BIORECOVERY OF COPPER FROM CONVERTER SLAGS:

SLAGS CHARACTERIZATION AND EXPLORATORY FERRIC LEACHING TESTS

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Abstract

In this paper the ferric sulphate leaching of converter slag (9% Cu) is studied in order to recover Cu through a process in which bacteria regenerate the leaching agent. The effect of variables such as pulp density, ferric concentration, temperature and size particle have been investigated.

As the Cu extraction is limited by the physical refractoriness of slag, a mild grinding is necessary.

In only 4 hours more than 93% of Cu is leached with 11.5 g/L of initial ferric sulphate, $D_{80}= 47.03$, 2% of pulp density at 60ºC.

1. INTRODUCTION

Copper extraction from Cu-Fe-S minerals is a pyrometallurgical process that entails obtaining a Cu-concentrate by froth flotation, smelting it to molten high-Cu matte, converting of molten matte to molten blister copper, which is finally electrorefining to ultra-pure copper.

In smelting and converting stages two molten phases are produced, one of them contains most of Cu as matte (in smelting) and impure Cu (in converting) and the other, the slag, as free as Cu as possible, is composed of oxides. Both phases are separated by sedimentation. It is well kwon that even in the most efficient pyrometallurgical method, copper is lost in discard slag. After cooling and solidification, slag consists of a matrix of iron silicates, where are included droplets of matte ($Cu_2S \cdot FeS$), white metal (Cu_2S) and blister copper (Cu^0) , that have failed to settle completely (Davenport et al, 2002).

The concentration of Cu in slag from smelting is typically in the range 0.5 to 2%, while converter slags can contain 2 to 15 % Cu. This is a considerable amount of copper very much higher than those of many ores. The high content in copper requires a treatment for Cu recovery. Slag cleaning is not only necessary because of economic reasons but also because of environmental implications (Bagahalha et al 2007). The procedures currently employed for Cu recovery from slag consist basically of returning slag to the pyrometallurgical process, following optionally two different pathways:

> 1. -Slag is sent to an electric furnace where the sedimentation time of Cu-bearing species is prolonged. The heaviest molten phase obtained is periodically tapped from the furnace and sent to a converter for conversion to blister copper.

> 2.- Slag is subjected to cooling/solidification, crushing, grinding and flotation to obtain a 30 to 60% Cu- concentrate (Rao, 1992).

In the electric furnace used for slag cleaning temperature is maintained or increased by passing electric current trough slag between submerged carbon electrodes. The furnaces are designed to give slag residence times of 1 to 10 hours. These settling times allow most of the matte drops to settle (Demetrio, 2000).

Slag cleaning by froth flotation entails solidifying slags in moulds, ladles or pits, cooling it for days and crushing and grinding the slag to 50 microns and smaller to obtain a 30 to 60% Cu concentrate that must to be totally resmelted increasing the smelting capacity or replacing some primary concentrate (Piret 2000).

It is logical to assume losses of Cu in both circuits of concentration, because the Cu is mostly included in very small particles that in the first case would need very long times to sediment in the electric furnace, remaining trapped in the slag phase; and in the second one are partially or totally occluded in the slag phase, unable to interact with the collector and therefore remain in the flotation tailings.

An alternative approach to the slag cleaning methods is to process the slag through hydrometallurgical routes. Leaching agents have included hydrochloric acid, sulphuric acid (in atmospheric and pressure leaching), ammonia, cyanide, ferric chloride, hydrogen peroxide and chlorine/chloride system (Anand et al 1980, Anand et al 1983; Herreros et al 1998; Basir et al 1999, Banza et al, 2002).

This paper is the first of a series about the treatment of converter slags by BRISA process, a biotechnological one based on the indirect bioleaching (Carranza et al 2009, Carranza et al 2004, Palencia et al 2002, Romero et al 2003).

The BRISA process consists, basically, of a dynamic leaching with ferric sulphate (ferric leaching stage) from ores and concentrates of metal sulphides (MeS), coupled with the biological regeneration (biooxidation stage) of the leaching reagent. The regenerated ferric iron is reused in the leaching step, running in a closed circuit. A scheme of the process is shown on figure 1.

The main chemical reactions that represent this process are:

$$MeS + 2Fe^{3+} \rightarrow S^o + Me^{++} + 2Fe^{++} \qquad \text{ferric leaching stage} \qquad (1)$$

$$2Fe^{++} + \tfrac{1}{2}O_2 + 2H^+ \xrightarrow{\;bacteria\;} 2Fe^{3+} + H_2O \qquad \text{biooxidation stage} \qquad (2)$$
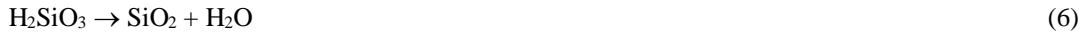
Both stages are carried out physically separated, allowing their individual enhancement: the ferric leaching by thermal activation, stirring and the use of catalysts (if it were necessary), and the biooxidation using high-efficiency bioreactors. In these bioreactors, the control of temperature, aeration, and residence time distribution is feasible in order to promote the growth and metabolic activity of bacteria (Mazuelos 2000, 2001).

