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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Physicochemical Simulation of Calcite (Dolomite)–$FeSO_4$–H_2O Open Systems

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Abstract—Effect of the chemical composition of carbonate minerals on the precipitation of iron from a Fe(II) sulfate solution was studied.

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This study proceeds with analysis of the interaction of calcite and dolomite with sulfate solutions of iron in order to determine the influence exerted by the composition of a neutralizing agent on the efficiency of water treatment to remove this component. It has been found that, upon addition of solid carbonates to a $Fe_2(SO_4)_3$ solution, the process of neutralization of the acid solution occurs with a higher intensity with calcite [1]. Under conditions of partly neutralized solutions, this leads to shorter onset time of iron precipitation and to precipitation to complete dissolution of the reagent. For two systems, with calcite or dolomite, the iron concentrations in solution upon complete dissolution of the minerals are the same. It is noteworthy that the experiments were performed at equal molar ratios between CO_3^{2-} contained in reagents and Fe^{3+} in the starting solution.

Under real conditions, hydroxo compounds of iron are predominantly formed with Fe^{2+} involved [2]. Iron-containing solutions are formed in oxidation zones of sulfide deposits and via weathering of stored sulfide wastes, discharge of acid wastewater, etc. In [3], the notion of the total acidity of water was introduced by which was understood the overall result of all processes occurring with release of H^+. It was found using a computer thermodynamic simulation that, upon interaction of acid water with calcite in a closed system, the hydrolysis of Fe^{3+} and precipitation of siderite $FeCO_3$ were principal processes determining the acidity [3]. In neutralization of acid water in an open system, the main acidity-determining processes are, owing to Fe^{2+} oxidation, the hydrolysis of Fe^{3+} and precipitation of $Fe(OH)_3$. The process of Fe^{2+} oxidation followed by hydrolysis was represented by Solomin G.A. et al. [3] by the following overall equation

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+. \qquad (1)$$

In an open system, in which the whole amount of iron(II) is oxidized, the total concentration of released protons, $\Delta H^+(Fe^{2+})$ (g-ion l^{-1}), is equal to its doubled concentration:

$$\Delta H^+(Fe^{2+}) = 2c(Fe^{2+}). \qquad (2)$$

It is known that, depending on the pH of the medium, the dissolution of calcite is described by the reactions

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-, \qquad (3)$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \qquad (4)$$

The concentration of dissolved carbonate components in an open system will only increase to an extent allowed by the equilibrium with atmospheric carbon dioxide [3]. It can be stated that, depending on conditions, one mole of $CaCO_3$ binds one to two moles of H^+ via hydrolysis of the carbonate ion. A similar process is observed in dissolution of dolomite. Consequently, the number of moles of the neutralizing component of the carbonate minerals is equal to the number of CO_3^{2-} moles. In this case, full neutralization of a $FeSO_4$ solution containing no additional impurities requires addition of reagents in an amount providing a $CO_3^{2-}/Fe^{2+} > 1$ ratio if the mechanism of reaction (4) is operative, or $CO_3^{2-}/Fe^{2+} > 2$ in the case of reaction (3).

It is known that such iron oxo hydroxides as goethite α-FeO(OH) and hematite α-Fe_2O_3 most widely occur in nature; substantially more rare are lepidocrocite γ-FeO(OH) and maghemite γ-Fe_2O_3 [2].

Lepidocrocite can be formed in those cases when $Fe(OH)_2$ is the starting substance and oxidation first yields "green" intermediates, protolepidocrocites, structurally close to $Fe(OH)_2$. This course of the oxidation process is possible at pH > ~4.5–5.5 and a moderate rate of Fe^{2+} conversion to Fe^{3+}. At pH lower than 4.5–5.5, iron(II) hydroxide is unstable, so that formation of protolepidocrocites is impossible and goethite is formed from $Fe(OH)_2$.

