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RECOVERY OF COPPER FROM SMELTING SLAG BY SULPHATION ROASTING AND WATER LEACHING

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Abstract: In this work extraction of copper and iron from a reverberatory furnace slag was studied. A two-step extraction procedure was followed. The first step was roasting of the slag in the presence of sulphuric acid at temperatures between 150 and 800 °C. The second step was leaching of the resulting calcine with distilled water. The maximum copper extraction of about 94% was achieved. In this case, the slag was roasted at 250 °C with sulphuric acid higher of about 33% than that stoichiometrically required, followed by water leaching of calcine at 50 °C. About 55% of iron was also dissolved under these conditions. On the other hand, for the calcine obtained at sulphation temperature of 600 °C, extraction of copper in a water leaching stage was still relatively high (about 79%), whereas that of iron was comparatively low (about 6%). Dissolution of copper and iron from the calcine was found to be very fast and was complete within the first few minutes. The water temperature in the leaching step was found to have no effect on extraction of copper and iron from the calcine in the range of 30 to 85 °C.

Keywords: copper, slag, sulphation, roasting, acid baking, leaching

Introduction

The environmental burden of waste disposal and decreasing metal ore grades make a strong case for implementation of alternative processes for metal recovery and metal recycling (Ochromowicz and Chmielewski, 2010; Schlesinger et al., 2011; Frandegard et al., 2013; Chmielewski, 2015). It has been estimated that landfills and other waste repositories (e.g., tailing ponds and slag heaps) around the world contain about 300 teragrams (Tg) of copper, which corresponds to more than 30% of the known remaining reserves (Kapur and Graedel, 2006). The situation is similar for other base metals, which has motivated a great deal of research on the base metal tailings over the past few years (Aromaa et al., 2013; Chen et al., 2014; Muravyov et al., 2014).

Likewise, studies on various non-ferrous slags has almost tripled since the early 1990s (Piatak et al., 2015).

Pyrometallurgical production of copper generates two slags: smelting furnace slag and converter slag which contain 0.5-2% Cu and 2-8% Cu, respectively. The following three methods are generally utilized for recovering the copper from these slags on an industrial scale: (i) recycling of the converter slag to the smelting furnace, (ii) cleaning of smelting and/or converter slags in electric furnaces and (iii) flotation. Metallic copper and sulphide copper present in these slags can be floated very effectively, provided that the mineral grains are large enough to be liberated by conventional crushing and grinding (Shen and Forssberg, 2003; Schlesinger et al., 2011).

The reverberatory furnace slag that has been discarded in the vicinity of the Bor Copper Smelter, Serbia, is currently processed by flotation at the nearby Bor Copper Concentrator. The copper recovery was rather low (about 40%) 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 and flotation of slag tailings using sulphuric acid solutions, without or with the addition of either ferric sulphate or hydrogen peroxide. However, the maximum copper extraction attained with the slag was modest at about 63%, whereas that obtained with the slag flotation tailings was as low as 33% (Urosevic et al., 2015). Accordingly, the objective of the present work was to investigate whether the introduction of a pyrometallurgical pre-treatment step to break down the slag structure, thereby rendering copper-containing phases amenable to leaching, would result in an increase in copper recovery.

Several studies on the recovery of metal values from various copper-containing slags by either chloriding or sulphation roasting followed by water leaching were reported. Thus, ammonium chloride was studied as a chloriding agent (D'yachenko et al., 2013; Nadirov et al., 2013), whereas the sulphating agents included ammonium sulphate (Sukla et al., 1986; Hamamci and Ziyadanogullari, 1991), ferric sulphate (Altundogan and Tumen, 1997), pyrite (Tumen and Bailey, 1990) and sulphuric acid (Sukla et al., 1986; Hamamci and Ziyadanogullari, 1991; Arslan and Arslan, 2002). However, all of these slags contained, in addition to copper, significant amounts of either cobalt or nickel or both. The slag studied in this paper is different from the previous studies since it contains no cobalt and very little nickel.