BRISA process has successfully applied to the treatment of Cu sulphides concentrates and ores (Palencia 2002, Romero 2003, Carranza 2004) and is a potential, innovative and environmental friendly technology to be applied to recovery copper from slags.

The main chemical reactions involved in the acid ferric leaching of copper from slag are the following:

Fayalite dissolution:

$$Fe_2SiO_4 \rightarrow SiO_4^{4-} + 2Fe^{++} \qquad (3)$$

$$SiO_4^{4-} + 4H^+ \rightarrow H_4SiO_4 \tag{4}$$

$$H_4SiO_4 \rightarrow H_2SiO_3 + H_2O \tag{5}$$

$$H_2SiO_3 \rightarrow SiO_2 + H_2O \tag{6}$$

Magnetite dissolution:

$$Fe_3O_4 + 2H^+ \rightarrow Fe^{++} + Fe_2O_3 + H_2O \tag{7}$$

Matte leaching:

$$Cu_2S \cdot FeS + 6Fe^{3+} \rightarrow 2S^o + 2Cu^{++} + 7Fe^{++} \tag{8}$$

White metal leaching:

$$Cu_2S + 4Fe^{3+} \rightarrow S^o + 2Cu^{++} + 4Fe^{++} \tag{9}$$

This reaction is carried out through two steps; in the first, very fast, the transformation of cuprous sulphide into blaubleibender coveline (Cu_6S_5) takes place:

$$5Cu_2S + 8Fe^{3+} \rightarrow Cu_6S_5 + 4Cu^{++} + 8Fe^{++} \tag{9a}$$

in the slower second step, sulphide oxidation produces elemental sulphur:

$$Cu_6S_5 + 12Fe^{3+} \rightarrow 5S^o + 6Cu^{++} + 12Fe^{++} \tag{9b}$$

the sum of the two last reactions corresponds to the global reaction (9)

Blister Cu leaching:

$$Cu^o + 2Fe^{3+} \rightarrow Cu^{++} + 2Fe^{++} \tag{10}$$

In the present work the ferric leaching of a sample of Pierce-Smith converter slag has been tested. Biooxidation stage has also been investigated and it will be reported in subsequent communications, together with an economic study and the selection of operational parameters for a continuous plant of this process.

2. MATERIALS AND METHODS.

2.1. Slag characterization

A sample of converter copper slag supplied by Atlantic Copper Company (Huelva, Spain) has been studied in this work. The sample as received was characterized as follows:

Chemical analysis.

Representative samples, obtained by a rotatory sample divider (Fritsch), were ground in a planetary monomill (pulverisette 6 Fritsch). After being subjected to attack with aqua regia, the resulting liquid from the digestion was analysed by atomic absorption spectrophotometry (Perkin Elmer AAS 3110). For the determination of S, a LECO titrator was employed.

Mineralogical analysis.

Metallographic samples were prepared by embedding the solid samples in epoxy resin, and polishing. They were visualised in a reflected-light optical microscope, fitted with polarised light, Nomarsky differential interferential contrast, and in a scanning electron microscope, fitted with elemental analysis by energy dispersion X-ray (EDX). The combination of the two techniques applied to the same fields of each sample enables identifying each species (by EDX spectra and elemental quantitative analysis in SEM).

Granulometry.

Sample as received were sequentially sieved using sieves of the ASTM series (#45, 50, 70, 100, 200, 230, and 400).

After grinding the particle size distribution of samples was analysed by laser diffraction (LS 13320 Beckman Coulter).

2.2. Leaching tests

The assays of dynamic leaching with ferric sulphate were carried out in Erlenmeyer flasks of 250 mL, stirred at 240 rpm on an orbital stirrer in a thermostatted chamber by forced air circulation. The water losses due to evaporation were determined by weight and were taken into account during recovery calculations. After each assay, the slurry was filtered, washed with distilled water, dried and weighed. Metallic ion concentrations in leaching liquors were determined by atomic absorption spectroscopy, except ferrous iron concentration that was analysed by titration with 0.05 N potassium dichromate in an automatic titrator (Radiometer Copenhagen) with potentiometric control of the endpoint. Initial pH was the equilibrium pH of the ferric solution used. The pH was measured at the beginning and at the end of each test. Solid residues were dissolved and analysed for copper and iron.

As preliminary tests, samples as received were leached with ferric sulphate solution at 20 and 75°C, after that, and in order to evaluate the physical refractoriness of slag to ferric leaching, a series of tests were performed on different size particle fractions after sieving the original samples. Each granulometric fraction was chemically characterized to determine the Cu extraction in ferric leaching.

To study the effect of grinding, samples were ground in a planetary monomill (Pulverisette 6 Fritsch) by hard metal tungsten carbide balls (93.5% WC + 6% Co) during different times (3, 5, 7, 10 and 15 minutes). 14 20-mm in diameter balls, 100 g of sample and 60 g of water were placed on the grinding bowl. After grinding the particle size distribution of samples was analysed by laser diffraction (LS 13320 Beckman Coulter).

