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SHORT COMMUNICATIONS

Modeling Cryogeochemical Processes in the Oxidation Zone of Sulfide Deposits with the Participation of Oxygen-Bearing Nitrogen Compounds

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The development of oxidation zones at sulfide deposits is largely controlled by active processes of sulfide oxidation, which produce chemically aggressive solutions of sulfuric acid (with pH 2 and lower) [1]. Some researchers believe that acid rains [2] may play a significant role in the transformations of ore and gangue minerals in technogenic landscapes, with genesis of acid rains in urbanized and industrially developed areas related to the anthropogenic emission of CO_2, SO_2 (up to 60%), and NO_x (up to 30–50%). It was experimentally established that nitrogen oxides and their interaction products with water play the role of catalysts during the oxidation and leaching of ore minerals, first of all, sulfides [3]. The freezing of weakly acidic (pH 3.0–5.0) natural sulfate water with low $[(0.2–5) \times 10^{-4}$ M] concentrations of N(III) compounds in cryogenic environments results in highly concentrated (with respect to HNO_2 and H_2SO_4) solutions and creates favorable conditions for active oxidation processes, as is also confirmed by the recently experimentally established fact of an anomalous increase in the HNO_2 oxidation rate (by a factor of 10^5) at negative temperatures [4]. These facts and considerations led us to suggest that nitrogen compounds can notably affect the chemical transformations of the near-surface levels of the cryolithozone.

According to literature data [1, 2] and our experimental results [3], the most chemically active oxygen-bearing nitrogen compound is nitrous acid. Its high activity is caused by the ambident properties of the HNO_2 molecule, which can act either as an oxidizer or a reducer depending on the composition of the system. Nitrous acid shows a high catalytic activity even at low concentrations (0.001 M) and normal temperature (298 K) and can manyfold intensify MeS oxidizing sulfate leaching. The activating effect of HNO_2 increases with an increase in its concentration and is limited only by HNO_2 disproportionation at positive temperatures and low pH values. It is now experimentally established that the stability of nitrous acid in cryogenic environments manyfold increases even under strongly acidic conditions.

EXPERIMENTAL METHODS

Cryogenic weathering was modeled using samples of sulfide ores from the Udokan deposits, whose major minerals are chalcosine, magnetite, quartz, feldspar, limonite, brochantite, ilmenite, and chalcopyrite. Our experiments were carried out with two size fractions of the samples: from –0.2 to +0.063 mm (in experiments aimed at examining the leaching kinetics) and –0.063 (in all other experiments). The samples contained the following concentrations (wt %) of ore elements: 20.50 Cu, 12.96 Fe_2O_3, 9.86 FeO, 6.89 S_{tot}, 0.14 S_{sulf}, and 199.33 ppm Ag (analyses were conducted in the LITsIMS, Chita, analyst T.G. Shevchenko).

Ore samples were leached in transparent polyethylene vessels, which allowed the experimentalist to observe the transformations at two regimes: at freezing (–20°C) and at room temperature (+20°C). The proportion of the solid and liquid phases (R/W) was equal to 1 : 5 (5 g of ore and 25 ml of solution) or 2.5 : 1 (5 g of ore and 2 ml of solution) depending on the purpose of the experiments.

The choice of the acidic regime during the modeling of the leaching process was dictated by two considerations: (1) the sulfuric acid concentration in natural waters in the oxidation zones of sulfide ore deposits (which broadly vary: according to field observations the pH ranges from 1–3 to, occasionally, 0.46 [5]) and (2) the transformation of the solution during its freezing, i.e., its cryogenic concentration. The cooling of the reaction mixtures (to –20°C) with various initial pH resulted in the equalization of sulfuric acid concentrations in the unfreezing volume of the liquid phase according to the diagram of state for the H_2O–H_2SO_4 system (Fig. 1) [6] with a proportional decrease in the solution volume. Thus, at negative temperatures, the leaching of ore in our experiments occurred at practically equal pH but at varying proportions of the liquid and solid phases. It should be mentioned that the pH values of the unfreezing solutions (when their temperature reached –20°C) somewhat differ from the values calculated from the data [6]. The thermal isolation of the reaction mixtures at the freezing technique used in our experiments (in a freezing chamber) takes approximately 10–15 min. This time span is characterized by the partial leaching of Cu, which can affect the cryogenic concentrating of sulfuric acid. We failed to directly measure the pH of solution in the interstitial space of the ice.

