SIMULATION OF CRYOGENIC WEATHERING PROCESSES OF SULPHIDES IN OXIDATION ZONE WITH THE ACTION OF OXYGEN COMPOUNDS OF NITROGEN

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The specificity of sulphide deposits oxidation zones forming is conditioned by active sulphides oxidation processes which cause creation of aggressive sulfuric solutions (to pH under 1) [1]. Acid rains are of great importance in ore minerals and non-metallic minerals transformation in technogenic landscapes [2]. Nitrogen oxides NO_x (to 30-50%) contained in acid precipitation and products of their interaction with water act as catalysis in the process of ore minerals oxidation and leaching, above all - sulphides, that have been presented in a number of experiments carried out by T.I. Markovich and her colleagues [3]. In the cryogenic conditions freezing of subacid sulphate (pH 3,0 -5,6) natural waters with low concentration ($(0{,}2 – 5)\cdot 10^{-4}$ M) of N(III) compounds lead to formation of film solutions and ones with strong concentration (by HNO_2 and H_2SO_4) on the surface of growing ice crystals and make conditions for active processing of oxidation, that has been recently confirmed by the experimental fact of abnormal increase of oxidation rate HNO_2 (10^5 times more) at the negative temperatures [4]. As a result, it can be suggested that nitrogen compounds noticeably affect chemical transformation of surface parts of cryogenic zones.

The simulation of cryogenic weathering was realized on the patterns of Udokan sulphide ore (fraction - 0,063 mm) of the following chemical and mineralogical composition: (Cu – 20,50 %; Fe_2O_3 – 12,96 %; FeO – 9,87 %; $S_{overall}$ – 6,89 %; $S_{sulphate}$- 0,14 %; Ag – 199,33 g/t), (Cu is presented by the following minerals: chalcosine - 13,87 %; magnetite - 6,89 %; quartz + feldspar - 38,84 %; limonite - 0,43 %; brochantite, ilmenite and chalcopyrite < 0,1 %). Ore leaching was performed in transparent polyethylene containers, in S:L proportions = 1:5 under two conditions: freezing temperature (- 20 C) and room temperature (+ 20 C). H_2SO_4 content in solution was 0.001; 0.01; 0.1; 0.5 mole/l. Nitrous acid of the given concentration (0.001, 0.01 и 0.1M) was obtained directly in reaction pulp according to metathesis reaction: $2NaNO_2 + H_2SO_4 = 2HNO_2 + Na_2SO_4$, by adding the portion of $NaNO_2$ solution (0.25 ml 0.02 M; 0.25 ml 0.2 M; 0.25 ml 2 M) into reactor. Leaching period was 90 days. After full thawing and filtering solutions were analyzed by the method of atomic absorption spectroscopy (determination mistake with the account of dilution did not exceed 6 %).

Under the cooling condition of reacting solutions with different starting pH up to - 20 °C, according to equilibrium diagram of the system $H_2SO_4 – H_2O$, sulphuric acid concentration in non-freezing liquid phase reached the same value 2,9 M [5]. The least subacid solutions underwent the greatest freezing in such circumstances - the change of liquid phase volume under 0,001, 0,01 and 0,1M sulfuric acid concentration was 2900, 290, 29 times, while under 0.5M was only 6. Taking into account what was stated above starting concentration of HNO_2 was chosen in such way that nitrous acid quantity contained in non-freezing portion of liquid was approximately the same (~5.8M). Exceptions were 0.5M H_2SO_4 solutions containing 0.1M HNO_2 (more concentrated nitrous acid is noticeably unstable). The minimal concentration HNO_2 in the system is conditioned by two factors: comparability with natural atmospheric precipitation (0.0005M [4]) and possibility to register considerable acceleration of sulphide oxidation during the experiment.

Experimental results of Udokan sulphide ore leaching by sulfuric solutions with and without $NaNO_2$ at different temperature conditions are presented in table 1. The greatest freezing effect on growth of ore reacted fraction reveals at the concentration H_2SO_4 = 0.01 and 0.001M. The copper extraction from solid phase increases 100; 30 times more (in sulfuric solutions with addition of nitrous acid) and 78; 80 times more (in sulfuric solutions) correspondingly. It is significant that solution in such range of acidity at freezing of - 20 °C undergoes the greatest modification (cryogenic strengthening factors are 290 and 2900 correspondingly).

Process activity in more acid medium at room temperature is 1.6 and 3.3 times more. In this case (when liquid phase dominates on solid phase (S:L = 1:5)), the changing of observed tendency can be concerned with diffusion factor influence. In the cryogenic conditions the growth of the processing rate due to of acid concentration increase is less than rate decrease of reagent diffusion in the solution towards reacting surface. To confirm this supposition we plan to carry out a number of experiments upon condition of different proportion of liquid and solid phases.

Table1. Temperature effect on copper leaching into solution

Concentration H_2SO_4, M	Concentration HNO_2, M	T = -20°C		T = +20°C		k*
		Concentration Cu, g/l	pH final	Concentration Cu, g/l	pH final	
0.5 0.5	0.1 -	8.6 2.8	0.87 0.61	14.1 9.3	1.62 0.95	0.6 0.3
0.1 0.1	0.1 -	3.5 2.1	3.00 1.87	1.9 2.8	4.45 4.18	1.8 0.7
0.01 0.01	0.01 -	0.7 0.7	4.41 4.29	0.007 0.009	6.63 6.72	100 78
0.001 0.001	0.001 -	0.09 0.08	4.66 4.62	0.003 0.001	6.65 7.32	30 80

*k = C_{Cu} (-20 °C)/C_{Cu} (+20 °C)
Numerator - experiment conditions and obtained results for oxidative system
$H_2SO_4 + O_2 + HNO_2$;
Denominator - experiment conditions and obtained results for oxidative system
$H_2SO_4 + O_2$.

Nitrous acid influence on acceleration of oxidation process becomes more apparent at negative temperature. The extraction of copper from solid phase (in 0.5 M solutions by sulphuric acid) increases in 3.1 times under - 20 °C, whereas under + 20 °C only 1.5 times. In the field of diluted solutions (0.01 - 0.001 M H_2SO_4) the missing of catalytic effect of HNO_2 on copper leaching may be conditioned by different starting ionic force of the solutions in the experiments with and without nitrous acid. In future experiments we plan to make systems equal by salt concentration of the solution - in the oxidative system $H_2SO_4 + O_2$ to reduce the starting concentration of sulphuric acid by value consumed for nitrous acid formation in the oxidative system $H_2SO_4 + O_2 + HNO_2$ and to add the equivalent quantity of sodium sulphate.

Obtained results can be applied to the development of chemical ore leaching technology (cryogeotechnology). Moreover results are closely connected with geoecology, since they allow to estimate mobility of heavy metals, copper in particular, and other contaminants as result of sulfuric-nitrous-acid leaching in zones of pergelisol and seasonal temperature variation on the ground surface and their negative influence on the environment.

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