Based on the above mentioned studies, sulphuric acid appears to be the best pre-treatment agent. Sulphuric acid has been utilized as the sulphation agent for various materials, and the sulphation process has also been referred to as acid baking, in particular when applied at temperatures up to 400 °C (Kul et al., 2008; Kim et al., 2009; Safarzadeh et al., 2012). Therefore, in the present work, roasting with sulphuric acid was adopted as a pretreatment step prior to the water leaching step.

Materials and experimental methods

Experiments were conducted using a reverberatory furnace slag from the Bor Copper Concentrator, Serbia. The slag was sampled from the crushing line before entering the milling section of the concentrator. The sample was ground to pass through a 75 μm sieve. Quantitative determination of elements in the sample was performed by the gravimetric analysis, volumetric analysis and atomic absorption spectrophotometry (FAAS/GFAAS). The chemical composition of the sample is given in Table 1.

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

Constituent	Cu total	Cu oxides	Cu sulphides	Fe total	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Fe ₃ O ₄	CaO	MgO
Content	0.97	0.15	0.82	39.09	33.75	3.78	8.05	33.80	9.39	6.00	1.66

XRD characterization of slag indicated that the major crystalline phases are magnetite, olivines (among which fayalite was found to be the most abundant), pyroxene and granate (Urosevic et al, 2015). Based on quantitative mineralogical analysis, the mineral composition was determined to be as follows: Cu-Fe-S sulphide solid solution, chalcocite (Cu₂S), covelite (CuS), pyrite (FeS₂), troilite (FeS), metallic copper, cuprite (Cu₂O), magnetite (Fe₃O₄), and gangue minerals. The sulphide content was 2.75%. The gangue minerals comprise fayalite glass, various dendritic ferrites and refractory aggregates. The mineral composition of these materials varies widely and is dependent on various factors (pH, Eh, cooling rate, number of crystallization centres, composition of the starting minerals, etc.). Among the copper sulphide minerals, the most abundant are complex compositions of the bornite-chalcocite (digenite), that is, Cu₅FeS₄-Cu₂S(Cu₉S₅) sulphide solid solution system. This system has continuous mixing series in all ratios, from temperatures of 300°C up to melting and formation of sulphide glass. With decreasing temperature, either metastable chalcopyrite (CuFeS₂) sulphide solid solution in bornite or chalcocite (digenite) sulphide solid solution in bornite are formed. They are formed in the absence of oxygen, when the sulphide minerals become trapped within the glass and start to crystallize as the temperature decreases. They occur most frequently as either inclusions or emulsions in the fayalite-glass phase (Fig. 1a). Most commonly, they are spherical in shape, from elongated to spindle-shaped drops of various cross sections (Fig. 1b). Slag minerals are characterized by microcrystal, coarse crystal and, most commonly, glass-like structures with the appearance of various eutectic dendrites and skeletons (fayalite, ferrites, magnetite, etc.), which is shown in Figs. 1c and 1d.

Roasting experiments were performed in a porcelain crucible. In each experiment, 5 g of slag was placed in the crucible. Then, a certain amount of sulphuric acid was added to the slag and thoroughly mixed. The crucible was transferred to a muffle furnace, which was preheated to the required temperature. The standard roasting experimental conditions were as follows: an amount of sulphuric acid larger by 33%

than that stoichiometrically required, a roasting temperature of 350 °C and a roasting time of 1 h. The calcine was cooled and ground prior to leaching.