With regard for the aforesaid, the initial HNO_2 concentration was chosen in such a way that the concentration of nitrous acid in a unit volume of the unfreezing liquid phase was roughly equal (~5.8 M). The only exception was 0.5 M solution of H_2SO_4 containing 0.1 M HNO_2 at +20°C and, correspondingly, ~0.6 M HNO_2 at –20°C (at higher concentrations in acidic solutions at positive temperatures: nitrous acid is notably unstable). The minimum HNO_2 concentration in the system was specified with regard for the following two considerations: its concentration in natural atmospheric precipitates (0.0005 M [7]) and the possibility of detecting a notable increase in the oxidation rate of sulfides in the experiments.

The working solutions were prepared of reagent-grade starting chemicals. The initial concentrations of sulfuric acid in the solutions was 0.001, 0.01, 0.1, and 0.5 M. Nitrous acid of specified concentration (0.001, 0.01, and 0.1 M) was synthesized in the reaction pulp by the following exchange reaction:

$$2NaNO_2 + H_2SO_4 = 2HNO_2 + Na_2SO_4,$$

by batching a calculated amount of $NaNO_2$ (0.25 ml of 0.02 M solution, 0.25 ml of 0.2 M solution, and 0.25 ml of 2 M solution) into the reaction vessel. To quantify the effect of nitrous acid on the sulfuric acid dissolution of the Udokan ore, half of our experiments were conducted under analogous conditions but without added sodium nitrate.

In studying the kinetics of the process, the duration of leaching was 5, 15, 30, 60, and 90 days and 90 days in the other experiments. Each point on the kinetic line is an average of two (5, 15, 30, and 60 days) and four (90 days) replicates.

The pH of the solutions before (for all experiments) and after (at R/W = 1 : 5) the experiments was measured by pH meters. The acidity of the liquid phase after ore leaching at R/W = 2.5 : 1 was assayed by universal indicator paper in view of the scarcity of the solution.

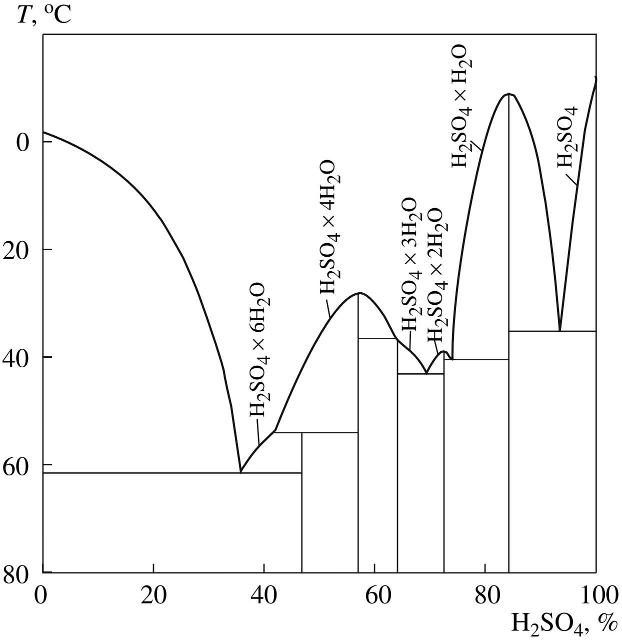

Fig. 1. Diagram of state for the H_2O–H_2SO_4 system [6].

Upon their complete melting and filtering, the solutions were analyzed for Cu by atomic absorption on a Perkin Elmer 303 OB spectrophotometer equipped with a MHS-20 analytical set at the Analytical Laboratory of the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences (analyst V.N. Il'ina). The analytical errors usually did not exceed 3% and 6% for concentrated solutions (>2 g/l, with regard for the dilution errors). Microprobe analyses were conducted at the Analytical Center of the United Institute of Geology, Geophysics, and Mineralogy, Siberian Branch, Russian Academy of Sciences.

EXPERIMENTAL RESULTS AND DISCUSSION

The rates of the leaching processes of most of the Cu sulfides proportionally increase with increasing acidity of the solutions, concentrations of the oxidizing agents, and temperature [3, 8]. The intensity of ore dissolution during freezing is controlled by two mutually compensating processes: the cryogenic concentrating of the reactants (which accelerates the processes) and a temperature decrease (which decelerates this process). Hence, the cooling of the reaction system can lead to either an increase or a decrease in the rate of the process depending on the predominance of one of the factors (or cannot change at all if the factors are balanced).

The results on the leaching of the Udokan sulfide ores with sulfate solutions (including those with added nitrous acid) at various temperatures are summarized in Table 1.

