MANAGEMENT OF A COPPER SMELTER DUST FOR COPPER PROFIABILITY

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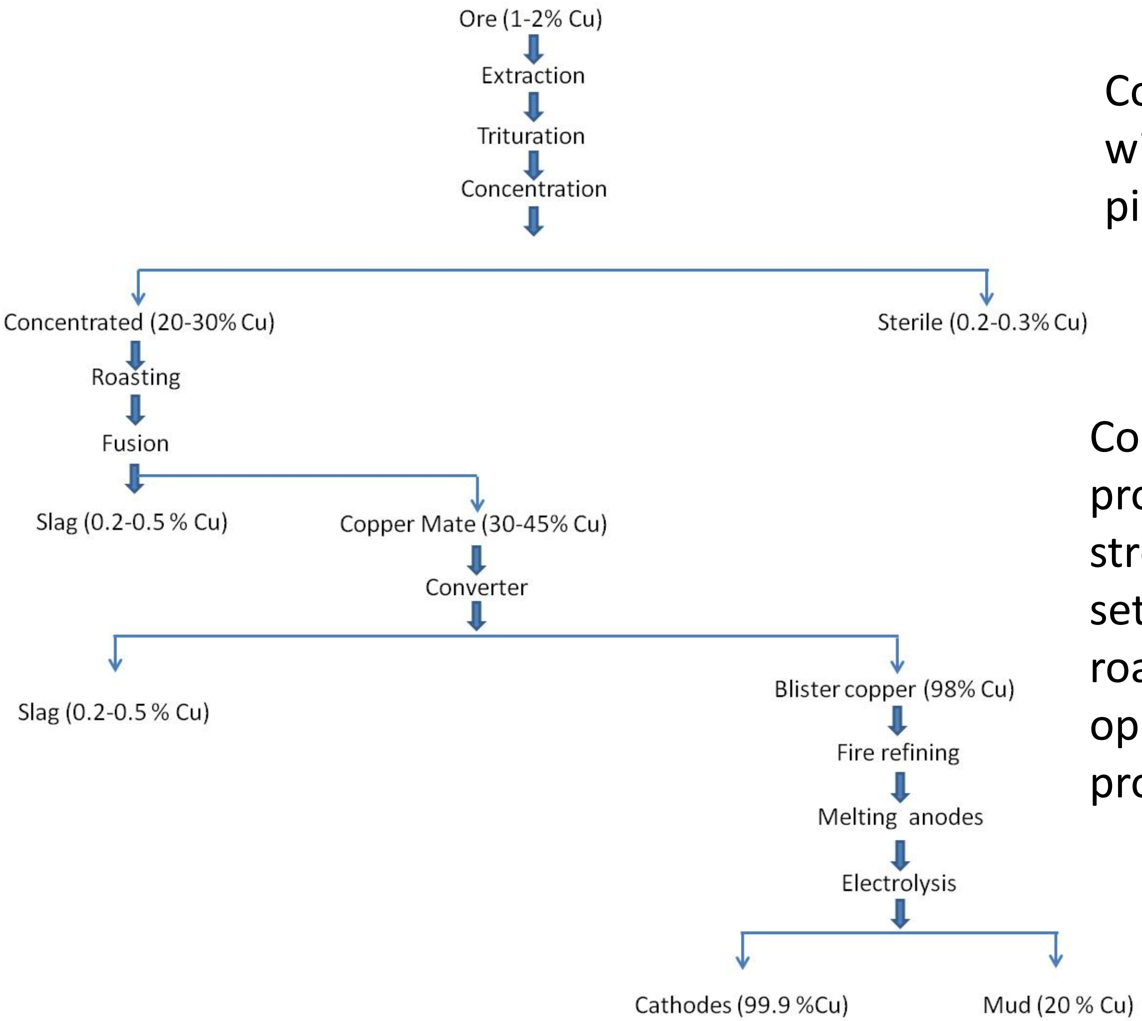
INTRODUCTION

