorption equilibria were determined for one or two solute components. In multicomponent solutions, such as natural and waste waters, these constants can be utilized only for very rough estimates.

² In these experiments, immobilization was referred to as adsorption immobilization provisionally, because the starting solutions were in equilibrium with the sold phases of heavy-metal carbonates, but the equilibrium could be shifted when the solutions occurred in contact with CaCO₃, and new phases could be formed, such as basic carbonates and oxihydrocarbonates of metals of lower solubility.

EXPERIMENTAL MODELING OF THE IMMOBILIZATION

Solid phase	Solution	μIJ	Me	Metal		
mass, g/L	Solution	рн	Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %
	-		Cu, calcite	•		•
2.3		2.29	89.1	89.1	0.0	0.0
2.6		6.96	"	75.9	13.2	14.8
3.0	0.5 M NaNO	8.08	"	5.04	84.1	94.3
4.0	0.0 101 1 (01 (03	8.10	"	6.45	82.6	92.8
5.0		8.16	"	2.52	86.6	97.2
6.0		8.17	<i>"</i>	0.94	88.2	98.9
2.3		2.29	89.1	88.6	0.5	0.6
2.6	0.5 M NaNO I	4.13		88.6	0.5	0.6
3.0	$0.5 \text{ M} \text{ NaNO}_3 + 0.005 \text{ M} \text{ NL} SO$	7.87		14.2	74.9	84.1
4.0	$0.005 \text{ M} \text{ Na}_2 \text{SO}_4$	7.79		20.3	68.8	77.2
5.0		8.15		4.56	84.5	94.9
6.0		8.19	00.1	0.4/	88.6	99.5
2.3		2.25	89.1	87.2	1.9	2.1
2.6	0.5 M NaNO ₂ +	3.38	"	89.0	0.1	0.1
3.0	0.01 M NaCl	7.95	.,	11.0	/8.1	87.0
4.0		8.06		/.9/	81.1	91.1
5.0		8.21	,,	1.90	87.2	97.9
			Same, dolomite	•		
2.1	0.5 M NaNO ₃	2.24	89.1	87.5	1.6	1.8
2.4		5.41	"	89.1	0.0	0.0
2.8		6.51	"	83.9	5.2	5.8
3.7		7.08	"	60.4	28.7	32.2
4.6		7.32	"	36.0	53.1	59.6
5.5		7.77	"	8.34	80.8	90.6
2.1		2.23	89.1	87.7	1.4	1.6
2.4		3.98	"	87.7	1.4	1.6
2.8	0.5 M NaNO ₃ +	4.46	"	87.4	1.7	1.9
3.7	0.005 M Na ₂ SO ₄	6.50	"	75.0	14.1	15.8
4.6	2 1	7.33	"	27.1	62.0	69.6
5 5		7.60	"	10.6	78.5	88.1
21		2 19	89.1	87.8	13	15
2.1		4 80	"	89.2	_ 0 1	_ 0.1
2.4	$0.5 \text{ M} \text{N}_{0} \text{NO} +$	6.41	,,	83.7	5.4	6.1
2.0	$0.3 \text{ M NaNO}_3 +$	6.90	,,	60.7	10.4	21.9
5.7	U.UI IVI INACI	0.07	,,	20 (17.4	21.0
4.6		7.20		38.6	50.5	56.7
5.5		7.59		14.9	74.2	83.3
	· ·		Zn, calcite	Γ	Γ	
2.3		2.29	93.9	92.8	1.1	1.2
2.6		6.96		90.1	3.8	4.0
3.0	0.5 M NaNO ₃	8.08		77.5	16.4	17.5
4.0	5	8.10	,,	71.1	22.8	24.3
5.0		8.16		55.9	38.0	40.5
6.0		8.17	"	28.8	65.1	69.3

Table 1. Immobilization of heavy metals by neutralizing acidic solutions by calcite and dolomite

