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METHODS FOR PROCESSING MINING WASTES FROM COPPER EXTRACTION FOR THE RECOVERY OF PRECIOUS METALS

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The tailings pond of the "Central Flotation" Baia Mare, Romania, poses a great ecological problem for the town, surrounding soils and watercourses. The paper reviews the current methods for the processing of the mine tailings. The results of preliminary acid leaching experiments are presented. The leaching carried out in successive steps lead to the significant concentration of the precious metals. The gold contents increased from 0.7 ppm to values 3 times higher in the resulting slime. The slime rich in Au and Ag will be subsequently processed using ionic liquids for a more efficient recovery of the precious metals.

Keywords: mining wastes, flotation tailings, metal recovery, leaching, ionic liquids

1. Introduction

The metal mining activity has been the source of large volumes of tailings that must be disposed and stored in special locations [1]. Mine tailings disposal methods include: dry-stacking of thickened tailings on land, backfilling into abandoned mines, direct disposal into rivers, lakes and seas/oceans, etc. [2]

Mine tailings consist of the remaining sterile ground-up rock after the valued minerals have been extracted from mined ore, as well as associated process water, which includes dissolved metals and ore processing reagents (for example: flotation reagents). In Cu extraction, tailings can account for 95-99% of the mined and processed ores [2, 3]. Since the mined tailings might contain remaining valuable metals that were not recovered in the ore processing, they represent potential resources and therefore they are objects of assessment studies and eventually of reprocessing [4]. From environmental point of view, the tailings pose a great ecological problem not only for the towns/people but also for the surrounding soils and watercourses, due to the fine particles (1-10 µm), heavy metals, toxic reagents used to ore processing (acids, alkalis, cyanides, etc.) [5].

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Over the last decades, many technologies for the recovery of valuable nonferrous and precious metals from flotation tailings have been developed [5]. These include, but are not limited to the following representative technologies:

i. acid leaching, ***ii***. bioleaching, ***iii***. re-flotation, ***iv***. pyro-metallurgy

Acid leaching is a simple and effective method for the extraction of some metals from tailings. Depending on the mineral acid used, metal-acid reactivity as well as the solubility of the metal salts formed, the metals could be extracted as soluble salt in solution (Cu, Zn, etc.) or concentrated in leaching residue/pulp (precious metals, Pb, etc.). The leachability of metals is usually affected by pH, temperature, particle size, contact time, stirring speed and pulp density [6]. The metals could be extracted from leached solution by electrowinning, cementation, ion-exchange resign, liquid-liquid extraction.

Bioleaching is the extraction of a metal from sulfide ores using materials found native to the environment; namely, water, air and microorganisms which catalyze the oxidation of sulfide minerals. Bioleaching, which is an emerging and frontier technology was applied successfully to extract Cu from low-grade sulfide ore [7, 11]. The development of bioleaching has attracted global attention as an alternative hydrometallurgy route for processing low-grade sulfide ore (Cu, Zn, Co, Cr, Fe, etc.) [8]. Furthermore, bioleaching has been applied successfully for the extraction of some nonferrous metals (Cu, Zn, Cr) from secondary sources (mine tailings, waste industrial solutions, etc.) [9, 10].

Flotation is a physicochemical separation process that exploits the differences in the surface properties of minerals and sterile and separates hydrophobic particles from hydrophilic particles [5]. Reprocessing tailings using flotation has proven to be more efficient and economical than other reprocessing methods, and the results up to day indicate that by re-flotation useful and precious metals concentrate have been obtained. Furthermore, the re-flotation considerable reduces the environmental impact of heavy metals and toxic reagents. [12, 13].

The mine tailings samples used in this study was taken from Baia Mare – Central Flotation Pond. The construction began in 1961 and finished at the end of 1962, when the pond was set into operation. The pond was passed into conservation at the end of 1975. The surface of the stock is approx. 50ha and the volume of tailings deposited was estimated at 8,500,000 t (5,700,000 cubic meter)
The mine tailing is in the form of mud containing flotation reagents and residual nonferrous metal sulfides: chalcopyrite, sphalerite, galena, pyrite.