In natural $FeSO_4$ solutions exhibiting an acid reaction, formation of lepidocrocite is almost impossible. This compound can only be formed in oxidation of iron sulfides in the presence of active neutralizers of sulfuric acid, and primarily carbonates. The most favorable conditions for formation of lepidocrocite in nature are created in a hypergenic change of siderite and other ferriferous carbonates, when iron passes into solutions in the form of $Fe(HCO_3)_2$. As a rule, lepidocrocite is formed in solutions with low content of Fe^{2+} and some amount of carbon dioxide. In more concentrated $Fe(HCO_3)_2$ solutions, in which Fe^{2+} oxidation is faster, goethite is synthesized.

Compared with other minerals, goethite is formed in the widest range of pH values, from the lowest to the highest. In the most acidic and the most alkaline solutions, goethite is the only stable iron oxide. At pH in the range from 4.5–5.5 to approximately 7.5, goethite can only be formed in the case of a very fast Fe^{2+} oxidation. In the pH range 7.5–12.5, goethite is not formed directly from Fe^{2+} compounds [2].

Thus, analysis of published data suggests that the most probable forms of iron precipitation in the interaction of sulfate iron solutions with carbonate minerals are goethite and lepidocrocite.

To study the mechanism and determine the effect of carbonate minerals on the nature of the precipitate formed in the interaction of a $FeSO_4$ solution with calcite and dolomite, we carried out model experiments whose results are reported in this communication.

EXPERIMENTAL

In view of the wide diversity and complexity of processes occurring in the interaction of calcite and dolomite with a $FeSO_4$ solution, we first performed experiments that can evaluate the degree of iron precipitation and the composition of the precipitated phase as functions of the relative amounts of the reagent and iron and the interaction time in a wide range of variation of these parameters.

We used in the study marbled calcite $CaCO_3$ from the Koelga deposit (Chelyabinsk oblast) and dolomite $CaMg(CO_3)_2$ from the Titan deposit (Murmansk oblast). The content of the impurity component, silica, was 0.1% for calcite and 21.4% for dolomite. Rock samples were crushed in a porcelain mortar. The fraction with grain size < 70 μm was taken for experiments. The starting suspensions with an iron concentration of 0.025 g-equiv l^{-1} (12.5 mM, 0.7 g l^{-1}) were prepared as follows. To diminish the oxidation rate of iron(II), 10 ml of 1 N HCl was added to a liter of the starting 0.125 N $FeSO_4$ solution prepared by dissolving a $FeSO_4 \cdot 7H_2O$ reagent of chemically pure grade in distilled water. Further, 2 ml of 0.1 N NaOH were added to a suspension of the reagent in 200 ml of distilled water in order to neutralize the excess amount of the acid in the starting $FeSO_4$ solution, and then 50 ml of the starting solution of iron sulfate were gradually poured in. The experiments were carried out under agitation with a magnetic rabble under conditions of a free access of air. After a prescribed time, the pH value of the suspension, pH_s, was determined and, upon filtration through a "blue band" filter, the solution pH was measured, pH_{sol}. The solutions were analyzed on Kortek Kvant AFA and Carl Zeiss AAS-30 atomic-absorption spectrometers. The sensitivity of the analysis for iron was 0.1 mg l^{-1}.

The change in the concentration of iron(II) in solution as a result of an interaction with neutralizing reagents was determined by the method of separate weighed portions. The dissolution of the minerals was monitored by X-ray phase analysis of the precipitates composed of iron compounds and the undissolved part of the reagent, and also by chemical analysis of solutions. The properties of the precipitated phase were studied by crystal-optical, X-ray diffraction, and electron-microscopic (SEM LEO 420 microscope) analyses.

A physicochemical study of the iron precipitation from sulfate solutions was carried out using the last version of the Selektor software complex [4].

For this purpose we used the model Al–B–Ar–Ne–C–Ca–Cl–F–K–Mg–Fe–Mn–N–Na–P–S–Si–Sr–Cu–Ni–Ti–H–O–*e* (*e* is electron) containing 104 components in the aqueous phase, 12 in the gas phase, and 155 solid phases. The calculations were made at a temperature of 25°C and pressure of 1 bar.