Copper production by pyrometallurgical processing is nowadays an important part of the metallurgy industry



Ore (1-2% Cu)
Extraction
Trituration
Concentration
Concentrated (20-30% Cu)
Sterile (0.2-0.3% Cu)
Roasting
Fusion
Slag (0.2-0.5 % Cu)
Copper Mate (30-45% Cu)
Converter
Slag (0.2-0.5 % Cu)
Blister copper (98% Cu)
Fire refining
Melting anodes
Electrolysis
Cathodes (99.9 %Cu)
Mud (20 % Cu)

re

Copper dusts production is inherent with all the furnace types used in pirometallurgy

Copper dusts are defined as the product recovered from exhaust gas streams found in furnace, flues, and setting chambers as a result of roasting, smelting, and converting operations from copper refining process

INTRODUCTION

Due to its physical and chemical characteristics, these copper dusts were categorized as hazardous wastes.

These residues must be stored in specialized landfills

Due their important amount of various form of copper compounds (even metallic copper) could be used as secondary raw material in the production of this metal

- Pyrometallurgy
- Hydrometallurgy

Several processes have the main idea the leaching with ammonium salts

Copper is stabilized in the aqueous solution as the corresponding ammine-copper complexes

The solutions are practically free of non-desired elements, remaining in the solid residue due to the alkalinity of the solutions

INTRODUCTION

A sequential process of a Chilean cooper flue dust is given based in:

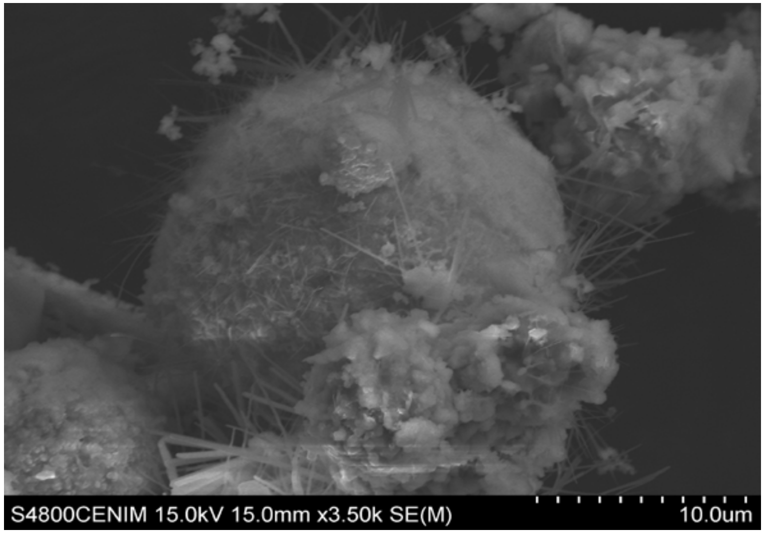
i) leaching with ammonium carbonate solution

ii a) cementation of copper from the solution using metallic zinc. Copper cement is the final product

ii b) liquid-liquid extraction of copper using LIX 54 as extractant and sulphuric acid as strippant. The final product could be copper cathode

EXPERIMENTAL

Materials



Dust from the flash furnace Chilean copper smelting plant

XRD Characterization				
Chalcocyanite	Maghemite	Sinnerite	Complex	Sulfide species
$CuSO_4$	Fe_2O_3	Cu_6As_4	Cu-Mo oxide	

Chemical Characterization (%)						
Cu	Fe	Mo	Pb	Al	As	Zn
24.5	14.0	0.45	0.08	1.2	0.9	0.15

EXPERIMENTAL

- i) Leaching
  - 1 L autoclave
  - Mild conditions- Reduce energy costs
- ii a) Cementation
  - Glass reactor- impeller
  - Stirring speed: 300 min^{-1}
- ii b)Solvent extraction
  - Batch conditions
    - Water jacketed (100 ml) separatory funnels
    - Mechanical shaking and thermostated (20ºC)
  - Continuous conditions
    - 2-4 Water jacketed mixer-settler
    - Mechanical shaking and thermostated