2. Experimental

The mine tailings sampling procedure was carried out in the following manner: an imaginary square grid was established over the tailings pond. The grid consisted of a base line of 10 m long, with line spacings every 2 m, resulting in 25 imaginary cells. Holes were made in the center of each grid cell with the help of an excavator. Samples of approximately 1 kg were taken from every hole from a depth of 0.5 – 2 m. In order to prepare a representative sample of the tailings, a mixture was made of the samples taken from each hole. The mixture was put on a flat surface in a circle format with a uniform height of approximately 5 cm. Two diagonal lines were drawn, and two opposite quadrants were eliminated. This procedure was continued up to a final sample of 1 kg remained.

The elemental analysis of the tailings sample was determined by induction coupled plasma optical emission spectroscopy (ICP-OES) and flame atomic absorption spectrometry (FAAS). The results are presented in the Table 1.

Table 1

Elemental analysis of the flotation tailing sample [g/t]

Element	**Au**	**Ag**	**Al**	**As**	**Ba**	**Bi**	**Ca**	**Cd**	**Co**
g/t	<0.7	<10.8	32070	610	362	<20	15060	8.4	15.8
Element	**Cr**	**Cu**	**Fe**	**Ga**	**K**	**La**	**Li**	**Mg**	**Mn**
g/t	46,3	562	70400	16	19300	8.5	20	5862	6195
Element	**Mo**	**Na**	**Ni**	**Pb**	**Sb**	**Se**	**Sn**	**Sr**	**Te**
g/t	<10	1200	13.2	2348	150	<10	24.6	54.7	<30
Element	**Ti**	**U**	**V**	**W**	**Zn**	**Zr**	S^{2-}	SO_4^{2-}	S_{Total}
g/t	1069	<127	70	<20	5890	20	17130	1630	18820

Sieve fraction of the flotation tailings sample are shown in Table 2.

Table 2

Sieve fraction of the flotation tailings

Sieve fraction (mm)	+0.3	-0.3+ 0.212	-0.212 +0.15	-0.150 +0.106	-0.106 +0.075	-0.075 +0.053	-0.053 +0.038	-0.038 +0.02	-0.02
Wt. % in the tailings	7.57	7.71	8.21	7.78	9.73	7.20	6.67	6.95	38.17

Preliminary acid leaching experiments of the tailings was performed in a 3000 ml glass reactor, equipped with a mechanical stirrer. A total of 1000 g dried tailings samples were leached using H_2SO_4 (2M) and HNO_3 (2M) respectively, at a solid/liquid ratio of 1:1.5. In the case of H_2SO_4, iron (III) sulphate as well as hydrogen peroxide (H_2O_2) were tested as oxidants. The experiments were carried out at room temperature, at a stirring speed of 120 min^{-1} and during a period of 7 days.

3. Results and discussion

3.1. 1st step leaching. The leaching results are presented in Table 3.

Table 3

The results of H_2SO_4 (2M) and HNO_3 (2M) leaching of flotation tailings

Leaching agent	Tailings leached (g)	Time (h)	Solid Residue (g)	Leached tailings (%)
H_2SO_4	1000.0	168	857	15
HNO_3	1000.0	168	693	31

Chemical contents of the leached solutions and solid residues obtained are shown in Table 4 and Table 5, respectively.

