DISSOLUTION OF COPPER FROM SMELTING SLAG
BY LEACHING IN CHLORIDE MEDIA

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Abstract

Leaching of copper smelting slag in chloride media was studied. The lixiviants used were aqueous solutions of hydrochloric acid (0.5-2.0 M HCl) as well as hydrogen peroxide and hydrochloric acid (0.5-3.0 M H_2O_2, 1.0 M HCl). The maximum final copper extraction from the slag of 73% was attained with 3 M H_2O_2, at room temperature after 120 minutes of reaction. At the same time, 55% of the iron from the slag was also dissolved. The copper extraction increased during the first 60 minutes of reaction and essentially ceased thereafter. Because of a rapid catalytic decomposition of hydrogen peroxide, it should be added contiuously to the leach suspension rather than at once at the begining of the experiment. In fact, it appears that almost complete dissolution of copper from the slag is achievable after about 4 hours of leaching by implementing the method of continuous lixiviant addition. Also, it seems that the final iron extraction could be limitied to as low as 20% by using this method.

Keywords: Copper, Slag, Leaching, Hydrochloric acid, Hydrogen peroxide.

1. Introduction

The worldwide landfills and other waste repositories (e.g., tailing ponds and slag heaps) have been estimated to contain more than 30% of the known remaining reserves of copper [1]. This situation has prompted much research on the recovery of copper and other base metals from copper metallurgical slags [2]. Most of the studies on the recovery of copper and other base metals from copper metallurgical slags have been conducted in acidic sulphate media, either in the absence or presence of an oxidant, in both atmospheric and pressure conditions [3-9]. In contrast, only a few papers have been published on the leaching of copper and other base metals from copper metallurgical slags in ammonia [7, 8, 10] and acidic chloride solutions [8, 11]. However, chloride media are generally known to be more aggressive than sulphate media [12]. In addition, research has been done into bioleaching [13, 14] and the effect organic (citric acid) on selective acid leaching [9]. Besides leaching, sulphation roasting of slag with sub sequential water leaching and flotation of the slag remained the two methods to which researchers most focused on copper extraction. Apart from copper, the copper smelter slag can also be a significant source of iron and silica [15-18].

The reverberatory furnace slag that was discarded in the vicinity of the Bor Copper Smelter, Serbia, is currently processed by flotation at the nearby Bor Copper Concentrator. The copper recovery has been rather low mainly due to the presence of oxide copper and insufficient mineral liberation. In our previous work, we investigated the technical feasibility of increasing copper recovery by leaching the slag using sulphuric acid solutions, without or with the addition of either ferric sulphate or hydrogen peroxide. However, the maximum copper extraction attained was modest at about 63% [6]. Accordingly, the objective of the present work was to investigate whether the implementation of leaching in chloride media would result in an increase in copper recovery.

2. Material, Characterization and Experimental Methods

The experiments were performed using reverberatory furnace slag from the Bor Copper Concentrator. The slag was sampled from the crushing line before entering the milling section of the

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concentrator. The sample was ground and sieved. The -75 µm size fraction was used for the experiments. This is because in mineral processing of copper ores, sieve fraction −75 µm is considered standard for determining the degree of liberation of copper minerals [19]. Quantitative determination of elements in the sample was performed by gravimetric and volumetric analysis, as well as atomic absorption spectrophotometry (FAAS M-403 or GFAAS M-1100B, Prkin Elmer). The chemical composition of the sample is presented in Table 1.

**Table 1**. *Chemical composition of the smelting slag (wt. %)*

Constituents	Content
Cu - total	0.97
Cu - oxides	0.15
Cu - sulphides	0.82
SiO_2	33.75
Al_2O_3	3.78
Fe_2O_3	8.05
FeO	33.8
Fe_3O_4	9.39
Fe - total	39.09
CaO	6
MgO	1.66

