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STUDY OF EXTRACTION OF COPPER AND IRON IONS FROM TECHNOGENIC SOLUTIONS USING SODIUM DIETHYLDITHIOCARBOMATE

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Abstract

This work presents the results of research on the processes of extracting copper (Cu^{2+}) and iron (Fe^{3+}) ions from technogenic solutions formed at the 3rd Hydrometallurgical Plant of the Navoi Mining and Metallurgical Combine. As an extractant, sodium diethyldithiocarbonate $NaS_2CN(C_2H_5)_2$ was used, which has the ability to form stable complex compounds with heavy metal ions. The experiments were conducted at various temperatures (25-45 ^{0}C), mixing duration (5-15 min), and dosing of the extractant (5-15 g) in an acidic environment (pH = 4). The degree of extraction was assessed using the PerkinElmer Lambda XLS photoelectric colorimeter. The obtained results showed that under certain conditions (experiment N^0. 3), a high degree of copper extraction (99.97%) is achieved, but at the same time, intensive extraction of iron ions (>99.99%) is observed, which indicates a low selectivity of $NaS_2CN(C_2H_5)_2$ in the studied conditions. Graphical analysis confirms that, despite the effectiveness of copper ion removal, the high degree of accompanying iron extraction necessitates the search for additional methods to increase extraction intensity.

Keywords: Technogenic solutions; heavy metals; extraction; copper ions; iron ions; sodium diethyldithiocarbonate; photoelectric analysis; hydrometallurgy; wastewater.

Introduction:

Wastewater from machine-building, non-ferrous metallurgy, and other enterprises contains heavy metal ions, which belong to priority pollutants and must be controlled in all environments.The greatest environmental hazard is posed by metals widely used in industry and possessing high toxicity and biological activity, such as Ni (II), Cr (III, VI), Zn (II), Cu (II), Cd (II), and others.Among modern wastewater treatment methods, physicochemical technologies that ensure the effective removal of heavy metal ions are of particular importance.[1]. Two-stage treatment scheme: first stage at 50 ^{0}C using mixotrophic S. thermosulfidooxidans, then at 37 ^{0} C - with the association of Sulfobacillus and Leptospirillum. This ensures efficient and accelerated biological extraction of iron from refractory gold-bearing ores.[2]. Biological oxidation of the sulfide concentrate of non-standard composition, containing 6.22% copper and 7.30% zinc, was carried out at a temperature of 40 ^{0} C using a mixture culture of acidophilic microorganisms. The main minerals of the concentrate are pyrite, chalcopyrite, sphalerite, and arsenopyrite tennantite. Bioprocess studies were conducted at two pulp density levels: 10% and 15%. In the first mode, copper and zinc extraction reached 17% and 70%, respectively, while in the second mode, copper extraction reached 15% and zinc extraction 72%. [3]. Low-temperature heap leaching was modeled in column bioreactors [4]. Genetic analysis revealed the presence of a psychrotolerant strain of Acidithiobacillus ferrooxidans (close to the SS3 strain) and a mesophilic Leptospirillum ferrooxidans. Comparative tests showed that the SS3 strain effectively oxidized pyrite, arsenopyrite, and chalcopyrite, however, at 5^{0}C, the leaching rate decreased due to the limited chemical dissolution of sulfides, despite the complete oxidation of iron.In column reactors, the negative influence of low temperatures was less pronounced compared to mixed systems. At 7 ^{0}C, oxidation proceeded more actively due to the preservation of iron in the solution, while at 21^0 C, its precipitation was observed. Thus, the existence of two temperature optimums for iron oxidation was established, and the ability of the culture to work at 5^{0}C was confirmed.

