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METAL RECOVERY FROM SLUDGE OBTAINED DURING THE NEUTRALIZATION PROCESSES OF AMD WATER

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ABSTRACT – Investigations of the metal recovery process from the sludge formed during the neutralization of acid mine drainage (AMD) water at pH 8 were performed at the laboratory level. The metal recovery process included the following technological phases: sludge leaching, solvent extraction (SX) of pregnant leaching solution in order to selectively separate copper from the leaching solution, and obtaining zinc-based products from the solution after the SX process. Preliminary results indicate a high degree of separation of copper (about 91%) and zinc (about 98%) from sludge.

Keywords: AMD Waters, Metal Recovery, Leaching, SX-EW, Neutralization.

INTRODUCTION

Acid mine drainage waters (AMD) are waters formed by the oxidation of pyrite and other sulfide minerals under the action of air and water. Wastewater generated in ZiJin Bor's plants (either directly during current production or indirectly due to decomposition of delayed mine overburden and flotation tailings by formation of acidic drainage waters) pollutes the Borska and Krivelj rivers, which merge to form the Bela river which flows into the river Timok, and Timok into the Danube river. These pollutants are most often represented by low pH value, increased content of heavy metal ions, suspended particles and fine particles of flotation tailings deposited in the valleys of these rivers on an area of over 2000 hectares. Robule Lake, formed at the base of mining overburden Ostreljski plans (Copper mine Bor), was created as a result of mining activities. It is a typical example of acidic drainage water whose pH value is around 2.5 [1-5].

EXPERIMENTAL

The content of heavy metals in AMD water is: Cu=34 mg/l, Fe=320 mg/l, Mn=90 mg/l, Zn=12 mg/l, As=0.004 mg/l. Sludge formed during the neutralization of acid mine drainage (AMD) water at pH 8 with $Ca(OH)_2$ was treated in aim to recover valuable metals [6,7].

Chemical characterization of sludge used for leaching process is presented in Table 1.

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Table 1 Chemical characterization of sludge obtained after neutralization with $Ca(OH)_2$ at pH 8

Element	Unit	Content	Element	Unit	Content
Al	%	7.58	Cr	ppm	4.60
Mg	%	3.19	Co	ppm	435.90
Mn	%	2.11	Ni	ppm	202.60
Fe	%	0.96	As	ppm	9.80
S	%	12.98	Cd	ppm	18.80
Zn	%	0.73	Cs	ppm	0.16
Cu	%	1.70	Pb	ppm	<10
Sr	%	0.0075	Mo	ppm	<10
Ca	%	14.88	-	-	-

Copper and zinc recovery process from neutralization sludge include four technological phases: sludge leaching, solvent extraction and electrowinning of copper (SX-EW), precipitation of zinc carbonate and obtaining zinc oxide.

Schematic representation of technological phases used for treatment of sludge are presented in Figure 1.

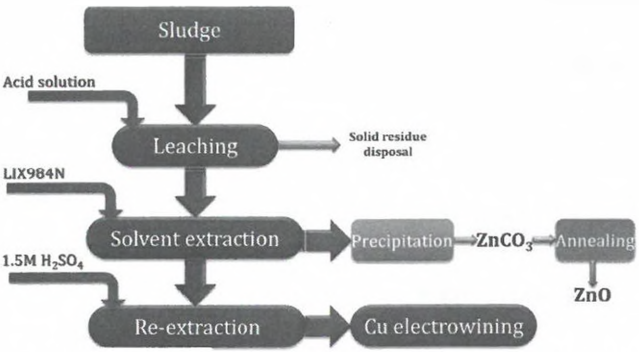


Figure 1 Schematic representation of the sludge treatment process

Leaching process

In aim of recovery of copper and zinc, sludge obtained after neutralization was leached at atmospheric pressure and temperature on following conditions: 1.2 M H_2SO_4 as leaching reagent, pulp density 20%, stirring speed 300 rpm, reaction time 60 min [8-11].

Solvent extraction process (SX)

The pregnant leaching solution (PLS) obtained after leaching process was treated in a solvent extraction process to selectively remove Cu from solution. Value of pH of solution was set from 0.94. at 1.49 using 10% solution of $Ca(OH)_2$, before starting of SX process. The influence of extractant type for the SX process was investigated. As solvent kerosene was used. For investigations of SX process four extractants were used: LIX984N, LIX622N, M5910 and M5640 with phase ratio org/aq=1:1, while re-extraction

process was performed with 1.5 M H_2SO_4 with phase ratio org/aq=5:1. Experiments of solvent extraction and re-extraction were performed in two stages. The duration of each of the processes was 15 min [10-13].