Table	1.	(Contd.)
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Solid phase	Solution	۳U	Me	Metal			
mass, g/L	Solution	рп	Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %	
2.3		2.29	93.9	91.7	2.2	2.3	
2.6		4.13		91.6	2.3	2.4	
3.0	$0.5 \text{ M NaNO}_3 +$	7.87	"	82.5	11.4	12.1	
4.0	$0.005 \text{ M Na}_2 \text{SO}_4$	7.79	"	82.4	11.5	12.2	
5.0		8.15		58.5	35.4	37.7	
6.0		8.19	,,	29.9	64.0	68.2	
2.3		2.25	93.9	91.1	2.8	3.0	
2.6		3.58		91.8	2.1	2.2	
3.0	$0.5 \text{ M} \text{ NaNO}_3 +$	7.95		82.6	11.3	12.0	
4.0	0.01 M NaCl	8.06		/4.3	19.6	20.9	
5.0		8.21	,,	52.0	41.9	44.6	
0.0		8.03	Same dolomite	08.2	23.7	27.4	
21		2 24	93.9	92.1	1.8	1.9	
2.1		5 41	93.9 "	92.1	1.0	1.9	
2.4		5.41		92.7	1.2	1.3	
2.8	0.5 M NaNO ₃	6.51 - 00		91.8	2.1	2.2	
3.7		7.08		89.9	4.0	4.3	
4.6		7.32	,,	88.7	5.2	5.5	
5.5		7.77	"	77.7	16.2	17.3	
2.1		2.23	93.9	93.9	0.0	0.0	
2.4		3.98	"	93.9	0.0	0.0	
2.8	0.5 M NaNO ₃ +	4.46	"	93.6	0.3	0.3	
3.7	$0.005 \text{ M} \text{ Na}_2 \text{SO}_4$	6.50	"	92.7	1.2	1.3	
4.6		7.33	"	90.2	3.7	3.9	
5.5		7.60	"	84.7	9.2	9.8	
2.1		2.19	93.9	93.3	0.6	0.6	
2.4		4.80	"	91.8	2.1	2.2	
2.8	0.5 M NaNO ₃ +	6.41	"	92.1	1.8	1.9	
3.7	0.01 M NaCl	6.89	"	91.4	2.5	2.7	
4.6		7.20	"	89.6	4.3	4.6	
5.5		7.59	"	82.8	11.1	11.8	
Pb, calcite							
2.3		2.29	26.8	26.2	0.6	2.2	
2.6		6.96	"	25.3	1.5	5.6	
3.0	$0.5 M N_0 NO$	8.08	"	5.07	21.7	81.1	
4.0	0.5 WI Main 0_3	8.10	"	1.85	25.0	93.1	
5.0		8.16	"	0.73	26.1	97.3	
6.0		8.17	"	0.39	26.4	98.5	
2.3		2.29	26.8	26.8	0.0	0.0	
2.6		4.13	"	26.4	0.4	1.5	
3.0	0.5 M NaNO ₃ +	7.87		4.67	22.1	82.6	
4.0	0.005 M Na ₂ SO ₄	7.79	"	3.75	23.0	86.0	
5.0		8.15	,,	1.23	25.6	95.4	
6.0		8.19	"	0.59	26.2	97.8	

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Table 1. (Contd.)

Solid phase	Solution	μIJ	Me	Metal		
mass, g/L		рн	Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %
2.3		2.25	26.8	26.0	0.8	3.0
2.6		3.58	"	25.9	0.9	3.4
3.0	0.5 M NaNO ₃ +	7.95	"	4.87	21.9	81.8
4.0	0.01 M NaCl	8.06	"	2.14	24.7	92.0
5.0		8.21	"	0.71	26.1	97.4
6.0		8.05	<i>"</i>	0.68	26.1	97.5
	1 1	2.24	Same, dolomite	26.2	0.6	
2.1		2.24	26.8	26.2	0.6	2.2
2.4		5.41	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	25.8	1.0	3.7
2.8	0.5 M NaNO ₂	6.51	"	25.8	1.0	3.7
3.7	$0.5 \text{ M} \text{ NaNO}_3$	7.08	"	21.6	5.2	19.4
4.6		7.32	"	15.9	10.9	40.7
5.5		7.77	"	6.89	19.9	74.3
2.1		2.23	26.8	26.7	0.1	0.4
2.4		3.98	"	26.1	0.7	2.6
2.8	0.5 M NaNO ₃ +	4.46	"	26.3	0.5	1.9
3.7	0.005 M Na ₂ SO ₄	6.50	"	25.0	1.8	6.7
4.6		7.33	"	16.4	10.4	38.8
5.5		7.60	"	10.9	15.9	59.3
2.1		2.19	26.8	26.2	0.6	2.2
2.4		4.80	"	26.2	0.6	2.2
2.8	$0.5 \text{ M NaNO}_3 +$	6.41	,,	25.9	0.9	3.4
3.7	0.01 M NaCl	6.89		24.8	2.0	7.5
4.6		7.20		16.4	10.4	38.8
5.5		7.59	Cd calaita	8.57	18.2	68.0
		2.20		41.7	0.0	0.0
2.3		2.29	41.7	41.7	0.0	0.0
2.6		6.96	,,	41.6	0.1	0.2
3.0	0.5 M NaNO2	8.08	"	37.0	4.7	11.3
4.0	010 111 1 (01 (0 3	8.10	"	30.6	11.1	26.6
5.0		8.16	"	18.0	23.7	56.8
6.0		8.17	"	7.26	34.4	82.6
2.3		2.29	41.7	40.8	0.9	2.2
2.6		4.13	"	40.8	0.9	2.2
3.0	0.5 M NaNO ₃ +	7.87	"	37.1	4.6	11.0
4.0	0.005 M Na ₂ SO ₄	7.79	"	32.2	9.5	22.8
5.0		8.15	"	17.2	24.5	58.8
6.0		8.19	"	8.33	33.4	80.0
2.3		2.25	41.7	39.7	2.0	4.8
2.6		3.58	"	39.8	1.9	4.6
3.0	0.5 M NaNO ₃ +	7.95	"	37.4	4.3	10.3
4.0	0.01 M NaCl	8.06	"	28.1	13.6	32.6
5.0		8.21	"	15.6	26.1	62.6
6.0		8.05	"	17.9	23.8	57.1

