Universidad Andrés Bello

# REUTILISATION OF PRIMARY METALLURGICAL WASTES: COPPER SLAG AS A SOURCE OF COPPER, MOLYBDENUM, AND IRON – BRIEF REVIEW OF TEST WORK AND THE PROPOSED WAY FORWARD


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THIRD INTERNATIONAL SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013

Leuven, Belgium

# Content

# Introduction

- Mining Residues = Waste ?

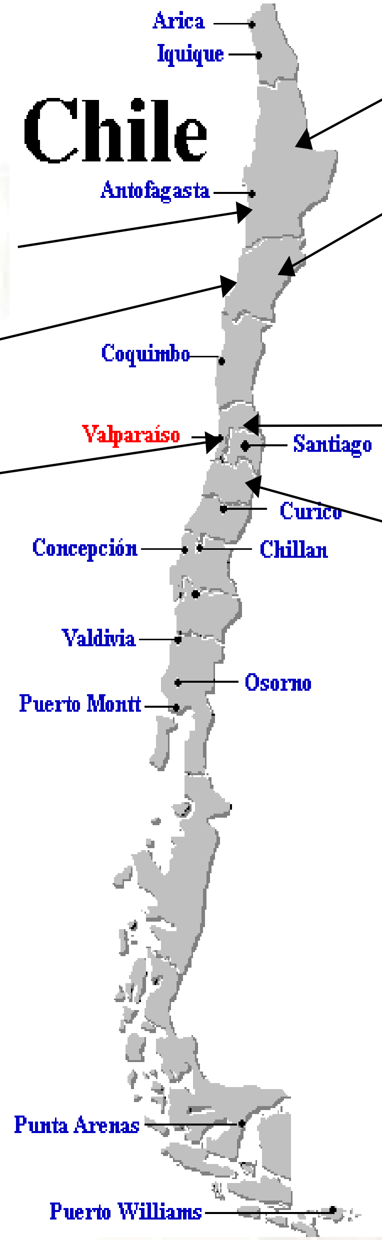
- …what about to consider "Wastes" as "Resources" ?

- Advantages of these "New Resources"…:
  - ✓ They are on surface (lower "mining costs").
  - ✓ They more or less characterized (lower "geological costs").
  - ✓ Their recovery, recycling and reutilization have a positive effect (lower "transport and disposal costs", and less environmental impact).

# Introduction

| Solid residues | Generation (ton/ton Cu) |
|---|---|
| Smelter Slags | ~ 2 |
| Tailings from Floatation | ~ 100 |
| Leaching Overburner | ~ 200 |
| Mine Sterile | ~ 400 |

# Introduction




CHUQUICAMATA (CODELCO)

POTRERILLOS (CODELCO)

ALTONORTE (XSTRATA)

PAIPOTE (ENAMI)

CHAGRES (ANGLOAMERICAN)

VENTANAS (CODELCO)

CALETONES (CODELCO)

