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Hydrometallurgical treatment of hazardous copper Cottrell dusts to recover copper

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Abstract: Copper flue dusts, or copper Cottrell dusts, from three types of copper smelting furnaces were leached with different ammonia-based reagents (ammonium chloride, ammonium carbonate and aqueous ammonia solutions) to dissolve the oxidised copper species via the formation of copper-ammonia complexes, so that most of the copper-accompanying metals, especially iron, remained in the solid residue. Such copper-bearing dusts are not only valuable secondary source of copper but also are considered as hazardous materials and cannot be dumped as such. Therefore, two procedures for copper dust treatment are proposed, one of them includes ammonium-based leaching, liquid-liquid extraction with LIX 860 (aldoxime), LIX 84 (ketoxime) or LIX 54 (β-diketone) and electrowinning to grade A copper cathode. The other one covers also ammonium-based leaching followed by cementation with zinc to copper cement as a final product.

Keywords: Cu solid wastes, leaching, solvent extraction, cementation

1. Introduction

The generation of solid wastes or secondary by-products is inherent to all the metallurgical plants, and among these wastes, flue dusts are always present in pyrometallurgical plants, thus different approaches for their treatment and/or profit had been considered before (Alguacil et al., 1996; Ruiz et al., 2007; Shin et al., 2013, Gonzalez et al., 2017).

Among copper-bearing secondary sources, copper flue dusts are of interest due to their relatively medium-high copper content and because they are considered as hazardous materials (i.e. due to the presence of arsenic in the dusts) and cannot be dumped as such. Moreover, their recycling to the correspondent furnace is not always desirable for different reasons, e.g. recycling of such dusts to the furnaces is considered as cold charge because they do not produce enough heat during reaction. On the contrary, copper sulfides that feed the furnaces, have an exothermic nature in the furnaces reactions due to the oxidation of sulfide to higher sulfur oxidation states. Thus, the feed with sulfides makes the process to be economically viable from the energy point of view, while the recycling of flue dusts to the furnaces increments the concentration of impurities (i.e. arsenic, antimony, etc.) in the material to be treated and consequently increases their concentrations in the end material obtained in each of the different steps of the copper pyrometallurgical process. Actual copper prices in the market amount to around 5690 US dollars/Mg (June 2017), hence the recovery of this metal from a given raw material and even secondary sources is of a profitable interest.

According to the data of the European Copper Institute a copper flue dust is defined as the product recovered from exhaust gas streams found in furnaces, flues and settling chambers as a result of roasting, smelting and converting operations from copper refining processes. The elements present in the final product can vary accordingly with the material used in a given furnace. The consideration of such dusts as hazardous materials is due to their toxicological and harmful properties causing various diseases (Table 1). Several investigations deal with the treatment of these copper dusts in order to

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recover copper or any of the elements presented in the dust (Martin et al., 2003; Morales et al., 2010; Vitkova et al., 2011; Bakhtiari et al., 2011; Liao et al., 2012; Montenegro et al., 2013; He et al., 2013; Qiang et al., 2014; Li and Zhao, 2014; Klink et al., 2016, Gonzalez et al., 2017). In all the investigations mentioned the copper leaching from starting materials was carried out with a variety of leachants but none of them included the use of ammonia-based leachants.

Table 1. Some harmful properties and effects of copper flue dusts.
Based on data from European Copper Institute (2016)

Hazard class and code	Effect
Acute toxicity 3 (inhalation)	Toxic if inhaled (H331)
Skin sensivity 1	Probable allergic skin reaction (H317)
Carcinogenic 1A	Probable cancer (H350)
Repetitive exposure 1 (inhalation or ingestion)	Damage to organs: central nervous system, blood, kidney (H372)

This work presents an investigation about the treatment of different copper flue dusts (copper Cottrell dusts) by the use of ammonia-based leachants, as the intimate relationship between copper(II) and ammonia to form soluble and stable complexes in aqueous solutions is known and helps to dissolve the oxidised copper(II) species. Further recovery of copper from the copper-bearing solutions via liquid-liquid extraction or cementation operations, resulting both in a final saleable copper material, copper cathode or copper cement, respectively, is proposed.

2. Materials and methods

The three copper flue dusts, considered in this work, are of Chilean nature and they come from flash, reverberatory and converter furnaces. Their copper content is shown in Table 2. Other elements (iron, arsenic, molybdenum, etc.) regularly appeared in the starting material. An X-ray diffraction sight showed that the mineralogical species found in these secondary materials are also of a various nature (Table 2) (Balladares et al., 2015). The physical aspect of the dusts is of typical powders, except for the converter dust which is formed of spherical or near-spherical balls (Fig. 1).

