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Recycling of copper flue dust via leaching-solvent extraction processing

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ABSTRACT

A laboratory-/bench-scale investigation relating to copper recovery from Chilean copper flue dust is described. Since the dust contained a high amount of copper (nearly 24%), the considered option consisted in the leaching of the metallic material with ammonium chloride solution, thus enabling the dissolution of copper via its ammoniacal complexes, and also rendering, due to the almost neutral conditions of the leaching solution, a near complete lean solution with respect to the presence of other metal accompanying in the dust. Results obtained show that with ammonium chloride solutions, nearly 90% of the copper contained in the dust can be leached at 20°C. Copper enters the solvent extraction-electrowinning circuit due to the following equilibria:

$$\mathrm{Cu(NH_3)^{2+}_{2aq}} + 2\mathrm{HR_{org}} \Leftrightarrow \mathrm{CuR_{2org}} + 2\mathrm{NH^{+}_{4aq}}$$

$$\mathrm{CuR_{2org}} + \mathrm{H_2SO_{4aq}} \Leftrightarrow 2\mathrm{HR_{org}} + \mathrm{Cu^{2+}_{aq}} + \mathrm{SO^{2-}_{4aq}}$$

regenerating both the leaching and the solvent extraction reagents. In the above equation, HR represented the active substance of the extractant (Acorga PT5050) used in the solvent extraction circuit; the first of the above equilibria is related to the extraction operation and the second to the strip stage.

Keywords: Copper flue dust; Leaching; Solvent extraction; Ammonium chloride; Acorga PT5050

1. Introduction

Copper production using pyrometallurgical processing in the copper output is nowadays an important part of the metallurgical industry. However, major pollution that is released into the atmosphere during the pyrometallurgical process includes, among others, copper flue dusts. These materials are defined as the product recovered from exhaust gas streams found in furnaces, flues, and setting chambers as a result of roasting, smelting, and converting operations from copper refining processes. Constituents found as

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end products are dependent upon the materials feeding the different operations.

Due to its physical and chemical (fine material and content of heavy metals) characteristics, these copper dusts were categorized as hazardous wastes [1,2]. Being considered as such, these residues must be stored in specialized landfills. Moreover, they may be used as intermediates under very strictly controlled conditions. On the other hand, these dusts, and due to their content in, i.e. copper, can be used as secondary raw material in the production of this metal.

Thus, there are two to three possibilities to manage these copper flue dusts in order to reduce their environmental impact and at the same time making them somewhat economically profitable. Two of them are related to the pyrometallurgical or hydrometallurgical processing of the dusts. They consist of the extraction of nonferrous metals, basically that of copper; however, the hydrometallurgical processes are considered by many as more eco-friendly than pyrometallurgical processing. The third option that can be considered for these dusts is their inactivation or stabilization, and disposal; however, this option seems arguable due to the high amount of copper which normally these dusts contain.

Considering the hydrometallurgical processing of the copper dusts, several options for the recovery of copper and other metals from these copper-bearing wastes have been proposed [3–10]. In a number of these procedures, the leaching-solvent extraction-electrowinning sequence, that is the same that is currently found for the treatment of copper-oxidized raw materials, has been applied for the recovery of copper.

For more than 50 years, the developments achieved by solvent extraction technology had improved the recovery of metals from a myriad of aqueous solutions, and thus, this is a useful technology when a metal is beneficiated by a hydrometallurgical flowsheet. In the particular case of copper, the great success of the coupling of sulfuric acid leaching-solvent extraction-electrowinning operations, in the treatment of oxidised copper ores, is nowadays one of the most important industrial uses of this technology.

In the present work, a lean copper (II) sulfate solution to feed an electrowinning operation, and thus obtaining copper grade A cathode, is obtained after the leaching of the copper flue dust with ammonium chloride solution and the subsequent solvent extraction operation.

2. Experimental method

The copper flue dust was a sample collected from a Chilean smelting company, and it is representative of the dust generated in the premises. This sample was characterized using the usual techniques for these purposes.