Table 1. (Contd.)

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Solid phase	Solution	лЦ	Me^{2+} concentration, μM			Metal
2.1 2.24 41.7 41.1 0.6 1.4 2.8 0.5 M NaNO ₃ 7.08 " 41.0 0.7 1.7 3.7 0.5 M NaNO ₃ 7.08 " 40.0 1.7 4.1 4.6 7.32 " 37.3 4.4 10.6 1.4 5.5 7.77 " 25.2 16.5 39.6 2.1 2.23 41.7 40.9 0.8 1.9 2.8 0.5 M NaNO ₃ + 4.46 " 40.9 0.8 1.9 2.8 0.5 M NaNO ₃ + 6.50 " 40.7 1.0 2.4 3.7 0.005 M Na ₂ SO ₄ 6.50 " 40.7 1.0 2.4 4.6 7.33 " 38.8 2.9 7.0 5.5 7.60 " 31.3 10.4 24.9 2.1 2.19 41.7 41.7 0.0 0.0 2.4 3.5 7.60 "	mass, g/L	Solution	рп	Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Same, dolomite			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.1		2.24	41.7	41.1	0.6	1.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.4		5.41	"	41.1	0.6	1.4
3.7 0.5 M NaNO^3 7.08 " 40.0 1.7 4.1 4.6 7.32 " 37.3 4.4 10.6 5.5 7.77 " 25.2 16.5 39.6 2.1 2.23 41.7 40.6 1.1 2.6 2.4 3.98 " 40.9 0.8 1.9 2.8 $0.5 \text{ M NaNO}_3 +$ 4.46 " 41.0 0.7 1.7 3.7 $0.005 \text{ M Na}_2 SO_4$ 6.50 " 40.7 1.0 2.4 4.6 7.33 " 38.8 2.9 7.0 5.5 7.60 " 31.3 10.4 24.9 2.1 2.19 41.7 41.7 0.0 0.0 2.4 4.80 " 41.4 0.3 0.7 2.8 $0.5 \text{ M NaNO}_3 +$ 6.41 " 41.2 0.5 1.2 3.7 0.01 M NaCl 6.89 " 40.9 0.8 1	2.8	0.5 M NaNO	6.51		41.0	0.7	1.7
4.6 7.32 " 37.3 4.4 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.6 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.7 10.	3.7	0.5 11 1 11 103	7.08		40.0	1.7	4.1
5.5 7.77 " 25.2 16.5 39.6 2.1 2.23 41.7 40.6 1.1 2.6 2.4 3.98 " 40.9 0.8 1.9 2.8 0.5 M NaNO ₃ + 4.46 " 41.0 0.7 1.7 3.7 0.005 M Na ₂ SO ₄ 6.50 " 40.7 1.0 2.4 4.6 7.33 " 38.8 2.9 7.0 5.5 7.60 " 31.3 10.4 24.9 2.1 2.19 41.7 41.7 0.0 0.0 2.4 4.80 " 41.4 0.3 0.7 2.8 0.5 M NaNO ₃ + 6.41 " 41.4 0.3 0.7 2.8 0.5 M NaNO ₃ + 6.41 " 41.2 0.5 1.2 3.7 0.01 M NaCl 6.89 " 40.9 0.8 1.9 4.6 7.20 " 38.0 3.7 8.9	4.6		7.32		37.3	4.4	10.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5.5		7.77	"	25.2	16.5	39.6
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2.1		2.23	41.7	40.6	1.1	2.6
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2.4		3.98	"	40.9	0.8	1.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.8	0.5 M NaNO ₃ +	4.46		41.0	0.7	1.7
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	3.7	0.005 M Na ₂ SO ₄	6.50		40.7	1.0	2.4