Stirred tank leaching tests were carried out in a 5L glass, baffle-stirred, thermostatted vessel. The solution volume was 4L and the stirred speed 500 min^{-1}. Samples of pulp were taken periodically, and after filtration were analysed for copper and ferrous iron.

3. RESULTS AND DISCUSSION

3.1. Characterisation of the material

Table I shows the chemical composition of the studied slag. As can be seen, it contains 9% of Cu, concentration very much higher than those of many ores (usually about 1% Cu).

Sample as received is composed of coarse particles, being 40% of then higher than 840 microns and 10% higher than 1.7 mm. (See second column on table III)

The microscopic observations of this material identified, as main constituents an amorphous glassy iron silicate phase with magnetite (Fe_3O_4) occluded into. Crystalline fayalite ($SiO_2 \cdot xFeO$) in minor proportion was observed as well. The main observed copper-bearing species are white metal (Cu_2S) and blister copper particles (Cu^0). Representative images of slag are shown on figures 2-4. Copper-bearing particles lower than 1 micrometer have been observed. According to the degree of liberation, it was observed occluded particles, totally surrounded by the matrix (fayalite/magnetite), mixed or partially free particles, which presented some zones in contact with the matrix and others not, and free particles, without matrix-Cu bearing species interphases.

3.2. Ferric leaching tests

3.2.1. Leaching of samples as received

As preliminary tests, sample as received was leached during 2 hours at 20 and 75°C with 3 different pulp densities (2, 5 and 10% wt). The initial ferric concentration of the leaching solution was 11 g/L. Results are shown in figures 5 and 6, where Cu concentration in g/L, the percentage of Cu extraction and the ratio [Fe(III)]/[Fe(II)] at the end of each test versus pulp density are plotted. A linear relationship between Cu concentration and pulp density is observed in cold leaching assays figure 5, however it does not mean higher Cu extractions. Copper extraction falls as pulp density increases, due to the depletion of ferric iron. By comparison of figures 5 and 6 thermal activation is observed. In hot leaching tests, there is not a linear relationship between Cu concentration and pulp density because of the lack of reagent. As can be seen in graphic, the ratio [Fe(III)]/[Fe(II)] drops, meaning more ferric consumption, more ferrous production and lower redox potential.

In short, two conclusions can be drawn from these results: firstly, the ferric leaching of slag is activated by temperature and, secondly, as this material is rich in copper, its leaching needs low pulp density or high ferric concentration.

3.2.2. Leaching of samples after sieving.

As it was observed that Cu-bearing particles were occluded in a silicate matrix, the contact between the reagent (ferric iron) and them will be limited. In order to study this effect, samples were sieved on different size-particle fractions and each fraction was leached with ferric iron. Experimental conditions were 70°C, 12 g/L of ferric iron, 2% of pulp density and 6 hours. On table II the initial Cu content of each granulometric fraction and the Cu recovery after ferric leaching are shown. Copper content (%) in residues is shown as well.

Copper seems to concentrate in fine fractions (see the second column) suggesting a preferential fracture at the fayalite / Cu-bearing particle interphase. Cu extractions (4th column) higher than 94% are only obtained after leaching fractions with size particle minor than 106 microns, leaving solid residues (3rd column) with less than 1.5% of Cu. As it was expected after the mineralogical analysis, there is physical refractoriness.

On figure 7 copper recoveries versus time for the different size fractions of sample is plotted. As regards size particle, fine fractions are leached quickly, in only 120 minutes, fractions minor than 44 microns

exceed 90% of Cu extraction. In contrast, fractions coarser than 106 microns do not reach this extraction level during the 6-hours test. In general, the curve of extraction flattens between 2 and 4 hours of leaching. This fact can be explained taking into account the reactions that take place. White metal particles (Cu_2S) leaching is carried out in two steps: the first one (reaction 9a) is very fast and the responsible of the quick initial leaching, the second one (reaction 9b) is slower because of the formation of a solid elemental sulphur layer. At the same time, blister copper leaching (reaction 10) is also fast due to the lack of reaction solid products.

3.2.3. Influence of grinding

Table III shows the granulometrical characterization of samples ground for different times and the granulometrical characterization of sample as received (without grinding). In this table mean particle size, median, standard deviation (S.D.), D_{10}, D_{20}, D_{80} and D_{90} are shown. From these statistical data it can be predicted that a longer grinding time will increase the fine fraction without dropping significantly the mean particle size.

After grinding and size distribution analysis, samples were leached at 70°C with 11.5 g/L of ferric iron for 8 hours, the pulp density in these assays was 2% and the pH 1.61.