**¿Why Slags are important for Chilean?**

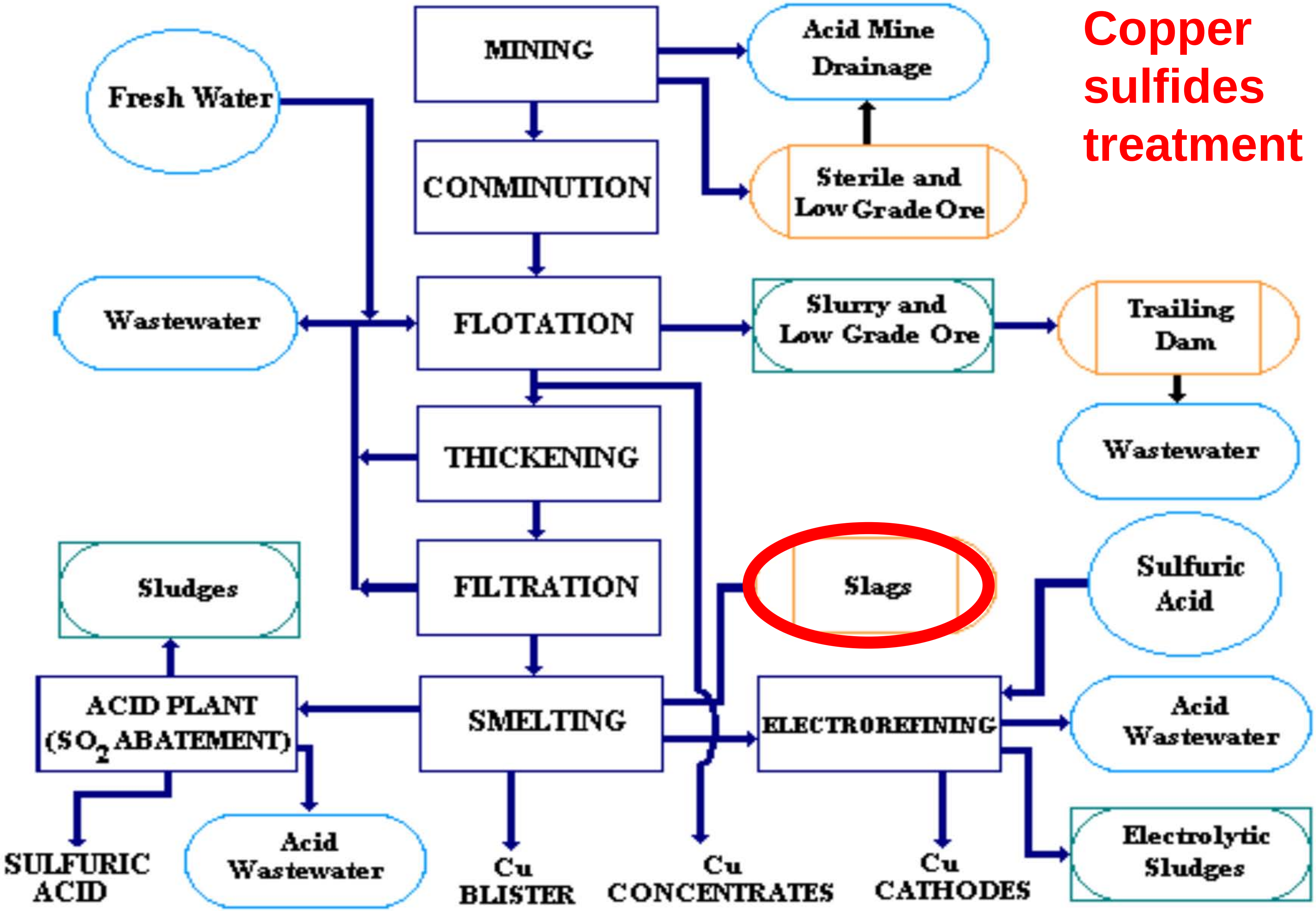
**7 Smelters**

**4 CODELCO**

**1 ENAMI**

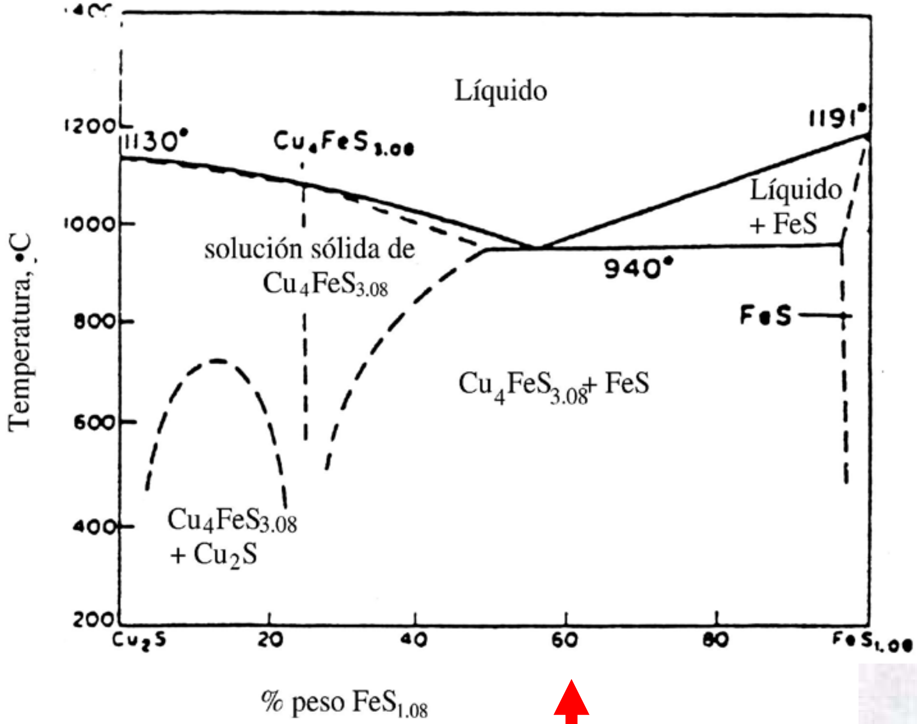
**2 Privates**

# Characterization




**Copper sulfides treatment**

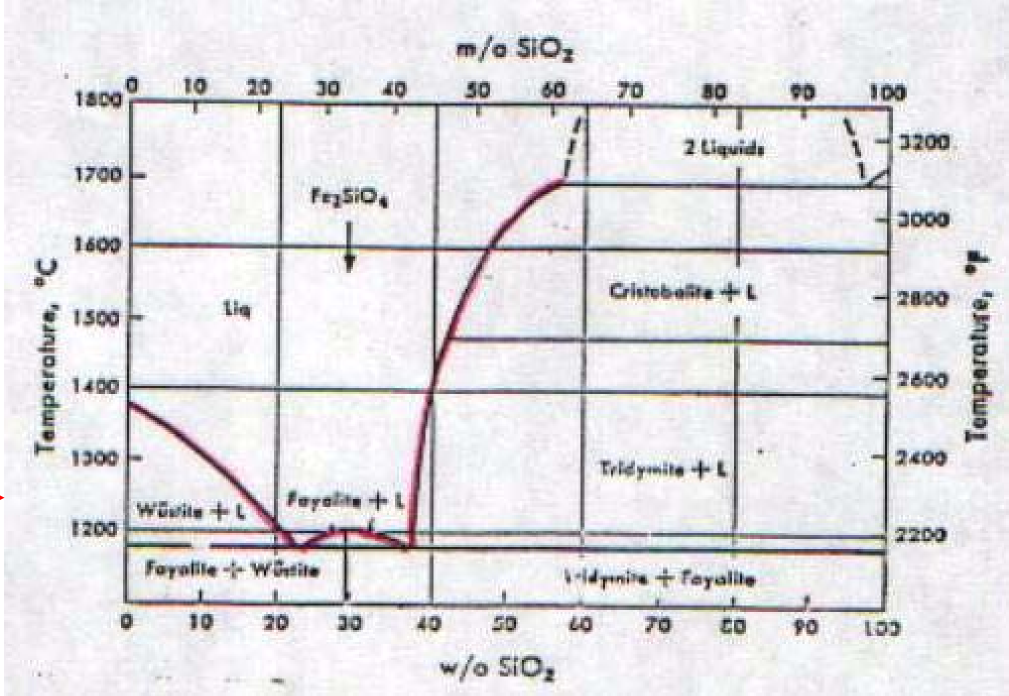
# Characterization




METALLIC PHASE IS NOT A RESTRICTION FOR THE WORKING TEMPERATURE. THE PROBLEM IS THE SLAG (HIGH SMELTING POINT AND VISCOSITY)

MATTE PHASE ($Cu_2S$+FeS) COULD BE OPERATED AT AROUND 1100 ºC.

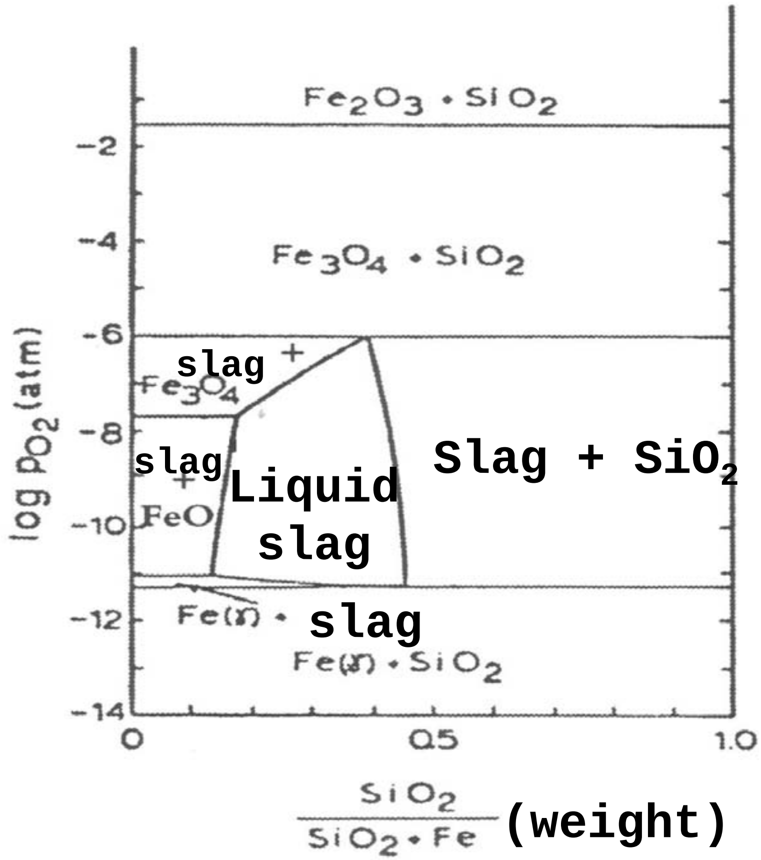
HOWEVER, TO KEEP FLUIDITY IN SLAG IT IS NECESSARY TO WORK OVER 1200 ºC.



# Characterization

## FeO-$SiO_2$ System

Note that the liquid region exists for a specific range of $SiO_2$ content…(fayalite formation)




PURPOSES OF SILICA ADDITION:

- To low the global melting point in the system

- To minimize free FeO and hence to decrease $Fe_3O_4$ formation

Fayalite and magnetite formation:

$2FeO + SiO_2 = 2FeOxSiO_2$

$6FeO + O_2 = 2Fe_3O_4 \quad K_{1200\ °C} = 15.8x10^8$

Note the competion between silica and oxygen to catch FeO

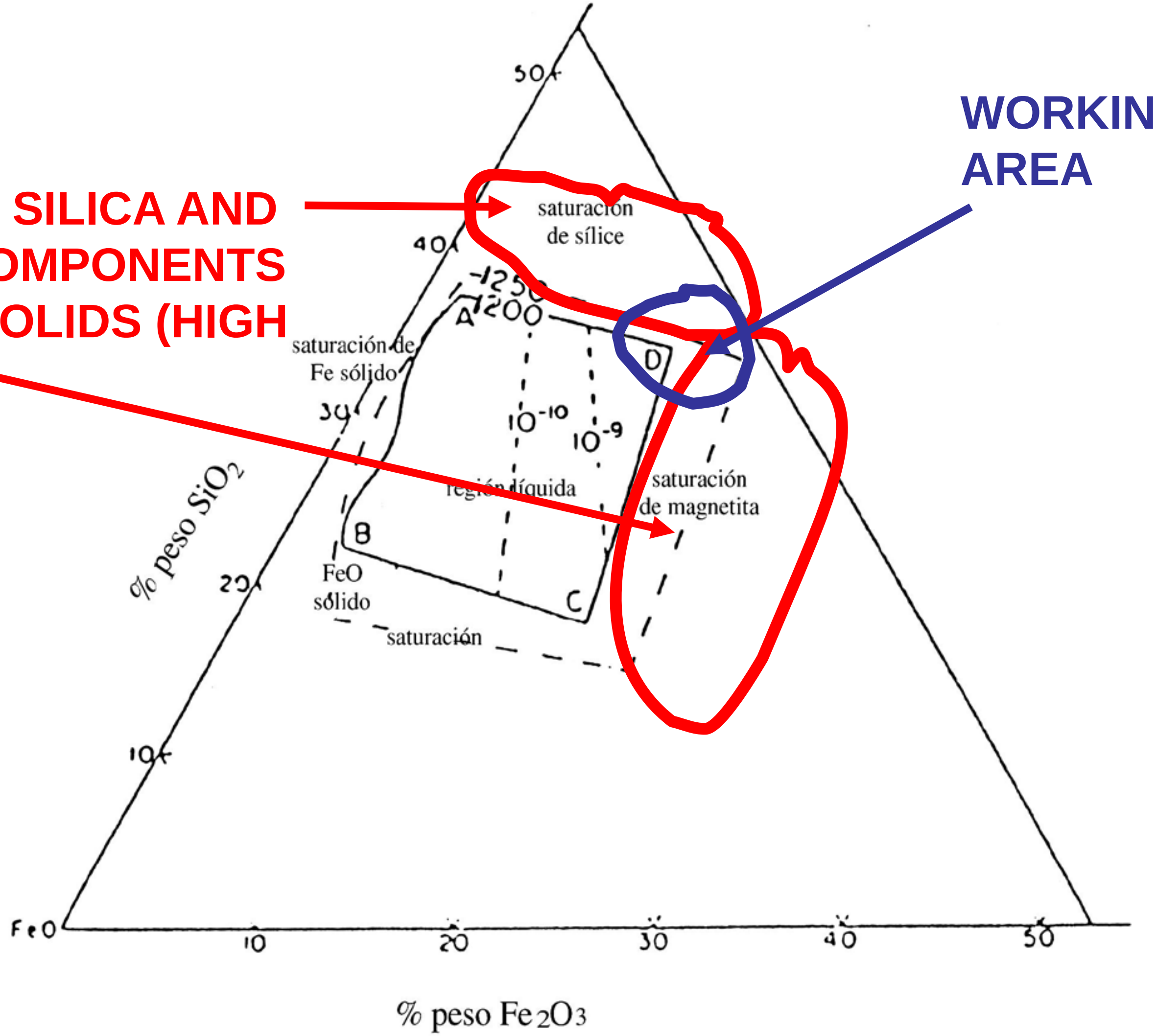
THERE IS A KIND OF COMPROMISE BETWEEN FREE $SiO_2$ AND $Fe_3O_4$ FORMATION

To obtain copper, oxygen potential must increase until $10^{-4}$ -$10^{-5}$ atm… then during slagging we will have magnetite formation … and magnetite currently entrape other metals (copper, molybdenum, etc)

# Characterization

SYSTEM SATURATED IN SILICA AND MAGNETITE → BOTH COMPONENTS WILL BE PRESENT AS SOLIDS (HIGH MELTING POINT)

WORKING AREA




$FeO-Fe_2O_3-SiO_2$ SYSTEM ASSOCIATED TO SLAGS

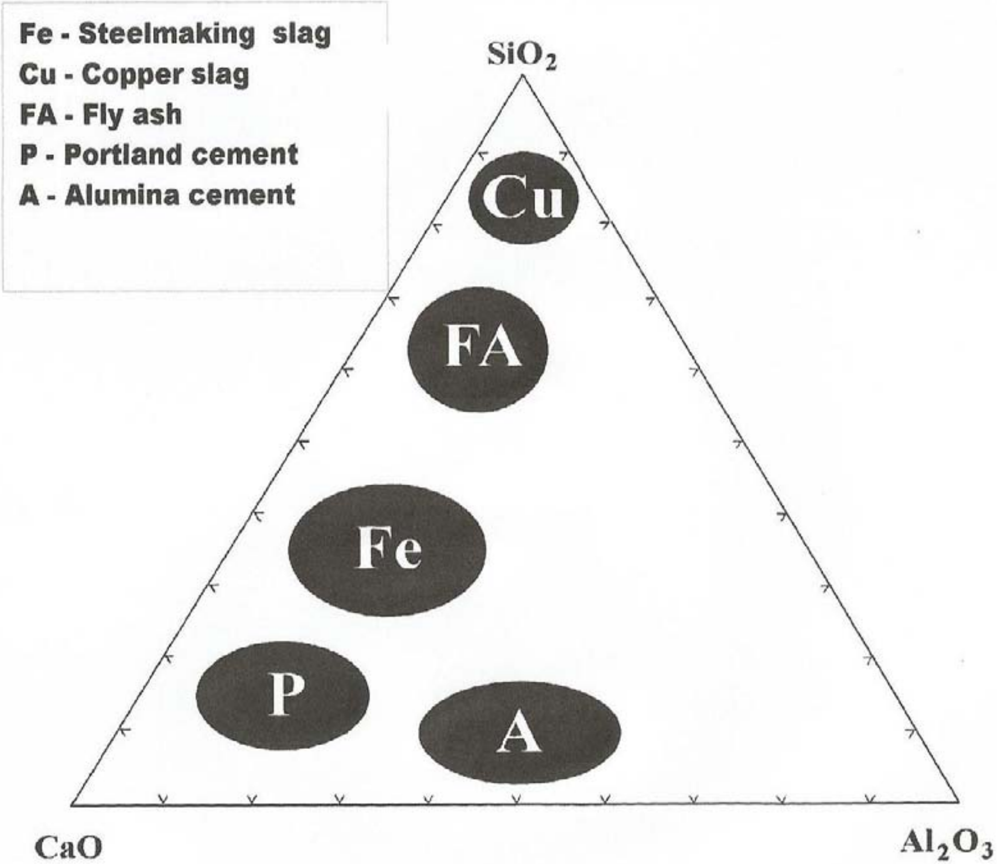
# Purpose of this work

- **Copper smelter slags** have seen limited use mainly as bulk products for road construction and abrasive material for cleaning metallic surfaces.
- This work is targeted at **revenue generation by the recovery of residual base metals as well as the bulk components**, iron and silica. The production of slag in the copper industry ranges **2.0-5.5 ton of slag per tonne of blister copper**.

# Purpose of this work

**As a first approach: the example of the iron making industry ➔ changing the composition of the slag to use by the cement industry**

**Recent work has focused on oxidation of slag to break some stable compounds and hence recover some valuable metals, as Molybdenum**



Comparison of Slag and Cement Composition

# Purpose of this work

- Traditionally, interest has been to recover copper. Historically some slags could have near 1% copper. However some others elements of interest could be found.
- Ref.: Table shows the content of copper, iron, molybdenum and silicon of an historically accumulated Chilean copper slag, quenched and slowly cooled.
- Technologies used today are able to ensure lower content of copper in the final slag (< 0.6%), but iron and silicon, as iron oxides and silica, remain approximately the same

| Slag Treatment | Composition (wt%) | | | |
|---|---|---|---|---|
| | Cu | Mo | Fe | Si |
| Quenched | 0.9 | 0.3 | 41.2 | 14.0 |
| Slowly cooled | 1.1 | 0.3 | 43.4 | 14.4 |

**Composition of a Chilean Copper Smelter Slag**

# Potential revenue

Additional potential production of bulk commodities from one tonne of fayalite slag containing 40% iron and 30% silica, after oxidation is 0.47 tonnes hematite and 0.30 tonnes silica.