Table 2. Copper content of the copper Cottrell dusts

Type	%Copper	Mineralogical species
Flash	25	copper sulfates and oxides, iron oxides, sulfides
Reverberatory	27	copper oxides and sulfates, sulfides, copper/iron oxides
Converter	74 (30% metallic copper)	metallic copper, copper/molybdenum/iron sulfides,arsenic-copper species

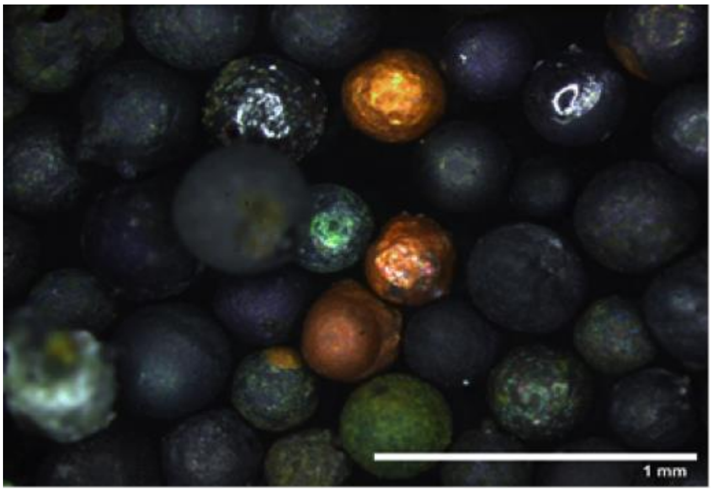

Fig. 1. Image of the converter dust (the orange forms are metallic copper)

All the reagents used in the present work were of AR (Analytical Reagent) grade, except the extractants LIX 860 (aldoxime), LIX 84 (ketoxime) and LIX 54 (β-diketone) which were supplied by Cognis Ltd. (Ireland). They were used as such by diluting them to the desired concentration with Exxsol D100 diluent, supplied by Exxon Chem. Iberia (Spain), which is a kerosene type diluent with >97% aliphatic components.

Leaching experiments were conducted under mild conditions, i.e. room temperature and atmospheric pressure, in a glass reactor, in order to decrease the operational costs, though these expenses were not evaluated within the frame of this investigation. Experiments were run up to three hours, however, different runs showed that two hours are often the limiting time to ensure a maximum copper recovery from the dusts.

Based on the previous batch experiments (Alguacil, 1999; Bermejo et al., 2000; Alguacil et al., 2002, Alguacil et al., 2015), continuous liquid-liquid extraction experiments were conducted in a unit of mixer-settlers. The unit has a maximum flow capacity of 100 cm^3/min for each phase (aqueous feed, organic and aqueous stripping), whereas mixing and settling volumes were 200 and 700 cm^3, respectively. The solutions in the mixers were mixed by impellers.

Cementation experiments were carried out in a glass reactor provided with a gently mechanical shake (200 min^{-1}) in order to maintain the solution under agitation. At this solution, the cementation agent was added.

Metals in solution were analysed by Atomic Absorption Spectrometry (Perkin Elmer 1100B, wavelength: 324.8 nm).

3. Results and discussion

3.1 Leaching

Leaching is often defined as solid-liquid extraction of metals from ores or solid waste (i.e. e-scrap) to solutions of leaching agents. Various concentrations of ammonia-based reagents as the leaching medium were investigated, these leachants have some singularities derived from the weak acid nature of the ammonium ions:

$$NH_4^+ \Leftrightarrow NH_3 + H^+ . \quad (1)$$

Thus, the leachants produce ammonia, which forms highly stable complexes with copper(II), increasing the solubilization of the species contained in the feed material, i.e.:

$$CuO + 4NH_3 + H_2O \rightarrow Cu(NH_3)_4^{2+} + 2OH^- . \quad (2)$$

However, and for all of the leachants investigated in this work, with the continuous generation of ammonia in the aqueous solution, the pH values of such solutions do not change significantly due to the fact that copper(II) forms highly stable ammonia complexes. The ammonia formed during leaching is bound in the form of copper-ammine complexes, and only an amount of non-bonded ammonia in equilibrium with the complexed ammonia remains as free ammonia in the solution. This results in a kind of a buffer system which keeps the pH value for each solution almost constant (Limpo et al., 1985). Besides the copper dissolution, the most important advantage of the ammonia leaching is high purity of the solution obtained, and, particularly, absence of iron – due to the high pH values of the solutions all the iron contained in the copper dusts remains in the solid residue, basically as iron(III) oxide. Though, in many cases acid leaching is more efficient (Roy et al., 2016), the alkaline leaching is considered less corrosive and low reagent consuming than the acid leaching (Bingol et al., 2005). Results of the leaching experiments are summarized in Tables 3-5.