Table 4

The chemical content of the solid residue (wt%) (g/t - for Ag and Au)

Leaching acid	Cu	Pb	Zn	Fe	Al	Si	Ca	Ag	Au
H_2SO_4	0.016	0.61	0.045	1.07	3.26	34.9	0.26	12.6	0.82
HNO_3	0.01	0.22	0.09	2.08	3.7	39.8	1.67	1.7	1.1

Table 5

Chemical composition of leached solution (g/l)

Leaching acid	Cu	Mg	Mn	Al	Co	Cr	Ag
H_2SO_4	0.31	3.43	4.14	2.46	0.01	0.013	0.001
HNO_3	0.45	3.49	4.46	1.78	0.008	0.006	0.01

The distribution of precious metals in are presented in Fig. 1.

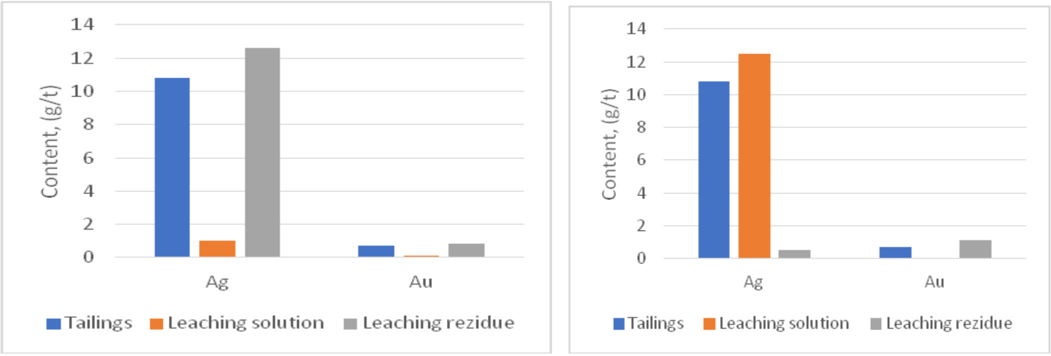

Fig. 1. Distribution of precious metals (a) H_2SO_4 leaching, (b) HNO_3 leaching

The presented results show that the leaching of the tailings in acid media leads to the dissolution of soluble compounds of Mg, Mn, Al and, as a consequence, to the increase of the precious metals contents in the solid undissolved residue.

3.2. 2nd Step leaching. The slime obtained at the 1st leaching operation were further leached in H_2SO_4 (2M solution) in order to concentrate the precious metals in the slime. A 500 g samples of dried slime were used; solid/liquid ratio of 1:1.5., at room temperature and at a stirring speed of 120 min-1, during a period of 7 days. The 2nd step leaching results are presented in Table 6.

Table 6

2nd step leaching parameters

Code	1st step leaching	2nd step leaching	Residue leached(g)	Time (h)	Slime mass (g)	Leached residue (%)
MSR1	H_2SO_4	H_2SO_4	500.0	168	421	16
MSR2	HNO_3	H_2SO_4	500.0	168	318	35

Chemical analysis of the slimes obtained are shown in Table 7 and the distribution of precious metals in Fig. 2.

Table 7

The chemical content of the solid residue (wt%) (g/t - for Ag and Au)

Code	Cu	Pb	Zn	Fe	Al	Si	Ca	Ag	Au
MSR1	0.0093	0.38	0.036	0.86	3.41	41.4	1.06	15.2	0.98
MSR2	0.004	0.13	0.041	1.02	3.57	44.9	0.16	0.02	1.91

Leaching in steps (in the same leaching acid or different acid media) also results in the dissolution of more soluble compounds and in an increased concentration of precious metals in residue.

3.3. The effect of the oxidizing agent. The parameters of leaching experiments (H_2SO_4 – 2M) with addition of oxidizing agents are shown in Table 8.