5.5 7.60 " 31.3 10.4 24.9 2.1 2.19 41.7 41.7 0.0 0.0 2.4 4.80 " 41.4 0.3 0.7 2.8 $0.5 \text{ M NaNO}_3 + 6.41$ " 41.2 0.5 1.2 3.7 0.01 M NaCl 6.89 " 40.9 0.8 1.9 4.6 7.20 " 38.0 3.7 8.9 5.5 7.59 " 29.7 12.0 28.8	4.6		7.33	••	38.8	2.9	7.0
2.1 2.19 41.7 41.7 0.0 0.0 2.4 4.80 " 41.4 0.3 0.7 2.8 0.5 M NaNO ₃ + 6.41 " 41.2 0.5 1.2 3.7 0.01 M NaCl 6.89 " 40.9 0.8 1.9 4.6 7.20 " 38.0 3.7 8.9 5.5 7.59 " 29.7 12.0 28.8	5.5		7.60		31.3	10.4	24.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2.1		2.19	41.7	41.7	0.0	0.0
2.8 $0.5 \text{ M NaNO}_3 + 0.41$ " 41.2 0.5 1.2 3.7 0.01 M NaCl 6.89 " 40.9 0.8 1.9 4.6 7.20 " 38.0 3.7 8.9 5.5 7.59 " 29.7 12.0 28.8	2.4		4.80		41.4	0.3	0.7
3.7 0.01 M NaCl 6.89 " 40.9 0.8 1.9 4.6 7.20 " 38.0 3.7 8.9 5.5 7.59 " 29.7 12.0 28.8	2.8	0.5 M NaNO ₃ +	6.41		41.2	0.5	1.2
4.6 7.20 " 38.0 3.7 8.9 5.5 7.59 " 29.7 12.0 28.8	3.7	0.01 M NaCl	6.89		40.9	0.8	1.9
5 5 7 59 " 29 7 12 0 28 8	4.6		7.20		38.0	3.7	8.9
	5.5		7.59		29.7	12.0	28.8
Co, calcite				Co, calcite			·
2.3 2.29 62.6 62.0 0.6 1.0	2.3		2.29	62.6	62.0	0.6	1.0
2.6 6.96 " 61.6 1.0 1.6	2.6	0.5 M NaNO ₃	6.96		61.6	1.0	1.6
$3.0 \qquad 0.5 \text{ M NaNO} \qquad 8.08 \qquad " \qquad 60.3 \qquad 2.3 \qquad 3.7$	3.0		8.08		60.3	2.3	3.7
4.0 (0.5 W Walko ₃) 8.10 " 59.8 2.8 4.5	4.0		8.10		59.8	2.8	4.5
5.0 8.16 " 56.8 5.8 9.3	5.0		8.16		56.8	5.8	9.3
6.0 8.17 " 50.8 11.8 18.8	6.0		8.17		50.8	11.8	18.8
2.3 2.29 62.6 61.1 1.5 2.4	2.3		2.29	62.6	61.1	1.5	2.4
2.6 4.13 " 61.6 1.0 1.6	2.6		4.13	••	61.6	1.0	1.6
3.0 $0.5 \text{ M NaNO}_3 + 7.87$ " 61.0 1.6 2.6	3.0	0.5 M NaNO ₃ +	7.87	"	61.0	1.6	2.6
4.0 $0.005 \text{ M Na}_2 \text{SO}_4$ 7.79 " 59.6 3.0 4.8	4.0	0.005 M Na ₂ SO ₄	7.79		59.6	3.0	4.8
5.0 8.15 " 56.2 6.4 10.2	5.0		8.15		56.2	6.4	10.2
6.0 8.19 " 51.9 10.7 17.1	6.0		8.19		51.9	10.7	17.1
2.3 2.25 62.6 62.6 0.0 0.0	2.3		2.25	62.6	62.6	0.0	0.0
2.6 3.58 " 62.5 0.1 0.2	2.6		3.58		62.5	0.1	0.2
3.0 $0.5 \text{ M NaNO}_3 + 7.95$ " 60.5 2.1 3.4	3.0	0.5 M NaNO ₃ +	7.95	"	60.5	2.1	3.4
4.0 0.01 M NaCl 8.06 " 60.3 2.3 3.7	4.0	0.01 M NaCl	8.06		60.3	2.3	3.7
5.0 8.21 " 54.8 7.8 12.5	5.0		8.21		54.8	7.8	12.5
6.0 8.05 " 56.8 5.8 9.3	6.0		8.05	"	56.8	5.8	9.3

GEOCHEMISTRY INTERNATIONAL Vol. 54 No. 8 2016

Table 1. (Contd.)