Value of these products would be dependent on recovery and physical form (size shape and hardness) and chemical quality (purity) of material resulting from separation techniques.

| Product | Copper (wt%) | Molybdenum (wt%) | Gross Value $/tonne* |
|---|---|---|---|
| Cu-Mo ore | 0.6 | 0.03 | 41 |
| Cu-Mo Slag | 0.6 | 0.3 | 90 |

*Gross Value = metal content x market price (Cu = $6/kg; Mo = $18/kg)

# Main Metals Recovery: Copper

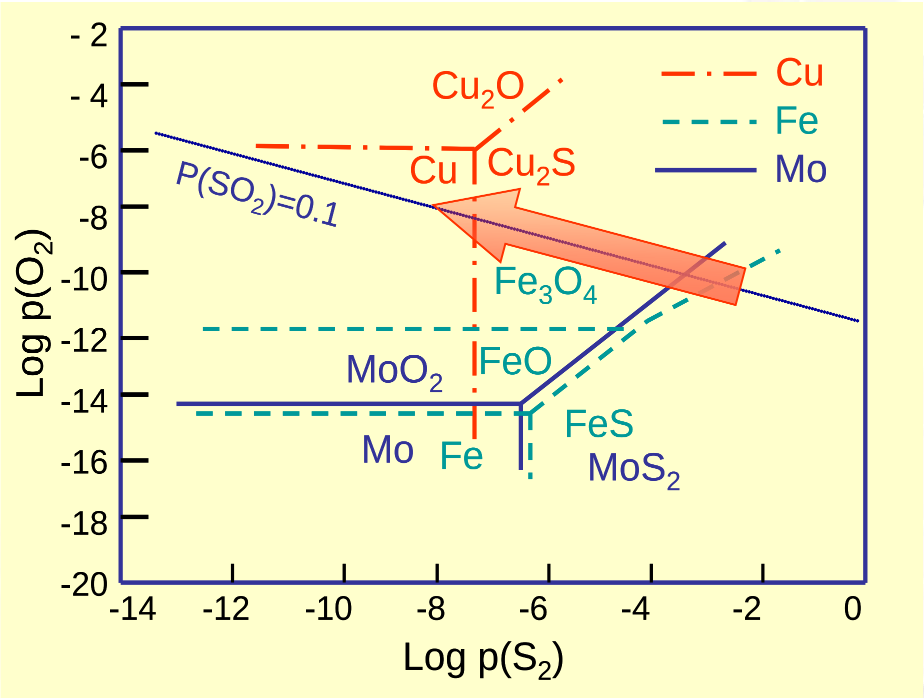
- Slag cleaning in slag cleaning furnace: pulverised coal is injected and temperature maintained with oxygen-fuel burners. Coal reduces the content of magnetite and slag viscosity. Copper particles are released to form a rich copper matte (>70% Cu)
- Slag cleaning in an electrical furnace: Copper is recovered by direct electrical reduction of magnetite, releasing the suspended inclusions while oxides are reduced by the graphite electrodes.
- Slag flotation: It requires slow cooling, crushing, grinding and flotation of slag with copper metal and sulphide particles reporting to the flotation concentrate.

# Main Metals Recovery: Molybdenum

- **Molybdenum is dispersed throughout the iron oxide phase**
- **At the copper-making step molybdenum is highly oxidised and associated to the magnetite structure**

**Selective flotation is imperfect and some $MoS_2$ remain in the copper smelter feed.**

**The molybdenum sulphide oxidizes readily and most of the Mo reports in the smelter slag as an insoluble spinel belonging to the $2FeO.MoO_2$-$Fe_3O_4$ series**




**Stability diagram of Cu-O-S, Fe-O-S and Mo-O-S systems at 1300 ºC**

# Main Metals Recovery: Molybdenum

| Slag | $Fe_3O_4$(%) | Cu(%) | Fe(%) | Mo(%) |
|---|---|---|---|---|
| Slag 1-S | 23.4 | 1.21 | 42.2 | 0.27 |
| Slag 1-R | 1.4 | 0.85 | 48.4 | 0.30 |
| Slag 2-S | 14.1 | 1.32 | 50.7 | 0.20 |
| Slag 3-S* | 7.9 | 1.19 | 45.7 | 0.40 |
| Slag 3-R | 13.4 | 0.77 | 43.0 | 0.40 |

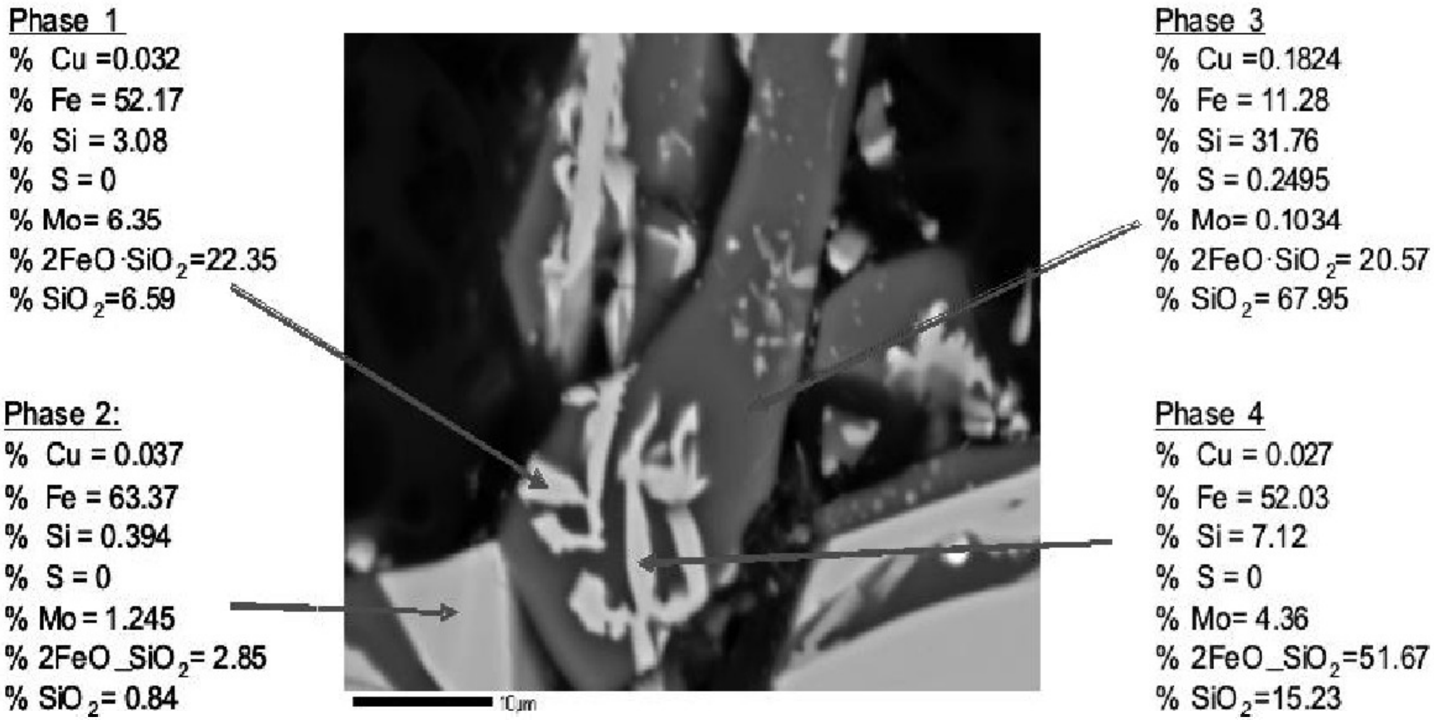
Composition and magnetite content of slowly and rapidly cooled slag

# Main Metals Recovery: Molybdenum

- Molybdenum form separate phases of Fe-Mo-O type:

  % Fe = 52.03-63.57%, Mo = 1.25-6.35% (phases 1, 2, 4)

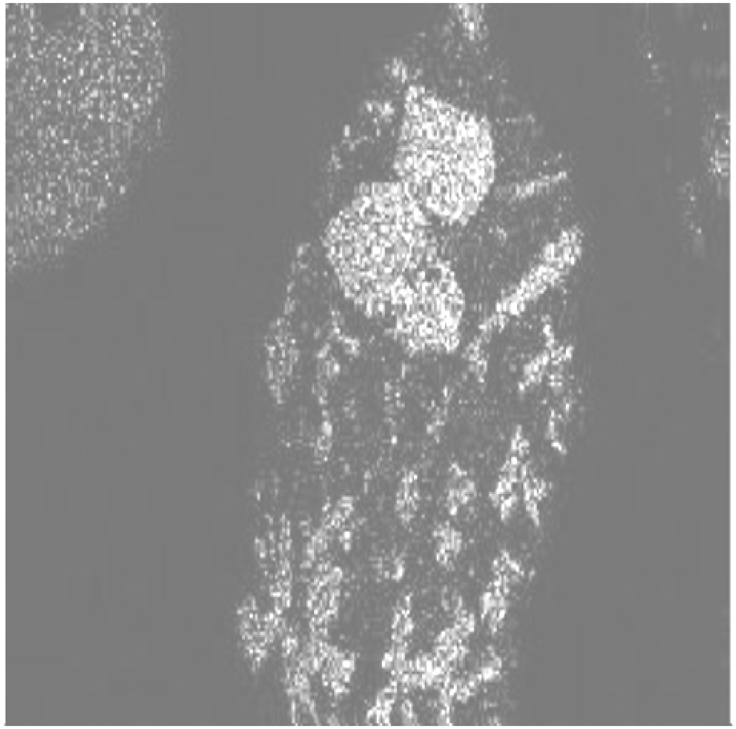
- These phases have low silica → iron could be present in a spinel structure type $FeO\text{-}MoO_2\text{-}Fe_3O_4$
- Phase 3 shows a glassy iron silicate type silica rich solution with low content of molybdenum.