It can be seen that with the flash dusts the maximum values of copper recovery are regularly obtained, whereas the minimum is obtained in the case of the converter dust. It results, probably, from the presence of considerable amount of zero valent or metallic copper when the feed material is the converter dust, which remained unattacked under the mild conditions used in the present work, and practically the same occurred with the sulfide species of the dusts. Also, the low percentages obtained in the case of the converter dust may be attributable to the morphology of the feed material, i.e. the converter dust forms almost spherical balls (Fig. 1) that can be viewed even at eye-view, whereas the others materials tested in the present work form unpalpable dusts of a greater specific surface area and, thus, resulting in a somewhat greater reactivity with respect to the leachants. Practically in all the cases, the percentage of the copper recovered increases with the decrease in the pulp density, probably due to the increase of ammonia ligands available to bond with copper, whereas in the case of aqueous ammonia leachant, the increase of the leachant concentration does not affect very appreciably the percentage of the copper recovered from the different dusts. In terms of copper dissolution, an apparent efficiency order can be established as: flash dust (ammonium chloride>ammonium carbonate=aqueous ammonia), reverberatory dust (ammonium carbonate=aqueous ammonia>ammonium chloride) and converter dust (ammonium chloride=ammonium carbonate>aqueous ammonia). The difference in the yields observed in Tables 3-5, and the various reactivities of the ammonium salts summarized above, is likely to be caused by the different pH values in which the leaching step occurs and also by probable formation of intermediate complexes such as $Cu(NH_3)_2Cl_2$. The complex can facilitate the dissolution of the various copper species found in the feed material.

Table 3. Leaching of dusts with ammonium chloride solutions

Run	Type of dust	Leachant	Pulp density, %wt	% Cu leached	Cu, g/dm^3
1	flash	1 M	4.8	90	11.3
2			0.99	90	2.5
3	reverberatory	1 M	4.8	14	1.9
4			0.99	28	0.76
5	converter	1 M	4.8	3	1.1
6			0.99	23	1.7

pH of solutions 5.5±0.3

Table 4. Leaching of dusts with ammonium carbonate solutions

Run	Type of dust	Leachant	Pulp density, %wt	% Cu leached	Cu, g/dm^3
7	flash	1 M	4.8	45	5.6
8			0.99	81	2.0
9	reverberatory	1 M	4.8	29	3.9
10			0.99	34	0.92
11	converter	1 M	4.8	7	2.6
12			0.99	19	1.4

pH of solutions 8.5±0.1

Table 5. Leaching of dusts with aqueous ammonia solutions

Run	Type of dust	Leachant	Pulp density, %wt	% Cu leached	Cu, g/dm^3
13	flash	15 M	0.99	81	2.0
14		1 M	0.99	75	1.9
15	reverberatory	15 M	0.99	34	0.92
16		1 M	0.99	31	0.84
17	converter	15 M	0.99	20	1.5
18		1 M	0.99	7	0.52

pH of solutions 11±0.2

3.2 Liquid-liquid extraction

The liquid-liquid extraction (LLE) operation transfers dissolved copper(II) from the low-copper and/or impure pregnant leach solution to high-copper pure electrowinning electrolyte solution, being this operation critical to ensure a correct copper solution to enter into the electrowinning operation. As it was shown in the previous work, LLE is an efficient technique to produce Cu-rich solution for electrowinning (Alguacil et al., 2015).

Basically, the LLE operation consists of four steps (Regel-Rosocka and Alguacil, 2013):

i) copper transfer from the leach solution into an organic phase,

ii) separation by gravity of the two phases or solutions,

iii) copper transfer from the loaded organic phase to an acidic solution (spent electrolyte), and

iv) separation by gravity of the two phases or solutions and recycling of the organic phase to a new extraction step.

Transfer of copper into the organic phase is favoured by the low acidity of the pregnant leach solution:

$$\mathrm{Cu}^{2+}_{\mathrm{aq}} + 2\mathrm{HR}_{\mathrm{org}} \Leftrightarrow \mathrm{CuR}_{2,\mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}} \tag{3}$$

shifting the above equilibrium to the right, whereas copper transfer from the organic phase to the spent electrolyte solution is favoured by the high acid concentration of the electrolyte, shifting the equilibrium to the left.

In practice, the conditions for LLE operation are summarized in Table 6.

Table 6. Conditions for copper LLE operation

Stage	Cu in aqueous, g/dm^3	Acidity	%v/v extractant
Extraction	1-5	low	5-20
Stripping	30-50	high	5-20

Very often, the acidity of the aqueous solution in the extraction stage is around pH 2 and higher, whereas in the stripping step the spent electrolyte contains 150-180 g/dm^3 sulfuric acid and 25-35 g/dm^3 copper(II), the advance electrolyte or the aqueous stripping solution exiting the LLE operation and entering the electrowinning operation contains near 30-50 g/dm^3 copper(II) and 150-170 g/dm^3 sulfuric acid. The LLE operation uses ketoximes, aldoximes, tailored mixtures of both and β-diketones, the latter commonly used when the pregnant solution is ammoniacal (pH>10) medium, as the organic extractants. These reagents are usually dissolved in kerosene type diluents to reach the desired extractant concentration necessary for each LLE operation.

