Udokan sulphide ore oxidativ leaching with acting oxygen compounds of nitrogen in the cryogenic conditions

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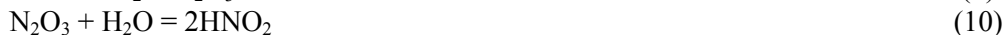
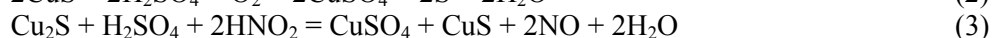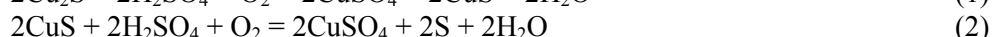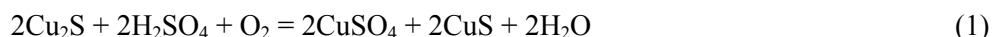mark@uiggm.nsc.ru, fax: (383) 333 2792, tel.: (383) 333 3112

Sulfide mining wastes, as well as the natural geochemical anomalies, represent an uncontrolled sources of heavy metals into the environment. As a result of a complex multifactorial process of chemical and biochemical weathering of ore minerals in these landscapes there is a formation of aggressive sulfuric acid solution (upto pH <1) promoting the mobilization of Fe, Cu, Zn and other elements [*Nordstrom*, 1991]. During the last decade a large number of works cover the development of geotechnical methods of migratory flows management in the fields of waste storing on the basis of experimental studies of the interaction of sulfide minerals with the components of the environment [*Alekhin ,et al.,* 2006].

It is known that the processes of chemical weathering with atmospheric oxygen are limited by the activation phase O_2 (E^o = + 1.23 B) and noticeably accelerated in the presence of catalysts, whose role in the oxidative horizon of sulphide dumps along with ions, Fe^{3+}, Cu^+ is acted by nitrogen oxycompounds coming from atmosphere in the form of acid deposition (dry and wet) [*Ptitsyn, et al.,* 2009].

From the point of view of thermodynamics, nitric oxides and products of their interaction with water have higher oxidation potential (E^o = + 0.85 ÷ + 1.77 B) than univalent copper ions (E^o = 0.15 B) and ferric (E^o = + 0.77 B).

The mechanism of catalysis is extremely complex and currently do not have details. During oxidation in the system there is a number of nitrogen compounds (NO, N_2O_3, NO_2, N_2O_4, HNO_2, NO_2^-, HNO_3, NO_3^-, NO^+, NO_2^+ etc.) with different catalytic activity and varying concentrations. According to numerous experimental studies kinetically most chemically responsive form is the nitrous acid and its dissociation products. At low concentrations (< 0.1 M) the activating effect of HNO_2 exceeds the catalytic activity of all other nitrogen oxycompounds by several times.

The complete opening of sulfides does not require significant amounts of activator, because the escaping nitric oxides are easily oxidized in the presence of oxygen, and again form nitric acid.

$$2Cu_2S + 2H_2SO_4 + O_2 = 2CuSO_4 + 2CuS + 2H_2O \qquad (1)$$
$$2CuS + 2H_2SO_4 + O_2 = 2CuSO_4 + 2S + 2H_2O \qquad (2)$$
$$Cu_2S + H_2SO_4 + 2HNO_2 = CuSO_4 + CuS + 2NO + 2H_2O \qquad (3)$$
$$CuS + H_2SO_4 + 2HNO_2 = CuSO_4 + S + 2NO + 2H_2O \qquad (4)$$

$$2NO + O_2 = 2NO_2 \qquad (5)$$
$$2NO_2 + H_2O = HNO_3 + HNO_2 \qquad (6)$$
$$2NO_2 = N_2O_4 \qquad (7)$$
$$N_2O_4 + H_2O = HNO_3 + HNO_2 \qquad (8)$$
$$NO + NO_2 = N_2O_3 \qquad (9)$$
$$N_2O_3 + H_2O = 2HNO_2 \qquad (10)$$

Activating effect of HNO_2 intensifies with its concentration increase and is limited by HNO_2 disproportionation in the range of positive temperatures and low pH values. Currently, it is experimentally determined that in cryogenic conditions nitrous acid stability increases many times, even in strongly acidic environment [*Takenaka, et al.,* 1992].