The results of experiments in the interaction of calcite and dolomite with a $FeSO_4$ solution demonstrated that, as in experiments with a sulfate solution of Fe(III), the composition of the neutralizing reagents affects the process of iron precipitation. In the early stage, at an interaction duration of 3 h, the difference between the reagents is manifested in the nature of the dependence of the iron concentration c_{Fe} in solution on the expenditure of a reagent. As the amount of the reagent increases in experiments with dolomite, the c_{Fe} steadily decreases and pH_s increases (Fig. 1a). Figure 1b shows results of similar experiments with calcite. The pH_s values increase with the expenditure of calcite, whereas a chaotic scatter of data is observed for c_{Fe}. After 24 h of interaction, the dependence of the concentration on the calcite expenditure becomes predictable nature (Fig. 2).

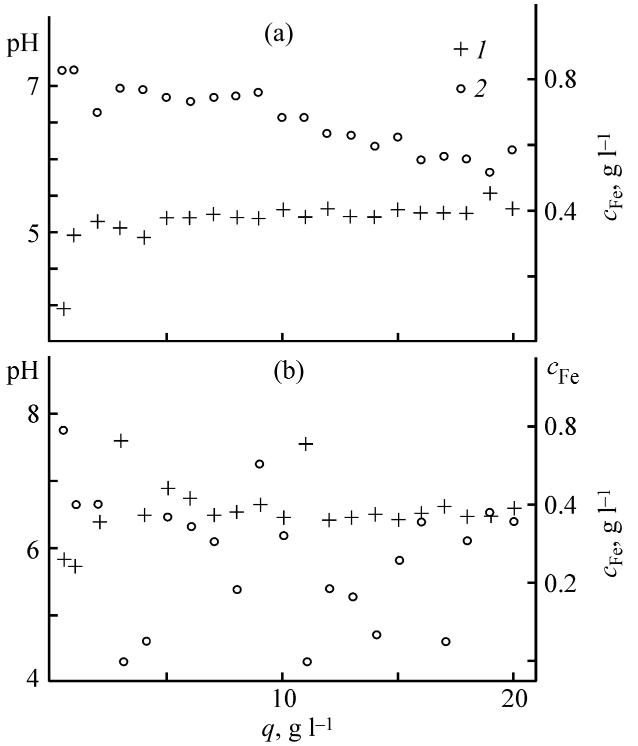

Fig. 1. (*1*) pH value and (*2*) iron concentration c_{Fe} in solution vs. the expenditure q of (a) dolomite and (b) calcite at an interaction duration of 3 h.

The experimental data can be accounted for by the higher chemical activity of calcite, compared with dolomite [1]. The rate of calcite dissolution considerably exceeds that of dolomite, which gives rise to local supersaturation regions in solution and favors precipitation of iron because of the excess amount of CO_2. The accumulation of CO_2 in early stages of neutralization in calcite decomposition was noted in [3]. A crystal-optical analysis demonstrated that siderite $FeCO_3$ is present in the precipitate, which indicates that the given system approaches the state characterized as the state of a limited access of air [3]. This state is not revealed by X-ray phase analysis. A possible reason is that $FeCO_3$ is precipitated as an amorphous deposit [2], similarly to amorphous $CaCO_3$. It is known that amorphous calcium hydroxide is formed, in addition to crystalline calcite and vaterite, in carbonization of a calcium hydroxide solution [5].

The higher rate of calcite dissolution, compared with dolomite, is confirmed by data on the chemical composition of the solutions (Table 1). The degree of

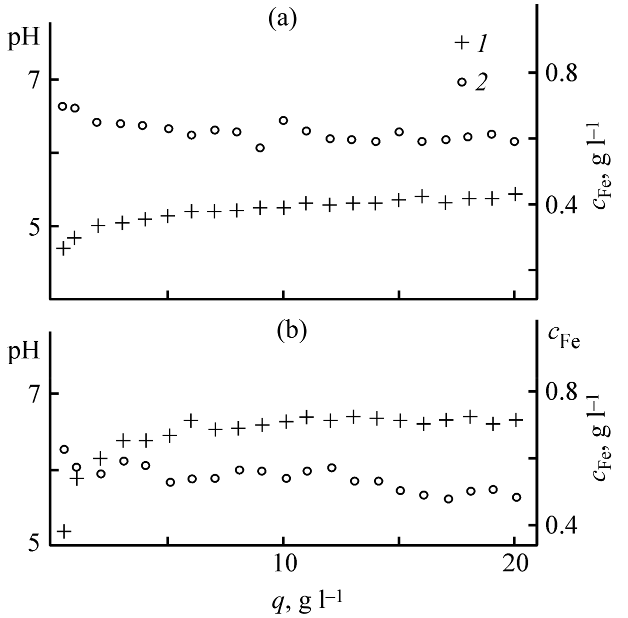

Fig. 2. (*1*) pH value and (*2*) iron concentration c_{Fe} in solution vs. the expenditure q of (a) dolomite and (b) calcite at an interaction duration of 24 h.