In the present investigation, LIX 860, LIX 84 and LIX 54 extractants were used to extract copper from three representative leach solutions generated in the treatment of copper dusts with ammonium chloride (pH 5.5), ammonium carbonate (pH 8.5) and aqueous ammonia solution (pH 11.0), in all the three cases, a solution of 180 g/dm^3 sulfuric acid was used as a strippant for the respective copper-loaded organic solutions.

In the present case, the copper extraction reaction represented by eq. (3) is substituted by:

$$\mathrm{Cu(NH_3)}^{2+}_{4,\mathrm{aq}} + 2\mathrm{HR}_{\mathrm{org}} \Leftrightarrow \mathrm{CuR}_{2,\mathrm{org}} + 2\mathrm{NH}^{+}_{4,\mathrm{aq}} + 2\mathrm{NH}_{3,\mathrm{aq}} \tag{4}$$

in which the protons resulting from the extraction of copper(II) and released to the aqueous solution are neutralized by the ammonia from the copper(II)-ammonia complex. The stripping reaction, as mentioned above, is maintained, and in this case serves to extract back the copper ions to an acidic solution suitable for electrowinning. In all the above eqs. (3 and 4), the subscripts aq and org denote the aqueous solution and the organic phase, respectively.

In the case of LIX 54, copper(II) extraction is feasible, because at these alkaline pH values, the β-diketone molecule is transformed to its tautomeric keto-enol form as:

$$\mathrm{R-CO-CH_2-CO-R'_{org}} \rightarrow \mathrm{R-COH=CH-CO-R'_{org}} \tag{5}$$

and copper(II) extraction and stripping occurs according to eq. (4).

The neat Cu gain (NCG) presented in Table 7 is defined as (Alguacil et al, 2002):

$$\mathrm{NCG} = [\mathrm{Cu}]_{\mathrm{ext,e}} - [\mathrm{Cu}]_{\mathrm{st,e}} \tag{6}$$

where $[\mathrm{Cu}]_{\mathrm{ext,e}}$ and $[\mathrm{Cu}]_{\mathrm{st,e}}$ are the copper concentrations in the exiting organic phases from the extraction and stripping stages, respectively. Table 7 summarizes the operational conditions for the three systems, whereas Fig.s 2-4 show schematic flowsheets for each of these operations, which were run for 20 hours each. Overall yields in terms of copper transfer exceed 98% for each of the three extractants, whereas the copper concentrations in the strip solutions are suitable to feed the electrowinning step.

Table 7. Operational conditions for the counter-current extraction of copper

Reagent[a]	Extraction+stripping stages	V_{org}/V_{aq} ratio in extraction	V_{org}/V_{aq} ratio in stripping	NCG, g/dm^3
LIX 860	1+2	1/1	2/1	1.9
LIX 84	2+2	1/2	2/1	7.7
LIX 54	1+2	1/2	2/1	5.7

[a] at 20% v/v in Exxsol D100. V_{org}: volume of organic phase. V_{aq}: volume of aqueous solution.

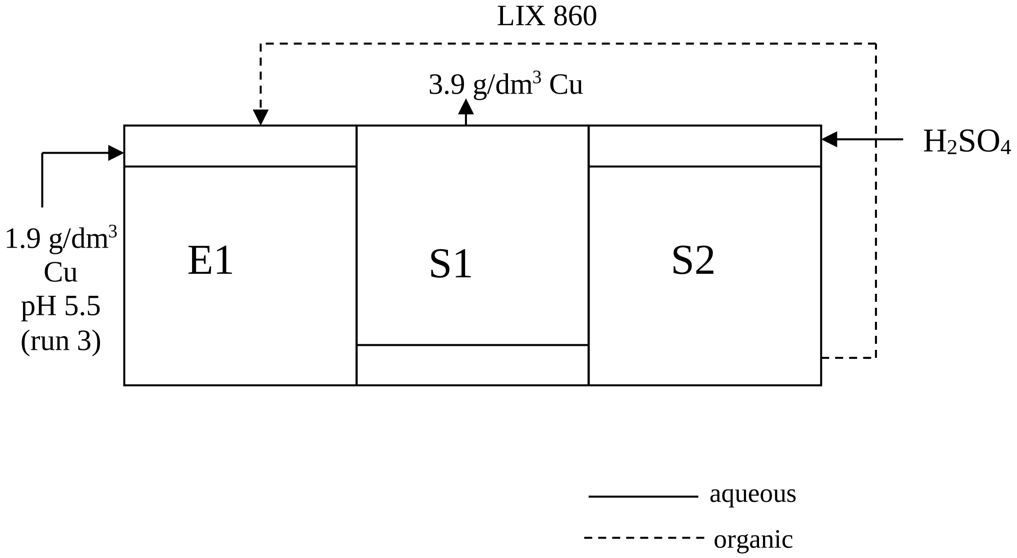

Fig. 2. Schematic flowsheet for the counter-current extraction-stripping circuit using LIX 860 as an extractant for copper ions. Aqueous feed solution from run 3 (Table 3). Temperature 20 °C