Materials and Methods:

Metallurgical and chemical industries' technogenic wastes contain significant amounts of iron, making them potential sources for obtaining iron oxide. Developing effective methods for processing such waste contributes to reducing the environmental burden and provides an additional source of valuable materials. [5]

In the work [6], hydrogels of iron III, chromium III, and zirconium IV were prepared by rapid alkaline hydrolysis with three washings of water. pH ranges: 4-13 for ferro and zirconogels, 6-12 for chromogels; sorbent concentration - 4 g/l.Sorbates: phosphate (Na_2HPO_4) 1-60·10^{-3} mol/l, arsenate (Na_2HAsO_4) 1-100·10–3 mol/l, ferrocyanide ($K_3[Fe\ (CN)_6]$) 1-10·10^{-3} mol/l; if there is an ionic background, the corresponding electrolyte was added. The experiments were conducted under static conditions at 20 ± 2 °C with magnetic stirring.The initial and residual concentrations of sorbates were measured by spectrophotometry (LOMO SF-26 or "Aquilon" SF-101). The pH of the zero-charge point of the hydrogels was determined by the Parks method on a 160 M ionometer [7], It has been determined that the application of limestone at 90 ^{0}C ensures the formation of the largest particles with excellent filtration characteristics. Introduction of a starter - a rotary sediment of 5-7% of the solid phase mass - further increases particle size by 20-25%. In the study [8], the influence of sulfur dioxide reduction process parameters (gas flow rate, reaction time, temperature, mixing rate) and diffusion dialysis parameters (incoming flow acidity, water and material flow rates) on copper separation efficiency was analyzed. Under these conditions, the degree of copper separation was 94.71%.

Results and Discussions:

The object of the research is the BIOX solution after biooxidation of refractory gold-bearing ores. After bacterial oxidation of sulfide minerals, the oxidized solid phase must be washed away from arsenic and dissolved iron before cyanidation. Acidic wastewater formed during flushing contains high concentrations of sulfuric acid, trivalent iron, and arsenic, and it must be neutralized before discharge to protect the environment. To form a stable and environmentally safe substance - iron arsenate, the effluents are neutralized using limestone pulp. Neutralization reactions:

Stage 1: $2H_3AsO_4 + Fe_2(SO_4)_3 + 3CaCO_3 \rightarrow 2FeAsO_4 + 3CaSO_4 + CO_2 + H_2O$

$Fe_2(SO_4)_3 + 3CaCO_3 + 3H_2O \rightarrow 2Fe(OH)_3 + 3CaSO_4 + 3CO_2$

Stage 2: $H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2$

To gradually extract the necessary components from the technogenic solution formed at the 3rd Hydrometallurgical Plant of the Navoi Mining and Metallurgical Combine, research was conducted on extracting copper from the solution only by extraction. Accordingly, the cation-exchange extractant sodium diethyldithiocarbonate $NaS_2CN(C_2H_5)_2$ was used as the extractant in the solution. To test the ability of this extractant to extract copper ions in the solution presented in Table 1 and to determine the optimal conditions for selective extraction of copper, a series of experiments were conducted under various conditions. The experiments were conducted in a magnetic stirrer with mixing durations of 5, 10, and 15 minutes at temperatures of 25 ^{0}C, 35 ^{0}C, 45 ^{0}C, and an extractant consumption of 5, 10, and 15 grams. During the extraction process, the solution medium is acidic, pH=4. When preparing the extractant solution, the ratio of solid to liquid was T: L=1:2 (i.e., 33.3% solution). The product obtained in each experiment was filtered and analyzed using the PerkinElmer LambdaXLS photoelectric calorimeter to determine the remaining copper and iron ions in the solution. The analysis results are presented in Table1. The purpose of photoelectric calorimetric analysis of copper and iron ions is to determine the experimental ratio of the extractant to copper ions in a given solution.

Table 1. Results of photoelectric calorimetric analysis of metal ions in the solution remaining after extraction

№	Mixing duration, min	Temperature °C	Extractant, g	Content of metal ions in the solution remaining after extraction, mg/l	
				Cu^{2+}	Fe^{3+}
1	5	25	5	0,01051	0,154
2	5	25	10	0,01043	0,126
3	5	25	15	0,00728	0,145
4	5	35	5	0,01379	0,141
5	5	35	10	0,01036	0,133
6	5	35	15	0,0121	0,113
7	5	45	5	0,0137	0,136
8	5	45	10	0,00954	0,131
9	5	45	15	0,00954	0,129
10	10	25	5	0,01226	0,447
11	10	25	10	0,01292	0,182
12	10	25	15	0,00785	0,177
13	10	35	5	0,01356	0,120
14	10	35	10	0,01155	0,169
15	10	35	15	0,01708	0,155
16	10	45	5	0,01122	2,132
17	10	45	10	0,01081	2,461
18	10	45	15	0,01084	1,059
19	15	25	5	0,01098	0,050
20	15	25	10	0,00965	0,014
21	15	25	15	0,00867	0,080
22	15	35	5	0,01171	0,545
23	15	35	10	0,01103	1,455
24	15	35	15	0,01275	0,026
25	15	45	5	0,01044	0,035
26	15	45	10	0,00921	0,094
27	15	45	15	0,0092	0,054

To simplify the comparative analysis of the results obtained in Table 1, it was depicted graphically (Figure 1).

