COMPARISON OF METHODS FOR RECOVERY OF VALUABLE COMPONENTS FROM METALLURGICAL SLAG

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ABSRACT The slag from lead-zinc metallurgy bears valuable components and its processing raises an increasing interest both from economic and environmental point of view. Low concentrations of metals and metals' presence as compounds different from natural minerals are the major obstacles in applying classical mineral processing technologies for metals' recovery. The paper compares results for copper extraction by application of different mineral processing technologies (hydrometallurgy, magnetic separation, classical flotation, electrochemically aided flotation, flotation of electrochemically pre-enriched material). Best results are obtained by electrochemically aided sulfide flotation, applied to electrochemically pretreated slag.

СРАВНЕНИЕ НА МЕТОДИ ЗА ИЗВЛИЧАНЕ НА ЦЕННИ КОМПОНЕНТИ ОТ МЕТАЛУРГИЧНА ШЛАКА

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РЕЗЮМЕ. Шлаката от оловно-цинковата металургия съдържа ценни метали и нейното преработване представлява интерес, както от икономическа гледна точка, така и от гледна точка на опазването на околната среда. Ниските концентрации на присъстващите метали и съществуването им под форма, различна от природните минерали, са основните пречки за прилагане на класическите обогатителни технологии за извличането на тези метали. В статията се сравняват резултатите за извличане на медта чрез прилагане на различни технологии за обогатяване (хидрометалургично третиране, магнитна сепарация, класическа флотация, електрохимично подпомогната флотация, флотация на електрохимично пре-третиран материал. Най-добри резултати са получени чрез електрохимично подпомогната флотация, приложена към електрохимично пре-третиран материал.

Introduction

Metals are needed for the well established technologies, machines and devices used in our everyday life, as well as for developing the latest green technologies in the area of transport, energy production and the environment protection.

At the same time, the worldwide reserves are being depleted. The metallurgical slag represents one of possible sources for ferrous and non ferrous metals. It often bears metals in higher concentration, compared to some of ores mined out in our days. Processing of slag also contributes to the environment protection by reserves preserving and decreasing the energy demand for the unit mass of metal production.

Slag from lead-zinc metallurgy is reach in copper, precious metals and other valuable components. According to some estimates, these components can be profitably extracted (Ayres et al., 2002; Jeanette et al. 2002).

Metallurgical slag is often processed by hydrometallurgy (Habashi, 1999). Sulfuric acid solutions are the cheapest industrially used reagent. They usually ensure high leaching rate and high recovery of metals (Jeanette et al, 2002). Some authors propose additional pressure to be applied in order to increase the leaching rate (Wesstrom, 2000). Ammonia and ammonia-carbonate solutions are among other leaching reagents that were studied and applied. An autoclave technology for recovery of copper, in presence of oxygen and water, from low grade concentrates and impoverished ores with Cu content less than 0.25%, or even less than 0.1% has been proposed (Jones, 1993). The working temperature was 180-220 ^{o}C, applied pressure - 150-300 psig and treatment time - 2 h. The following generalized reaction takes place:

$$4CuFeS_2 + 17O_2 + 4H_2O \rightarrow 4CuSO_4 + 4H_2SO_4 + 2Fe_2O_3$$

The resulting acidic solution is rich in Cu.

A hydrometallurgy technology is patented for nonferrous metals leaching from impoverished ores and waste materials where chloride bearing solutions are used (Hoboy, et al. 2004).

Increased attention is paid recently to the possibility to facilitate metals recovery from waste materials and low grade ores with the aid of an electrochemical treatment (Fetisov et al., 2004; P. Gramatyka et al., 2007).

This paper presents a comparison of laboratory results for copper extraction from lead-zinc metallurgical slag by application of different mineral processing technologies (hydrometallurgy, magnetic separation, classical sulfide ore flotation, and classical and electrochemically aided sulfide ore flotation of electrochemically pre-enriched material).

Methods and materials

Experiments were carried out with slag from lead-zinc metallurgy with the following content of the major metals: Cu 1.75 %, 0.72 Zn %,0.29 Pb %, and Fe 24.55 %.

Mineralogical studies showed that the copper was concentrated predominately inside the iron sulphides (troilite and pyrrhotite). It exists mainly as micron-sized copper sulphides (chalcopyrite, halcozine, and covellite) and elemental copper under the form of small copper grains or veins inside the iron sulphides. Intermetallic compounds bear around 2 % of copper and the coke – around 1 %.