Solid phase	Solution	Solution pH	Me	Metal		
mass, g/L	Solution		Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %
-	1 1		Same, dolomite	1		
2.1		2.24	62.6	62.3	0.3	0.5
2.4		5.41	"	62.8	-0.2	- 0.3
2.8	0.5 M NoNO	6.51	"	61.9	0.7	1.1
3.7	$0.5 \text{ M} \text{ NaNO}_3$	7.08	"	61.5	1.1	1.8
4.6		7.32	"	60.4	2.2	3.5
5.5		7.77	"	56.3	6.3	10.1
2.1		2.23	62.6	62.1	0.5	0.8
2.4		3.98	"	62.8	-0.2	- 0.3
2.8	0.5 M NaNO ₃ +	4.46	"	61.0	1.6	2.6
3.7	0.005 M Na ₂ SO ₄	6.50	"	62.7	-0.1	- 0.2
4.6		7.33	"	61.4	1.2	1.9
5.5		7.60	"	60.3	2.3	3.7
2.1		2.19	62.6	61.8	0.8	1.3
2.4		4.80	"	62.3	0.3	0.5
2.8	0.5 M NaNO ₃ +	6.41	"	61.9	0.7	1.1
3.7	0.01 M NaCl	6.89	"	61.7	0.9	1.4
4.6		7.20	"	60.6	2.0	3.2
5.5		7.59	"	59.9	2.7	4.3
			Ni, calcite			I
2.3		2.29	93.0	91.9	1.1	1.2
2.6	0.5 M NaNO ₃	6.96	"	91.4	1.6	1.7
3.0		8.08	"	88.8	4.2	4.5
4.0		8.10	"	88.2	4.8	5.2
5.0		8.16	"	85.7	7.3	7.8
6.0		8.17	"	71.9	21.1	22.7
2.3		2.29	93.0	91.5	1.5	1.6
2.6		4.13	"	90.4	2.6	2.8
3.0	$0.5 M NaNO_{2} +$	7.87	"	89.1	3.9	4.2
4.0	$0.5 \text{ WI NaINO}_3 + 0.005 \text{ M Na}_3 \text{SO}_4$	7.79	"	88.6	4.4	4.7
5.0		8.15	"	82.6	10.4	11.2
6.0		8 19	"	73.4	19.6	21.1
2.3		2.25	03.0	90.7	2.3	21.1
2.5		3.58	<i>7</i> 5.0 "	92.2	0.8	0.9
3.0	0.5 M NaNO ₃ +	7.95	"	86.9	6.1	6.6
4.0	0.01 M NaCl	8.06	"	86.1	6.9	7.4
5.0		8.21		78.0	15.0	16.1
6.0		8.05	,,	84.1	8.9	9.6

 Table 1. (Contd.)

Solid phase	se Solution pH		Me	Metal		
mass, g/L	mass, g/L	pm	Starting	Equilibrium	$-\Delta[Me^{2+}]$	removed, %
			Same, dolomite	•		
2.1		2.24	93.0	91.8	1.2	1.3
2.4		5.41	"	91.4	1.6	1.7
2.8	$0.5 \mathrm{M} \mathrm{NeNO}$	6.51	"	91.0	2.0	2.2
3.7	0.5 IVI INAINO ₃	7.08	"	89.4	3.6	3.9
4.6		7.32	"	87.3	5.7	6.1
5.5		7.77	"	84.0	9.0	9.7
2.1		2.23	93.0	93.0	0.0	0.0
2.4		3.98	"	91.3	1.7	1.8
2.8	0.5 M NaNO ₃ +	4.46	"	91.2	1.8	1.9
3.7	0.005 M Na ₂ SO ₄	6.50	"	91.2	1.8	1.9
4.6		7.33	"	87.9	5.1	5.5
5.5		7.60	"	85.6	7.4	8.0
2.1		2.19	93.0	92.3	0.7	0.8
2.4		4.80	"	91.8	1.2	1.3
2.8	0.5 M NaNO ₃ +	6.41	"	91.0	2.0	2.2
3.7	0.01 M NaCl	6.89	"	89.9	3.1	3.3
4.6		7.20	"	87.4	5.6	6.0
5.5		7.59	"	84.6	8.4	9.0

Given the constancy of the total amount of atoms adsorbed on the surface of a solid phase

$$\Gamma_{\infty} = \overline{[\mathrm{Ca}_{1-x}\mathrm{Mg}_{x}]} + \overline{[\mathrm{Me}]}$$
(7)

