

Geochemical Processes Occurring in Cryogenic Zones of Sulphide Deposits Oxidation Assisted by Nitrogen Compounds

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Abstract

Sulphuric acid leaching of sulphide ores assisted by nitrous compounds in Udokan copper deposits was studied regarding the effect of low and high temperatures. Negative temperatures were found to intensify the leaching of copper dramatically. Nitrous acid appears to be the catalyst of the process. Experimental results show that heavy metals in the cryogenic zones of sulphide ores demonstrate high mobility at oxidation processes assisted by nitrous compounds.

INTRODUCTION

Oxidation zones in sulphide ore deposits form owing to intensive processes of sulphides oxidation yielding aggressive sulphuric acid solutions. Solutions acidity may essentially decrease depending on the ores mineralogical composition. The most concentrated solutions (pH < 1) are produced, when pyrite is oxidized [1].

Cryogenic conditions at sulphide ore oxidation help both formation and conservation of well dissolving sulphate minerals, crystal hydrates in particular [2]. The pioneer experimental studies related to sulphides leaching by sulphuric acid solutions at negative temperatures reported in [3] were followed by others [4].

It is widely assumed that in man-caused landscapes acid rains, provided by increasing nitrogen sulphur emissions, have essential effect on the transformation of ore and non-ore minerals [5]. Nitrogen oxides and products of their interaction with water in acid rains catalyze oxidation and leaching of ore minerals, especially sulphides, as is shown in studies [7, 8].

Among nitrogen oxides nitrous acid, HNO₂, is mostly significant. Its high kinetic activity is

provides by its instability and disproportionation ability. Its chemical nature is unique, and remains unstudied yet. Recent experimental facts demonstrate the abnormally (by 10⁵ fold) higher rate of HNO₂ oxidation at negative temperatures [9]. This fact allows one to assume that nitrogen compounds have significant effect on the chemical transformations occurring in the cryolite zone subsurface.

This study is related to the Udokan pyrite leaching with nitrous acid containing sulphuric acid solutions performed in cryogenic conditions.

This process is mostly actual for the territories of severe climate and widely spread permafrost.

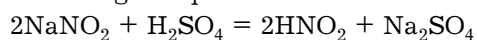
EXPERIMENTAL

Udokan ore concentrate used in experiments had the following composition (mass %): Cu 20.50, Fe₂O₃ 12.96, FeO 9.87, S_{total} 6.89, S_{sulphide} 0.14, Ag 199.33 g/t. Fraction with large ore particles (0.2–0.063 mm) was exposed to leaching. According to mineral analysis this fraction contains the following minerals: chalcocite,

magnetite, quartz + feldspar, limonite, brochantite, ilmenite, and chalcopyrite. Isolated inclusions of bornite, zircon and native silver were noticed.

Experiments were performed at two temperature regimes: freezing ($-20\text{ }^{\circ}\text{C}$) and ambient temperature ($+20\text{ }^{\circ}\text{C}$).

Standard procedures [10] and chemical pure grade reagents were used for solution preparations. Sulphuric acid solutions (0.5, 0.05, 0.005 and 0.0005 M) were prepared by standard H_2SO_4 solution dilution. Nitrous acid solutions (0.001, 0.01 and 0.1 M) were obtained in reaction pulp according to equation:



by dosing the calculated quantity of NaNO_2 solution (0.25 ml 0.02 M, 0.25 ml 0.2 M, 0.25 ml 2 M) into reaction vessel.

Solution acidity was measured with pH meter combined with millivoltmeter pH-673.M.

Ore leaching was performed in transparent polyethylene and polypropylene vessels for better observation. According to leaching kinetics leaching duration was 5, 15, 30, 60 and 90 days. Each point on kinetic curve was determined for a separate ore sample by two (5, 15, 30, 60 days) and four (90 days) parallels.

Mass ratio solid : liquid was 1 : 5 and 2.5 : 1. In all cases ore sample mass was 5 g, starting solution volume being 25 and 2 ml, respectively.

After complete solution melting and filtering copper content was determined with atomic absorption using Perkin Elmer 303 OB equipped with MHS-20 (Analytical Centre of United Institute of Geology, Mineralogy, Geophysics, SB RAS). Experimental error was usually no larger than 3 %, for concentrated solutions (more than 2 g/l) – no larger than 6 % (with correction for dilution error).