Table IV shows Cu recoveries, D_{80} and final pH for different grinding times. It can be observed that finer grinds give better Cu extractions. Cu extraction increases as D_{80} decreases, extractions higher than 90% are obtained for sample ground to D_{80}=83,54 microns. Because most of Cu-bearing particles is occluded in fayalite matrix, it is logical the observed inverse relationship between size particle and copper extraction. In relation to the time of grinding, it is noticeable that an increase in the time of grinding 10 to 15 minutes does not mean a significant increase in copper recovery. Even though, D_{80} drops from 47.03 to 37.45, it is not enough to liberate the finest Cu-bearing particles (particles smaller than 1 micron have been observed). Even if it were technically possible, to liberate these small Cu-bearing particles by grinding is not economically profitable. However, a mild grinding is advisable as Cu recovery improves and the residues content less than 0.6% of copper. An economic evaluation of grinding is necessary.

For the following study, a time of grinding of 10 minutes was selected because it warrants copper recoveries higher than 90% and it has been observed that an increase to 15 minutes does not mean a significant increase in copper recovery.

In relation to the final pH, it can be observed a soft increase respect to the initial one (1.61), final pH varies from 1.65 to 1.70. Acid is consumed by fayalite and magnetite dissolution (reactions 3-7).

3.2.4. Temperature

As thermal activation was observed, the influence of temperature has been studied in the range 20-80°C. After grinding for 10 minutes (D_{80} = 47.03), samples were leached at 25, 40, 50, 60, 70 and 80°C, with 11.5 g/L of ferric iron during 8 hours; the pulp density in these assays was 2%. Figure 8 shows Cu extractions against temperature.

A linear increase of Cu recovery is observed in the range 25 - 50°C. Temperature values higher than 60°C do not significantly improve Cu extraction. For this reason, the evolution of leaching at 60°C in a stirred tank was studied; data are plotted in Figure 9. It can be observed that in only 10 minutes more than 70% of Cu is recovered, this fast leaching can be justified because the reactions of blister Cu and white metal with ferric sulphate (reactions 9a and 10) are very fast. In only 4 hours more than 93% of Cu is leached at 60°C.

4. CONCLUSIONS AND CONSIDERATIONS

The copper extraction yield is limited by the physical refractoriness of slag, due to the high degree of occlusion in a silicate matrix of the copper-bearing species. Copper seems to concentrate in fine fractions suggesting a preferential fracture at the fayalite / Cu-bearing particle interphase. The physical refractoriness of slag makes necessary a mild grinding.

The ferric leaching of slag is activated by temperature, a linear increase of Cu recovery is observed in the range 25 - 50°C. Temperature values higher than 60°C do not significantly improve Cu extraction.

In only 4 hours more than 93% of Cu is leached from this rich in copper converter slag in the following conditions: 11.5 g/L of ferric iron (pH=1.67), D_{80} = 47.03, 2% of pulp density and 60°C.

6. REFERENCES

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Table I: Chemical composition of slag

% Cu	% Zn	% Cd	% Ni	% S	% Fe	As (g/t)	Sb (g/t)
9.13	1.356	0.002	0.007	1.070	40.03	510	223

Table II: Initial and final Cu content of each granulometric fraction and Cu recovery after ferric leaching

Size fraction (microns)	% Cu initial	% Cu after leaching	% Cu recovery
<22	18.27	0.66	99.1
22-44	15.42	0.78	97.7
44-106	14.68	1.43	94.2
106-297	10.99	2.41	86.7
297-840	8.25	3.31	73.2
>840	6	4.02	34.9

Table III: Statistical characterization of particle size distribution for the sample as received and for the sample ground during different times.

(µm)	Grinding time (min)					
	0	3	5	7	10	15
Mean		88,62	51,66	40,59	31,6	27,04
Median	640	63,39	42,2	30,95	21,92	17,09
S.D.		123,3	40,83	35,73	34,03	34,45
D_{10}	44	9,33	7,296	5,24	3,46	2,81
D_{20}	106	19,7	15,28	10,62	7,21	5,74
D_{80}	1378	130	83,54	65,36	47,03	37,45
D_{90}	1680	168,7	110,8	89,18	68,03	55,69

Table IV: Cu recovery and D_{80} versus grinding time. Experimental conditions: $[Fe(III)]_0=12g/L$, $T=70ºC$, pulp density= 2%, initial pH=1.61.

Grinding time (min)	% Cu recovery	D_{80}	Final pH
3	88.43	130.00	1.71
5	90.14	83.50	1.65
7	91.73	65.36	1.70
10	93.54	47.03	1.70
15	94.15	37.45	1.66

Figure 1:

Figure 2: Representative optical microscope image of slag showing the main constituents: fayalite and magnetite and , also the copper-bearing particles.
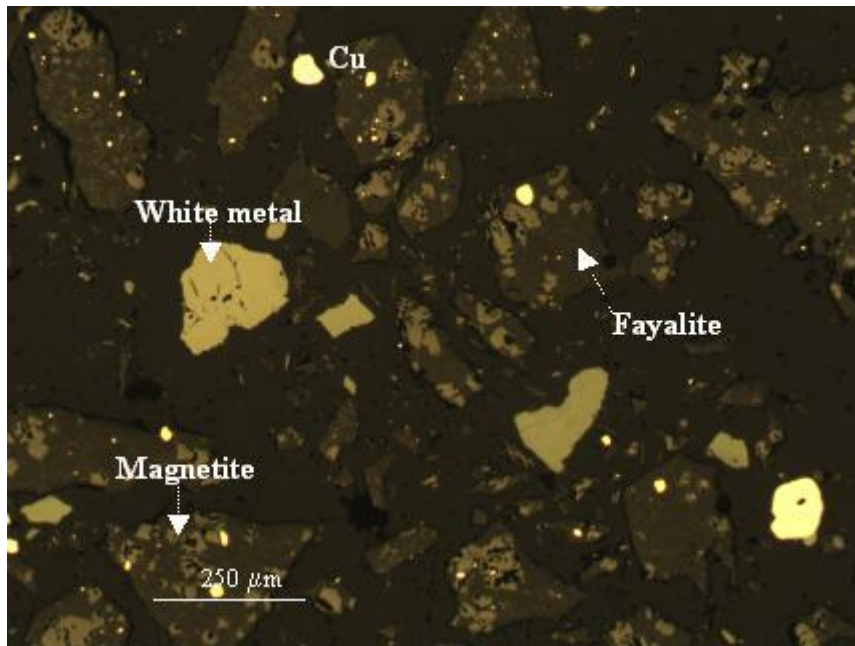
Figure 3: Optical micrograph of slag showing very small particles of Cu occluded in silicate matrix.