Leaching experiments have been carried out in a 1L autoclave and in the presence of mild conditions, principally to reduce energy costs. Solvent extraction experiments were performed both in batch and continuous conditions. Batch tests were carried out in water-jacketed 100 mL separatory funnels provided with mechanical shaking and thermostated at the required temperature, and using an organic-to-aqueous phase relationship of 1:1, except when the copper extraction equilibrium isotherms were generated in which the sequential organic to aqueous phases relationship variation was used as the methodology. Continuous investigations were conducted in a 2–4 cell water-jacketed mixer–settler unit, also thermostated at the required temperature and mechanically shaken. The unit had various flow capacities for each phase (maximum 100 mL/min), whereas mixing and settling volumes were 200 and 700 mL, respectively. The extractant used in this series of solvent extraction experiments was Acorga PT5050 (Cytec Ind.), its active substance being 5-nonylsalicylaldoxime (Fig. 1), and was used as received by diluting it to the desired concentration with Exxsol D100 (aliphatic diluent) obtained from Exxon Chem. Iberia, Spain.

All other reagents used in the present investigation were of AR grade, and metals were analyzed either by AAS or ICP-MS.

3. Results and discussions

3.1. Characterization of the copper flue dust

The dust from the flash furnace of the Chilean copper smelting plant is collected by electrostatic filters and is relatively fine (Fig. 2), some well-defined spherically shaped particles can be observed, but not

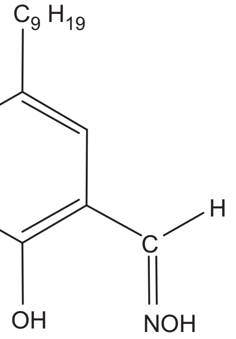

Fig. 1. 5-Nonylsalicylaldoxime.

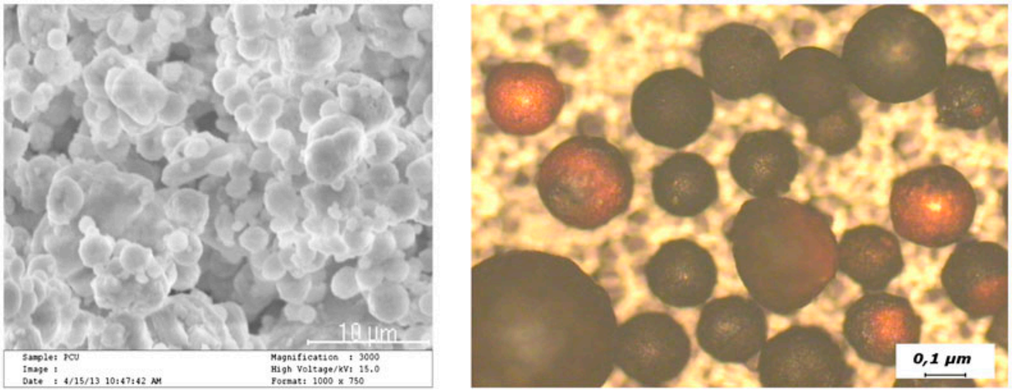

Fig. 2. SEM image of the copper flash smelter flue dust (left), and comparison with that of a copper converter flue dust (right, the orange spheres are metallic copper).

at the same extent as those found in the morphology of a typical copper converter dust.

The composition of the flash dust is shown in Table 1; the richness in copper that this flue dust presents is evident.

The X-ray diffraction (XRD) characterization of the flash flue dust sample indicates the complexity of this copper (in general, of all) flue dusts. It consists mainly of oxidized species (chalcanthite ($CuSO_4{\cdot}5H_2O$), copper (II) oxide ($CuO{\cdot}3H_2O$), cuprospinel ($CuFe_2O_4$), and hematite (Fe_2O_3)) with a few sulfide species, though the presence of amorphous species, which were not identifiable by XRD, may be considered.

3.2. Leaching

The results derived from leaching experiments using ammonium chloride solutions and various experimental variables on the copper flue dust are summarized in Table 2.

From the series of experiments, it can be deduced that under the various experimental conditions investigated, the percentage of copper dissolved is around 90%; this should indicate that nearly 10% of the copper contained in the flue dust is in the form of sulfides or even metallic copper, fractions which are not solubilized by this leachant under these mild experimental conditions. Other conclusions derived from the above table is that neither the variation in the ammonium chloride concentration nor the variation in the L/S ratio affects appreciably the percentage of copper dissolved, and the same conclusion is drawn with respect to the increase of the temperature, since the increment of this variable from 25 to 45°C only increases the percentage of copper recovered by nearly 1%. It should also worth to be mentioned here that practically the same results are obtained when reaction times of 1 h, or even less, are used.