The XRD characterization of the samples of the copper slag and leach residue was conducted using a Philips PW-1710 X-ray diffractometer with a CuKα radiation (λ = 0.154178 nm, 40 kV, 30 mA) at the scanning rate of 0.02 °2θ/s vary from 5 to 70 °2θ. XRD analysis of the slag indicated that its main crystalline constituents are magnetite, olivines (among which fayalite was found to be the most abundant), pyroxene and granate (Figure 1). The composition, structure and textures of the copper slag was evaluation by polarising reflected light
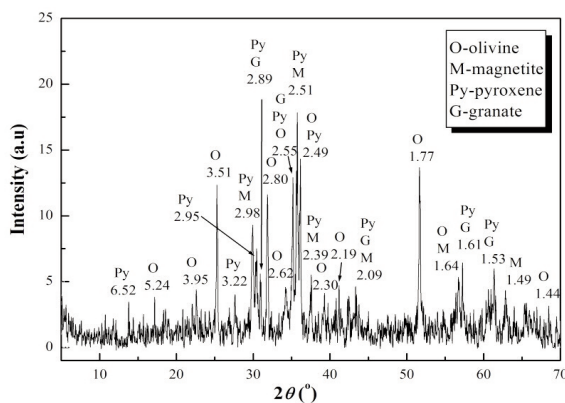
Figure 1. *XRD pattern for the copper slag sample*

microscopy (Carl Zeiss Axioskop 40). This analysis demonstrated that the slag is composed of a fayalite and ferite structure that contains small grains of magnetite, pyrite, chalcopyrite, chalcocite, bornite, copper matte and elemental copper (Figure 2).
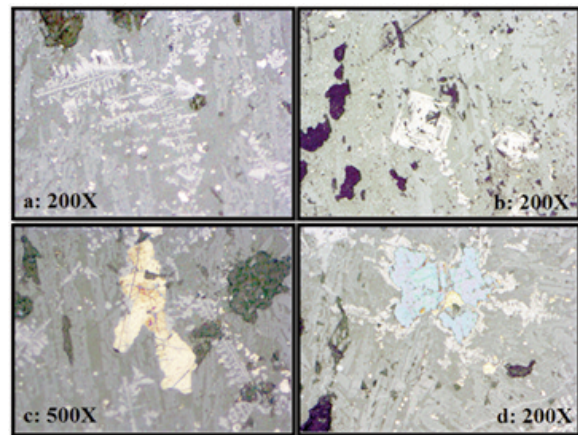
Figure 2. *Photomicrographs of the smelting slag (reflected light, air, II N): a – ferrite dendrites in the fayalite structure, b – magnetite shaped as a cube in the fayalite structure, c – chalcopyrite in the fayalite structure, d – copper matte in the fayalite structure.*

The standard experimental procedure involved leaching 5 g of the slag with 150 mL of lixiviant, at room temperature and atmospheric pressure. These standard experiments were conducted in a 250 mL glass beaker at a stirring speed of 350 min^{-1} using a magnetic stirrer. The experiments investigating the effect of temperature on metal dissolution were conducted in a three-necked glass reactor immersed in a thermostatic water bath and equipped with a glass stirrer, condenser and thermometer. The reaction time was 120 minutes. Sampling was performed at regular time intervals by taking 1 mL of the leach liquor with a pipette. The leach liquor sample was filtered and the filtrate was transferred to a 50 mL volumetric flask. The flask was filled with distilled water to the mark. The diluted solution was analyzed by atomic absorption spectrophotometry. All experiments were repeated at least twice to ensure consistent results.

3. Results and discussion
3.1. Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration on metal dissolution from the slag was studied at initial hydrochloric acid concentrations ranging from 0.5 M to 2.0 M. The results are shown in Figure 3. It can be seen that copper dissolution increased slightly with increasing hydrochloric acid concentration. However, the final copper extractions were realatively low (28-36%). Further, the copper dissolution essentially