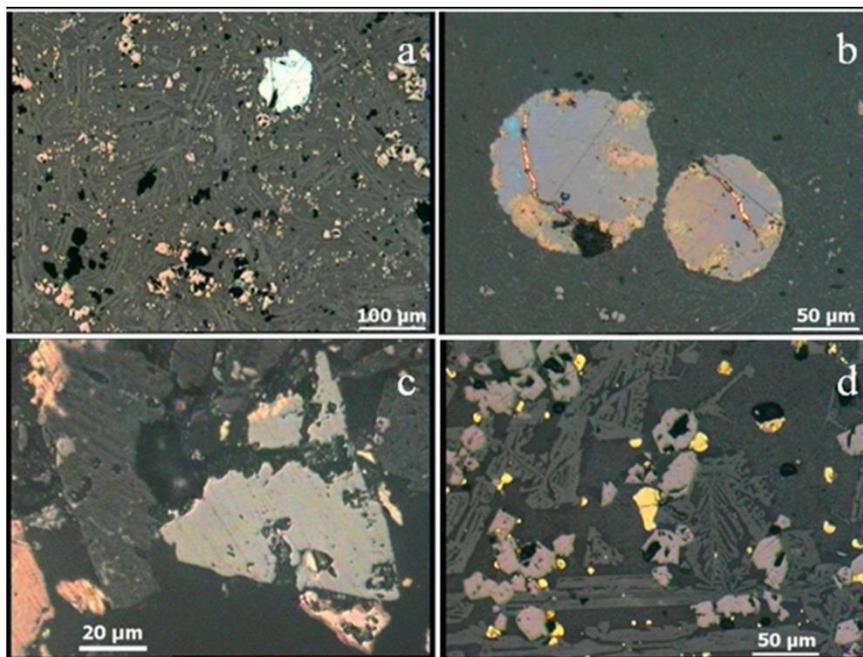


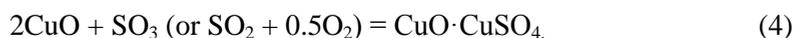
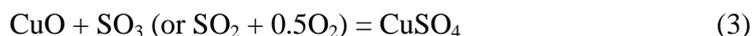
Fig. 1. Photomicrographs of smelting slag (reflected light, air, II N); (a) droplet and/or emulsion inclusions of sulphide solid solution in fayalite-glass matrix, (b) circular sections of complex sulphides of Cu-Fe-S system, (c) skeletal growth of magnetite from silicate melt, (d) coarse crystal aggregate of smelting slag with clearly distinguishable areas of troilite (yellow), magnetite (light-brown) and fayalite dendrite in glass

Leaching experiments at room temperature were conducted in a glass beaker using a magnetic stirrer, whereas those at set temperatures were performed in a three-necked glass reactor immersed in a thermostatic water bath and fitted with a glass stirrer, condenser and thermometer. The sample was leached with 150 cm³ of distilled water. Standard conditions for the leaching experiments were as follows: leaching time of 30 min and stirring speed of 350 min⁻¹. Sampling was performed by taking 1 cm³ of the leach liquor with a pipette. The leach liquor sample was filtered and the filtrate was transferred to a 50 cm³ volumetric flask. The flask was filled with distilled water to the mark. The diluted solution was acidified to prevent metal precipitation. The diluted, acidified solution was analyzed by atomic absorption spectrophotometry. All the experiments were repeated at least two times and some of them several times to establish the reproducibility of the results.

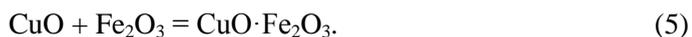
Results and discussion

Roasting

Roasting with sulphuric acid results in production of metal sulphates which are readily soluble in water. The reactions occurring during sulphation roasting of metallic copper and copper compounds may be represented as follows (Altundogan and Tumen, 1997):



Reactions similar to those presented in Eqs. 2 to 4 may be written for compounds containing ferrous iron (i.e., FeO and FeSO₄), whereas additional equations need to be considered in the case of compounds containing ferric iron (i.e., Fe₂O₃ and Fe₂(SO₄)₃). In addition, ferrites may be formed according to the following reaction (Tumen and Bailey, 1990):



The effect of sulphuric acid dosage in the roasting stage on extraction of copper and iron in the subsequent leaching stage was studied by addition of 5 g of slag to different quantities of concentrated sulphuric acid (2, 3, 4, and 5 cm³) followed by roasting the mixture. The stoichiometric requirement of sulphuric acid (96%, ρ=1.84 g/cm³) was calculated to be 3 cm³ based on the amount of copper and iron phases present in the slag. Roasting was performed at 350 °C for a duration of 1 h. The resulting calcine was leached with distilled water at room temperature.