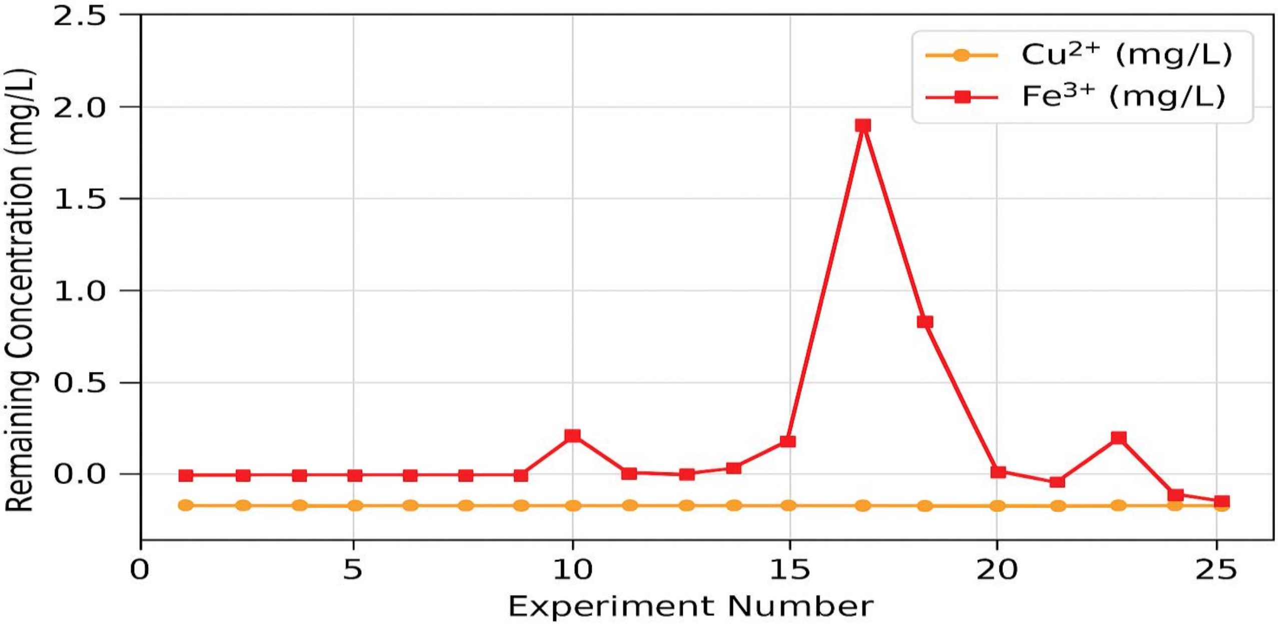

Fig. 1. Residual amount of Cu2+ and Fe3+ ions in raffinate - solution remaining after extraction, mg/l

From the graph shown in Figure 1, it can be immediately observed that the quantities in which less copper ions and more iron ions remained in the solution were in experiments No. 10, 16, 17, 18, 22 and 23, between which a sharp difference in concentration was observed in experiment No. 17. In experiments conducted based on the biooxidized technogenic solution of GMZ-3 of the Navoi Mining and Metallurgical Combine, extraction with sodium diethyldithiocarbonate $NaS_2CN\ (C_2H_5)_2$ was carried out to separate the main metal ions - Cu^{2+} (22.2 mg/l) and Fe^{3+} (7290 mg/l) in the solution, which confirmed the high ability of the extractant to extract copper ions from this solution. In particular, under the conditions of Experiment No. 3 (5 minutes, 25°C, 15 g of extractant), the extraction of Cu^{2+} was 99.97% (Fig. 1). However, under these conditions, more than 99.99% of Fe^{3+} ions were also subjected to extraction. This indicates that the $NaS_2CN\ (C_2H_5)_2$ extractant has a high extraction capacity not only for Cu^{2+} ions but also for Fe^{3+} ions, i.e., it is not selective under these conditions. The results of the graphical analysis conducted based on Table 1 also confirm this situation: despite the high degree of copper extraction in all experiments, the fact that iron is also extracted together indicates a low level of selectivity.