Besides the above, the most important feature of the leaching results is the higher copper concentrations yielding in the solutions after leaching with ammonium chloride solutions, by far more than adequate to feed the solvent extraction operation and the characteristics of the operation derived with the use of ammonium chloride [11]. Due to the weak acidic nature of the ammonium ion, the next reaction takes place:

$$NH_4^+ \rightarrow NH_3 + H^+ \quad (1)$$

and the resultant ammonia forms highly stable complexes with copper (II) ($Cu(NH_3)_n^{2+}$, n = 1–4), increasing the dissolution power of this leaching medium. Also, the leaching with ammonium chloride solutions normally runs at near constant and near neutral pH value range. Despite the above equation and the generation of ammonia, the pH of the solution does not vary appreciably since most of the generated ammonia is complexed by copper (II), with the uncomplexed ammonia and the ammonium salts resulting in a

Table 1
Main elements of the flash flue dust

	Copper	Iron	Molybdenum	Lead	Aluminum	Arsenic	Zinc
%	24.5	14.0	0.45	0.08	1.2	0.9	0.15

Table 2
Results of the leaching of the copper flue dusts under various experimental variables

Leachant	L/S ratio	Temperature (°C)	Time (h)	% Cu leached	Copper concentration in the solution (g/L)
NH_4Cl 1 M	10	25	2	89.9	22.0
2.5 M				90.3	22.1
5 M				90.5	22.2
NH_4Cl 2.5 M	10	25	2	90.3	22.1
	20			89.4	10.9
	40			88.2	5.4
NH_4Cl 1 M	10	25	2	89.9	22.0
	40			87.2	5.3
NH_4Cl 5 M	100	25	2	90.5	2.2
		45		91.5	2.2

buffer system that maintains an almost fixed pH of the solution. With this pH being nearly neutral, the solution obtained from the leaching operation is very pure, having very low values (in the range of few mg/L) of other impurities found in the flue dust and free of iron, which remains in the residue probably as an iron (III) oxide species.

3.3. Solvent extraction

As mentioned earlier, ammonia is generated in the process when copper flue dust is leached with ammonium chloride solution; this ammonia is coordinated with copper (II) to form the various copper (II) ammine complexes and can be used to neutralize the protons generated during the extraction process of copper (II) by oxime derivatives. Thus, the general equation to describe the extraction of copper (II) by these oxime derivatives (HR) changes from:

$$Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow CuR_{2_{org}} + 2H^{+}_{aq} \tag{2}$$

to

$$Cu(NH_3)^{2+}_{2_{aq}} + 2HR_{org} \Leftrightarrow CuR_{2_{org}} + 2NH^{+}_{4_{aq}} \tag{3}$$

where the subscripts aq and org represented the various aqueous and organic solutions involved in the process. At the same time, and in accordance with the last equation, the leaching reagent is regenerated in the process.

The effect of equilibration time on the extraction of copper by Acorga PT5050 was investigated using aqueous solutions of 2 g/L Cu (II) and 5 M ammonium chloride at a pH of 6.1, and 10% v/v organic solutions of the extractant in Exxsol D100. The temperature was 20°C and the equilibration time was varied from 1 min to 1 h, whereas the organic to aqueous phase relationship was maintained at 1:1. The results obtained indicated that copper extraction equilibrium (nearly 99% metal extraction) is reached within 2.5 min of contact.

The variation of the pH of the aqueous solution containing 2 g/L Cu (II) and 5 M ammonium chloride showed a gradual decrease in the extraction of the metal by 5% v/v Acorga PT5050 in Exxsol D100 with the decrease of the pH values in the more acidic range (Fig. 3). It is clear from this figure that at the pH values normally encountered in the solutions resulting from the treatment of the copper flue dust with ammonium chloride solutions greater than 4, the extraction of copper is near quantitative.

Once the feasibility of extracting copper using Acorga PT5050 had been investigated, detailed investigations were carried out to optimize conditions for the

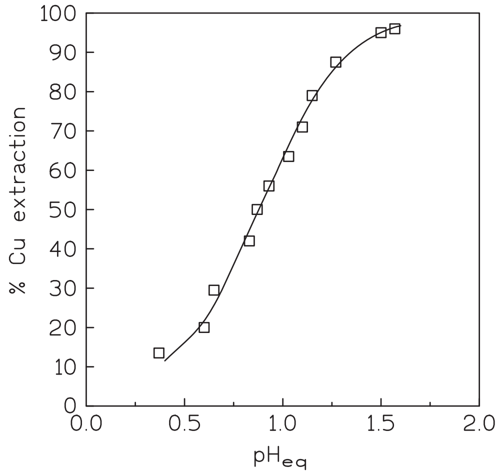

Fig. 3. The effect of pH on copper extraction. Equilibration time: 10 min. Organic/aqueous phases relationship 1:1. Temperature: 20°C.