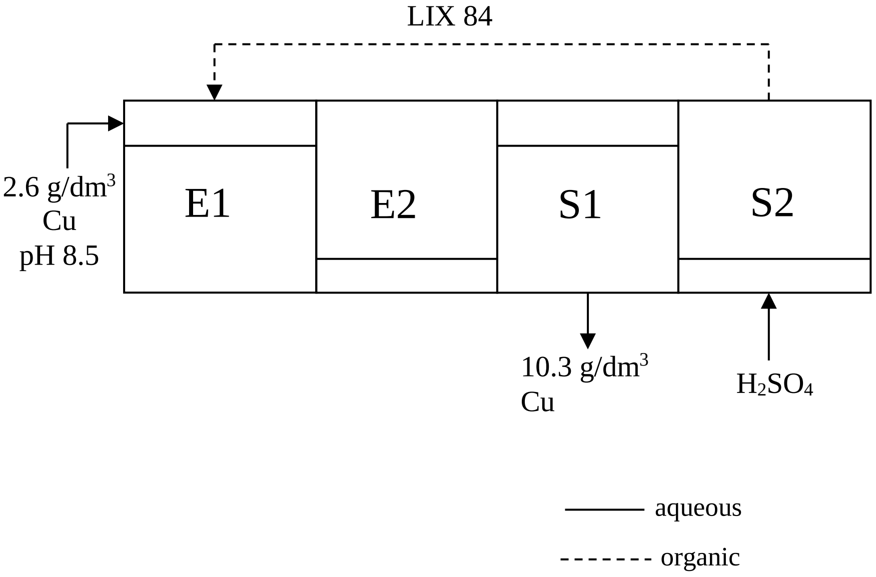

Fig. 3. Schematic flowsheet for the counter-current extraction-stripping circuit using LIX 84 as an extractant for copper ions. Aqueous feed solution from run 7 (Table 4). Temperature 20 °C

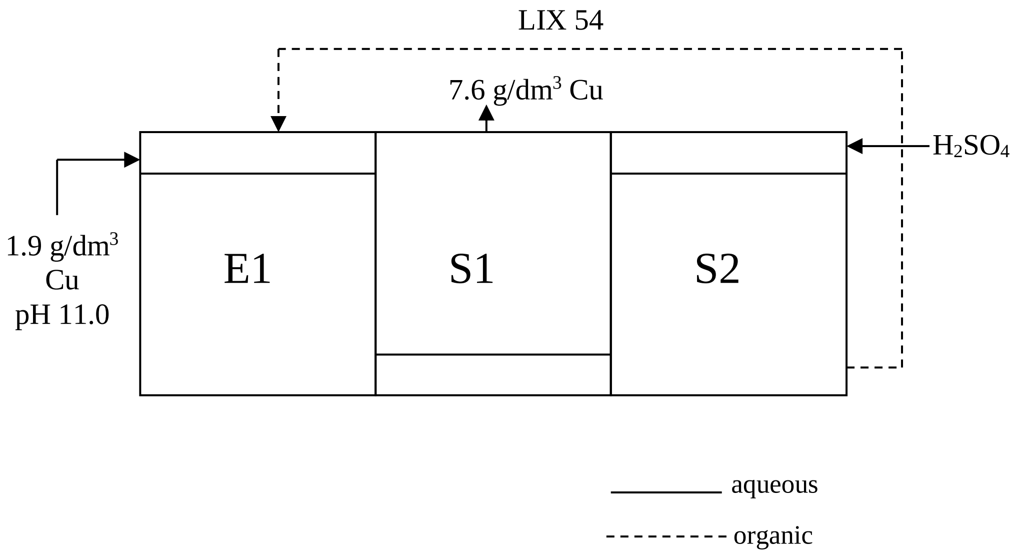

Fig. 4. Schematic flowsheet for the counter-current extraction-stripping circuit using LIX 54 as an extractant for copper ions. Aqueous feed solution from run 14 (Table 5). Temperature 20 °C

3.3 Cementation

Cementation is a hydrometallurgical operation in which a metal, in its ionic form, is precipitated from the aqueous solution by another but zero valent metal. In this process, the metal with more positive oxidation potential, as given in the electromotive series, goes to the solution and displaces or reduces a metal with less positive potential. In practice, several cautions must be obeyed due to the probable side-reactions which take place during the operation, i.e. excessive dissolution of the cementing metal, redissolution of the precipitated metal, precipitation of hydrolytic products, etc.