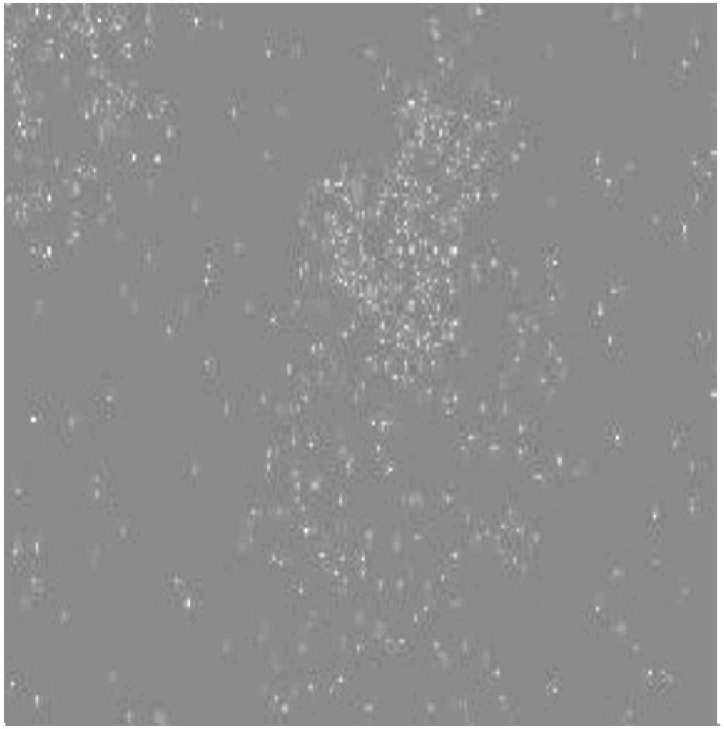

SEM image of copper slag showing phase composition

# Main Metals Recovery: Molybdenum

- Microprobe analysis shows distribution of iron and molybdenum and association between both elements in the slag



(a)



(b)

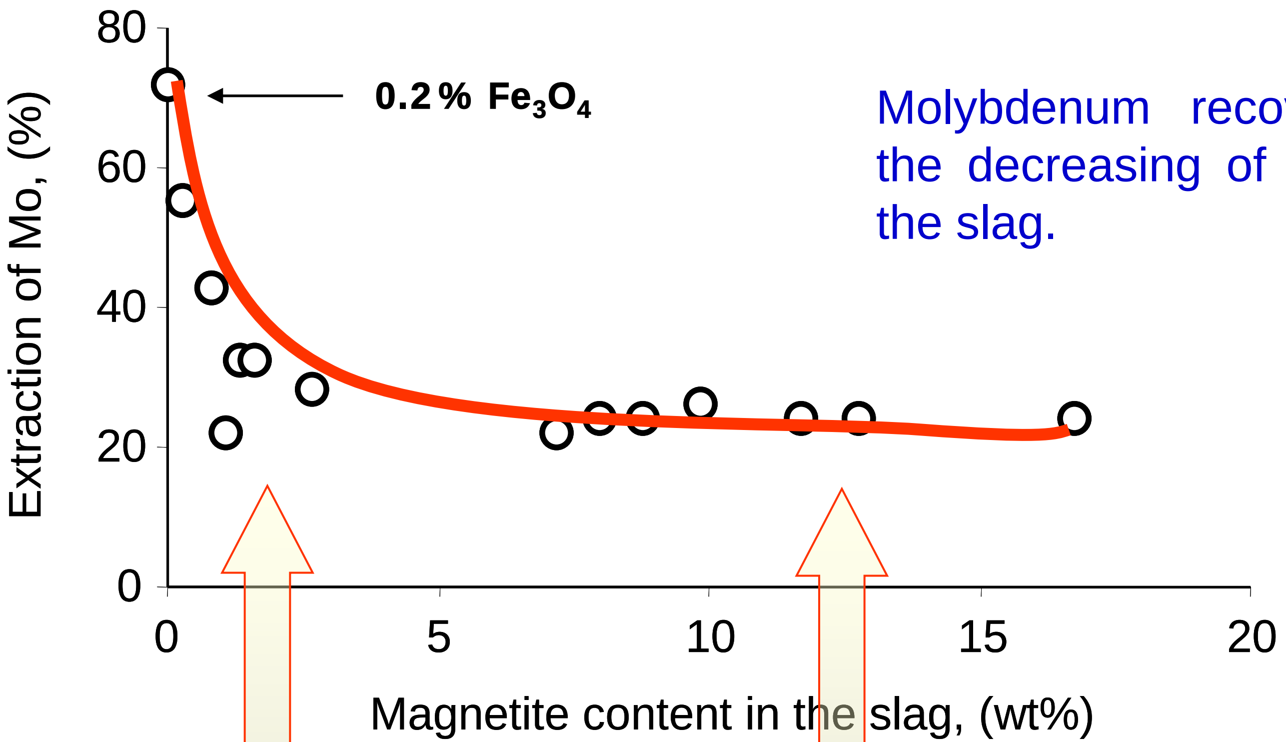
**Microprobe Analysis of Copper Slag showing iron (a) and molybdenum (b)**

# Main Metals Recovery: Molybdenum

| Slag | $Fe_3O_4$(%) | Extraction of Fe (%) | Extraction of Mo (%) |
|---|---|---|---|
| Slag 1-S | 23.4 | 82 | 22 |
| Slag 1-R | 1.4 | 65 | 95 |
| Slag 2-S | 14.1 | 57 | 30 |
| Slag 3-S* | 7.9 | 77 | 18 |
| Slag 3-R | 13.4 | 47 | 30 |

**Acid leaching of slag showing link between molybdenum solubility and magnetite**

# Main Metals Recovery: Molybdenum and magnetite content in the slag




Molybdenum recovery increases with the decreasing of magnetite content in the slag.

Rapidly cooled slag.

Slow cooled slag.