EXPERIMENTAL

Extraction agent → LIX 54 (β-diketone)

$R\text{-}CO\text{-}CH_2\text{-}CO\text{-}R'$

R y R'- Alkyl chains

Property	Kerosene
Aliphatic	98%
Boiling range	210-284ºC
Flash point	96ºC

RESULTS

i) LEACHING

Leaching reagent:

a) It must dissolve the targeted metal as rapidly as possible to make commercially feasible the operation, and it should no attack the non-desiderable elements or gange of the initial material

b) It must be cheap ount

$(NH_4)_2CO_3$

b) It is better that it can be regenerated within the whole process

RESULTS

i) LEACHING

Ammonium carbonate concentration no affect on leaching cooper percentage

$(NH_4)_2CO_3$ (g/L)	L/S ratio	pH	%Cu leached	Cu in solution (g/L)
260	100	8.6	79.6	1.95
130	100	8.7	82.4	2.02
65	100	8.7	81.2	1.99

$(NH_4)_2CO_3$ (g/L)	L/S ratio	pH	%Cu leached	Cu in solution (g/L)
260	100	8.6	79.6	1.95
260	10	8.5	79.9	19.6
65	200	8.8	92.2	1.13
65	100	8.7	81.2	1.99
65	20	7.8	45.1	5.50
65	10	7.3	9.8	2.40

L/S ratio no affect in the %Cu leached when concentrated $(NH_4)_2CO_3$ solution are used

However, the %Cu drops as the initial L/S ratio decrease when the dilute $(NH_4)_2CO_3$ solution are used

This is due to the decrease of the number of ammonia ligands available per copper atom

RESULTS

i) LEACHING

Higher copper concentrations can be yield in the solutions after leaching with ammonium carbonate solutions

$$NH_4^+ \longleftrightarrow NH_3 + H^+$$

$$Cu(NH_3)_n^{2+} \qquad n= 2 \text{ or } 4$$

Despite 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 slightly alkaline, the leaching solution is very pure, having very low values of other impurities found in the flue dust and free of iron, which remained in the residue probably as an iron (III) oxide species.

RESULTS

i) LEACHING

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65	10	7.3	9.8	2.40

The pH is slightly alkaline, 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.

RESULTS

ii a) CEMENTATION

The cementation of copper from a alkaline solution was done by metallic zinc, according with the overall reaction