In the examined range of the starting pH of the H_2SO_4 solutions, we observed all possible relations between the rates of the processes at negative and positive temperatures correlated with the cryogenic con-

Table 1. Conditions and results of experiments on the leaching of the Udokan ore by an H_2SO_4 solution with the addition of HNO_2 (numerators) and without it (denominators) (τ = 90 days, R/W = 1 : 5, printed in upright type, and 2.5 : 1, printed in italics)

Concentration, M		T = –20°C			T = +20°C			k*	
H_2SO_4	HNO_2	Concentration Cu, g/l		pH**	Concentration Cu, g/l		pH		
0.5 0.5	0.1 –	8.6 2.8	*23.1* *21.0*	0.87 0.61	14.1 9.3	*24.6* *22.9*	1.62 0.95	0.6 0.3	*0.9* *0.9*
0.1 0.1	0.1 –	4.1 2.1	*0.2* *4.9*	3.00 1.87	1.9 2.8	*0.06* *0.42*	4.45 4.18	2.2 0.7	*3.3* *11.7*
0.01 0.01	0.01 –	0.7 0.7	*0.04* *0.3*	4.41 4.29	0.007 0.009	*0.03* *0.02*	6.63 6.72	100 78	*1.3* *15.0*
0.001 0.001	0.001 –	0.09 0.08	*0.02* *0.02*	4.66 4.62	0.003 0.001	*0.02* *0.01*	6.65 7.32	30 80	*1.0* *2.0*

Notes: * $k = C_{Cu}(-20°C)/C_{Cu}(+20°C)$.

** pH was measured after melting.

Table 2. Changes in the Cu concentration (g/l) in the solution with time during the leaching of the Udokan ore with the addition of HNO_2 (numerators) and without it (denominators) (R/W = 2.5 : 1)

Acid concentration, M		T = –20°C					T = +20°C				
		Duration of experiment									
H_2SO_4	HNO_2	5	15	30	60	90	5	15	30	60	90
0.5 0.5	0.1 –	24.3 20.3	25.1 20.0	23.7 21.0	22.5 17.6	23.1 21.0	22.7 21.8	23.9 21.5	24.2 22.7	23.4 20.0	24.6 22.9
0.1 0.1	0.1 –	2.5 4.7	1.9 5.0	1.3 5.2	0.1 4.1	0.2 4.9	0.4 2.9	0.1 2.1	0.2 2.0	0.06 0.5	0.06 0.4
0.01 0.01	0.01 –	0.3 0.5	0.3 0.5	0.2 0.6	0.07 0.3	0.04 0.3	0.08 0.03	0.02 0.03	0.03 0.03	0.04 0.01	0.03 0.02
0.001 0.001	0.001 –	0.03 0.02	0.02 0.03	0.03 0.04	0.02 0.01	0.02 0.02	0.02 0.02	0.07 0.02	0.04 0.09	0.04 0.03	0.02 0.01

centration coefficients: an increase in the intensity of Cu extraction by factors of 30–100 in weakly acidic solutions, the deceleration of the processes by factors of 1.6–3.3 in acidic solutions (0.5 M H_2SO_4), and the minimum difference between the leaching rates (by factors of 0.7–2.2) in 0.1 M H_2SO_4 solution.

Our experiments aimed at studying the kinetics of the process (Table 2, Fig. 2) demonstrate that leaching is a fairly fast process: a Cu^{+2} concentration commonly reached its maximum in the solutions within five days, the activating action of nitrous acid was detected mostly during the stage of active leaching, and the acceleration of the process in cryogenic experiments was greater during the initial stages. A decrease in the Cu concentration in the solutions during the final leaching stages testifies to the formation of secondary Cu-bearing phases, which were detected among the experimental products (Fig. 3).

The acicular crystals (Fig. 3) are, according to microprobe data, brochantite $Cu_4(OH)_6SO_4$, which could be formed in the course of chalcosine dissolution