Table 1. Content of components in solutions obtained upon interaction of the starting $FeSO_4$ solution (concentration 12.5 mM) with calcite and dolomite[a]

Reagent composition	Amount of a reagent		3 h		7 days		14 days		60 days	
	q, g l^{-1}	n_{in}, mM	pH_s	n_{in}, mM	pH_s	n_{in}, mM	pH_s	n_{in}, mM	pH_s	n_{in}, mM
Calcite	4	40	6.50	10.8	6.45	7.21	6.94	14.2	7.65	–
	9	90	6.65	5.7	6.55	0.61	7.70	12.4	7.70	–
	14	140	6.50	14.5	6.65	0.01	–	–	7.75	–
	19	180	6.45	8.2	6.65	0.3	7.75	12.0	7.75	–
Dolomite	4	34	4.95	1.5	5.05	7.2	5.93	13.8	6.85	14.4
	9	78	5.20	2.2	5.30	8.91	6.75	13.3	7.45	14.4
	14	121	5.2	3.2	5.45	0.3	6.70	12.8	7.45	15.3
	19	156	5.3	4.4	5.45	8.7	6.74	14.9	7.45	15.4

[a] q, reagent expenditure; nin and nsolv, initial and dissolved amounts of the reagent in terms of carbonate ions; dash, data unavailable.

calcite dissolution at an experiment duration of 3 h substantially exceeds that of dolomite. As the weighed portion becomes larger, the amount of dissolved dolomite increases, whereas for calcite, irregular variations of this parameter are observed.

According to the results of thermodynamic simulation, the equilibrium with calcite is attained at pH 5.3–6.3 in a closed system and at pH 7.4–8.1 in an open system [3]. The pH values of ~6.5 in 3-h experiments with calcite also indicate that the experimental conditions approach those of a closed system. As the interaction duration increases,

Table 2. Content of the components in solutions obtained upon interaction of the starting $FeSO_4$ solution (concentration 12.5 mM) with calcite and dolomite

n_{in}, mM	14 days			60 days		
	n_{solv}, mM	$n_{pr.Fe}$, mM	pH_s	n_{solv}, mM	$n_{pr.Fe}$, mM	pH_s
Calcite						
5	5.0	2.4	3.7	–	3.1	3.4
10	10.0	8.2	4.0	–	8.4	3.7
20	14.8	12.1	6.3	–	11.4	6.0
30	12.2	12.1	6.4	–	12.5	7.5
Dolomite						
4.3	4.3	4.3	4.1	5.2	3.6	3.6
8.7	8.7	8.6	4.5	10.6	8.9	3.9
17.4	12.7	12.4	5.1	14.2	12.2	4.8
26.0	13.8	12.2	5.3	14.3	12.5	6.9

[a] $n_{pr.Fe}$, amount of precipitated iron.