(6) yields an expression for the amount of heavy metal Γ_{Me} adsorbed on the surface of Ca-Mg carbonate Ca_{1-x}Mg_xCO₃

$$\Gamma_{\rm Me} = \frac{\Gamma_{\infty} K[{\rm Me}^{2+}]}{[{\rm Ca}^{2+}]^{1-x} [{\rm Mg}^{2+}]^x + K[{\rm Me}^{2+}]},$$
(8)

where *K* is the equilibrium constant of reaction (6). Multiplying the numerator and denominator of the right-hand part of Eq. (8) by $[CO_3^{2--}]$ and dividing by the concentration solubility product $L'_{Ca_{1-x}Mg_xCO_3}$ of $Ca_{1-x}Mg_xCO_3$, we obtain

$$\Gamma_{\rm Me} = \frac{\Gamma_{\infty} K \left(\frac{\dot{L}_{\rm MeCO_3}}{\dot{L}_{\rm Ca_{1-x}Mg_xCO_3}} \right) \Omega_{\rm MeCO_3}}{1 + K \left(\frac{\dot{L}_{\rm MeCO_3}}{\dot{L}_{\rm Ca_{1-x}Mg_xCO_3}} \right) \Omega_{\rm MeCO_3}}, \qquad (9)$$

where L'_{MeCO_3} is the concentration solubility product of the heavy-metal carbonate, and $\Omega_{MeCO_3} = \frac{[Me^{2^+}][CO_3^{2^-}]}{L'_{MeCO_3}}$ is the degree of solution saturation with respect to $MeCO_3$. The form of Eq. (9) corresponds to that of the Langmuir adsorption isotherm

$$\Gamma_{\rm Me} = \frac{\Gamma_{\infty} K^*[{\rm Me}^{2+}]}{1 + K^*[{\rm Me}^{2+}]},\tag{10}$$

in which
$$K^* = K\left(\frac{L'_{MeCO_3}}{L'_{Ca_{1-x}Mg_xCO_3}}\right)$$
, and the equilibrium

concentration of the metal [Me²⁺] is substituted for the degree of saturation with the sold phase MeCO₃. According to (9), Γ_{Me} is constant for solutions saturated with MeCO₃ ($\Omega_{MeCO_3} = 1$).

The results of experiments on modeling the adsorption immobilization of Zn, Cd, Co, and Ni on calcite (Table 2) show that the concentrations of the dissolved metals nonlinearly vary with increasing solid phase/solution mass ratio (Fig. 2). The most efficient removal from solution is typical of Cd: at a CaCO₃ mass of 21 g/L and starting calcite content of 10 mM, 95% (720 μ M) Cd was removed from the solution. The adsorption of Co, Ni, and Zn under analogous conditions is remarkably lower: 57% (100 µM), 14% $(27 \,\mu\text{M})$, and 33% $(12 \,\mu\text{M})$, respectively. An increase in the starting concentrations of dissolved Ca from 10 to 50 µM leads to a significant decrease in the immobilization of the metals: by 76-80% for Zn, 12-24% for Cd, 44-69% for Co, and 47-54% for Ni, as follows from exchange adsorption reaction (6).



Fig. 1. Dependences of the heavy-metal concentrations in equilibrium with calcite and dolomite on pH. (1) Calcite, 0.5 M NaNO₃; (2) same, 0.5 M NaNO₃ and 0.005 M Na₂SO₄; (3) same, 0.5 M NaNO₃ and 0.01 M NaCl; (4) dolomite, 0.5 M NaNO₃; (5) same, 0.5 M NaNO₃ and 0.005 M Na₂SO₄; (6) same, 0.5 M NaNO₃ and 0.01 M NaCl.

At the same time, the dependences of the specific adsorption of Zn, Co, and Ni on the equilibrium concentrations of these metals in the solutions notably differ in form from adsorption isotherms (Langmuir's, Freundlich's, and others). For Ni and Co, extrapolation of the linear segment of the dependence Γ_{Me} – $[Me^{2+}]$ to the low-concentration region results in $\Gamma_{Me} = 0$ at $[Me^{2+}] > 0$ (Fig. 3), which has no physical meaning. The $d\Gamma_{Me}/d[Me^{2+}]$ derivative for Ni

increases with increasing equilibrium concentration of the metal in the solution, whereas it should have decreased according to the adsorption theory. This can likely be explained as follows. The maximum adsorption of the metals is likely reached at lower concentrations than those in the experiments. At higher concentrations, the metal is removed from the solution by precipitating the solid phase of the basic carbonate $Me(OH)_x(CO_3)_{1-0.5x}$, whose solubility is lower than that of $MeCO_3$. The precipitation process is initiated