$$6Cu_2S + 3H_2SO_4 + 15O_2 = Cu_4(OH)_6SO_4 + 8CuSO_4, \quad (1)$$

or by the hydrolysis of Cu sulfate

$$4CuSO_4 + 6H_2O = Cu_4(OH)_6SO_4 + 3H_2SO_4. \quad (2)$$

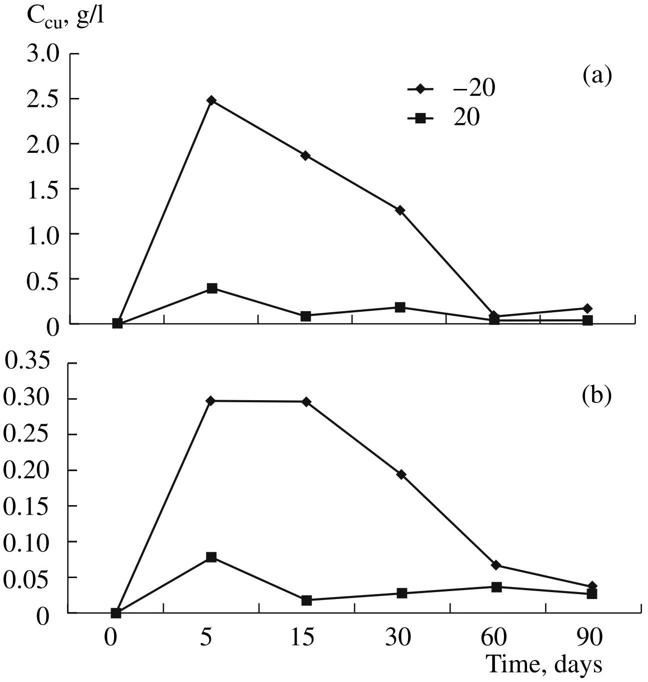

Fig. 2. Dependence of Cu concentration in solution on time at various temperatures at initial pH equal to (a) 1 and (b) 2.

Reaction (1) requires acidic conditions, and reaction (2) produces H_2SO_4, and, hence, brochantite precipitation can somewhat counterbalance acid consumption onto chalcosine dissolution and prolong the process.

The formal recalculation of the data of Table 1 with regard for cryogenic concentration according to the $H_2O–H_2SO_4$ diagram yields the results presented in Table 3.

Cryogeochemical systems are characterized by the action of freezing, a mechanism able to buffer (at negative Celsius temperatures) the concentration of the dissolved component (freezing). If the temperature does not vary, the consumption of the solute component by some reactions automatically results in a decrease in the volume of the unfreezing solution *at its constant concentration*. With reference to our example, this implies that acid consumption by, for example, the reaction

$$Cu_2S + H_2SO_4 + 5/2O_2 = 2CuSO_4 + H_2O, \qquad (3)$$

should not lead to a decrease in its concentration and, hence, to an increase in the pH. In other words, the leaching process at negative temperatures proceeds at an *unchanging* concentration of the solvent but at a continuous decrease in the volume of the unfreezing solution and a corresponding increase in the R/W ratio. Although the mass of the solid phase thereby slightly decreases (because of its dissolution), the area of the reacting surface simultaneously increases because of the disintegration of the ore in the process of its leaching. This process is significantly intensified at temperature variations due to cracking.

Hence, while the parameter of the process characterizing acid consumption at positive temperatures is pH, such a parameter at negative temperatures is the R/W ratio. Figure 4 shows the dependence of the Cu concentration in the unfreezing solution (recalculated from

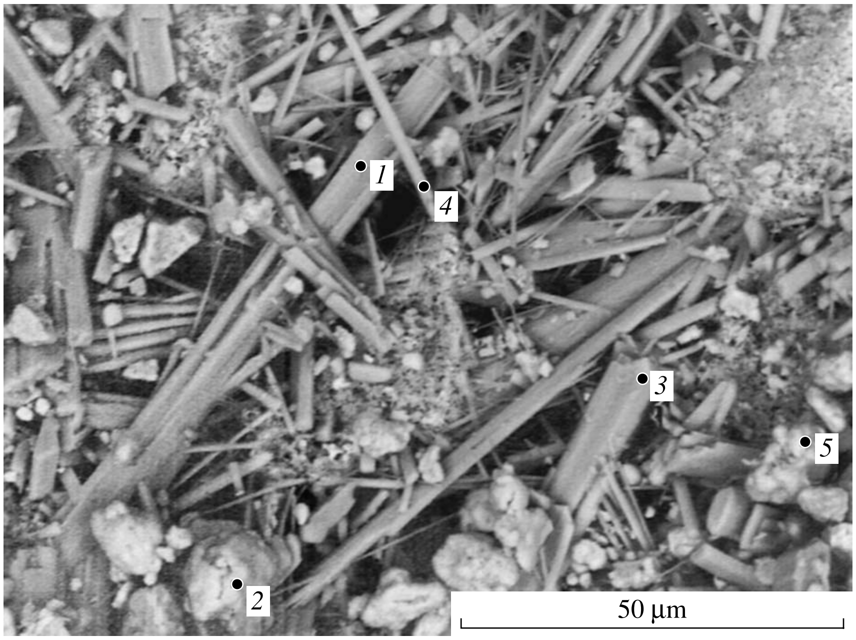

Fig. 3. Newly formed phases in the products of our experiments at negative temperatures. The acicular crystals correspond to $Cu_4(OH)_6SO_4$ (microprobe data).

