Impurity Control in Copper Metallurgical Plants with Special Focus on Arsenic

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Towards Sustainable Metallurgical Processes

• Impurity control- a must in making the Copper metallurgical industry sustainable!

• Development of sustainable processes means innovation

• Meet economic and environmental goals simultaneously

• Innovation needs research collaborations

• This series of seminars is an excellent initiative...
Sustainability Aspects of Impurity Control Technologies-1

• Consider deportment of impurities throughout the whole process flowsheet for best intervention strategy

• Work towards clean impurity-specific separation approaches to minimize valuable metal loss, reagent usage, or intro of new pollutants:
  - SX (residual organics?), IX, Molecular Recognition Technology (MRT), magnetic resins, selective precipitation, Sorption/Adsorption etc.

• Equally important to get enrichment-concentration to facilitate economic recovery and/or disposal
Sustainability Aspects of Impurity Control Technologies-2

- Consider **recovery** if there is demand of the impurity as by-product;
  - Example: Se, Te, Sb, Bi in Cu industry: Can be sold as feedstock for electronic/PV applications

- **Disposal**: sustainable approach; not only removal from solution but also economic disposal in compact stable matrix (unleachable)!
Minor Impurities - Removal

- **As, Sb, Bi**
  - Cu refineries mostly
    - Electrolytic stripping
    - SX for As
    - IX for Sb and Bi

- **Se, Te**
  - Cu, Zn plants
    - Oxidation state (VI vs IV)
    - Cementation with Cu or Ag
    - Sulphide precipitation
    - Reduction (Se)

IBC Bi removal as bisulfate salt (picture above) >200 TPY Bi
Impurity control studies at McGill

- **Arsenic** immobilization as scorodite etc (last 25 years) PLUS

- **Antimony** removal from acidic solutions by precipitation as stable ferric antimonate (2012-2015)

- **Selenium(IV)** elimination from acid plant effluents by reduction (2007-2011)

- **New project** on **Se(VI)** reduction/removal via designing of a photocatalytic-assisted nanocomposite filtration material (2017-

- **Ni** recovery from spent Cu electrolyte by solvent displacement crystallization (1998-2003)

- **Mn** removal by SO2/O2-patented process (1998-2001)

- Impurity control by cementation in Zn plants (**Co, Cd**) (1996-2002)
Arsenic in the Non-ferrous Industry

- It reports in flue dusts, acid bleed streams, various wastes, autoclave discharge solutions, process solutions-effluents/residues and ultimately tailings.
- Safe disposal (residue stability) much more challenging than its removal from plant streams.
- Leachability/pore water limit: <1 mg/L As.
- But TCLP-type testing not necessarily the appropriate measure when it comes to long term stability!
Hydrometallurgical Arsenic Fixation—Which Method to Use?

>- Depends on arsenic oxidation state and concentration

  - Arsenic retention is favoured when in its V state
  - Various methods available to oxidise As\textsuperscript{III} (not reviewed here; at McGill we have worked with H\textsubscript{2}O\textsubscript{2} and SO\textsubscript{2}/O\textsubscript{2}; see new Barrick work with O\textsubscript{2}/C)

>- Low concentration (<3 g/L As) sources in plant effluents ➔ Ambient T co-precipitation with Fe(III)
>- Arsenic-rich industrial solutions and solid wastes ➔ Scorodite ($\text{FeAsO}_4\cdot2\text{H}_2\text{O}$)

>- Other stabilization methods?
**Arsenic Fixation Methods:** Co-precipitation with Fe(III)

1. **Arseonic-laden effluent**
2. **CaO** → Neutralization → **Fe₂(SO₄)₃**
   - $\text{(Fe/As} \geq 3)$
3. **S/L Separation** → **Solids**
4. **Long-term storage**

**Arsenic-bearing phases:**
- AsO₄⁻⁻⁻FeOOH
- CaSO₄·2H₂O
- FeAsO₄·xH₂O, $x = 2-3$

McGill staged Co-precipitation Circuit: 10 yrs research*

Arsenic Fixation Methods

Arsenic sulphide precipitation from solution

- It can work as bulk As removal method with further treatment, but not as direct viable disposal option
- Precipitate rather poorly crystalline and difficult to separate; difficult to handle reagent
- Not satisfactory for disposal!