$$Cu^{2+} + Zn^{0} \longrightarrow Cu^{0} + Zn^{2+}$$

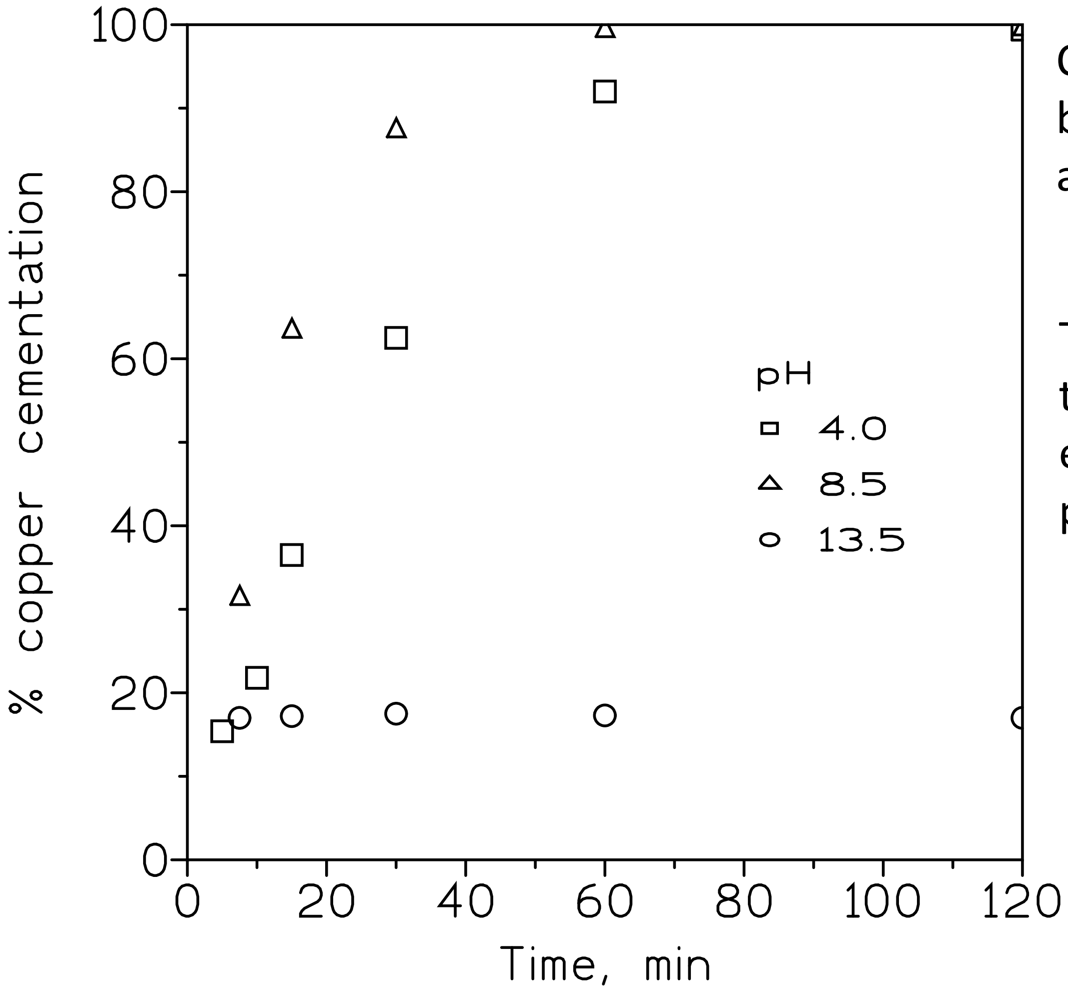
Cu^{2+}/Cu^{0} =0.34

ΔG^{0}_{298} = -35.19 -15.54 = -50.73 Kcal

Zn^{2+}/Zn^{0}= -0.76

RESULTS

ii a) CEMENTATION: pH effect

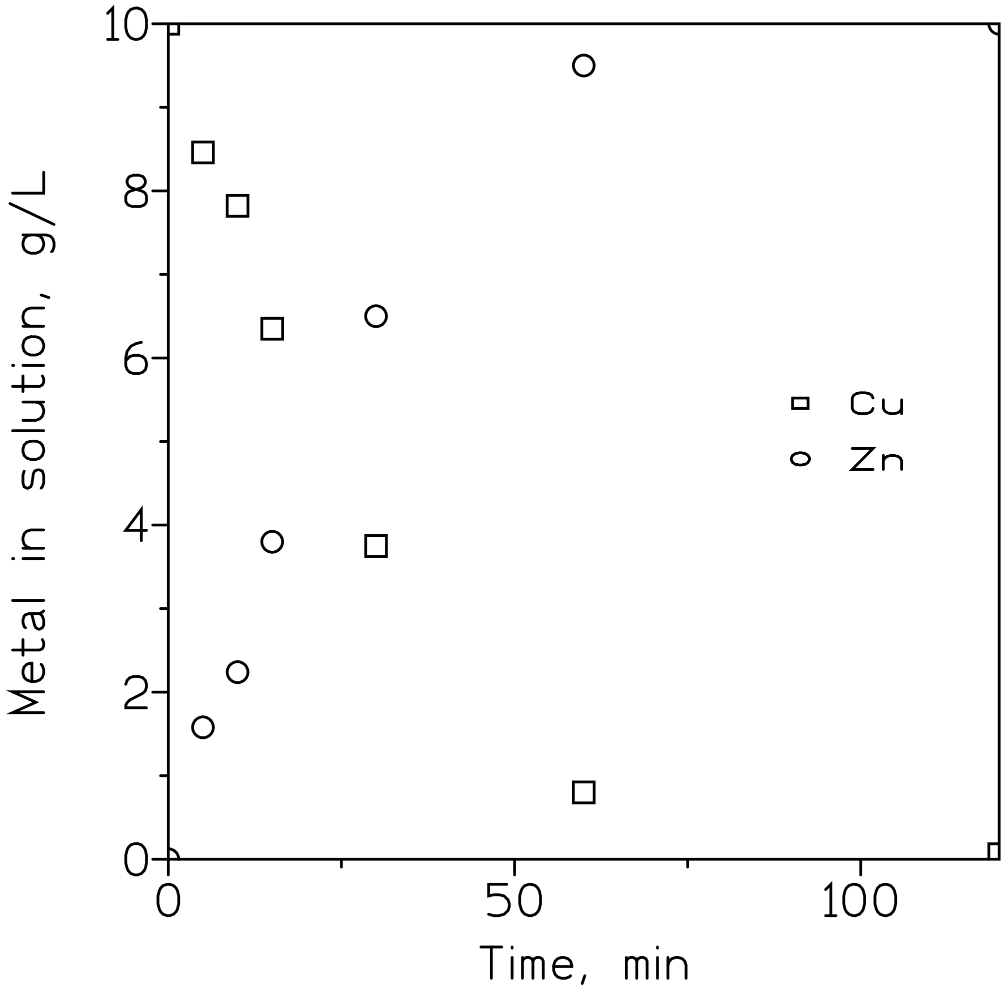


Cu^{2+} is well cementated a pH=4 but bad precipitated form ammonical alkaline solution.

This situation can be remediated if the aqueous solution contain an excess of ammonia ligands and the pH is maintained in 8-9 range.

RESULTS

ii a) CEMENTATION: metal concentration



At the end. the molar relationship $Zn^{2+}_{(liq)}/Cu^{0}_{(sol)} \approx 1$