Table 3. Data of Table 1 at $T = -20°C$ and initial R/W = 1 : 5 recalculated with regard of cryogenic concentrating

H_2SO_4, M/l	HNO_2, M/l	V_{sol}, ml	Cu, g/l	R/W
0.5	0.1	4.16	51.6	1.2
		4.16	16.8	1.2
0.1	0.1	0.83	123.5	6.0
		0.83	63.2	6.0
0.01	0.01	0.08	218.8	62.5
		0.08	218.8	62.5
0.001	0.001	0.008	281.0	625
		0.008	250.0	625

analytical data with allowance made for concentrating) on variations in the R/W ratio, regardless of the initial R/W ratio and the starting concentrations of the reactants. It can be seen that the Cu concentration first increases, and the addition of HNO_2 intensifies this process, but then the tendency changes to the opposite one. At very high R/W ratios (small solution amounts), a significant error is likely introduced by the incomplete wetting of the solid phase, and thus, these results seem to be not reliable enough and are not displayed in the diagram.

It follows that the acidity of the solutions in our experiments at negative temperatures should have not decreased with time, as is the case at positive temperatures. However, a decrease in the volume of the solution should result in a decrease in its dissolving capacity with respect to solute components and, hence, to the possibility of oversaturation with respect to them. Because of this, if the leaching mechanism of chalcosine corresponds to reaction (1), Cu sulfate should necessarily precipitate as a solid phase at concentrations higher than 12.3 wt % $CuSO_4$ (approximately 55 g/l Cu).

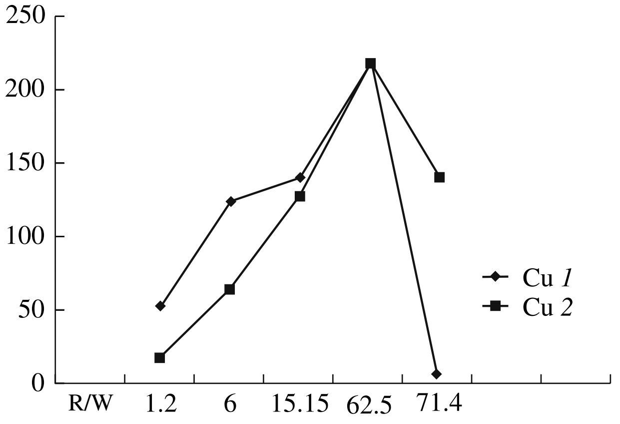

Fig. 4. Dependence of Cu concentration (g/l) in the unfreezing solution on the R/W ratio, which varied in the course of the experiments (regardless of the initial R/W and the initial concentrations of reactants). Cu 1—with the addition of HNO_2; Cu 2—without HNO_2.

In Fig. 4, points lying above the value of 55 g/l are virtual, and excess Cu should be contained in the form of solid Cu sulfate. Copper sulfate was detected in the products of some of our experiments. The decrease in the Cu concentration in the experiments at positive temperatures could also be induced by the precipitation of Cu hydroxide (which becomes unstable at room temperature at pH > 5). However, it was not detected among the experimental products.

The termination of the leaching process at negative temperatures can be caused by one of the following factors:

* exhaustion of the leached mineral (chalcosine in our experiments);

* lack of oxygen, because the reaction vessel was hermetically sealed; and

* exhaustion of the acid and a decrease in the volume of the liquid phase below a certain critical level.

The depletion of the acid and the corresponding increase in the Cu concentration in the solution gradually transfers the solution from the $H_2O–H_2SO_4$ system into the $H_2O–CuSO_4$ system, whose eutectic temperature is equal to –1.5°C [9]. The free liquid phase should completely disappear from this system at –20°C in the absence of nitrous acid. The facts and considerations presented above highlight the need for experimental diagrams of three-component (and more) systems at negative temperatures.

An additional factor complicating the behavior of cryogeochemical systems is the origin of film solutions: nonautonomous phases [10], whose position in the diagrams of state was considered in our earlier publication [11]. Film solutions have notably different physicochemical characteristics and freeze at lower temperatures than free concentrated solutions.

CONCLUSIONS

1. Processes of chemical interactions in water–rock systems at negative temperatures are principally different from analogous processes at positive temperatures because of the action of cryogenic concentrating.

2. Negative temperatures can (at favorable combinations of other factors) notably intensify heterogeneous chemical reactions.

3. The addition of nitrous acid exerts a catalytic effect on the sulfate leaching of sulfides at both positive and negative temperatures, but this effect is more significant at negative temperatures and during early stages of the process.

4. Our experimental data indicate that the rate of the acidic leaching of sulfides is fairly high: the maximum Cu concentrations in the solutions were reached within a few days.

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