Equipment used for all the experiments were glass separation funnels and shaker with regulated time and intensity of mixing the phases. At the end of two-step extraction and two-step re-extraction experiments, separated aqueous phase were analyzed by the ICP method in order to determine the metal concentration.

Precipitation of zinc

After solvent extraction of copper using LIX984N as extractant, from aqueous phase zinc was precipitated in the form of zinc carbonate by a two-stage neutralization process. The first stage of neutralization process was performed in order to remove iron from the solution, and the second stage in order to precipitate zinc in the form of zinc carbonate.

Two samples of obtained zinc carbonate were annealed in a chamber furnace at 450 °C, for 2 h and 4 h in aim to obtain zinc oxide. Samples of both zinc oxides were analyzed by the ICP method.

RESULTS AND DISCUSSION

Leaching process

Chemical composition of pregnant leaching solution (PLS), used for investigation of solvent extraction process, is given in Table 2.

Table 2 Concentrations of metals in PLS

Element	Fe	Mn	Cu	Mo	Zn	As	Ni	Pb	Cd	Cr	Se
Conc. (mg/l)	1549.7	1798.2	3104.4	1.2	1317.1	<0.02	22.7	<0.02	1.9	0.16	<0.033

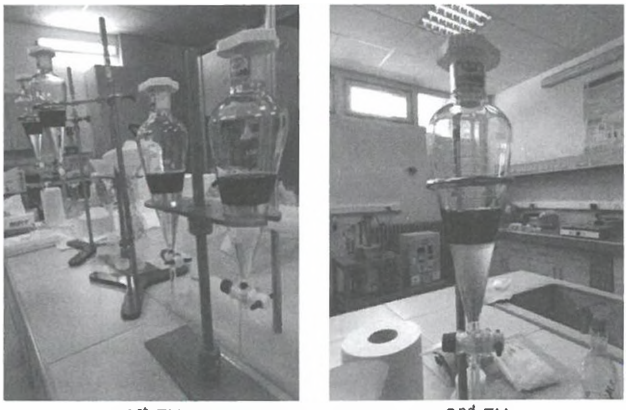
Achieved leaching degree for Cu was 99.3%, and for Zn 99.4%.

Solvent extraction process

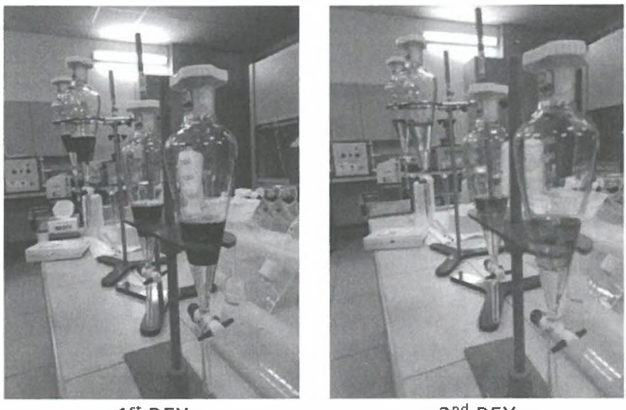
Figure 2 shows separating of phases in process extraction and re-extractions. In Table 3 are presented extraction and re-extraction degrees of Cu, Fe and Zn depending on the type of extractant.

Table 3 Extraction and re-extraction degrees od Cu, Fe and Zn

Extractant	Extraction degree $1^{st}+2^{nd}$ (%)			Re-extraction degree $1^{st}+2^{nd}$ (%)		
	Cu	Fe	Zn	Cu	Fe	Zn
LIX984N	98.55	14.38	15.69	73.31	13.98	10.99
LIX622N	99.30	19.03	30.41	68.65	10.62	1.44
M5910	98.17	17.95	18.21	65.87	7.43	6.44
M5640	98.89	69.29	40.00	73.01	5.19	1.22



1st EX 2nd EX



1st REX 2nd REX

Figure 2 Separating of phases in process extraction and re-extractions

Best selectivity for copper in relation to iron and zinc was achieved using LIX984N as extractant.

Solution obtained after re-extraction process is suitable for further investigations of electrowinning process in aim to obtain copper commercial quality.

Precipitation of zinc

After a two-stage process of neutralization and precipitation of zinc carbonate in the annealing process in the time of 2h (sample I ZnO) and 4 h (sample II ZnO), zinc oxides were obtained with contents of Zn 72% and 75% respectively.