Table 2. Adsorption immobilization of heavy meta	ls on calcite
--------------------------------------------------	---------------

Solid phase	Ca(NO ₃) ₂		Me^{2+} concentration, μM			Metal removed
mass, g/L	concentration,	pH	Starting	Equilibrium	$-\Delta [Me^{2+}]$	%
	mM		Starting	Equilionum		
	1		Zn	1		1
1.4	10	7.75	36.1	34.9	1.22	3.4
4.3	"	7.70	"	32.6	3.52	9.7
7.1	"	7.66	"	30.7	5.35	14.8
10.0	"	7.69	"	29.1	7.03	19.5
14.3		7.68		27.1	9.02	25.0
21.4		7.69	"	24.2	11.9	33.1
1.4	50	7.47	112.6	111.6	0.92	0.8
4.3		7.42		110.1	2.45	2.2
7.1		7.38	"	108.9	3.67	3.3
10.0		7.45	"	107.4	5.20	4.6
14.3		7.36	"	106.7	5.81	5.2
21.4		1.35		105.1	7.49	0.7
	10	6.54	Cd			
1.4	10	6.54	758	714	44.5	5.9
4.3		6.51		603	156	20.5
7.1		6.57		520	238	31.4
10.0		6.63		407	351	46.3
14.3		6.75		250	508	67.0
21.4	50	7.14		32.9	726	95.7
1.4	50	6.63	823	785	37.8	4.6
4.3		6.64		692	131	15.9
7.1		6.65		596	227	27.6
10.0	"	6.68	"	499	324	39.3
14.2		6.67	,,	370	453	55.0
21.4		0.81	<u> </u>	225	398	12.1
	10	7 72	175.6	067	70.0	44.0
5./	10	1.13	1/5.6	96.7	/8.9	44.9
9.9	,,	7.04	"	03.0 70.4	91.8	54.9
14.2	"	7.00	"	79.4 77 0	90.2	56.0
24.1	"	7.67	"	75.0	98.4 100.6	57.3
24.1	"	7.03	"	73.0	103.0	58.6
57	50	7.38	175.6	151.5	24.1	13 7
0.0		7.35	"	130.3	24.1	20.7
14.2	"	7.35	"	137.5	50.5 44 1	25.1
18.5	"	7.20	"	126.1	49.6	23.1
24.0	"	7.31	"	123.5	52.1	20.2
31.3	"	7.32	"	117.6	58.0	33.0
			Ni			
57	10	7 56	190.3	169.5	20.8	10.9
99	"	7.50	"	167.7	20.0	11.9
14.2	"	7.12	"	165.8	24.5	12.9
18.5	"	7.43	"	164.3	26.1	13.7
24.0	"	7.47	"	162.0	28.3	14.9
31.2	"	7.65	"	159.3	31.0	16.3
5.7	50	7.33	175.2	166.3	8.86	5.1
9.9	"	7.32		164.4	10.7	6.1
14.1	"	7.36	"	164.8	10.4	5.9
18.5	"	7.42	"	163.2	11.9	6.8
24.1	"	7.40	"	161.9	13.3	7.6
31.3	"	7.34	"	160.2	15.0	8.6
	1		1			1

GEOCHEMISTRY INTERNATIONAL Vol. 54 No. 8 2016



Fig. 2. Dependences of the adsorption removal of heavy metals from solutions on the calcite mass. Starting Ca concentrations: (1) 10 mM, (2) 50 mM.

by changes in the physicochemical parameters of the liquid phase at interaction of the starting solution with $CaCO_3$.

The theoretical form of an adsorption isotherm is consistent only with the data on Cd, which indicate the constancy of Γ_{Cd} , which corresponds to the process asymptotically approaching the maximum adsorption value. Because the solubility of CdCO₃ is the lowest among the examined carbonates, it is realistic to suggest that saturation with respect to CdCO₃ was reached under these conditions, and according to (9), $\Gamma_{Cd} = \text{const.}$

A fact that was demonstrated in earlier experiments (Sergeev et al., 2000) and was hard to explain is that heavy metals can be significantly immobilized by the carbonate volcanic rock calcarinite in the presence of large amounts of dissolved organic compounds (DOM), which forms stable complexes and should be favorable for retaining heavy metals in solution. Theoretical analysis of this issue makes it possible to explain this phenomenon by the effect of the Fe³⁺ admixture in calcarinite. As is known, the stability constants of Fe³⁺ complexes with organic ligands are usually much higher

than the constants of other heavy metals (Table 3), and hence, Fe^{3+} ions coming from the absorbent into solution substitute heavy metals in the organic complexes

$$Fe^{3+} + Me^{2+} - DOM = Fe^{3+} - DOM + Me^{2+}$$
, (11)

which are then again able to form individual solid phases involved in the adsorption process.