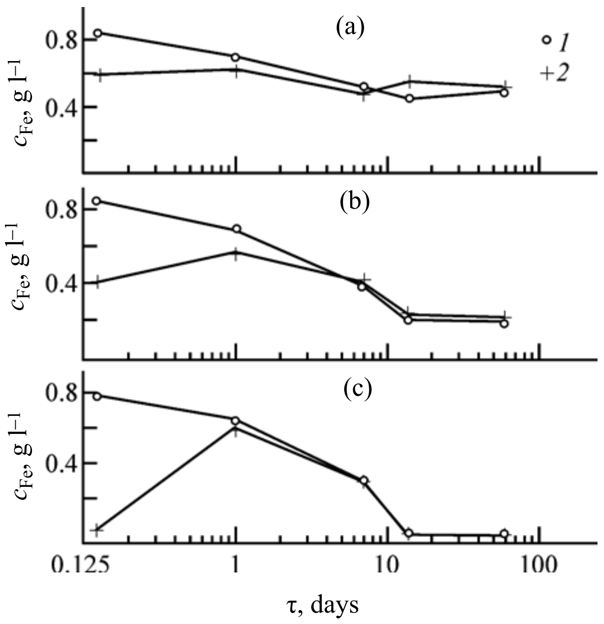

Fig. 3. Iron concentration c_{Fe} in solution vs. the interaction duration τ. (*1*) Calcite and (*2*) dolomite. Ratio between the amounts of the minerals (in terms of carbonate ions) and the content of iron in the starting solution, n_{in}/c_{Fein} for calcite (dolomite) (mol/mol): (a) 0.40 (0.36), (b) 0.80 (0.70), and (c) 2.40 (2.10).

Table 3. Results of a thermodynamic simulation of the interaction in an open system constituted by calcite or dolomite and a $FeSO_4$ solution (concentration 12.5×10^{-3} mol kg^{-1})

$n_{in} \times 10^3$, M	pH	Amount of solid phases $n \times 10^3$, mol		Concentration of main Fe-containing species in solution, mol kg^{-1}
		α-FeO(OH)	$CaCO_3$	
Calcite				
10.0	2.53	12.49	0.00	$FeSO_4^+$ 4.24×10^{-6}, Fe^{3+} 3.38×10^{-7}, $FeOH^{2+}$ 3.25×10^{-7}
12.0	3.24	12.49	0.00	$FeSO_4^+$ 3.40×10^{-8}, Fe^{3+} 2.65×10^{-9}, $FeOH^{2+}$ 1.27×10^{-8}
12.5	5.57	12.50	0.00	$Fe(OH)_2^+$ 1.65×10^{-12}
12.6	7.20	12.50	0.00	$Fe(OH)_3$ 2.76×10^{-13}
13.0	7.61	12.50	0.232	$Fe(OH)_3$ 2.76×10^{-13}, $Fe(OH)_4^-$ 8.0×10^{-14}
Dolomite				
10.0	2.55	12.49	0.00	$FeSO_4^+$ 4.20×10^{-6}, Fe^{3+} 3.20×10^{-7}, $FeOH^{2+}$ 3.15×10^{-7}
12.0	3.26	12.49	0.00	$FeSO_4^+$ 3.30×10^{-8}, Fe^{3+} 2.50×10^{-9}, $FeOH^{2+}$ 1.20×10^{-8}
12.5	5.58	12.50	0.00	$Fe(OH)_2^+$ 1.60×10^{-12}
12.6	7.19	12.50	0.00	$Fe(OH)_3$ 2.77×10^{-13}
13.0	7.63	12.50	0.00	$Fe(OH)_3$ 2.77×10^{-13}

the pH grows and reaches a value of 7.7 (Table 1), characteristic of the open system, in two months.

Thus, the rate of calcite dissolution in the initial stage of the interaction exceeds the rate of CO_2 removal from the reaction medium, with $FeCO_3$ precipitated under the high supersaturation conditions. As carbon dioxide is removed, the iron concentration grows, with the dependence of c_{Fe} on the calcite expenditure becoming similar to that for dolomite already after 24 h of interaction (Fig. 2). Further precipitation of iron in experiments with calcite is apparently due to Fe(II) → Fe(III) oxidation to give FeO(OH). In the case of dolomite, siderite is not formed and only the last mechanism of iron precipitation is operative. Figure 3 illustrates these considerations. Under conditions of a considerable deficiency of the reagent ($CO_3^{2-}/Fe^{2+} \approx 0.4$), the dependences for calcite and dolomite almost coincide. As the calcite expenditure increases, c_{Fe} substantially decreases in experiments with an interaction duration of 3 h. In 24 h, the iron-containing precipitated phase dissolves, with the iron concentration in solutions reaching values recorded in similar experiments with dolomite. In experiments with dolomite, c_{Fe} gradually decreases during the entire experiment.