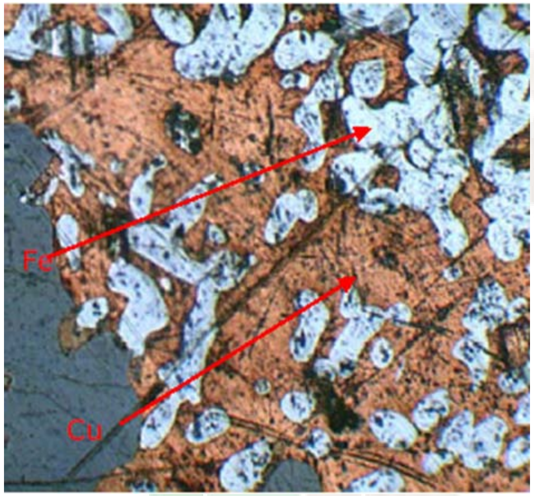
**700 – 750°C**

**Air + 10 % $SO_2$**

# Main Metals Recovery: Iron

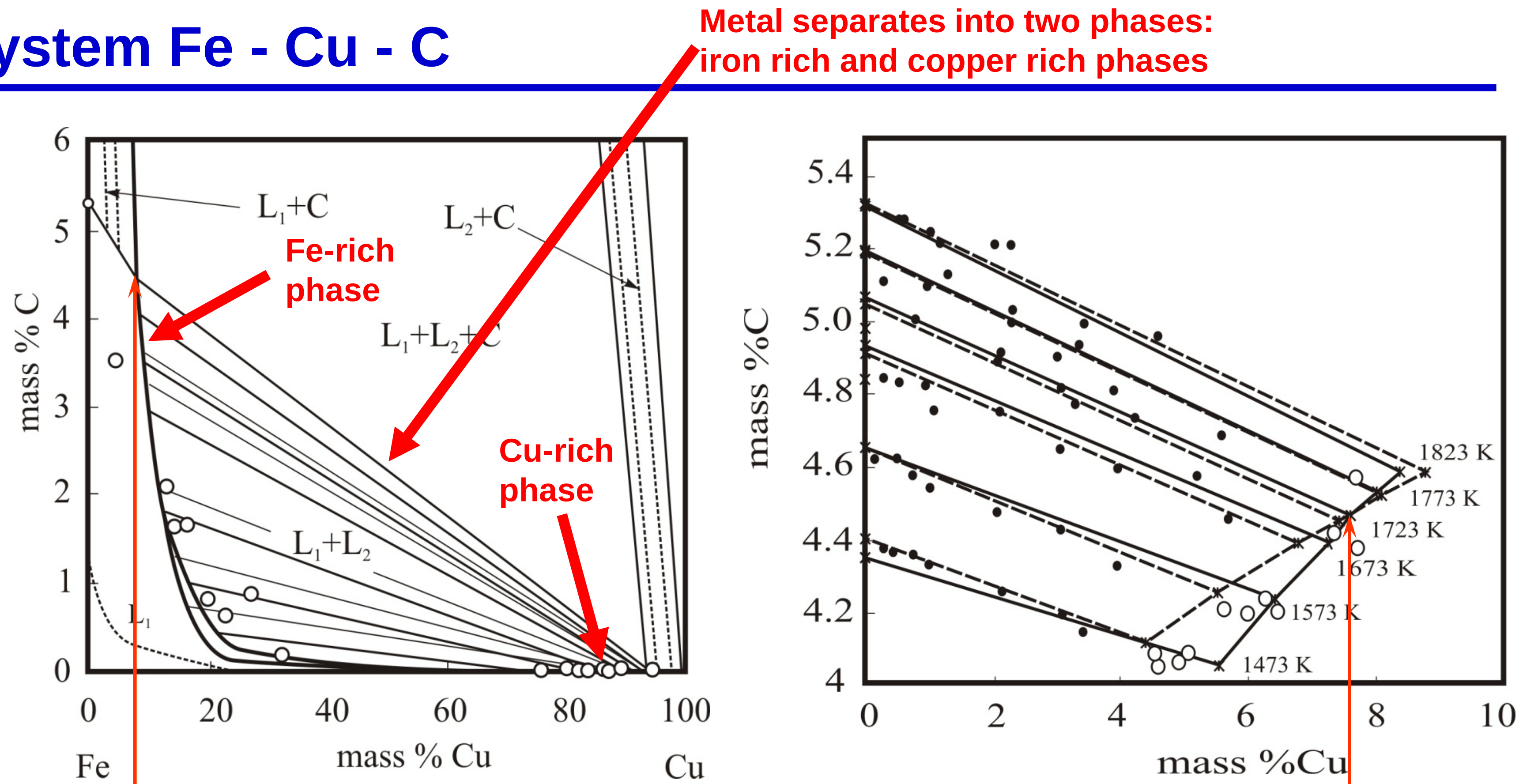
- Iron is a major element in the final slag and can be recovered as metal in an additional reducing step.
- Slag out from smelter operations are cleaned in an electric furnace using coke as a reductant
- Solubility of carbon in the Fe-Cu-C system is a function of

  (a) copper content and (b) temperature
- When an excess of carbon is present, reduction of slag results in the formation of an Fe-Cu-C alloy



# Main Metals Recovery: Iron

## System Fe - Cu - C



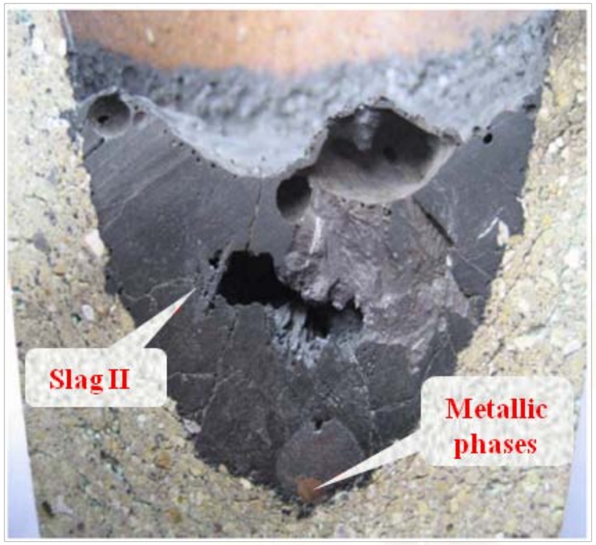

Copper and carbon saturated iron alloy at 1723 K

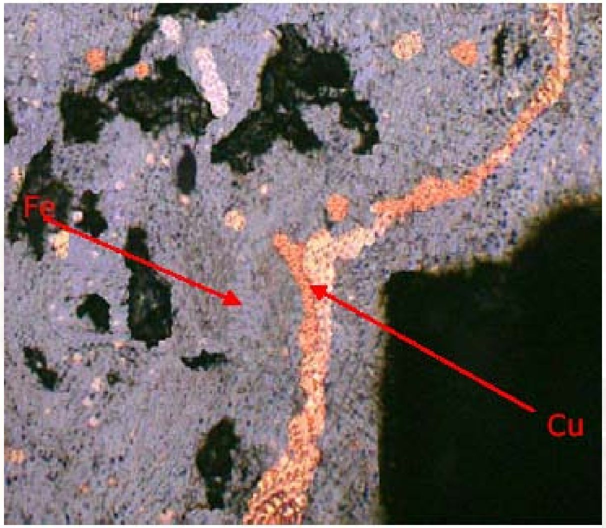
**- Solubility of carbon in copper is negligible. While the melt rich in iron dissolves copper and carbon, solubility of copper decreases with the increasing of carbon content**

# Main Metals Recovery: Iron

| Compound | $Cu_2O$ | $Cu_2S$ | FeS | FeO | $Fe_3O_4$ | $SiO_2$ | $Al_2O_3$ | CaO | Other |
|---|---|---|---|---|---|---|---|---|---|
| Wt% | 0.76 | 2.00 | 1.17 | 40.61 | 12.38 | 33.00 | 2.12 | 0.69 | 7.27 |
| | | | | | | | | | |
| Element | Cu | Fe | S | Si | Al | Ca | As mg/kg | | |
| Wt% | 2.27 | 41.3 | 0.83 | 15.4 | 1.60 | 0.49 | 74 | | |