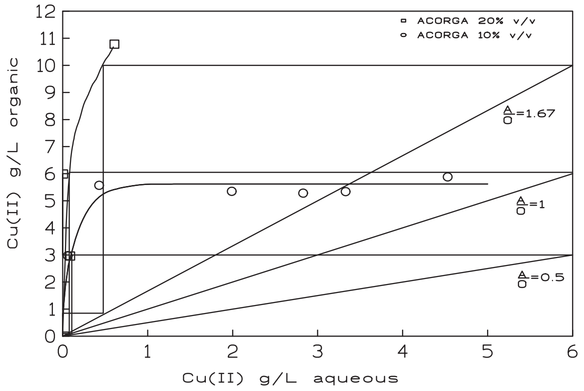

Fig. 4. Copper isotherms and McCabe–Thiele diagrams for copper extraction.

extraction of copper using a typical solution containing 6 g/L of copper and 5 M ammonium chloride. To determine the number of stages required at a chosen volume phase ratio, extraction isotherms, at the temperature of 20˚C, were obtained with 10 and 20% v/v Acorga PT5050 in Exxsol D100 (Fig. 4).

As can be observed from the above figure, the number of stages required for the extraction of the metal decreases as the extractant concentration increases, but often, the number of stages required to yield 98% copper extraction is in the 1–2 mixer–settler units.

Also, the stripping of copper was investigated, and in this case, this meant the reversal of the extraction reaction; thus:

$$\mathrm{CuR}_{2_{\mathrm{org}}} + 2\mathrm{H}^{+}_{\mathrm{aq}} \Leftrightarrow \mathrm{Cu}^{2+}_{\mathrm{aq}} + 2\mathrm{HR}_{\mathrm{org}} \qquad (4)$$

and the extractant is regenerated and recycled to a new extraction step. In copper terms, the stripping of the metal is carried out using spent electrolyte solutions, about 180 g/L sulfuric acid, and this solution was used to strip the organic-loaded phase with 3 g/L Cu at an organic/aqueous phase ratio of 1:1 at 20˚C, showing that nearly 99% stripping efficiency was achieved after less than 5 min of contact.

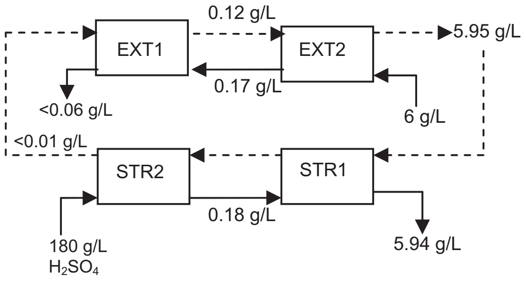

Fig. 5. Schematic flowsheet for the treatment of the copper solution via solvent extraction technology. Continuous lines: aqueous streams. Broken lines: organic streams. All the numbers represent copper(II) concentrations.

Counter-current extraction in the mixer–settler unit containing two extraction stages and two stripping stages were carried out to test the performance of the system on a continuous basis. In this context, a feed solution containing 6 g/L Cu (II) and 5 M ammonium chloride at pH 5.5 was extracted by a 20% v/v solution of Acorga PT5050 in Exxsol D100, at a phase ratio of 1:1; a 180 g/L sulfuric acid solution was used as the strip solution. The conditions and results used in the counter-current run are showed in the flowsheet given in Fig. 5. After a 50 h run operation, an average of 99.2% of copper extraction and 99.8% copper stripping, respectively, are achieved.

4. Conclusion

The use of ammonium chloride solution as a leaching reagent for copper flue dust allowed the solubilization of most of the copper (around 90% leaching yield under various operational conditions) contained in the starting material, and at the same time, obtaining very pure copper solutions which feed the solvent extraction operation. This operation had been investigated using the oxime Acorga PT5050, and results showed that nearly 99% extraction and stripping yields could be achieved under continuous operational basis. Both the leaching and the solvent extraction reagents are regenerated within the given process.

Results obtained from this investigation showed that the introduction of rich copper aqueous streams derived from the treatment of the copper dusts with ammonium chloride solutions in electrowinning operations is feasible.

Acknowledgment

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