$$Cu^{2+} + Zn^{0} \longrightarrow Cu^{0} + Zn^{2+}$$

RESULTS

ii a) CEMENTATION: salt addition

$(NH_4)_2CO_3$ (g/L)	15 min	30 min	60 min
65	13.1	13.3	13.5
89	34.5	46.4	44.7
113	65.0	86.8	97.4
160	91.0	99.1	>99.5
210	65.2	91.8	>99.5
260	68.5	87.5	>99.5

Aqueous solution: 10 g/L Cu^{2+} in $(NH_4)_2CO_3$, pH 8.5 ±0.02
Zn/Cu molar ratio: 2
Temperature:20ºC

The salt addition, ammonium carbonate, increases the copper cementation percentage

RESULTS

ii a) CEMENTATION: influence Zn/Cu ratio

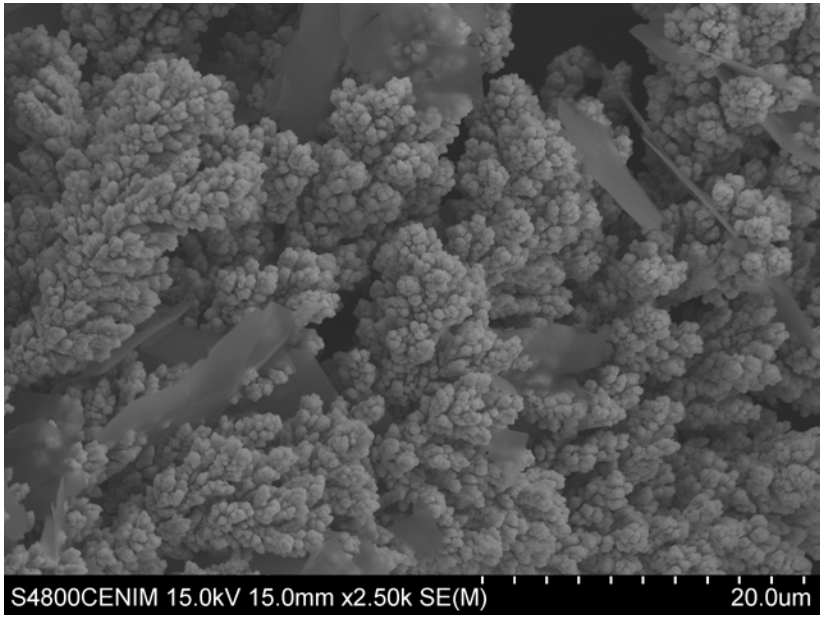
Zn/Cu	15 min	30 min	60 min	2 h
8	84.2	95.0	99.5	>99.5
6	53.2	63.6	80.5	98,3
4	48.5	61.1	73.0	97,6