ceased after 60 minutes. Also, the final iron extractions were higher than those of copper. Thus, the final iron extractions were around 55% at 1.5 M and 2.0 M HCl. Moreover, except for the lowest concentration of hydrochloric acid, the iron dissolution practically stopped after 90 minutes. Chen et al. [11] studied leaching of copper slag with hydrochloric acid. They were able to dissolve as much as 91% of the copper from the slag with 35% HCl at 80-90 ºC. However, these extreme conditions also resulted in almost complete dissolution of iron (i.e., 99%). For this reason, in the present work, the effect of temperature on metal dissolution was not investigated in hydrochloric acid solutions alone.
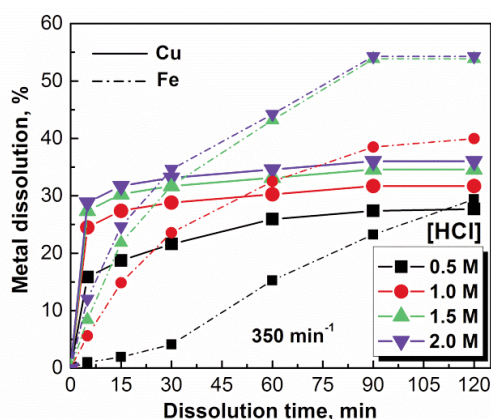

Figure 3. *Copper and iron extractions from the slag as a function of time at different initial hydrochloric acid concentrations*

By comparing the results obtained in the present work with those found during leaching of the slag with sulphuric acid [6], it can be seen that the kinetic curves have a somewhat similar shape. The copper extractions are about 10% higher in hydrochloric acid than those in sulphuric acid [6], which can be expected as chloride media are known to be more aggressive than sulphate media [12]. On the other hand, the iron extractions are similar in the two media [6].

3.2. Effect of hydrogen peroxide concentration

As the copper extraction from the slag with hydrochloric acid was relatively low, a new set of experiments was performed using hydrogen peroxide as a strong oxidant. The experiments were conducted in acidic chloride solutions (1.0 M HCl) at different initial hydrogen peroxide concentrations (0.5-3.0 M). The results are depicted in Figure 4.

It can be seen that the copper extractions in the presence of hydrogen peroxide are higher when compared to those in the presence of hydrochloric acid alone. As the oxidant concentration increases so

does the copper extraction, that is, from 46% to 73% for the lowest and highest hydrogen peroxide concentration, respectively.
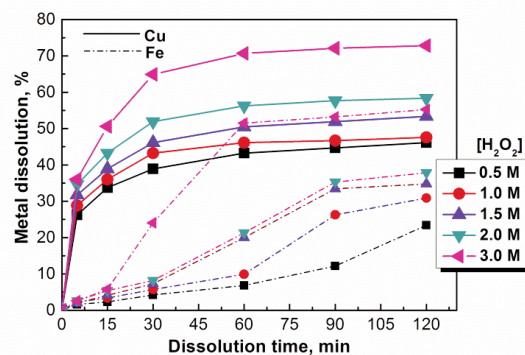

Figure 4. *Copper and iron extractions from the slag as a function of time at different initial hydrogen peroxide concentrations (1.0 M HCl, 350 min⁻¹)*

These extractions are approximately twice as high as those obtained in the presence of hydrochloric acid alone. This finding indicates that an oxidant is necessary to achieve a meaningful copper dissolution from the slag. With regard to the iron extractions, they are lower than the copper extractions, and vary from 31% to 55%. From Figure 4, it can also be seen that a significant iron dissolutiuon from the slag starts only after the copper dissolution has almost stopped. This finding suggests that hydrogen peroxide has a greater affinity towards the copper compounds when compared to the iron compounds in the slag. In other words, the copper amenable to leaching is present in forms that are more succeptible to oxidation than the iron compounds in the slag. The copper dissolution is most rapid within the first 60 minutes of reaction. The reaction itself is vigorous in the first 60 minutes, which was observed during the experiments, but can
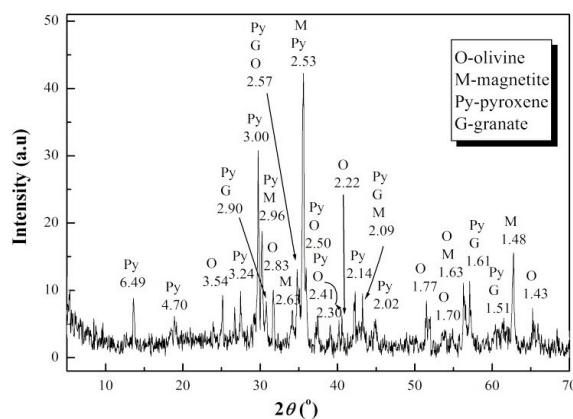