As can be seen in Table 2, sulphuric acid dosage had no effect on the copper and iron extractions obtained, except for a dosage equal to 67% of the stoichiometric requirement, where the extractions were slightly lower. The subsequent roasting experiments were performed with an amount of sulphuric acid corresponding to 133% of that stoichiometrically required in order to ensure complete dissolution of copper.

Table 2. Effect of sulphuric acid dosage in roasting on extraction of copper and iron in leaching

H ₂ SO ₄ , cm ³	2	3	4	5
H ₂ SO ₄ dosage ^a , %	67	100	133	167
Cu extraction, %	81.73	87.75	86.54	87.94
Fe extraction, %	46.90	49.74	48.90	51.17

^a percentage of stoichiometric requirement of sulphuric acid

The effect of roasting time on extraction of copper and iron in the subsequent leaching stage was investigated using calcines roasted at 350 °C for 0.5, 1, 2, 3, and 4 h. The calcines were obtained by roasting slag with an amount of sulphuric acid equal to 133% of the stoichiometric requirement. The leaching experiments were conducted at room temperature. The copper and iron extractions obtained in these experiments are shown in Table 3. It can be seen that increasing the duration of roasting from 0.5 h to 4 h had no effect on copper and iron extraction. Further roasting experiments were conducted for 1 h as in some of the experiments the roasting temperature was lower than 350 °C.

Table 3. Effect of roasting time on extraction of copper and iron in leaching

Time, h	0.5	1	2	3	4
Cu extraction, %	87.26	86.54	88.13	87.75	86.54
Fe extraction, %	49.31	48.90	49.74	49.74	48.30

The effect of roasting temperature on extraction of copper and iron in the subsequent leaching stage was studied in a relatively wide temperature range of 150 to 800 °C. Following roasting with a quantity of sulphuric acid corresponding to 133% of the stoichiometric requirement for 1 h, the calcines were cooled, ground and leached with distilled water at 50 °C. The results obtained are presented in Table 4 and Fig. 2. It can be seen that copper extractions are similar (between 91.35 and 93.74%) for the calcines obtained in the temperature range of 200 to 550 °C and decrease for temperature higher than 600 °C. The iron recoveries are rather high (between 51.17% and 57.32%) in the temperature range of 200 to 450 °C and start to decline at 500 °C. Also, the pH values of the leach solution gradually increase with increasing roasting temperature (Table 4).

The effect of roasting temperature higher than 400 °C on copper and iron extraction obtained in the subsequent leaching step can be compared with the data presented in the literature. Hamamci and Ziyandogulari (1991) and Arslan and Arslan (2002) found that roasting in the presence of sulphuric acid conducted at temperatures up to 300 °C did not decrease the copper and iron recovery. Sukla et al. (1986) conducted experiments at temperatures up to 600 °C but nevertheless found no decline in copper extraction, which remained close to 100% at temperatures higher than 150 °C. Moreover, they observed the maximum iron extraction of about 85% at roasting temperature of 50 °C, which then decreased gradually to about 50% at 400 °C, and thereafter remained unchanged. This behaviour is in contrast to that found in the present study where iron extraction decreased slightly from 60 to 54% at temperature between 100 and 400 °C, and then sharply dropped from 51 to 6% at temperature between 450 and 600 °C (Fig. 2).