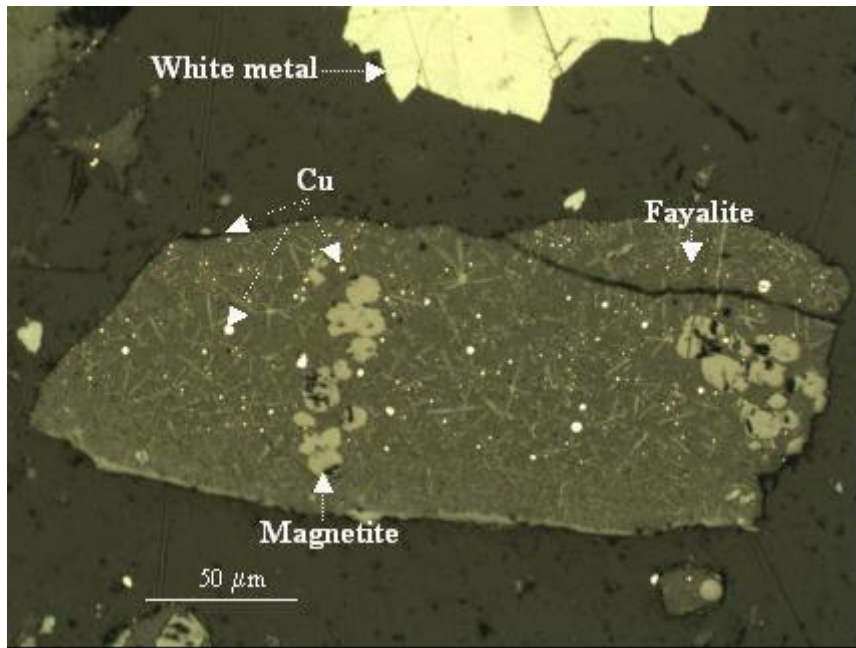
Figure 4: Optical micrograph of slag showing copper – white metal particles
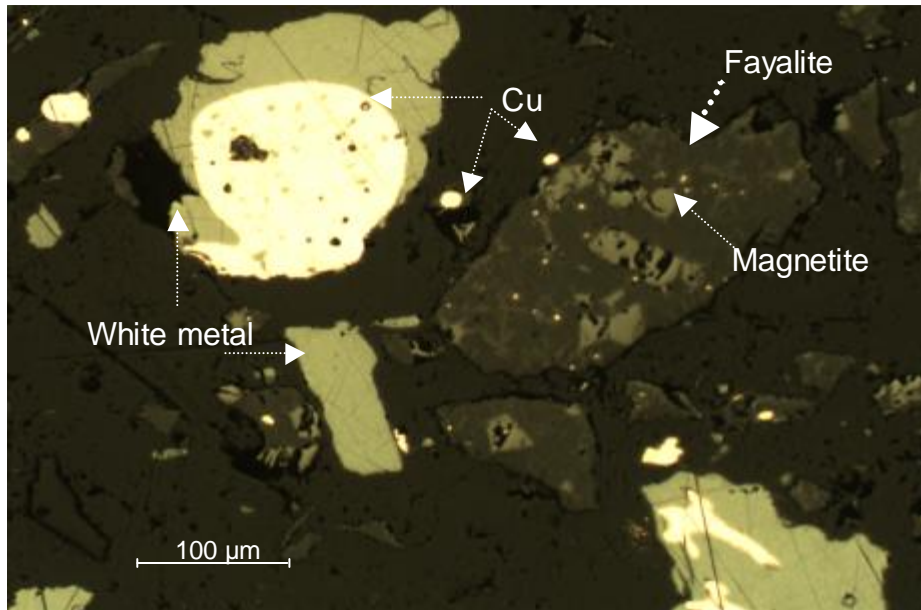
Figure 5: Influence of pulp density. Experimental conditions: $[Fe(III)]_0=11$g/L, T=20ºC, t=120 min.
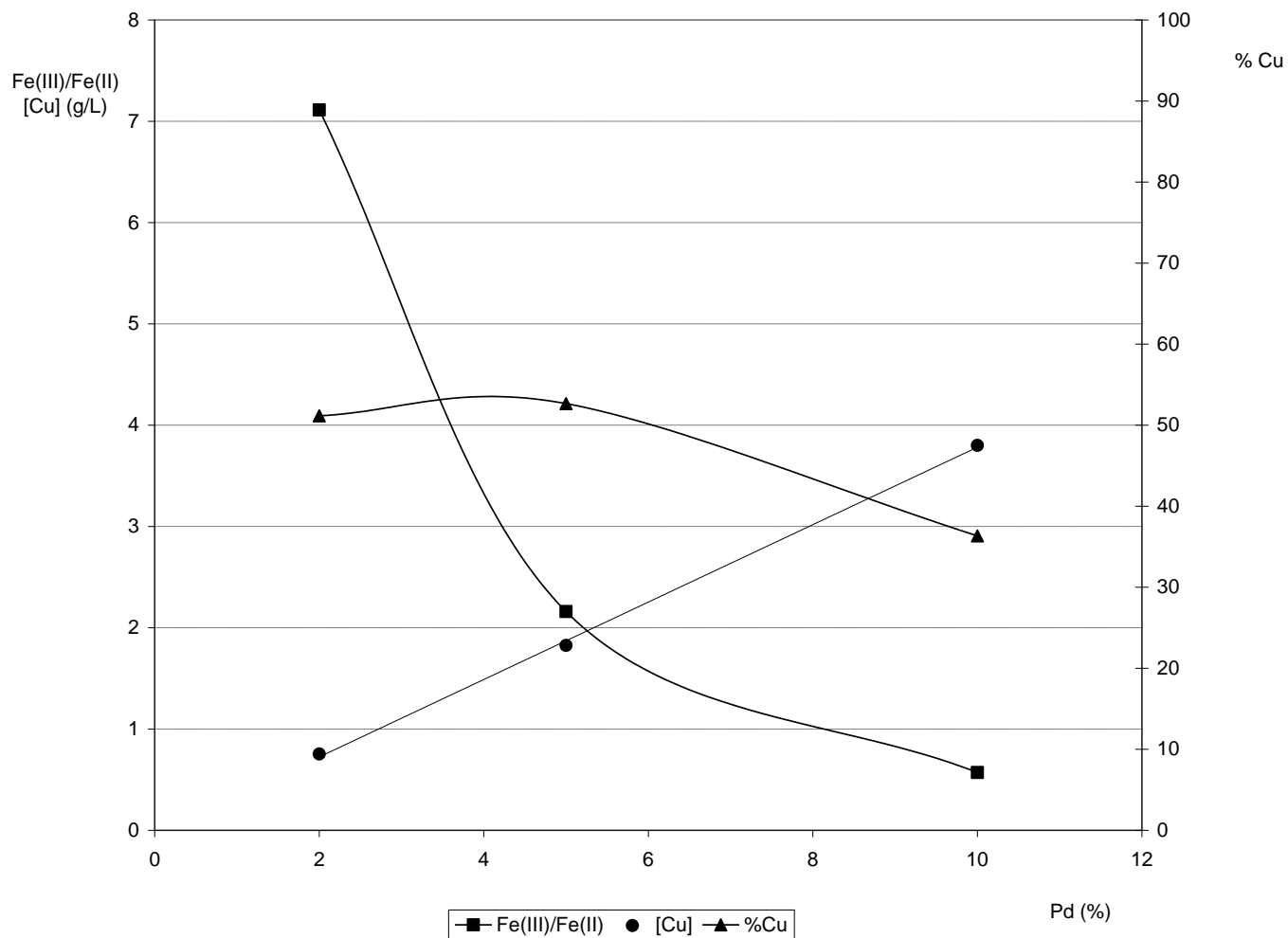