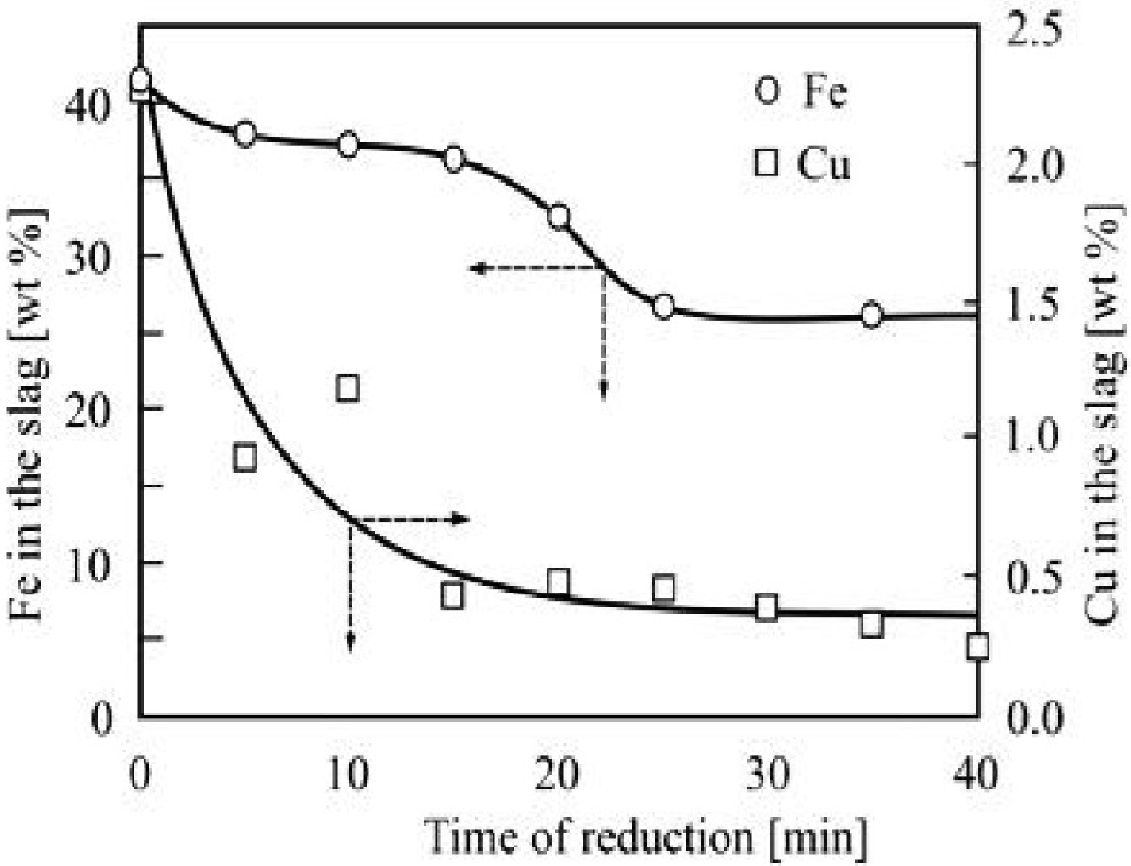
**Analysis of slag from flash furnace used for iron reduction research**



# Main Metals Recovery: Iron

- **Reduction kinetic of copper oxide and magnetite was studied by using graphite rod as reducing agent at 1450 $^{o}C$.**

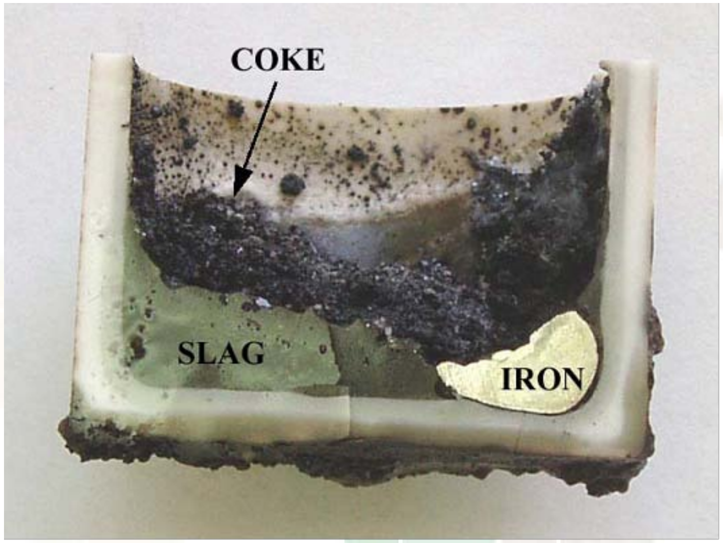



**Preferential removal of copper during slag reduction**

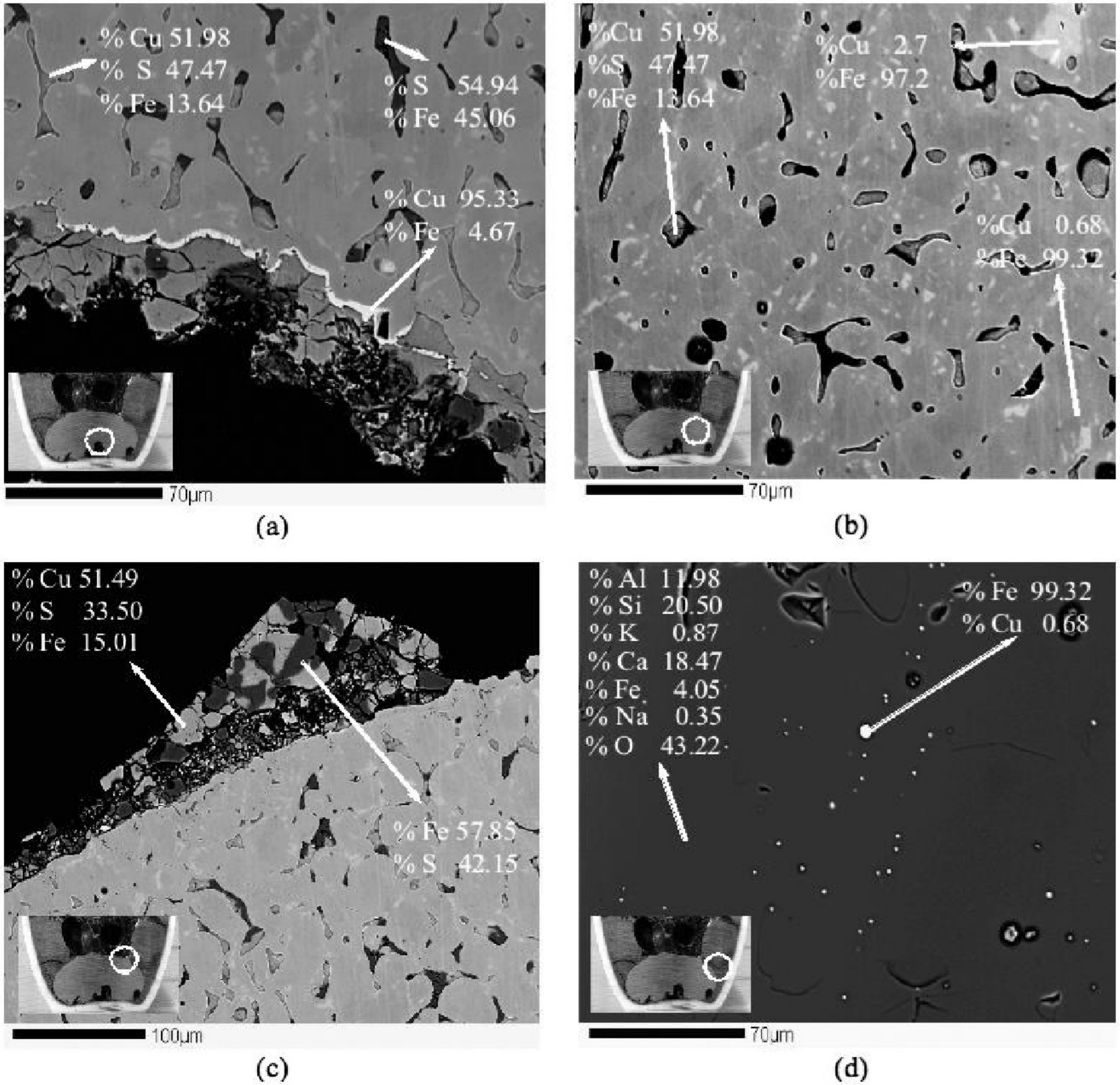
# Main Metals Recovery: Iron

| Carbon addition wt% | 1st. Step: selective copper reduction | | | | | 2nd. Step: reduction to metallic iron | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | First slag rich in iron | | | Metallic phase | | Final slag | | | Iron Alloy | |
| | %Cu | %Fe | %S | %Cu | %Fe | %Cu | %Fe | %S | %Cu | %Fe |
| 100 | 0.32 | 24.6 | 0.5 | 51.0 | 48.2 | 0.02 | 3.8 | 0.26 | 1.36 | 98.0 |
| 150 | 0.20 | 30.1 | 0.45 | 12.2 | 87.0 | 0.24 | 4.2 | 0.25 | 0.84 | 98.9 |