Since in the present case, the copper-bearing solutions obtained from the leach operation have pH values above 2-3 (the pH range in which iron(III) precipitates), the use of zero valent iron is not recommendable because this new precipitate will contaminate the cemented copper. Instead, a metal which remains solubilized in the ammoniacal medium should be used, and in the present investigation zero valent zinc was used as cementing agent for copper.

According to the electromotive series, zero valent zinc:

$$\mathrm{Zn/Zn^{2+}} \quad E = +0.763 \text{ V}$$

can be used to cement copper:

$$\mathrm{Cu/Cu^{2+}} \quad E = -0.337 \text{ V}$$

and the dissolved zinc is stabilized in the aqueous solution via the formation of the zinc-ammonia complexes, i.e.:

$$\mathrm{Zn^{2+}} + 4\mathrm{NH_3} \rightarrow \mathrm{Zn(NH_3)_4^{2+}}. \tag{7}$$

In the case of solutions in ammonium carbonate medium, the increase in the Zn/Cu molar relationship increased the cementation kinetics, and after two hours the extent of copper cementation is greater than 95% (Table 8).

Table 8. Influence of the Zn/Cu molar relationship on the percentage of copper(II) cementation

Zn/Cu	15 min	30 min	60 min	2 h
8	84	95	>99	>99
6	53	64	81	98
4	49	61	73	98

Aqueous solutions: 5 g/dm^3 copper and 0.6 M ammonium carbonate, pH 8.5. Temperature 20 °C

When the aqueous solution contained different concentrations of ammonium carbonate, it was found that the presence of this salt in the feed solution influences the copper cementation, increasing this cementation as the salt concentration is increased (Table 9). However, at the lowest ammonium carbonate concentrations the cementation of copper by zinc is feasible if an excess of the cementation agent is used, as the results in Table 8 show.

The presence of aqueous ammonia in the solution decreased the percentage of copper cemented by zinc, as it is shown in Table 10. Probably this can be attributable to the presence of an excess of the complexing agent in the most ammoniacal concentrated solution, which (besides the pH of the solution) probably also changes the stoichiometry of copper(II)-ammonia complexes $Cu(NH_3)_n^{2+}$ (n= 1 to 4).

Table 9. Influence of the ammonium carbonate concentration on the percentage of copper(II) cementation

Ammonium carbonate, M	15 min	30 min	60 min
0.6	13	13	14
0.8	35	46	45
1	65	87	97
2.4	69	88	>99

Aqueous solution: 10 g/dm^3 copper in ammonium carbonate, pH 8.5. Zn/Cu molar ratio: 2. Temperature 20 °C

Table 10. Influence of the aqueous ammonia concentration on the percentage of copper cementation

Aqueous ammonia concentration, M	% Copper cemented[a]
15	75
1.8	82
0.88	93

Aqueous solution: 2 g/dm^3 Cu in aqueous ammonia, pH 8.9-11. Zn/Cu molar ratio 2. Temperature: 20 °C .[a]After 1 hour.

The final material obtained in the cementation from a 0.88 M aqueous ammonia medium, consisted of 55% copper, 35% zinc and probably 10% balance oxygen (attributable to a certain degree of oxidation during the cementation process), whereas the molar ratio of zinc dissolved against the copper cemented is near 1, as expected by the reaction:

$$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+} . \quad (8)$$

This is not the case of the cementation from higher concentrated ammonia solutions in which the molar ratio of zinc dissolved against the copper cemented is near 2, indicating that such side reactions occur as an excessive dissolution of the cementing agent, probably due to the medium in which cementation takes place.