Figure 6: Influence of pulp density. Experimental conditions: $[Fe(III)]_0=11g/L$, $T=75^oC$, $t=120$ min.
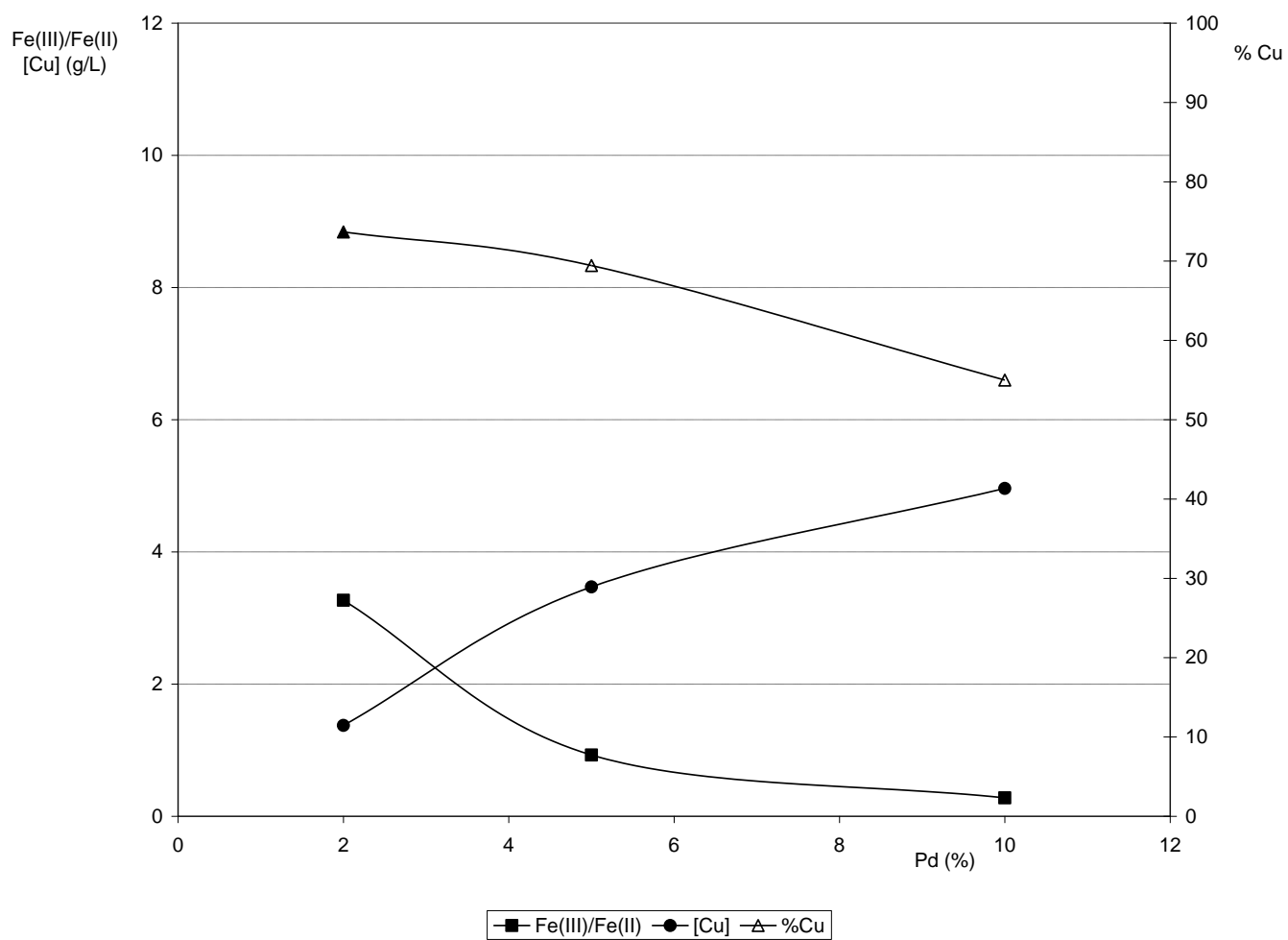
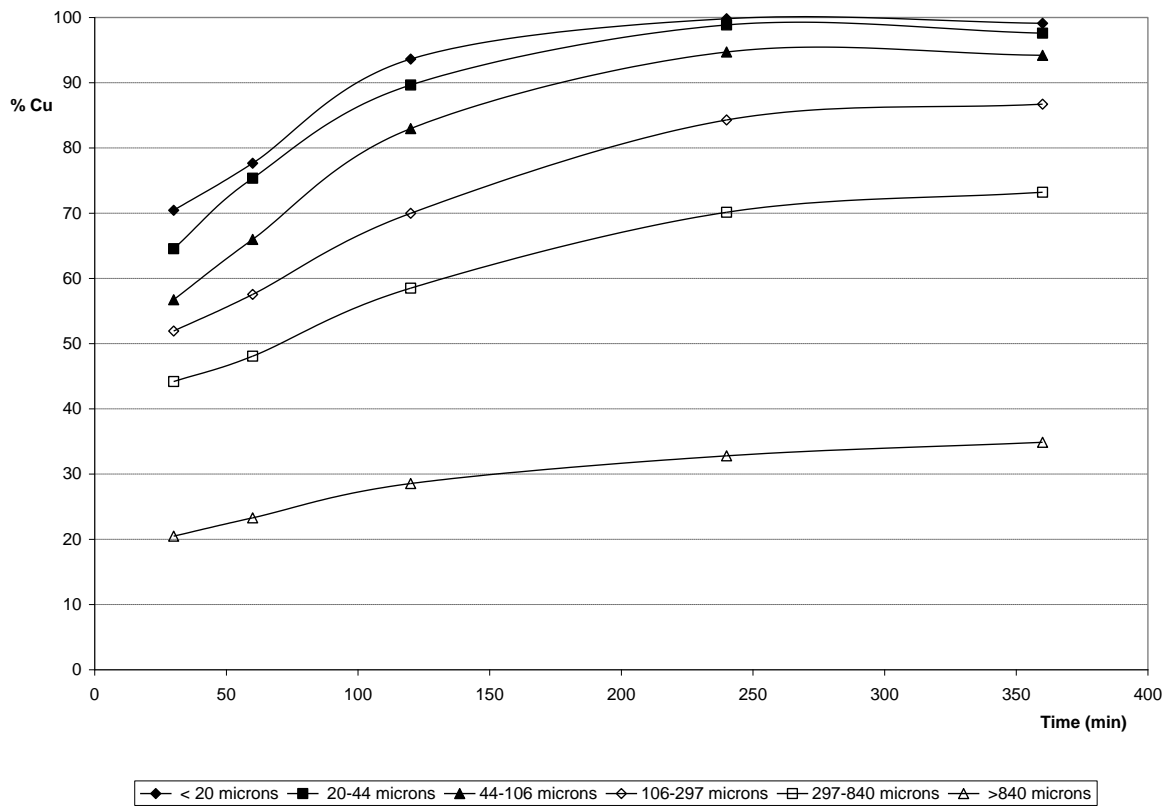Figure 7: Copper recovery versus time for different size fractions of sample. Experimental conditions: [Fe(III)]$_0$=12g/L, T=70ºC, pulp density= 2%.

