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Recycling of a copper flue dust *via* leaching-solvent extraction processing

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Abstract

A laboratory/bench scale investigation relating the copper recovery from a Chilean copper flue dust is described. Since the dust contained a high amount of copper (near 24 %), the considered option consists in the leaching of the metallic material with ammonium chloride solution, thus enabling the dissolution of copper *via* either of 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 copper metal-accompanying in the dust. Copper enters the solvent extraction-electrowinning circuit due to the next equilibrium:

which regenerates the leaching reagent. In the above equation, HR represented the active substance of the extractant (Acorga PT5050) used in the solvent extraction circuit.

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

Due to its physical and chemical (content of heavy metals) characteristics, these copper dusts were categorized as hazardous wastes. [1,2]. Being considered as hazardous wastes, these residues must be stored in specialised 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 metals.

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 consisted in 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 seemed arguably due to the high amount of copper which normally these dusts contained.

Considering the hydrometallurgical processing for the copper dusts, several options for the recovery of copper and other metals from these copper-bearing wastes have been proposed [3-6]. In a number

of these procedures the sequence leaching-solvent extraction-electrowinning, that is the same that is currently found for the treatment of copper oxidised raw materials, has been applied to the recovery of copper.

In the present work, a lean copper (II) sulphate 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 solutions and the subsequent solvent extraction operation.

2. MATERIALS AND METHODS

The dust from the flash furnace of a Chilean copper smelting plant is collected by electrostatic filters and is relatively fine (Figure 1), some well defined spherical-shaped particles can be observed but not at the same extent than these found in the morphology of a typical copper converter dust.

Figure 1. Aspect 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).

The XRD characterization of the flash flue dust sample indicates the complexity of this copper (in general all) flue dusts. It consists mainly in oxidized species (chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), copper (II) oxide ($\text{CuO} \cdot 3\text{H}_2\text{O}$), cuprospinel (CuFe_2O_4), hematite (Fe_2O_3)) with a few sulphide species, though the presence of amorphous species, which were not identifiable by XRD, may be considered. The composition of the flash dust is shown in Table 1, it is evident the richness in copper that this flue dust presents.

Table 1. Main elements of the flash flue dust

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

Leaching experiments have been carried out in a 1 liter autoclave and in the basis 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, whereas 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 (Figure 2) 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 analysed either by AAS or ICP-MS.

Figure 2. 5-nonylsalicylaldehyde

3. RESULTS AND DISCUSSION

3.1. 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.

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

Leachant	L/S Ratio	Temperature	Time	% Cu leached	Copper concentration in the solution
NH ₄ Cl 1 M 2.5 M 5 M	10	25° C	2 h	89.9	22.0 g/L
				90.3	22.1 g/L
				90.5	22.2 g/L
NH ₄ Cl 2.5 M	10	25° C	2 h	90.3	22.1 g/L
	20			89.4	10.9 g/L
	40			88.2	5.4 g/L
NH ₄ Cl 1 M	10	25° C	2 h	89.9	22.0 g/L
	40			87.2	5.3 g/L
NH ₄ Cl 5 M	100	25° C	2 h	90.5	2.2 g/L
		45° C		91.5	2.2 g/L

From this series of experiments it can be deduced that under the various experimental conditions investigated the percentage of copper dissolved is around 90 %, this should indicated that near 10 % of the copper contained in the flue dust is in the form of sulphides or even metallic copper, fractions which are not solubilized by this leachant using 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 to the percentage of copper dissolved, and the same conclusion is raised with respect to the increase of the temperature, since the increment of this variable from 25° C to 45° C only increased the percentage of copper recovered by near 1 %. It should also worth to be mentioned here that practically the same results are obtained when reaction times of 1 hour, 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, and the characteristics of the operation derived with the use of ammonium chloride [7]. Due to the weak acidic nature of the ammonium ion, the next reaction takes place:

and the resultant ammonia forms highly stable complexes with copper (II) ($\text{Cu}(\text{NH}_3)_n^{2+}$, $n=1$ to 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), while the uncomplexed ammonia and the ammonium salts resulting in a buffer system which maintained the pH of the solution almost fixed. Being this pH near 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 remained in the residue probably as an iron (III) oxide species.

3.1. Solvent extraction

From more than fifty years, the developments achieved by solvent extraction technology had improved the recovery of metals from a miriade of aqueous solutions, and, thus, this is an useful technology when a metal is beneficiated by a hydrometallurgical flow-sheet. In the particular case of copper, the great success of the coupling of sulphuric 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.

As it is mentioned above, ammonia is generated in the process when the copper flue dust is leached with ammonium chloride solutions, 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:

to:

where the subscripts aq and org represented the various aqueous and organic solutions involved in the process. At the same time, and according 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 of 20° C and the equilibration time was varied from 1 min to 1 hour, whereas the organic to aqueous phase relationship was maintained as 1:1. The results obtained indicated that copper extraction equilibrium (near 99 % metal extraction) is reached within 2.5 min of contact.

The variation of the aqueous 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 aqueous pH values to the more acidic range

(Figure 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.

Figure 3. The effect of pH on copper extraction. Equilibration time: 10 min. Organic/aqueous phases relationship 1:1.

Once the feasibility of extracting copper using Acorga PT5050 had been determined, detailed investigations were carried out to optimize to determine conditions for the extraction of copper for 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 (Figure 4).

Figure 4. Copper isotherms and McCabe-Thiele diagrams for copper extraction.

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.

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

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 sulphuric acid, and this solution was used to strip organic loaded phase with 3 g/L Cu at an organic/aqueous phase ratio of 1 and 20° C, showing that near 99 % stripping efficiency was achieved after less than 5 min of contact.

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 in 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 sulphuric acid solution was used as the strip solution. The conditions and results used in the counter-current run are showed in the flow-sheet given in Figure 5. After 50 hours run operation an average 99.2 % of copper extraction and 99.8 % copper stripping are achieved.

Figure 5. Schematic flow-sheet for the treatment of the copper solution *via* solvent extraction technology. Continuous lines: aqueous streams. Broken lines: organic streams. All the numbers represented copper(II) concentrations.

CONCLUSIONS

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

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