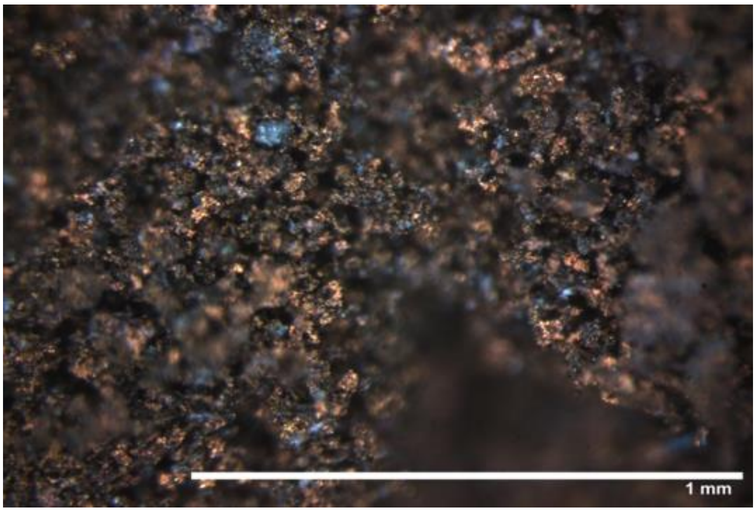

Fig. 5. Copper cement. Grey particles are of unreacted zero valent zinc

A typical appearance of copper cement is shown in Fig. 5. After the cementation step, the Cu-Zn cement needs to enter smelting operation to further refine copper from the the cement.

Fig. 6 shows a general scheme for the treatment of the copper dusts using ammonium carbonate solutions as leachant, and LLE or cementation as separation/purification technologies for the metal. The overall scheme is the same for other two leachants used in the present investigation.

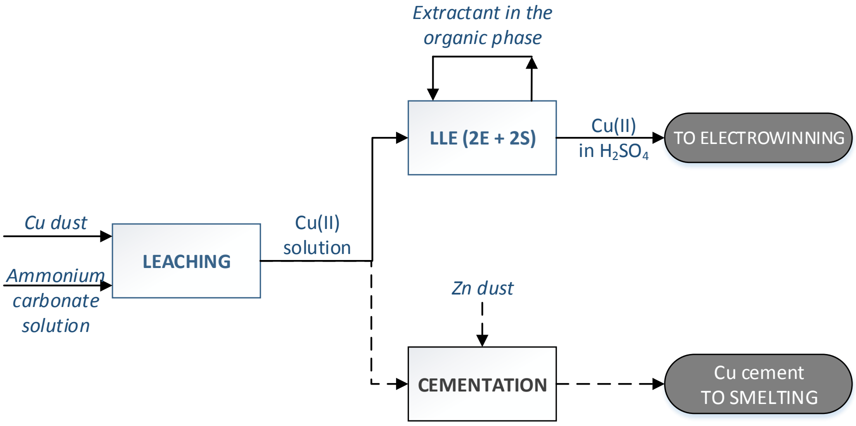

Fig. 6. Proposal of two procedures for copper dust treatment

4. Conclusion

The use of ammonia-based leachants, in mild conditions, for the recovery of copper from copper flue dust is attractive when the starting materials have a minimum of non-soluble species such as sulfides and metallic copper. Besides the copper dissolution, the most important advantage of the ammonia leaching is high purity of the solution obtained, and, particularly, absence of iron. The most suitable leachant for copper dissolution depends on the type of the copper dust, i.e. ammonium chloride>ammonium carbonate=aqueous ammonia for flash dust, ammonium carbonate=aqueous ammonia>ammonium chloride for reverberatory dust and ammonium chloride=ammonium carbonate>aqueous ammonia for converter dust.

The main advantage of the procedure proposed in this work is generation of copper solutions of great purity, and for that reason recovery of the final saleable copper products via liquid-liquid extraction or cementation. Liquid-liquid extraction with LIX 860 (aldoxime), LIX 84 (ketoxime) or LIX 54 (β-diketone) (overall yield of copper transfer > 98%) resulted in solutions which can enter to a copper electrowinning plant to yield grade A copper cathode as the end product.

Cementation with zinc is also attractive, due to the easiness of the operation and low costs, though the purity of the final product, Cu cement, is less than in liquid-liquid extraction practice and needs further refinement. The final material obtained in the cementation from a 0.88 M aqueous ammonia medium, consisted of 55% copper, 35% zinc and probably 10% balance oxygen (attributable to a certain degree of oxidation during the cementation process).

To sum up, two procedures for copper dust treatment are proposed, one of them includes ammonium-based leaching, liquid-liquid extraction with oxime derivatives or β-diketones and stripping with sulfuric acid, that could be followed by electrowinning to grade A copper cathode. The other procedure covers also ammonium-based leaching followed by cementation with zinc dust to copper cement as a final product.

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References

ALGUACIL, F.J., 1999. *Recovery of copper from ammoniacal/ammonium carbonate medium by LIX 973N,* Hydrometallurgy 52, 55-61.

ALGUACIL, F.J., COBO, A., ALONSO, M., 2002. *Copper separation from nitrate/nitric acid media using Acorga M5640 extractant. Part I: solvent extraction study*, Chem. Eng. J. 85, 259-263.

ALGUACIL, F.J., MAGNE, L., NAVARRO, P. SIMPSON, J., 1996. *Hydrometallurgical treatment of copper flue dusts. Removal of arsenic from the leaching solutions*, Rev. Metal. Madrid 32, 400-407.