To diminish the effect of the supersaturation factor, we carried out experiments with gradual (set 1) and single-portion (set 2) pouring of a $FeSO_4$ solution into a calcite suspension. According to the results of an X-ray phase analysis, precipitates of set 1 are less crystallized than those of set 2, in agreement with the results of an analysis of their morphology with a SEM LEO 420 microscope. In set 1, loose flaky new formations are produced, whereas in set 2, the precipitate is more aggregated because iron oxo hydroxides formed from $FeCO_3$ in set 1 have not enough time to be crystallized to the same extent as the precipitates in set 2.

Table 4. Lepidocrocite/goethite ratio in precipitates produced in interaction of a $FeSO_4$ solution with calcite or dolomite for 60 days

pH_c	γ-FeO(OH)/α-FeO(OH)
Calcite	
3.40	0.20
7.65	0.64
7.75	0.63
7.75	0.79
Dolomite	
3.55	0.17
6.85	1.74
7.45	1.08
7.45	1.22

As the interaction duration increases to 60 days, the transformation of the iron-containing precipitate is due to gradual oxidation of iron(II) to iron(III) and formation of a mixture of α-FeOOH and γ-FeOOH. The precipitate has the form of lamellar crystals, which results from their growth under conditions of a gradual decrease in the iron concentration in the solution [6].

In 60 days, c_{Fe} decreases to less than 0.1 mg l^{-1}. The only exception are experiments with the smallest amount of reagents, for which Table 2 lists results of determination of the chemical composition of solutions. At a deficiency of the reagent with respect to the amount of iron(II) in the starting mixture ($CO_3^{2-}/Fe^{2+} < 1$, n_{in} 5.0 and 10.0 mM for calcite, 4.3 and 8.7 mM for dolomite), iron is not completely precipitated. As the reagent expenditure is raised to n_{in} 20.0 and 30.0 mM (calcite) and 17.4 and 26.0 mM (dolomite), the degree of solution purification reaches values of 97–100%, with the ratio between the amount of minerals that have passed into solution and that of precipitated iron is 1.0–1.1 mol/mol, which points to a predominant occurrence of reaction (4) in the systems under consideration.

To the ratio $CO_3^{2-}/Fe^{2+} > 1$, at which iron is the most completely precipitated, also point the results of a thermodynamic simulation. Table 3 lists data on the content of solid phases and concentration in solution of those iron-containing species which make the main contribution to the total concentration of dissolved iron. Under the thermal equilibrium conditions, formation of electrically neutral $Fe(OH)_3$ species, i.e., the onset of precipitation, is observed when the ratio $CO_3^{2-}/Fe^{2+} = 1$ is exceeded (Table 3). At the same time, experimental data demonstrate that, even in 60 days, the reagent is not completely dissolved and its excess at ratios n_{in}/c_{Fein} = 1.6–2.4 mol/mol is required for complete precipitation of iron (Table 2).

The approach of the systems to the equilibrium state is accompanied by a change in the shape of the $c_{Fe} = f(pH)$ dependence (Fig. 4). In the set of experiments with calcite, the initially fast precipitation of iron (Interaction duration 3 h), subsequent dissolution (124 h), and following gradual decrease in c_{Fe} mostly occur in the pH range 6–7. Two oppositely directed processes, dissolution