Figure 5. *XRD pattern for the leach residue (1.0 M HCl, 2.0 M H₂O₂)*

also be concluded based on Figure 4. During this time, intense decomposition of hydrogen peroxide accompanied with oxygen effervescence was observed. The suspension itself appeared as if it was boiling, in particular at higher hydrogen peroxide concentrations (i.e., above 1.5 M H_2O_2). The results obtained in the present work are similar to those found when the slag was leached with hydrogen peroxide in acidic sulphate solutions [6]. XRD analysis of the leach residue (Figure 5) showed the same mineral phases as those found in the copper slag sample, but with more pronounced peaks. The crystallinity of the residue was higher than that of the copper slag sample, but nevertheless low.

3.3. Effect of stirring

The decomposition of hydrogen peroxide is known to be catalysed by a number of ions and compounds, as well as by stirring, shaking and heating [20]. For this reason, the effect of stirring on copper and iron extractions was studied. Two experiments were perfromed, one without stirring the suspension and the other one at a strring speed of 350 min^{-1}. The results are shown in Figure 6. It can be seen that stirring the suspension has a positive effect on metal dissolution when compared to the unstirred suspension. This phenomenon may be due to a better contact of the lixiviant with the slag that has a high density (i.e., 3600 kg m^{-3}).
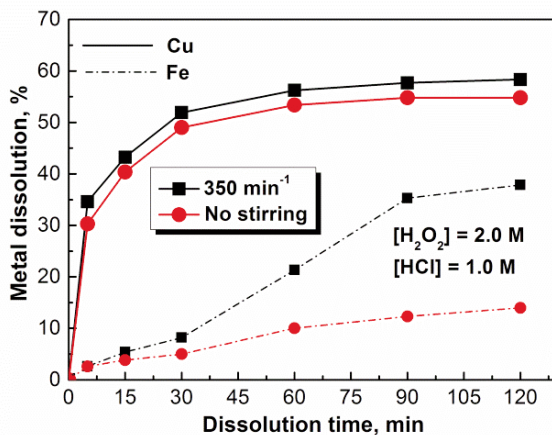

Fiure 6. Copper and iron extractions from the slag with and without stirring

3.4. Effect of temperature

The effect of temperature on metal dissolution was studied in a narrow temperature range (32-54 °C) because hydrogen peroxide tends to decompose at temperatures above 40 °C. The results obtained (Figure 7) show that the final copper extraction was not affected significantly in this temperature range.
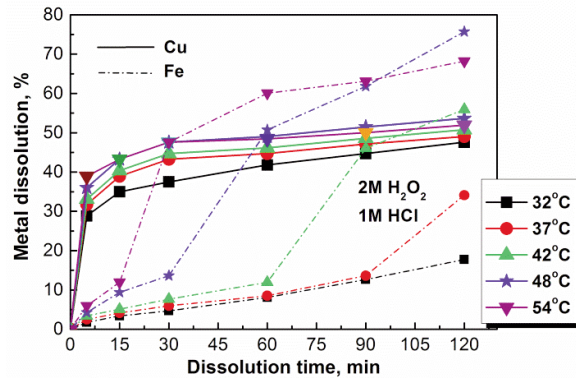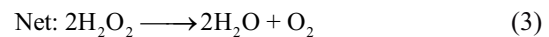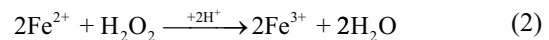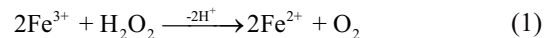

Figure 7. Copper and iron extractions from the slag as a function of time at different temperatures

From Figure 7, it can be concluded that the leaching of copper from the slag is the dominant process until a specific critical concentration of iron ions in solution has been reached (i.e., until about 10% of the iron has been dissolved from the slag). Following that, as the concentration of iron in solution increases, the reaction becomes faster because of the catalytic decomposition of hydrogen peroxide to oxygen and water through a redox process caused by the Fe^{3+}/Fe^{2+} redox couple (equations 1, 2 and 3) [21]. The higher the decomposition of hydrogen peroxide (i.e., the more intense oxygen effervescence), the higher the dissolution of iron, both of which increase as the temperature increases. This is the reason that the final iron extractions at 48 °C and 54 °C are considerably higher than the final copper extractions at these temperatures.