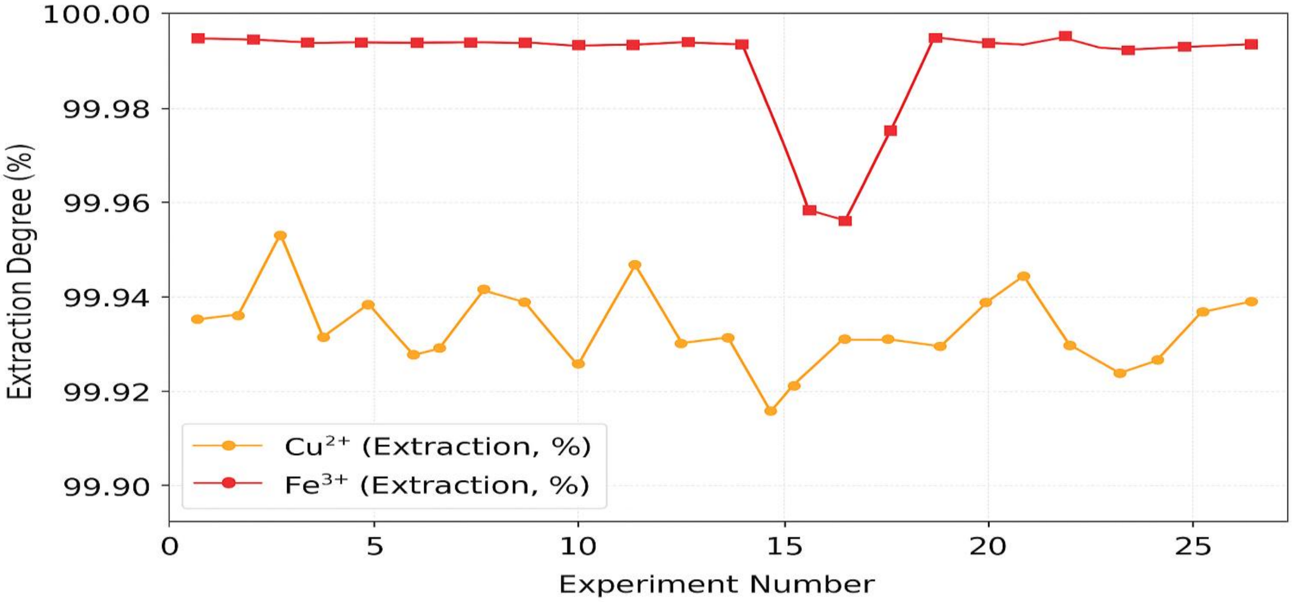

Fig. 2. Degree of extraction of Cu^{2+} and Fe^{3+} ions from the solution into the organic phase during extraction

Conclusion:

Studies have shown that sodium diethyldithiocarbonate ($NaS_2CN\ (C_2H5)\ _2$) effectively extracts copper ions from biooxidized technogenic solutions formed during the washing of the solid phase of refractory gold-bearing ores. Under optimal conditions (experiment N^0. 3: 5 min, 25 °C, 15 g of extractant), a high copper extraction rate of 99.97% was achieved. However, at the same time, intensive extraction of iron ions is observed (more than 99.99%), which indicates a low selectivity of the extractant under these conditions. Graphical analysis confirms that, despite the high efficiency of copper extraction, $NaS_2CN(C_2H_5)\ _2$ practically does not distinguish copper and iron ions in an acidic environment (pH = 4), which limits its use for selective copper extraction. The obtained results indicate the need to modify the extraction conditions or introduce additional stages of preliminary iron separation in order to increase the selectivity of the process and the practical value of the method for industrial application.

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