ALGUACIL, F.J., GARCIA-DIAZ, I., LOPEZ, F., RODRIGUEZ, O., 2015. *Recycling of copper flue dust via leaching-solvent extraction processing*, Des. Water Treat. 56:5, 1202-1207.

BAKHTIARI, F., ATASHI, H., ZIVDAR, M., SEYEDBAGHERI, S., FAZAELIPOOR, M.H., 2011. *Bioleaching kinetics of copper from copper smelter dusts*, J. Ind. Eng. Chem. 17, 29-35.

BALLADARES, E., KELM, V., HELLE, S., PARRA, R., ARANEDA, E., 2015. *Chemical-mineralogical characterization of copper smelting flue dust*, DYNA 82, 90-95.

BERMEJO, J.C., ALONSO, M., SASTRE, A.M., ALGUACIL, F.J., 2000. *Solvent extraction of Cu(II) by LIX 54-100 and its application to a solid supported liquid membrane system*, J. Chem. Res. (S) 9, 479-481.

BINGÖL, D., CANBAZOGLU, M., AYDOGAN, S., 2005. *Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching*, Hydrometallurgy 76, 55-62.

EUROPEAN COPPER INSTITUTE, http://www.copperalliance.eu (accessed September, 2016).

GONZALEZ, A., FONT, O., MORENO, N., QUEROL, X., ARANCIBIA, N., NAVIA, R., 2017. *Copper flash smelting flue dust as a source of germanium*, Waste Biomass Valor 8, 2121-2129.

HE, X., CHAI, Z., SHI, J., LI, Y., FANG, Z., LI, F., 2013. *Leaching of elements from flue dust produced in copper scrap smelting process*, Toxicol. Environ. Chem. 95, 184-189.

KLINK, C., EISEN, S., DAUS, B., HEIM, J., SCHLOMANN, M., SCHOPF, S., 2016. *Investigation of Acidithiobacillus ferrooxidans in pure and mixed-species culture for bioleaching of Theisen sludge from former copper smelting*, J. Appl. Microbiol. 120, 1520-1530.

LI, Q., ZHAO, Y.Z., 2014. *An environmentally friendly process to recover zinc from flue dusts of secondary copper industry*, Res. J. Chem. Environ. 18, 13-19.

LIAO, T., CHEN, B., CHEN, Y., 2012. *Preparation of high-purity sponge bismuth from copper converter flue dusts by hydrometallurgical process*, J. Rare Metals 36, 966-972.

LIMPO, J.L., LUIS, A., HERNANDEZ, A., ALGUACIL, F.J., 1985. Spanish Patent 545698.

MARTIN, M.I., LOPEZ-DELGADO, A., LOPEZ, F.A., COEDO, A.G., DORADO, M.T., ALGUACIL, F.J., 2003. *Treatment of copper converter flue dust for the separation of metallic/non-metallic copper by hydrometallurgical processing*, J. Chem. Eng. Japan 3, 1498-1502.

MONTENEGRO, V., SANO, H., FUJISAWA, T., 2013. *Recirculation of high arsenic content copper smelting dust to smelting and converting processes*, Min. Eng. 49, 184-189.

MORALES, A., CRUELLS, M., ROCA, A., BERGO, R., 2010. *Treatment of copper flash smelter flue dusts for copper and zinc extraction and arsenic stabilization*, Hydrometallurgy 105, 148-154.

QIANG, L., PINTO, I.S.S., YOUCAI, Z., 2014. *Sequential stepwise recovery of selected metals from flue dusts of secondary copper smelting*, J. Clean. Prod. 84, 663-670.

REGEL-ROSOCKA, M., ALGUACIL, F.J., 2013. *Recent trend in metals extraction*, Rev. Metal. Madrid 49, 292-315.

ROY, S., SARKAR, S., DATTA, A., REHANI, S., 2016. *Importance of mineralogy and reaction kinetics for selecting leaching methods of copper from copper smelter slag*, Sep. Sci. Technol. 51, 135-146.

RUIZ, O., CLEMENTE, C., ALONSO, M., ALGUACIL, F.J., 2007. *Recycling of an electric furnace flue dust to obtain high grade ZnO*, J. Hazard. Mat. 141, 33-36.

SHIN, S.K., KIM, W.-I., JEON, T.-W., KANG, Y.-Y., JEONG, S.-K., YEON, J.-M., SOMASUNDARAM, S., 2013. *Hazardous waste characterization among various thermal processes in South Korea: A comparative analysis*, J. Hazard. Mat. 260, 157-166.

VITKOVA, M., ETTLER, V., HYKS, J., ASTRUP, T., KRIBEK, B., 2011. *Leaching of metals from copper smelter flue dust (Mufulira, Zambian Copperbelt)*, Appl. Geochem. 26, 5263-5266.