$$2Fe^{3+} + H_2O_2 \xrightarrow{-2H^+} 2Fe^{2+} + O_2 \tag{1}$$

$$2Fe^{2+} + H_2O_2 \xrightarrow{+2H^+} 2Fe^{3+} + 2H_2O \tag{2}$$

$$Net: 2H_2O_2 \longrightarrow 2H_2O + O_2 \tag{3}$$

3.5. Effect of the solid/liquid ratio

The effect of the solid/liquid ratio on metal dissolution was studied by leaching 5, 10, 15 and 20 g of slag with 150 mL of lixiviant (2.0 M H_2O_2, 1.0 M HCl) at room temperature during 120 min, which corresponds to the solid/liquid ratios of 1:30, 1:15, 1:10 and 1:7.5. As seen in Figure 8, the highest final copper extraction and the lowest final iron extraction were obtained in the most dilute suspension (i.e., when 5 g of slag was used). As the solid/liquid ratio increases, the final copper extraction slightly decreases whereas that of iron somewhat increases.

Suspension temperatures were recorded during these experiments and are given in Figure 9. This figure shows that hydrogen peroxide decomposition accelerates with increasing suspension densities,

which translates into higher suspension temperatures. However, very fast hydrogen peroxide decomposition during the first 15 minutes of leaching in more dense suspensions (i.e., when between 10 g and 20 g of slag was used) leads to a lower final copper extraction.
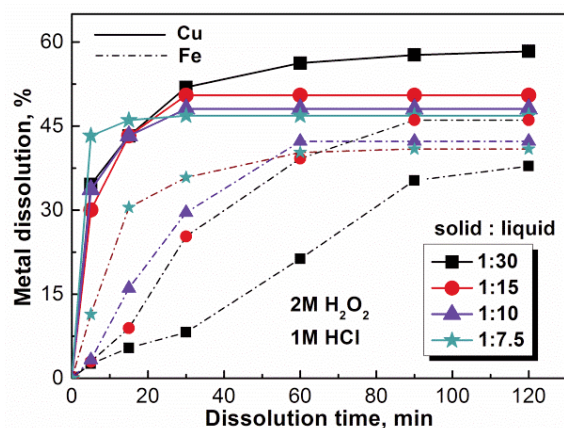

Figure 8. Copper and iron extractions from the slag as a function of time at different solid/liquid ratios
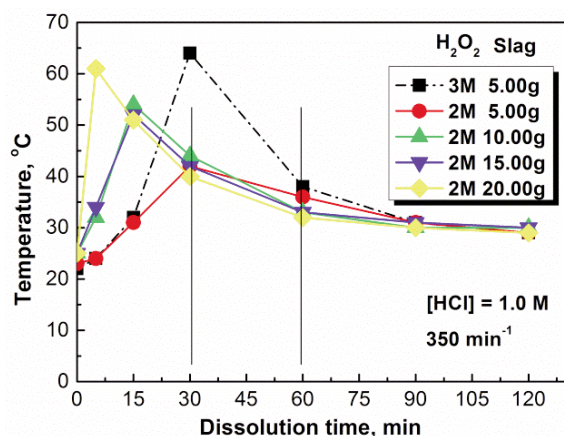

Figure 9. Suspension temperatures as a function of time at different solid/liquid ratios

Figure 9 also implies that most of the copper and iron have been dissolved from the slag after the first 60 minutes of reaction, which is in fact equal to the time during which most of the hydrogen peroxide have been decomposed.

For comparison, the suspension temperature recorded during leaching with 3.0 M hydrogen peroxide is also shown in Figure 9. It is evident that the suspension temperature is 20 °C higher after 30 minutes of leaching with 3.0 M H_2O_2 when compared to 2.0 M H_2O_2. This rise in temperature is responsible not only for higher final copper and iron extractions with 3.0 M H_2O_2 when compared to 2.0 M H_2O_2 (see Figure 4) but also for faster hydrogen peroxide decomposition.