Table 4. Effect of roasting temperature on extraction of copper and iron as well as on pH of leach solutions in the leaching stage

T, °C	Cu extraction, %	Fe extraction, %	pH
150	79.32	59.69	1.49
200	89.78	57.32	1.66
250	93.74	54.72	2.17
300	92.98	53.59	2.32
350	93.74	53.30	2.42
400	93.18	53.72	2.48
450	92.70	51.17	2.50
500	92.31	42.64	2.53
550	92.62	38.37	2.58
600	79.32	5.97	2.66
650	51.05	1.34	3.33
700	34.85	0.024	4.27
800	2.16	0.008	5.39

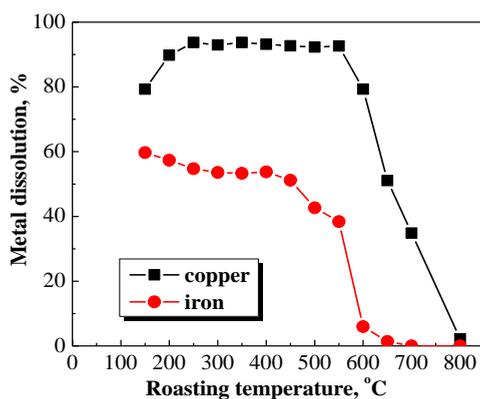
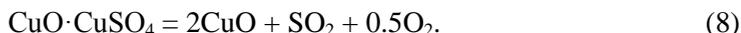
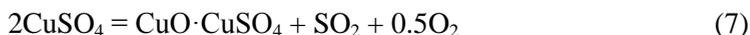


Fig. 2. Copper and iron extractions attained upon water leaching of calcines obtained at different roasting temperatures

Tumen and Bailey (1990) investigating roasting with pyrite and ferric sulphate reported results which are similar to those found in the present study. Tumen and Bailey (1990), after roasting reverberatory furnace slag without pyrite, observed the maximum copper extraction of about 78% at 550 °C, which thereafter steadily decreased to a value close to zero at 750 °C. In addition, they reported the maximum iron extraction of 4% at 450 °C, which decreased gradually to essentially zero at 650 °C. Altundogan and Tumen (1997) reported the maximum copper extraction of about 90% following roasting at 500 °C, which then decreased, first slightly to 85% at 600 °C, then sharply to practically zero at 700 °C. With regard to behaviour of iron,

Altundogan and Tumen (1997) followed the concentration of iron in the leach solution (in contrast to extraction of iron due to iron added in the form of ferric sulphate) and observed steady decline in the iron concentration from about 28 g/dm³ for a roasting temperature of 450 °C to close to zero g/dm³ for 650 °C.

These decreased metal recoveries at high temperatures may be due to the transformation of water-soluble copper and iron sulphates to copper and iron compounds which are not soluble in water. Thus, the decomposition temperature of copper sulphate is 650 °C, whereas that of iron sulphate is 480 °C (Tumen and Bailey, 1990; Altundogan and Tumen, 1997). These temperatures are consistent with the data presented in Table 4 and Fig. 2. Decomposition of iron and copper sulphates may be illustrated by the following reactions (Tumen and Bailey, 1990):



Also, the lower metal recoveries at high temperatures may be attributed to evaporation of sulphuric acid (the boiling point of sulphuric acid is 337 °C) (Sukla et al., 1986; Altundogan and Tumen, 1997). This explanation is in line with the increase in pH of leach solutions with temperature presented in Table 4.

Finally, the lower extractions of iron obtained for higher roasting temperatures may be due to precipitation of ferric iron, which can start to occur at pH 2 (Gupta, 2003).

Sulphation roasting at 550 °C was conducted not only for 1 h but also for 2, 3 and 4 h. The intent was to determine how the increase in roasting time would affect extraction of copper and iron. The results are given in Table 5. The copper extraction obtained was unaffected, whereas that of iron slightly decreased with increasing roasting time, that is, from 38.37 for 1 h to 31.98% for 4 h.

Table 5. Effect of time at roasting temperature of 550 °C on extraction of copper and iron in leaching

Time, h	1	2	3	4
Cu extraction, %	92.62	91.85	92.09	92.70
Fe extraction, %	38.37	36.14	33.51	31.98

In terms of selectivity, the optimum roasting temperature appears to be 600 °C as this temperature leads to a sharp drop in extraction of iron. On the other hand, with regard to the maximum extraction of copper, the optimum roasting temperature seems to be 250 °C as this temperature results in the highest copper extraction. However, a process including the roasting step at 250 °C would normally involve an iron removal step prior to the recovery of copper from the leach solution.