Aqueous solution: 5 g/L Cu^{2+} and 65 g/L $(NH_4)_2CO_3$, pH 8.5 ±0.02
Temperature:20ºC

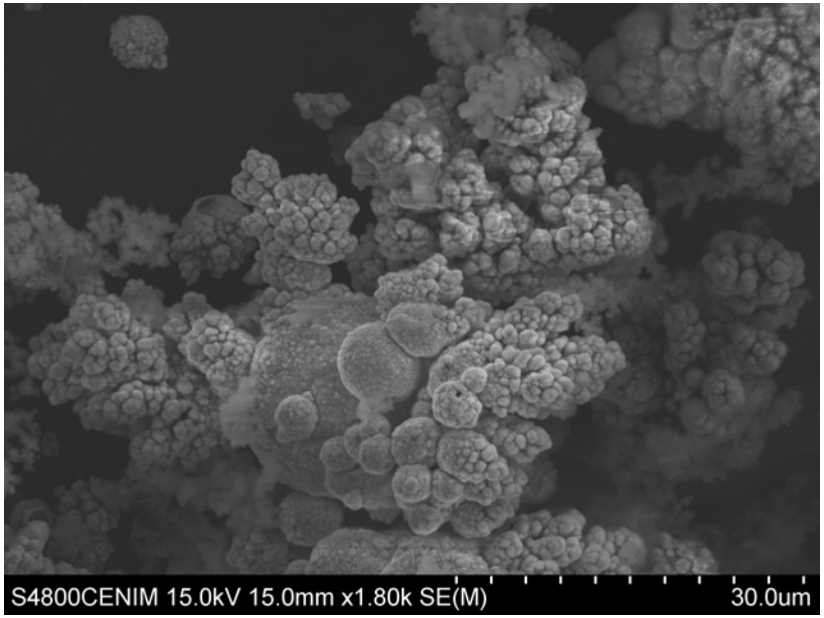
Zn/Cu molar ratio increased a increases the Cu^{2+} percentage cementated

The same tendency is observed to a concentration of ammonium carbonate 260 g/L. The maximum percentage of copper cementated is obtained to 1.5 Zn/Cu ratio

ii a) CEMENTATION: cement morphology



Aqueous solution: 5 g/L Cu^{2+} and 160 g/L
$(NH_4)_2CO_3$, pH 4.0 ±0.02
Temperature:20ºC



Aqueous solution: 5 g/L Cu^{2+} and 160 g/L
$(NH_4)_2CO_3$, pH 8.5 ±0.02
Temperature:20ºC

The copper cementated has the form of granular particles. The unreacted zinc is represented by the non-granular specimes

RESULTS

ii b) LIQUID-LIQUID EXTRACTION

Too much dilute copper (i.e. below 5 g/L) or complex solutions result unpractical for direct production of copper cathodes

Liquid-liquid extraction is the technology which ensures the production of lean copper solution with the adequate concentration to be their direct feeding to the electrowinning plant and to yield a grade A copper cathode

- First step: Metal extraction
- Second step: Metal stripping from loaded organic solution