CONCLUSION

After investigations of proposed technological processes of copper and zinc recovery from sludge obtained by neutralization of AMD water, following results were achieved:

- leaching degree of zinc was 99.4% and copper 99.3%;
- extraction degree of Cu using LIX984N was 98.55%,

- satisfactory degree of selective separation of copper in relation to zinc and iron has been achieved,
- zinc oxide with content of Zn 72-75% was obtained.

Advantage of the proposed procedure is the possibility to valorize copper from neutralization sludge, as well as valorize zinc to zinc oxide products.

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REFERENCES

1. Stevanović, Z., Obradović, Lj., Marković, R., Jonović, R., Avramović, Lj., Bugarin, M., Stevanović, J. (2014) Mine Waste Water Management in the Bor Municipality in Order to Protect the Bor River Water, https://www.researchgate.net/publication/268815386_Mine_Waste_Water_Management_in_the_Bor_Municipality_in_Order_to_Protect_the_Bor_River_Water.
2. Avramović, Lj., Stevanović, Z., Bugarin, M., Jonović, R., Marković, R., Gardić, V., Jonović, M., Đorđević, J. (2016) Characterization of Soil in the Coastal Area of the Bor River. Journal Materials Protection, 57 (3) 378–382.
3. Gardić, V., Marković, R., Masuda, N., Sokolović, J., Petrović, J., Đorđievski, S., Božić, D. (2017) The study of leachability and toxicity of sludge after neutralization of Saraka and Robule AMD wastewaters. Journal of Mining and Metallurgy, 17-29.
4. Dimitrijević, M. (2012) Acid mine drainage, Copper, 33-44.
5. Dimitrijević, M., Nujkić, M., Milić, S. (2012) The lime treatment of acid mine drainage, Copper, 45-56.
6. Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Wang, S., Sillanpää, M., (2015) Acid mine drainage (AMD) treatment: Neutralization and toxic elements removal with unmodified and modified limestone. Ecological Engineering, 30-40.
7. Marković, R., Masuda, N., Bessho, M., Avramović, L., Gardić, V., Stanković, S., Sovrlić, Z. (2015) Neutralization of Artificial Acid Mine Drainage with Different Cu, Al and Fe Ions Content. In: 47th International October Conference on Mining and Metallurgy. Bor Lake, Serbia, 415-418.
8. Avramović, Lj., Jonović, R., Stevanović, Z., Shibayama, A., Haga, K., Takasaki, Y., Han, B., Urošević, D., Dimitrijević, S. (2018) Beaker Leaching and High Pressure Leaching of Flotation Tailings. In: International Satreps Conference Mining & Environment in Future. Bor Lake, Serbia, 39-44.
9. Avramović, Lj., Jonović, R., Trifunović, V., Gardić, V., Dimitrijević, S., Jonović, M., Haga, K. (2019) Treatment of flotation tailing using high pressure leaching and solvent extraction process. In: 51th International October Conference on Mining and Metallurgy. Bor Lake, Serbia, 175-178.

10. Haga, K., Godirilwe, L., Takasaki, Y., Ishiyama, D., Shibayama, A., Han, B., Avramović, Lj., Jonović, R., Dimitrijević, S., Stevanović, Z. (2019) Metal Recovery and Reducing of Environmental Loading of Copper Mine Tailings by High Pressure Leaching and SX-EW Process. In: 58th Annual Conference of Metallurgists (Com). Vancouver, Canada, 24-27.
11. Han, B., Altansukh, B., Haga, K., Stevanović, Z., Jonović, R., Avramović, Lj., Urosević, D., Takasaki, Y., Masuda, N., Ishiyama, D., Shibayama, A. (2018) Development of copper recovery process from flotation tailings by a combined method of high-pressure leaching solvent extraction. Journal Of Hazardous Materials, vol. 352, 192-203.
12. Conić, V., Avramović, Lj., Jonović, R., Marković, R., Bugarin, M. (2015) SX-EW Treatment of the Solution Obtained After Acid Leaching RTB Bor Flotation Tailing. In: XVI Balkan Mineral Processing Congress. Belgrade, Srbija, Proceedings, Volume II, 827-829.
13. Avramović, LJ., Jonović, R., Marković, R., Shibayama, A., Haga, K., Baisui, H., Urošević, D. (2017) Separation of copper and iron using LIX-984N by the solvent extraction. In: XII International Symposium on Recycling Technologies and Sustainable Development. Bor Lake, Bor, Serbia, 237-242.