Figure 8: Influence of temperature in Cu extraction. Experimental conditions: $[Fe(III)]_0$=11.5g/L, pulp density= 2%, D_{80}=47.03, t=8h, initial pH=1.67. Final pH data are plotted as ♦.
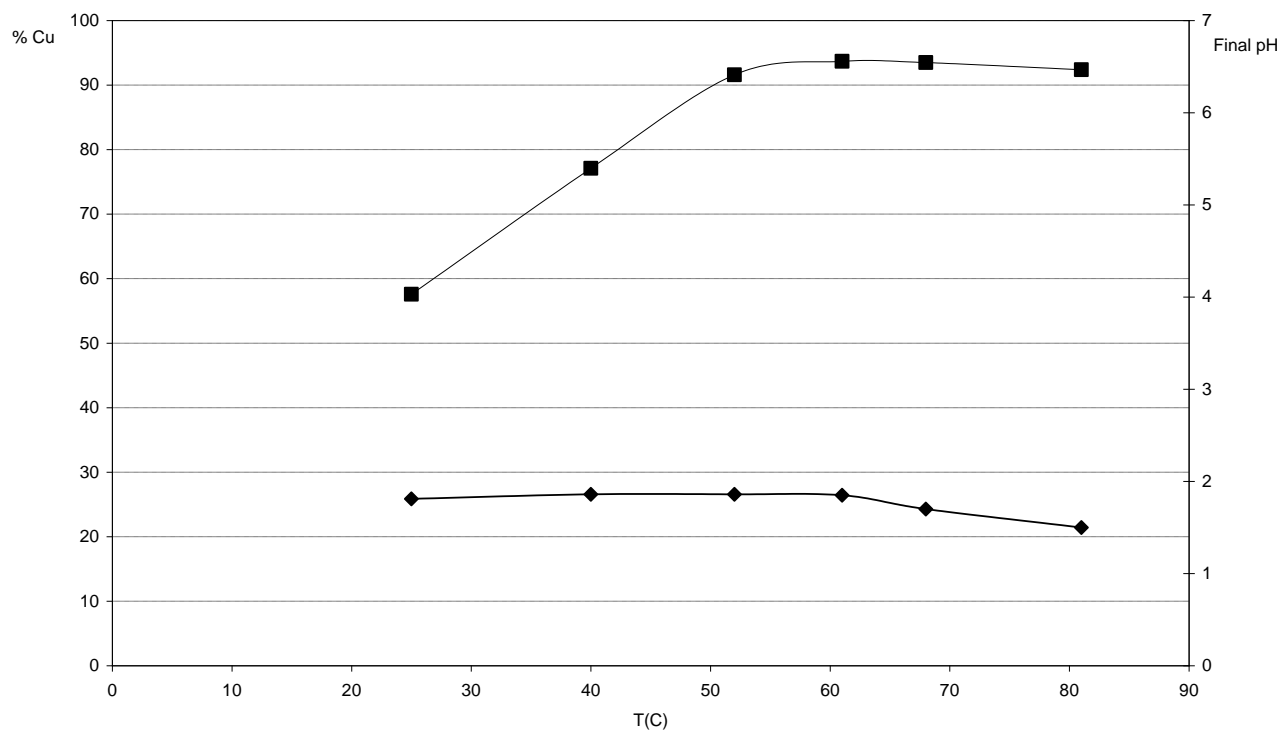
Figure 9: Cu recovery versus time and ferrous and ferric iron evolution. Experimental conditions: [Fe(III)]$_0$=11.5g/L, T=60°C, pulp density= 2%, D$_{80}$=47.03, initial pH=1.67, final pH=1.87.