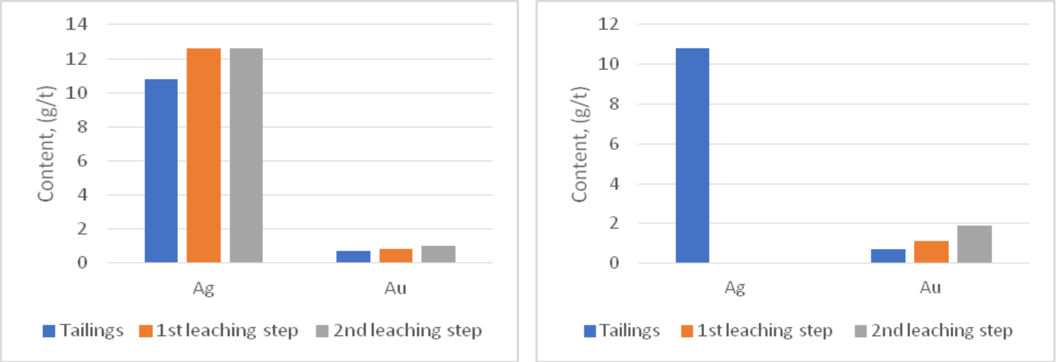

Fig. 2. Distribution of precious metals in 1st and 2nd leaching steeps solid residues
(a) 1st leaching: H_2SO_4 , 2nd leaching: H_2SO_4 , (b) 1st leaching: HNO_3 , 2nd leaching: H_2SO_4

Table 8

Parameters of leaching with oxidizing agent additions

Leaching acid	Oxidizing agent	Oxidizing quantity	Tailings leached (g)	Time (h)	Solid Residue (g)	Leached tailings (%)
H_2SO_4	$Fe_2(SO_4)_3$	50 g/l	1000.0	168	836	16.4
H_2SO_4	H_2O_2	10ml/daily	1000.0	168	842	15.8

Chemical contents of the solid residues are shown in Table 9

Table 9

The chemical content of the leach residue (wt%) (g/t - for Ag and Au)

Oxidizing agent	Cu	Pb	Zn	Fe	Al	Ag	Au
H_2O_2	0.025	0.23	0.15	3.47	2.95	11.3	0.83
$Fe_2(SO_4)_3$	0.016	0.14	0.05	1.54	2.94	12.3	0.88

The effect of oxidizing agents on the precious metals concentration in leach residue are shown in Fig. 3.

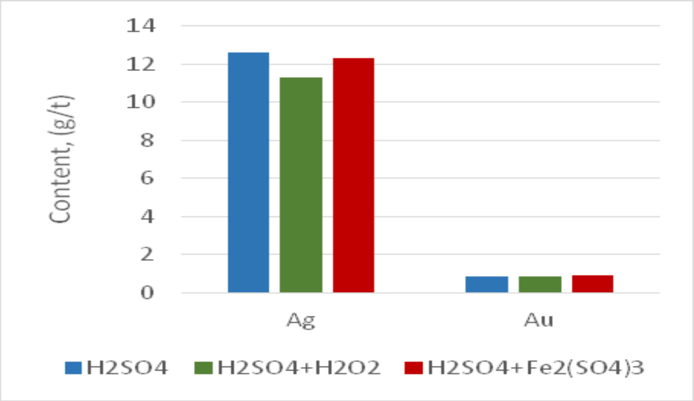

Fig. 3. Effect of leach solution composition on precious metals concentration in leach residue

The addition of an oxidizing agent (H_2O_2 or $Fe_2(SO_4)_3$) in the H_2SO_4 leaching solution had no significant influences on the leaching efficiency. This could be a consequence of the fact that most compounds in the tailings are already in some oxidized state due to the contact with atmospheric media (air, rain, gases).

6. Conclusions

Based on the preliminary experiments, the following conclusions can be drawn:

- By acid leached of the flotation tailings, slimes enriched in precious metals could be obtained.
- HNO_3 leaching are more effective than H_2SO_4 leaching: 31 % of the tailings was leached comparatively with 15%, having as results increasing Au content in the slime (1.1 vs. 0.82 g/t).
- Further leached of the slime in H_2SO_4 solution has a result an increase of Au content in the new slime up to 3 times comparative with tailings (1.9 vs. 0.7 g/t)

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