Simulation of cryogenic weathering was realized on the patterns of Udokan sulphide ore (fraction - 0.2÷+0.063 mm) of the following chemical and mineralogical composition: (Cu – 20.50 %; Fe_2O_3 – 12.96 %; FeO – 9.87 %; $S_{overall}$ – 689 %; $S_{sulphite}$- 0.14 %; Ag – 199.33 g/t), (chalcosine – 13.87 %; magnetite – 6.89 %;

quartz + feldspar – 38.84 %; limonite – 0.43 %; brochantite, ilmenite and chalcopyrite < 0.1 %). Leaching of ore by the sulphuric solutions (0.5 M) was carried out in closed polyethylene containers (500 ml) at - 20 and + 20 °C. The initial ratio of solid and liquid phases (S: L) is 1:5 (5 g of ore: 25 ml of solution). Nitrous acid (0.1 M) was obtained directly in the reaction pulp according to the exchange reaction: $2NaNO_2 + H_2SO_4 = 2HNO_2 + Na_2SO_4$, by adding a calculated amount of $NaNO_2$ solution (0.25ml 2 M) in the reaction vessel. The leaching periods were 2, 24 and 144 hours. Solutions after complete thawing and filtering were analyzed for copper content by atomic absorption (determination mistake with the account of dilution does not exceed 6%).

Preliminary investigations showed that the acid opening of Udokan ore in a wide range of pH values from 0.39 (0.5 M H_2SO_4) upto 3.01, (0.0005 M H_2SO_4) both in cryogenic conditions and at positive temperatures consisted of two stages: the initial oxidative leaching (according to eq. 1–4) and secondary mineralization (precipitation of soluble hydrosulfate).

The choice of sulfuric acid concentration (0.5 M) in these series of experiments has been determined by the following circumstances:

- opening of the ore by concentrated solutions of H_2SO_4 is limited by oxygen content in the closed system and does not go beyond the first stage, that allows us to investigate the activating effect of nitrous acid directly on the oxidation process without imposing the stage of brochantite loss.

- in cryogenic conditions environment acidity does not depend on the initial content of H_2SO_4 in the solution and it is determined by the preset temperature. According to the diagram of system of H_2SO_4–H_2O - T thermostating at – 20 °C of model solutions containing 0.5 M H_2SO_4 + 0.1M HNO_2 and 0.0005 M H_2SO_4 + 0.0001M HNO_2 – close to natural waters (pH 3, the content of NO_2^- in the mist $1–5 \cdot 10^{-4}$ M, in the rain $0.02–2 \cdot 10^{-5}$ M) leads to equalization of values upto 2.9 M H_2SO_4 + 0.58 M HNO_2.

- freezing of more acid solutions allows leaching at lower S:L values, that is, with a larger amount of unfrozen liquid phase. This circumstance can reduce the diffusion constraints and enhance the mass transfer processes.

The experimental results of the sulfuric acid leaching of Udokan sulfide ores (including the addition of $NaNO_2$) at different temperatures are presented in Table 1.

Table 1. Changing the copper concentration in solution* during leaching of Udokan ore

Acid concentration, M		Concentration Cu^{2+}, g/l			$k = C_{Cu}(-20 °C)/ C_{Cu}(+20 °C)$		
		Experiment duration, hours			Experiment duration, hours		
H_2SO_4	HNO_2	2	24	144	2	24	144
0.5	0.1	<u>4.10</u> 3.52	<u>6.32</u> 4.92	<u>7.56</u> 7.56	1.16	1.28	1.00
0.5	-	<u>1.44</u> 1.48	<u>1.55</u> 1.82	<u>1.64</u> 2.77	0.97	0.85	0.59

* – values were averaged over the three parallels;
in the numerator - the concentration of copper at T = - 20 C°
in the denominator - the concentration of copper at T = + 20 C°

According to the introduced results there is the positive dynamics in the process of copper extraction into the solution under all experimental conditions. Obviously even at subzero temperatures after complete freezing of the reaction mixture (20–50 minutes from the start of the experiment), the concentration of copper continues to rise.

Cooling of the system from 20 to 0 C° increases the solubility of oxygen from 6.94 to 10.19 ml per 1000 ml of water. According to the stechiometry of 1–2 equations with the full consumption of oxygen dissolved in the liquid phase at the beginning of the experiment, the copper content in the solution reaches approximately only 0.058 and 0.040 g/l (that is much lower than the values listed in the table). This fact indicates that O_2 molecules diffuse from the free volume of the reactor to the surface of sulfide not only at room temperature, but also in cryogenic conditions.

Probably, in this case the volume of unfrozen liquid phase located in the intergranular space of polycrystalline ice is of significant importance.

Oxidation of copper sulfides is much faster with nitrous acid and proceeds with almost equal intensity on the entire range of parameters. Activating action of HNO_2 is more pronounced during freezing. Extraction of copper from the solid phase increases by 2.7 times at room temperature and 4.7 times in cryogenic conditions.

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