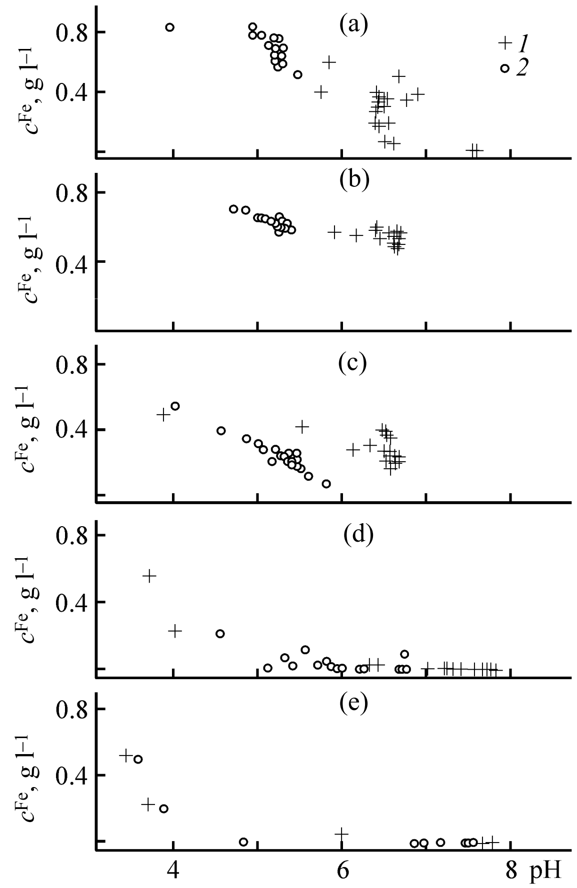

Fig. 4. Iron concentration c_{Fe} in solution vs. the precipitation pH in systems with (*1*) calcite and (*2*) dolomite. Interaction duration: (a) 3 h, (b) 24 h, (c) 7 days, (d) 14 days, and (e) 60 days.

of the reagent and hydrolysis of Fe^{3+}, result in that pH decreases to 3.5 in experiments with a small amount of calcite, whereas at an excess of the reagent, pH increases to 7.7. In the set with dolomite, the pH values change from 4.5 to 5.5 (interaction duration 3 and 24 h). The same types of variation with time of the dependences $c_{\mathrm{Fe}} = f(\mathrm{pH})$ in two sets indicate that there occur similar processes in which the neutralizing agent is consumed and an iron-containing precipitate is formed. In 60 days, these dependences obtained in experiments with calcite and dolomite almost coincide. The equilibrium thermodynamic data for the systems under consideration differ only slightly (Table 3).

The experimental data reflecting the dependence of the iron concentration in solution on the precipitation pH exceed the calculated values by several orders of magnitude. This discrepancy can be attributed to presence in solution of not only monomer hydroxo forms of Fe(III) taken into account in calculations, but also the disregarded hydroxo forms [7, 8].

As follows from the experimental data, formation of iron oxo hydroxides is a consequence of gradual oxidation of iron(II) to iron(III) under conditions corresponding to precipitation of a mixture of α-FeO(OH) and γ-FeO(OH) [9]. The results of X-ray phase analysis were used to determine the ratio between the concentrations of polymorphic modifications of FeO(OH) in precipitates obtained in systems with calcite and dolomite at an interaction duration of 60 days and varied $n_{\mathrm{in}}/c_{\mathrm{Fein}}$ ratio (Table 4). The experimental data give no way of deriving a certain dependence of the lepidocrocite/goethite ratio on $\mathrm{pH_s}$. At the same time, it can be seen from the results obtained that predominantly goethite is formed in an acid medium, and the fraction of lepidocrocite substantially increases in neutral and weakly alkaline media.

CONCLUSIONS

(1) A physicochemical simulation of calcite (dolomite)–$FeSO_4$–H_2O open systems demonstrated that the onset of precipitation, to which corresponds appearance of predominantly electrically neutral $Fe(OH)_3$ species in solution, is observed at a $CO_3^{2-}/Fe^{2+} > 1$ ratio between reagents (in terms of carbonate ions) and iron(II) in the starting solution.

(2) It was found experimentally that the degree of solution purification was as large as 97–100% if the ratio between carbonate minerals that passed into solution (in terms of carbonate ins) and precipitated iron was $n_{\mathrm{solv}}/n_{\mathrm{prFe}}$ = 1.0–1.1 mol/mol. At the same time, the reagent is not completely dissolved in the experimental conditions even after 60 days. Complete precipitation of iron requires an excess amount of the reagent at $n_{\mathrm{in}}/c_{\mathrm{Fein}}$ = 1.6–2.4 mol/mol.

(3) It was shown that calcite is dissolved substantially faster than dolomite, which creates local supersaturation regions in solution. In the first stage of the process at an excess of the reagent and an interaction duration of 3 h, the large amount of dissolved CO_2 favors precipitation of iron in the form of siderite $FeCO_3$. As carbon dioxide is removed, the concentration of iron grows. Further, precipitation of iron is due to the Fe(II) → Fe(III) oxidation to give FeO(OH). If dolomite is used, no siderite is formed and only the last mechanism of iron precipitation is operative.

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