RESULTS AND DISCUSSION

Sulphuric acid concentration (from 0.5 to 0.0005 M) was chosen with regard to a wide range of H_2SO_4 content in the natural waters of sulphide oxidation zones [1]. According to the state diagram for system $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at freezing of reaction mixtures of various starting pH to $-20\text{ }^{\circ}\text{C}$ sulphuric acid concentration in non-freezing liquid phase attains 2.9 M in all cases

TABLE 1

Temperature effect on copper leaching into the liquid phase (solid : liquid = 1 : 5)

Concentration, mol/l		C_{Cu} , g/l,		K
H_2SO_4	HNO_2	at temperature, $^{\circ}\text{C}$		
		$-20\text{ }^{\circ}\text{C}$	$+20\text{ }^{\circ}\text{C}$	
0.5	0.1	9.6	16.5	0.6
0.05	0.1	3.6	2.0	1.8
0.005	0.01	0.8	0.08	10
0.0005	0.001	0.09	0.003	30

Note. Here and in Table 2: $K = C_{\text{Cu}}(-20\text{ }^{\circ}\text{C})/C_{\text{Cu}}(+20\text{ }^{\circ}\text{C})$.

[4]. Under these conditions the least acid solutions are mostly frozen out. In particular, liquid phase volume at sulphuric acid concentrations of 0.0005, 0.005 and 0.05 M changes by 6000, 600 and 60 fold, respectively, but only by 6 fold, if sulphuric acid concentration is 0.5 M. With this regard HNO_2 concentration was adjusted so that in non-freezing liquid volume it always was the same, i.e. 5.8 M. Exclusions are solutions 0.5 M H_2SO_4 containing 0.1 M HNO_2 (at higher concentrations nitrous acid is very unstable). The minimum content of HNO_2 in the system was caused by two factors: comparability with natural precipitates (0.0005 M [11]) and capability of following the noticeable acceleration of sulphides oxidation under experimental conditions.

Freezing effect on the leaching of Udokan sulphide ore by sulphuric acid solutions with NaNO_2 was studied at ratio solid : liquid = 1 : 5. Table 1 shows the obtained and averaged results.

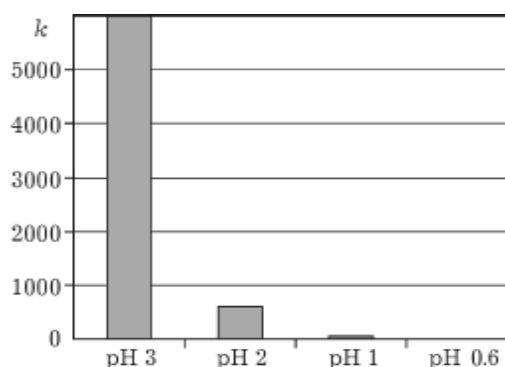


Fig. 1. Cryogenic concentration coefficient k versus starting pH:

pH	3	2	1	0.6
k	6000	600	60	6

TABLE 2

Influence of ratio solid : liquid on copper leaching efficiency ($t = 90$ days)

Concentration, mol/l		C_{Cu}^* , g/l,		K	
H_2SO_4	HNO_2	at solid : liquid		at solid : liquid	
		1 : 5	2.5 : 1	1 : 5	2.5 : 1
0.5	0.1	9.6/16.5	23.1/24.6	0.6	0.9
0.05	0.1	3.6/2.0	0.2/0.06	1.8	3.3
0.005	0.01	0.8/0.08	0.04/0.03	10	1.3
0.0005	0.001	0.09/0.003	0.02/0.02	30	1.0

Note. For designation see Table 1.

*First value for temperature -20 °C, second value for temperature $+20$ °C.

The maximum increase of ore opening degree occurs at H_2SO_4 concentrations equal to 0.005 and 0.0005 M. Copper extraction from the solid phase also increases by 10–30-fold. Note, that in this acidity range solutions change remarkably (cryogenic concentration coefficients $k = C_{H_2SO_4}(-20\text{ °C})/C_{H_2SO_4}(+20\text{ °C})$ are 600 and 6000, respectively), see Fig. 1.

At stronger acidity (0.5 M H_2SO_4) process intensity at room temperature is 1.7-fold higher. In this case, that is when liquid phase dominates over the solid one (solid : liquid = 1 : 5), the observed tendency change is most likely caused by the diffusion factor influence. Under cryogenic conditions process rate increase due to acidity increase is less than the decrease of rate of reagent diffusion from the solution volume to reaction interface.