RESULTS

ii b) LIQUID-LIQUID EXTRACTION

First step: Metal extraction

Liquid-liquid Cu(II) extraction the agent extraction most widely used are:

Ketoxine Salicyaladoximes Salicyaladoximes

$$\mathrm{Cu^{+2}_{aq} + 2\ HR_{org} \longrightarrow R_2Cu_{org} + 2\ H^{2+}_{aq}}$$

β-diketone (LIX 54)

aq- aqueous
org-organic

$$\mathrm{Cu(NH_3)_2{}^{+2}_{aq} + 2\ HR_{org} \longrightarrow R_2Cu_{org} + 2\ NH_4{}^{+}_{aq}}$$

The extraction of the diammine-copper(II) complex $\mathrm{Cu(NH_3)_2{}^{+2}_{aq}}$, product of the leaching step, result in the neutralization of the protons released to the aqueous solutions by the agent extraction, and regenerating the leaching reagent

RESULTS

ii b) LIQUID-LIQUID EXTRACTION

Second step: Metal stripping

$$R_2Cu_{org} + H_2SO_{4aq} \longrightarrow 2HRorg + Cu^{2+}{}_{aq} + SO_4{}^{2-}{}_{aq}$$

The stripping agent was a H_2SO_4 solution (i.e. 160-180 g/L H_2SO_4), this solution represented the advanced electrolyte whcih feed the electrowinning operation

RESULTS

ii b) LIQUID-LIQUID EXTRACTION

Preliminary studies

Experiments conditions:

Liquid phase: 2 g/L Cu(II) in 65 g/L $(NH_4)_2CO_3$ pH 8.5 ± 0.02
Organic phase: 10 %V/V LIX 54 + Kerosene

First step: Metal extraction

Equilibrium time= 2.5 min (98.8 %)

Endothermic reaction

An increase in the ammonium carbonate in the aqueous solution decrease the percentage of copper extraction , from 98.9-80.3 % Cu for ammonium carbonate solutions in 65 to 260 g/L

RESULTS

ii b) LIQUID-LIQUID EXTRACTION

Preliminary studies

Experiments conditions:

Liquid phase: 2 g/L Cu(II) in 65 g/L $(NH_4)_2CO_3$ pH 8.5 ± 0.02
Organic phase: 10 %V/V LIX 54 + Kerosene

Second step:
Metal stripping

The stripping of the metal carried out using spent electrowinning solutions (160-180 g/L H_2SO_4) ensured the strip of the metal from the loaded organic phase to the aqueous solution, which represented the advanced electrolyte