XRD analysis of the calcine produced at 550 °C revealed the presence of hematite, maghemite and magnetite crystalline phases. However, it should be noted that the

phase composition was difficult to determine due to a very high content of amorphous material.

Leaching

Four samples of slag weighing 1, 5, 10 and 20 g were roasted with the appropriate quantity of sulphuric acid under the standard experimental conditions. After cooling and grinding the calcines, they were leached with 150 dm³ distilled water at temperature of 50 °C. By performing nine roasting experiments at 350 °C, the mass of calcine was found to be by 45.3% larger than the initial mass of slag. Therefore, the solid-to-liquid ratios in the leaching stage were approximately 1:100, 1:20, 1:10 and 1:5. The results are given in Table 6.

Table 6. Effect of solid-to-liquid ratio in leaching on copper and iron extractions

Solid : Liquid	Cu extraction, %	Fe extraction, %
1 : 100	92.30	52.50
1 : 20	93.74	53.30
1 : 10	88.94	51.17
1 : 5	76.92	46.33

As seen in Table 6, the copper and iron extractions are unaffected in dilute slurries, whereas thicker slurries lead to a decrease in extractions. It should be noted that the increased mass of the calcine with respect to the initial mass of slag is dependent on the roasting temperature. Thus, the mass increase is 33.4 and 9.3% at roasting temperatures of 550 °C and 650 °C, respectively. This trend may be attributed to conversion of copper and iron sulphates to the corresponding oxides.

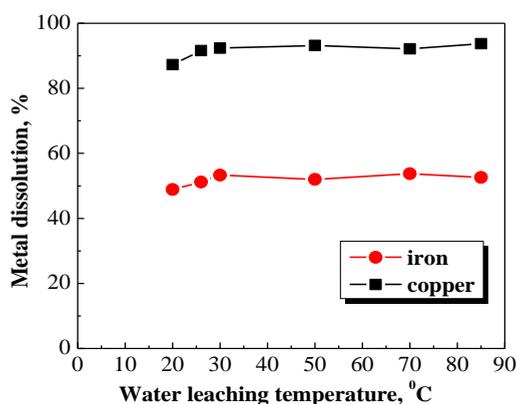


Fig. 3. Copper and iron extractions at different water leaching temperatures

Water leaching of the calcine, which was produced by roasting under standard experimental conditions, was conducted at different temperatures of 20, 26, 30, 50, 70 and 85 °C for a duration of 30 min to elucidate the effect of water temperature on extraction of copper and iron. The results illustrated in Figure 3 show that water temperature has a negligible effect on the dissolution of copper and iron above 30 °C. It can be also concluded that the copper-bearing compounds formed during sulphation roasting of the calcine are readily soluble in water.

The copper and iron extractions obtained during leaching of calcine, which was produced under standard roasting conditions, with distilled water at 50 °C are shown in Table 7 as a function of leaching time. The results indicate that leaching time has essentially no effect on extraction of copper and iron after 15 min of leaching.

Table 7. Effect of leaching time on extraction of copper and iron

Time, min	Cu extraction, %	Fe extraction, %
15	92.65	52.92
30	93.74	53.30
60	94.05	53.72
90	93.15	52.86

For this reason, experiments with shorter leaching times were then conducted, namely: 1, 3, 5, and 10 min. The experimental procedure was changed so that 1 cm³ of leach liquor was sampled directly from the leach slurry (i.e. without stopping the mixing) at the time intervals noted above. The samples were filtered into 50 cm³ volumetric flasks and analysed. As these experiments demonstrated that the copper and iron extractions obtained were stable and did not change with time after 3 min of leaching, a series of experiments was performed at different temperatures (as noted above under the effect of water leaching temperature). The duration of these experiments was 5 min, and the samples were taken every minute according to the same direct sampling procedure as that explained above. These experiments showed the same trend, that is, copper and iron extractions obtained were maximum after 2-3 min of leaching and thereafter remained unchanged. It should be also noted that copper and iron extractions after 1-2 min of reaction were only about 4% lower than those listed in Table 7, which implies very fast leaching kinetics of copper and iron from the calcine.