In order to confirm this idea we performed a series of experiments at ratio solid : liquid = 2.5 : 1 (5 g of ore per 2 ml of solution). Table 2 shows the averaged experiments results.

Liquid volume decrease in reaction mixture removes diffusion limitations and helps the leveling of process rates at -20 and $+20$ °C in the whole range of H_2SO_4 concentrations ($K \approx 1$).

The less pronounced freezing effect on ore opening degree at weak acidity (0.0006 and 0.005 M) is most likely caused by two reasons. First, pulp neutralization at leaching (up to pH 6.0–7.0) and long term experiment (90 days) create favourable conditions for Cu^{2+} isolation from the solution, as water insoluble copper sulphates form such as brochantite and anthlerite. Second, the rate of copper extraction from the ore is proportional to the solid phase surface area. Therefore, when leaching at solid : liquid = 2.5 : 1 (5 g of ore per 2 ml of solution) is completed considerably faster than at solid : liquid = 1 : 5 (5 g of ore per 25 ml of solution), other conditions being the same.

In order to check this assumption we have studied copper leaching kinetics. Experimental results, presented in Table 3, confirm our assumption that process acceleration under cryogenic conditions occurs at earlier stages (k is 6.2 and 3.7 at H_2SO_4 concentrations equal to 0.05 and 0.005 M, respectively).

It is obvious (see Table 3) that leaching goes fast enough: in most cases copper content in the solution attains its maximum during the first 5 days of the experiment (15 days, when H_2SO_4 concentration is 0.0005 at $+20$ °C). Further system transformations are related to the liquid phase stability, which depends on neutralization degree.

For the estimation of changes happening the second stage, we give the ratios of copper content in the liquid phase after the 5th and 90th

TABLE 3

Copper content in the liquid phase (solid : liquid = 2.5 : 1) versus time, g/l

Concentration, mol/l		C_{Cu}^* versus time (days)					C_{Cu} (5 days)/ C_{Cu} (90 days)	
H_2SO_4	HNO_2	5	15	30	60	90	at temperature	
							-20 °C	$+20$ °C
0.5	0.1	24.3/22.7	25.1/23.9	23.7/24.2	22.6/23.4	23.1/24.6	1.0	0.9
0.05	0.1	2.5/0.4	1.9/0.1	1.3/0.2	0.1/0.06	0.2/0.06	12.5	6.7
0.005	0.01	0.3/0.08	0.3/0.02	0.2/0.03	0.07/0.04	0.04/0.03	7.5	2.7
0.0005	0.001	0.03/0.02	0.02/0.07	0.03/0.04	0.02/0.04	0.02/0.02	1.5	1.0

*First value – for temperature -20 °C, second – for temperature $+20$ °C.

day of experiment. When H_2SO_4 concentration is 0.5 M, pH after leaching does not exceed 4.5, which is typical for the start of copper compounds precipitation from the liquid phase (brochantite, anthlerite) [4]. In other cases neutralization is deeper (up to pH 6.0 and higher), and therefore we observe the decreasing content of soluble Cu^{2+} compounds, as a new solid phase forms. When H_2SO_4 concentration is 0.0005 M, copper content in the liquid phase changes at the earlier stage of leaching. This assumption, however, requires further investigations.

Therefore, copper content in the liquid phase at various temperatures (-20 and $+20$ °C) at first grows dramatically, and then decreases. These results once again confirm a rather specific character of chemical processes in the water-ore system under cryogenic conditions.

CONCLUSIONS

Experiments show that ore opening attains its maximum degree at negative temperature, when sulphuric acid concentration is 0.0005 and 0.005 M. Under these conditions copper extraction from the solid phase increases by 10–30-fold. It is remarkable that in the same range system acidity changes dramatically (cryogenic concentration coefficient k is 600 and 6000, respectively).

Moreover, at both negative and positive temperatures copper content in the liquid phase at first grows essentially, and then decreases owing to the secondary mineralization processes.

These results are directly related to geo ecology, since allow one to estimate the mobility of heavy metals such as copper and other toxicants, when sulphuric-nitric leaching happens under the permafrost conditions.

Therefore, one should take in account the temperature effect on the process of sulphides

oxidation, assisted by nitric compounds, when designing ore leaching technologies (cryogeotechnologies). With this regard it is actual to study the kinetic and mechanisms of oxidative leaching of sulphide minerals, which go in specific man-caused formations, such as waste banks of mining and metallurgy, and thus are harmful to environment.

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