Our results show that the adsorption precipitation immobilization of heavy metals on Ca and Mg carbonates is highly efficient, and it is thus expedient to use the carbonate geochemical barrier to prevent environmental contamination with heavy metals from various industrial waste waters. This pertains first of all to the ecological rehabilitation of acidic mining waters and products of acid leaching of rare elements. First, the low-solubility heavy-metal carbonates should be immobilized, and then the remaining Zn, Cd, Co, and Ni concentrations should be removed by adsorption on CaCO₃. An even greater efficiency may be shown by composite clay-carbonate and/or clay-sulfitecarbonate geochemical barriers, whose nonsilicate components should effectively immobilize heavy metals at their high concentrations.

SAVENKO



Fig. 3. Dependences of the specific adsorption of heavy metals on calcite on the concentrations of the heavy metals in the solution. Starting Ca concentrations: (I) 10 mM, (2) 50 mM.

CONCLUSIONS

1. It is experimentally proved that interaction of calcite and dolomite with solutions of heavy metals (Cu, Zn, Pb, Cd, Co, and Ni) at pH > 7.8-8.1 leads to

a significant decrease in the concentrations of the metals because of the precipitation of individual carbonate phases of these metals. Except Pb, which is equally efficiently removed by both minerals, the

Table 3. Stability constants of MeL complexes with organic ligands

Ligand I	$\log K_1^0$ (Lur'e, 1989)					
	Fe ³⁺	Cu ²⁺	Zn^{2+}	Pb ²⁺	Cd^{2+}	
Acetate CH ₃ COO ⁻	3.38	2.23	1.57	_	1.93	
Oxalate COO_2^{2-}	9.40	6.70	4.85	—	4.00	
Oxyquinoline $C_9H_6NO^-$	12.30	12.20	8.50	_	7.20	
Salicylate $C_6H_4(COO)O^{2-}$	15.35	12.02	6.85	—	—	
Sulphosalicylate $C_6H_3O(COO)(SO_3)^{3-}$	14.05	9.52	6.05	_	_	
Tartrate (CHOH) ₂ (COO) ₂ ^{2–}	7.49	3.00	3.31	2.92	_	
Citrate $(CH_2)_2 C(OH) (COO)_3^{3-}$	11.40	5.90	4.98	4.34	5.36	
Citrate (monohydro) (CH ₂) ₂ C(OH)(COOH)(COO) $_3^{3-}$	6.30	3.42	2.98	5.72	2.20	

other metals are more efficiently immobilized by dolomite than calcite at any pH.

2. Residual Zn, Cd, Co, and Ni concentrations are immobilized by chemosorption, which is more efficient for Cd than for Co, Ni, and Zn. An increase in the starting content of dissolved calcite suppresses the immobilization of the metals.

3. The high efficiency of adsorption—precipitation immobilization of heavy metals on Ca and Mg carbonates can be used to engineer artificial geochemical barriers on the basis of carbonate rocks to protect the environment from contamination with heavy metals.

REFERENCES

- Yu. Yu. Lur'e, "Handbook on Analytical Chemistry (Khimiya, Moscow, 1989) [in Russian].
- A. E. Martell, R. M. Smith, and R. J. Motekaitis, Critically Selected Stability Constants of Metal Complexes Database. Version 3.0 (A&M University, College Station, 1997).

- G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, *Handbook of Thermodynamic Values* (Atomizdat, Moscow, 1971) [in Russian].
- A. I. Perel'man, E. N. Borisenko, N. F. Myrlyan, and M. P. Tentyukov, "Anthropogenic geochemical barriers," in *Geochemistry of Anthropogenic Processes*, Ed. by I. K. Karpov (Nauka, Moscow, 1990), pp. 14–26.
- V. I. Sergeev, A. V. Savenko, and L. Gatto, "Application of calcarenite for removal of heavy metals from waters bearing dissolved inorganic matter," Geoekologiya, No. 3, 229–233 (2000).
- K. N. Trubetskoi, and A. E. Vorob'ev, "Classification of methods of raw mineral reproduction," Gornyi Zh., No. 1, 30–34 (1998).
- G. A. Volkov, and G. A. Solomin, "Assessment of the stability constants of complex compounds in relation with problems of element migration in underground waters," Gidrogeol. Inzhenr. Geol. Ekspress-Informatsiya, No. 3, 1–24 (1983).

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