3.6. Effect of the mode of lixiviant addition

According to the standard experimental procedure, a copper extraction of about 60% was attained when leaching with 2.0 M H_2O_2 + 1.0 M HCl. Hydrogen peroxide decomposition when in contact with the slag is recognized as the main limiting factor to achieving higher copper extractions [6]. For this reason, two experiments were performed using modified experimental procedures. In the first experiment, 6 mL portions of lixiviant A (6.5 mL conc. HCl + 23.5 mL conc. H_2O_2) were added at 10, 30, 50, 80, 110 and 140 minutes of reaction into a beaker containing initially 120 mL of lixiviant B (6.5 mL conc. HCl + 7.1 mL conc. H_2O_2 + water) and 5g of the slag. In the second experiment, the lixiviant (1.0 M HCl + 2.0 M H_2O_2) was added continuously using an automatic burette at a rate of 1.44 mL/min into a suspension containing 5 g of the slag and 50 mL of water. The lixiviant concentrations in both experiments were adjusted so as to correspond to the standard experimental conditions for easier comparison. The results are illustrated in Figure 10.
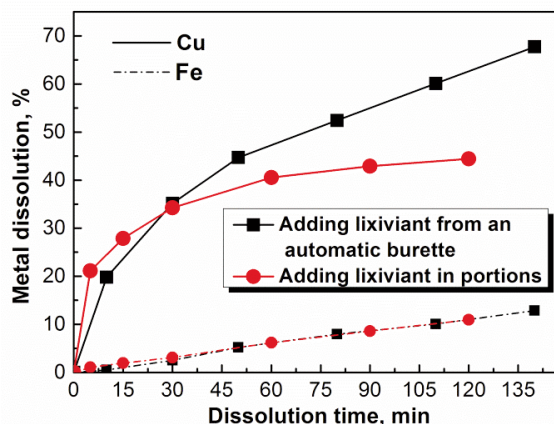

Figure 10. Effect of the mode of lixiviant addition on metal dissolution from the slag

The final iron extraction in both experiments is almost the same (i.e., around 11%) and about three times lower than that obtained according the standard experimental procedure. However, adding lixiviant in portions resulted in a low final copper extraction (i.e., about 40%). On the other hand, although the copper extraction attained at 120 minutes of leaching using the method of continuous lixiviant addition is similar to that obtained according to the standard experimental procedure (i.e., about 60%), the former seems to be better. That is, by extrapolating the copper leaching curve in Figure 10, it can be concluded that almost complete dissolution of copper from the slag could be achieved after about 4 hours of leaching, whereas copper dissolution from the slag essentially

stops after 60 minutes when leaching is performed according to the standard experimental procedure (Figure 4). Also, it seems that the iron extraction after 4 hours of leaching using the method of continuous lixiviant addition could be as low as 20%.

4. Conclusions

Leaching of the copper smelting slag was performed using hydrochloric acid solutions, without or with the addition of hydrogen peroxide. Three experimental procedures were tested. The first experimental procedure involved adding the lixiviant at the beginning of the experiment. When leaching with hydrochloric acid alone, the final copper extraction was only 36% after 2 hours of reaction. The maximum final copper extraction of 73% was attained in the presence of 3.0 M hydrogen peroxide after 2 hours of leaching. This observation indicates that much of the copper (in the form of fine particles) that is locked within the slag matrix was not liberated prior to leaching. Further, leaching was not selective, that is, around 55% of the iron from the slag was also dissolved. Copper dissolution from the slag was the dominant process until a specific critical iron concentration in solution was reached (i.e., until about 10% of the iron was dissolved). The second and third experimental procedures consisted in adding the lixiviant in portions at specific time intervals as well as continuously using a burette, respectively. Experiments performed according to these two procedures resulted in low iron extractions after 2 hours of leaching (i.e., about 11%). However, a low copper extraction was obtained using the second procedure (i.e., about 40%). On the other hand, the method of continuous lixiviant addition seems to be promising. That is, by using extrapolation, it can be concluded that 4 hours of leaching would be needed to achieve nearly complete dissolution of copper. At the same time, it appears that the iron extraction would be limited to as low as 20%.

Acknowledgments

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