Phase composition during the selective reduction of slag



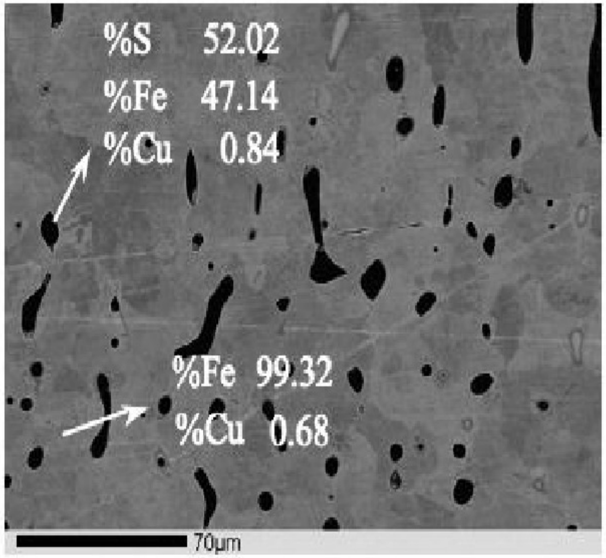
# Main Metals Recovery: Iron



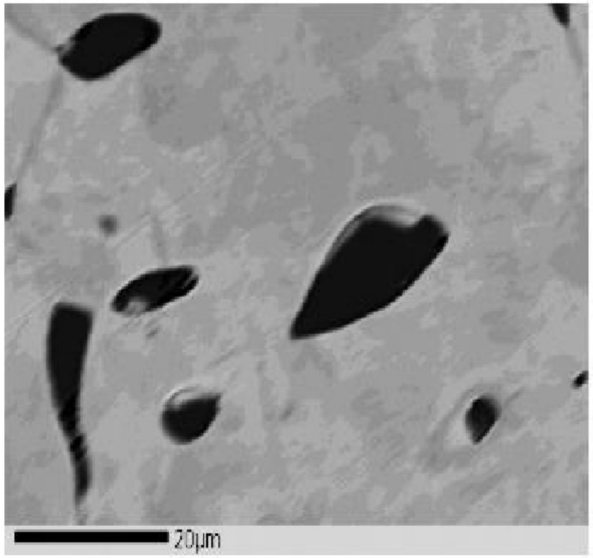

**Microstructure of metal and final slag phases for (a) lower part of the m.a., (b) central part of the m.a., (c) upper part of the m.a. in contact with the s.p., (d) final s.p. (m.a. = metallic alloy, s.p. = slag phase)**

# Main Metals Recovery: Iron

- During the first stage, both copper and iron are reduced and a copper rich metallic alloy is obtained, and, in the second stage, a rich iron alloy is obtained, The copper content decreases to 0.24% in the final slag, and to 0.84% in the final metallic alloy.
- The iron alloy obtained by using 150% of carbon addition was micro-analysed in order to observe the copper-iron interaction.



(a)



(b)

# Summary & Perspectives

- Public & regulatory attitudes to mine wastes have been undergoing a progressive change over time, from the perspective of something of no value to be discarded to that of a potential resource.
- Other factors bearing on this new view include: desire to conserve resources, minimize mine foot-print, avoid air and water contamination, reduce closure and decommissioning costs and eliminate the need for perpetual maintenance of sites.
- Social pressures and economic factors both encourage a search for economic ways to turn wastes into useful commodities.

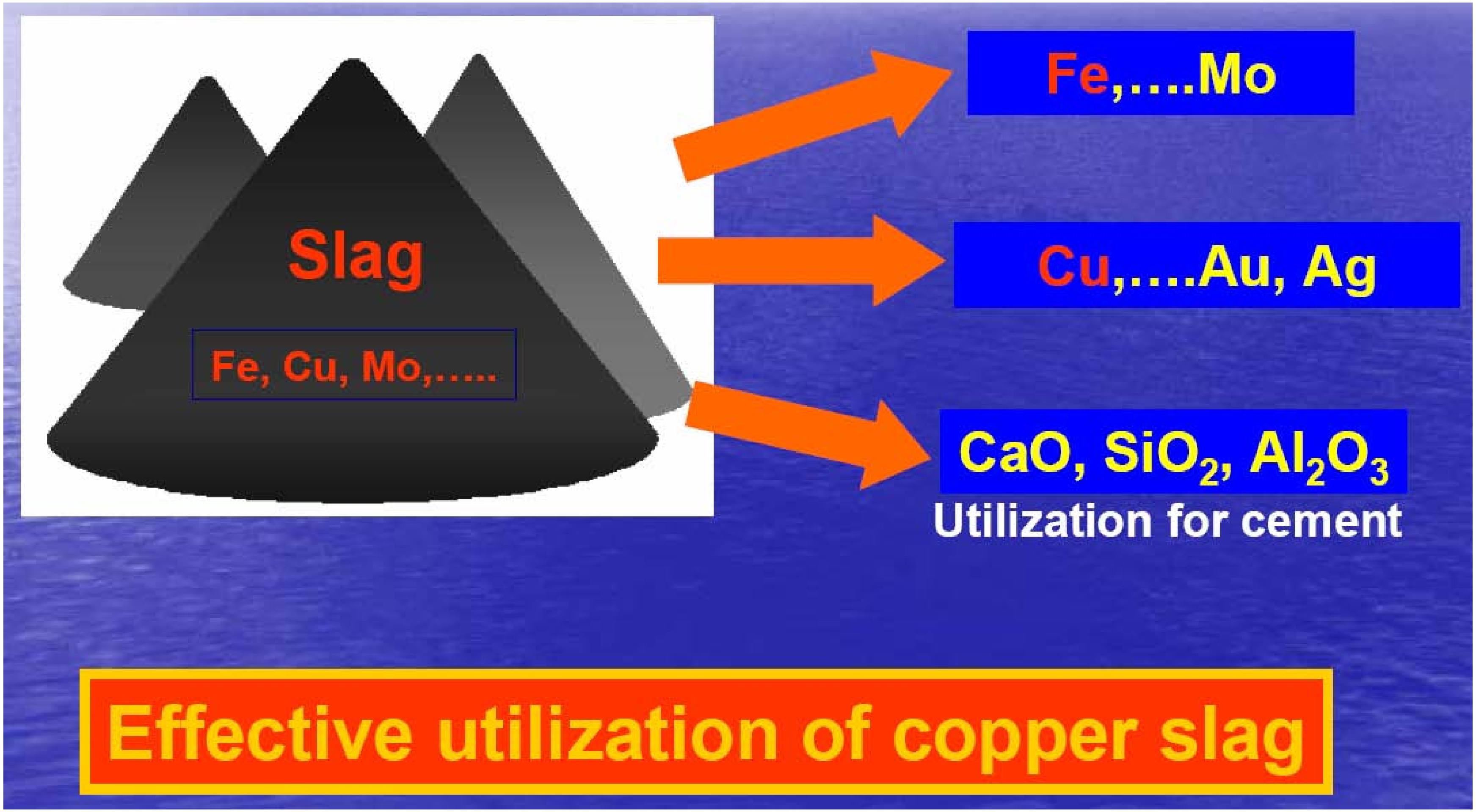
# Summary & Perspectives

- Smelter slag is one class of waste that is a prime target for investigation.
- A primary objective of recent investigations has been to find ways of separating residual pay metals from the bulk of the slag and more particularly from copper smelter slag that contain additionally molybdenum.
- An alternative approach is to cool the slag slowly, grind finely and then recover solid copper metal or sulphide inclusions to be recovered by flotation. Neither technique recovers cobalt or molybdenum if present

# Summary & Perspectives

- Leaching of slag without a preliminary thermal treatment does not appear promising as dissolution of the iron matrix also occurs.
- The authors preference for a possible future pilot scale investigation is fluid bed oxidation with modest fossil fuel addition for temperature control.

# Summary & Perspectives: our purpose !!!



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