Process flowsheet

A simplified process flowsheet for the recovery of copper from the reverberatory furnace slag using sulphation roasting (i.e., acid baking) and water leaching is shown in Figure 4. Assuming that the calcine was produced at 350 °C and subsequently water leached at 20% solids (i.e., at a solid-to-liquid ratio of 1:5), then it can also be assumed that copper and iron extractions of 77% and 46%, respectively, could be achieved (see Table 6). Based on this data, it can be calculated that the concentrations

of copper and iron in the pregnant leach solution would be about 1 g/dm^3 and 24 g/dm^3 , respectively. This concentration of copper would be high enough for solvent extraction with oxime based reagents such as LIX[®] 84-I or LIX[®] 984N, but iron would have to be reduced to levels below about 2 g/dm^3 prior to the copper solvent extraction step (Schlesinger et al., 2011). However, despite the fact that the proposed process flowsheet appears to be technically feasible, it is less likely that it would be financially viable as compared to dump leach operations with similar copper tenors.

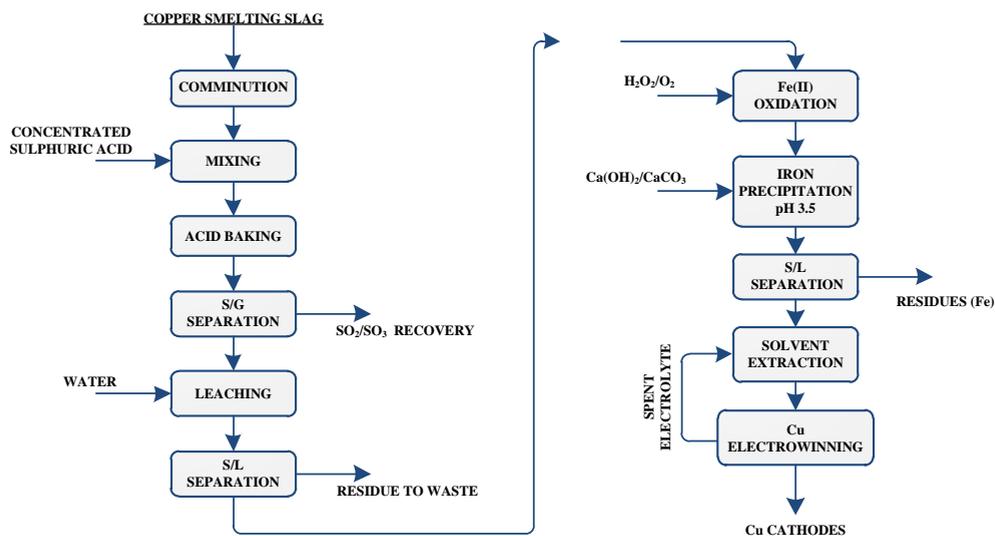


Fig. 4. Flowsheet for the recovery of copper from smelting slag

Conclusion

Treatment of smelting slag by the combined sulphation roasting-water leaching procedure resulted in high copper extractions. However, high copper extractions were accompanied by rather high iron extractions, which is unfavourable in terms of further treatment of the leach liquor. In terms of selectivity, the optimum sulphation temperature was determined to be $600 \text{ }^\circ\text{C}$. For the calcine produced at this temperature, the copper extraction attained was relatively high (about 79%), whereas that of iron was comparatively low (about 6%). On the other hand, with regard to the maximum extraction of copper, the optimum sulphation temperature was found to be $250 \text{ }^\circ\text{C}$ as this temperature resulted in the highest copper extraction (about 94%). However, in this case, the iron extraction obtained was comparatively high (about 55%). The temperature of the leach water had no effect on the copper and iron extractions obtained, except for temperatures below $30 \text{ }^\circ\text{C}$, where extractions were slightly lower.

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