The material was ground until reaching 95 % of it to be with a size less than 0.076 mm.

Leaching experiments were carried out for 5 hours at room temperature, atmospheric pressure, stirring rate of 600 rev/min and at ratios of solid to liquid = 1:5 and 1:10. Leaching solutions were 10 % H_2SO_4, 30 % H_2SO_4, 10 % H_2SO_4 plus and oxidizing reagent (Panayotov and Panayotova, 2009), 10 % HNO_3, 10 % HCl and 10 % HCl bearing 0.2 M $FeCl_3$. The obtained leachates were analyzed in the central laboratory "Geochemistry" at the University of Mining and Geology.

The finding that the Cu was concentrated predominately inside the iron sulphides and in intermetallides lead us to the idea to try magnetic separation and subsequently the scheme of copper sulfides' flotation to be applied. Classical flow sheet of copper sulfides' flotation was applied to material without any pretreatment and to electrochemically pretreated material for valuable metals pre-concentration. The treatment for valuable metals pre-concentration is described elsewhere (Panayotova and Panayotov, 2011). The generalized flow-sheet of the carried out open cycle flotation is presented in Fig. 1.

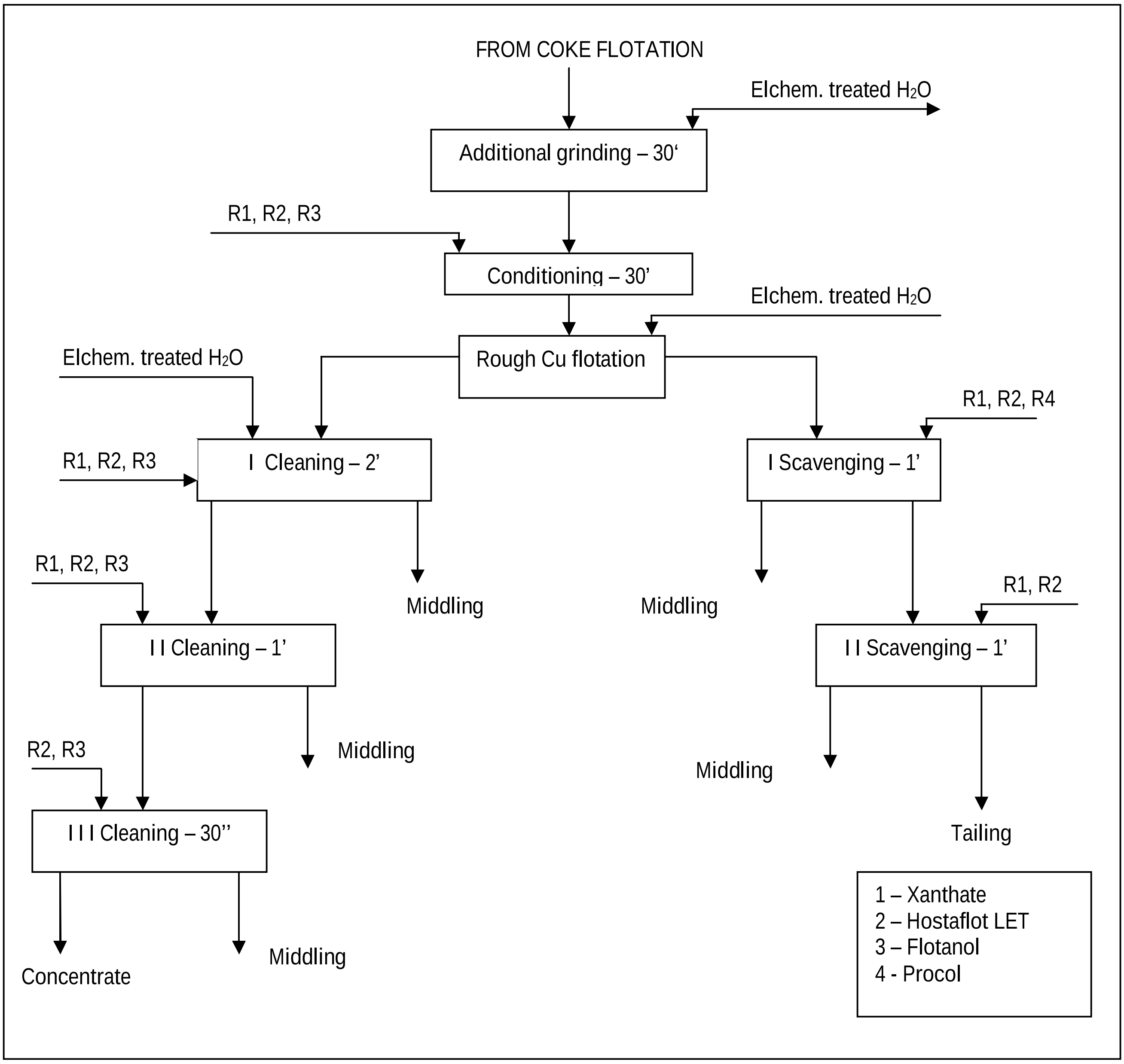

Fig.1. Generalized applied flotation flow-sheet – difference between the classical and electrochemically aided flotation scheme is the addition of electrochemically treated water

Results and discussion

The magnetic separation divided the material into magnetic and non-magnetic fractions - however neither of them was enriched in copper. Both fractions were further subjected to classical flotation. The amount of copper in the initial material, and in the flotation product of passed through flotation magnetic and non-magnetic fraction remained the same.

The results from hydrometallurgical experiments are presented in Table 1. Each result, presented in Table 1, is an average of 3 parallel experiments.

The results, presented in Table 1, show that very small amount of copper available in the raw material is dissolved, most probably due to the available shell made of iron intermetalides and minerals which shields copper minerals.

Table 1.
Results from hydrometallurgical treatment

Leaching solution	Cu in leachate, % from initially available Cu in the solid raw material	
	Solid:liquid=1:5	Solid:liquid=1:10
10 % H_2SO_4	4.9	7.1
30 % H_2SO_4	6.4	8.7
Oxidizing reagent–o.r.	9.6	13.8
10 % H_2SO_4 + o.r.	10.1	14.3
10 % HNO_3	12.6	17.2
10 % HCl	5.1	6.8
10%HCl+0.2M $FeCl_3$.	5.7	7.3