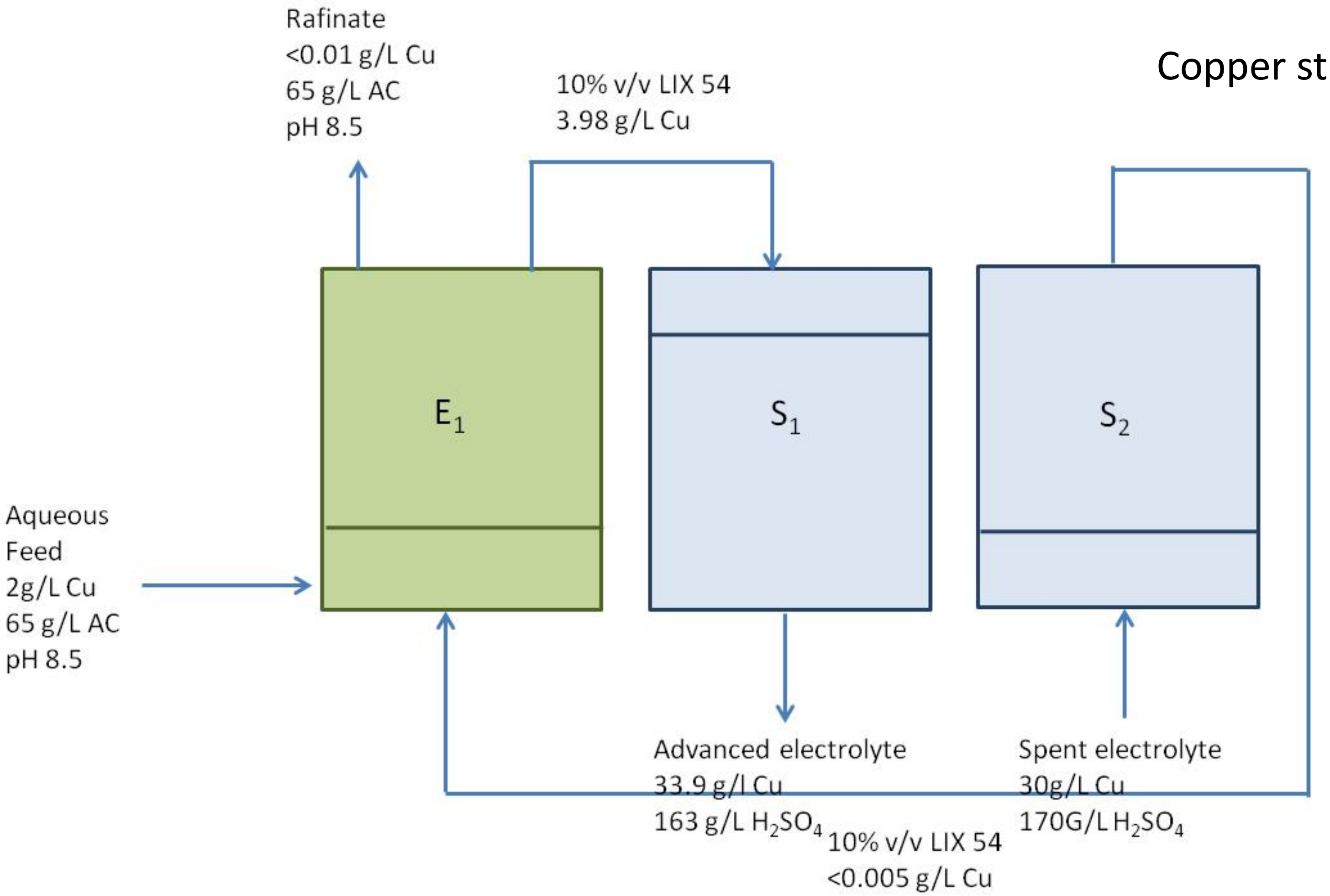
RESULTS

ii b) LIQUID-LIQUID EXTRACTION

After 100 h

Copper extractoin 99.5 %

Copper stripping 99.9 %



Rafinate
<0.01 g/L Cu
65 g/L AC
pH 8.5

10% v/v LIX 54
3.98 g/L Cu

E_1

S_1

S_2

Aqueous
Feed
2g/L Cu
65 g/L AC
pH 8.5

Advanced electrolyte
33.9 g/l Cu
163 g/L H_2SO_4

10% v/v LIX 54
<0.005 g/L Cu

Spent electrolyte
30g/L Cu
170G/L H_2SO_4

CONCLUSION

$(NH_4)_2CO_3$ solution allowed the dissolution of Cu(II) from copper flue dust

$$CuSO_4 + (NH_4)_2CO_3 \longrightarrow Cu(NH_3)_2^{2+} + SO_4^{2-} + CO_3^{2-} + 2H^+$$

The metal-lean solution can be processed

ii a) Cementation

$$Cu^{2+} + Zn^0 \longrightarrow Cu^0 + Zn^{2+}$$

Cement copper is the final product

ii b) Liquid-liquid extraction

$$Cu(NH_3)_2{}^{+2}{}_{aq} + 2\ HR_{org} \longrightarrow R_2Cu_{org} + 2\ NH_4{}^{+}{}_{aq}$$

The final product could be copper cathode

THANK YOU
FOR
YOUR ATTENTION