Different degrees of grinding do not substantially alter the results. Observed higher concentration of Cu in leachate, obtained after the material has contacted with 10 % HNO_3, may be assigned to dissolution of metallic copper presenting in the material. Generally, results obtained show that non-pressure hydrometallurgy is not suitable for treating the studied material. Classical electrolysis of leachates with copper concentration over 10 % did not reach yield higher than 50 %.

Application of classical sulfide flotation did not achieve the desired separation. The attempt to expose copper to flotation reagents by achieving a higher degree of grinding did not change the situation.

Table 2 presents a comparison of results from application of classical sulfide ore flotation to non-pretreated material and classical and electrochemically aided sulfide ore flotation to electrochemically pre-enriched material. The electrochemically aided flotation differs from the classical one by addition of electrochemically treated water in the additional grinding process after coke flotation and before rough and first cleaning flotation. More details are given elsewhere (Panayotov et al., 2008). Each result, presented in Table 2, is an average of 2 parallel experiments.

As it can be seen from Table 2, the best results were obtained when electrochemically aided flotation is applied to electrochemically pretreated (pre-concentrated) material. Better results obtained with electrochemically pretreated material could be attributed to facilitated disclosure of copper minerals by the simultaneous action of applied direct current and leaching solution.

Table 2.
Comparison of results from classical and electrochemically aided flotation

Flotation scheme	Concentrate grade	Tailings	Recovery*
	Cu,%	Cu,%	Cu,%
Classical – non pretreated material	6.12	1.02	50.2
Classical - pre-treated material	9.56	0.80	67.5
Electrochemically aided, pretreated material	11.57	0.66	70.56

*% from initially available Cu in the solid raw material

The comparison of results presented in Tables 1 and 2, considered together with the electrolysis results, reveal the advantage of electrochemically aided flotation over hydrometallurgy, carried out at normal pressure and temperature, in terms of copper recovery from the studied material.

Conclusions

Electrochemically aided sulfide flotation, applied to electrochemically pretreated slag from lead-zinc metallurgy, appears to be promising method for copper extraction – both from the viewpoint of copper recovery and grade of the obtained concentrate.

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