- But As-S from pyrometallurgical processing/inert roasting and subsequent melting (@250°C) is reported by JX Nippon MM to be stable (TCLP < 0.2 ppm As)*

*Akira Yoshimura, presentation at CESCO Impurity Seminar, April 2017 in Santiago, Chile
Arsenic Fixation Methods

Production of scorodite (FeAsO$_4$.2H$_2$O)

- Production in **autoclaves** (*i.e.* 140°C < T < 180°C)\#

- McGill research led to the development of **The Atmospheric Process**; this became a commercial reality in Chile in 2012 by ECOMETALES

↑ A variation of atmospheric precipitation based on oxidation forms the basis of the **Dowa Metal Scorodite Process (High As solution)** and **Bioscorodite Process (Dilute As solution)**

↑ Also it can be produced by conversion of amFA to scorodite* → the **Outotec Scorodite Process**


Scorodite Production - The Atmospheric Process

- Supersaturation-controlled process concept*
- Work within “heterogeneous” zone
- Self-seeded in continuous reactors
- “Self-corrected” in case of pH overshooting

*Demopoulos, Hydrometallurgy 96 (2009) 199–214
Laboratory Crystallization

2H₃AsO₄ + Fe₂(SO₄)₃ + 4H₂O → 2FeAsO₄·2H₂O + 3H₂SO₄

NEW-GEN SCORODITE*
→ FREE of GYPSUM!

*Patent application pending
Atmospheric Precipitation of Scorodite

- Well grown solids (20-30 μm)
- Excellent S/L separation & washing characteristics
Atmospheric Scorodite Process Flowsheet* (implemented by Ecometales in Chile)

- Arsenic Sludge
- CaCO₃
- Weak Acid
- Fume Dust
- Iron Source
- As₂O₃ Dissolution and As(III) (Fe(II)) Oxidation
- SO₂/O₂
- Atmospheric Scorodite Precipitation
- Recycle of Seed
- Scorodite Gypsum to disposal
- Leach Residue (optional)
- Recovery of Metal Value
- Polishing
- Copper Cathode
- Arsenic-Free Solution (As < 0.1 mg/L)

*Demopoulos et al., paper in Copper 2003
Arsenic stabilization via Scorodite Production in CHILE!

• The atmospheric scorodite process became an industrial reality after 20 yrs research in 2012!
• ECOMETALES – a subsidiary of Codelco – operates a 5,000 TPY As fixation plant in Northern Chile

➢ Ecometales Product: scorodite (1/3)/gypsum (2/3) mixture*

Dowa Scorodite Process*

The process was tested at a demonstration plant (30 t/month of As fixed as scorodite) in Dowa’s copper smelter site in Kosaka—refer to Dowa presentation.

Scorodite Stability

- Scorodite passes EPA’s new TCLP test limit of 1 mg/L As involving testing @ pH 5 for 20 hr

- What about its long term dissolution kinetics over a wider range of pH and ORP?

- Note that not all scorodites are equal!

Scorodite solubility data as a f(pH)

Figure from Bluteau & Demopoulos, Hydrometallurgy, 2007.
As release from atmospheric scorodite as a function of redox potential*

- pH 7 CaO and gypsum saturated
- Significant release when \(E_h < 150\text{mV}\)

*Cesar Verdugo, Gustavo Lagos, Levente Becze, Mario Gómez and George Demopoulos, Submitted to Hydrometallurgy
Development of scorodite encapsulation technology-the next generation!

- Scorodite’s stability is a function of pH;
- Scorodite unstable under reducing conditions;
- Enhance its stability by encapsulation with inert materials;
- Stabilization/solidification (S/S) of mineral-derived arsenical residues (including scorodite) using cement as in “Jarofix”) not appropriate.

→ PERFECT FOR INTEGRATION WITH OUR NEW GYPSUM-FREE SCORODITE PROCESS!
Metal phosphates (AlPO₄·1.5H₂O, and Ca₅(PO₄)₃OH,F)

- Aluminum hydroxyl gels

Encapsulation materials:

- Metal phosphates (AlPO₄·1.5H₂O, and Ca₅(PO₄)₃OH,F)
- **Aluminum hydroxyl gels**

**Stabilization technology based on encapsulation***

Aluminum hydroxyl gels

Aluminum hydroxyl gels

Aluminum Salt Solution + Base → Aluminum hydroxyl gels

Stabilizing scorodite by mineral coating!

Naked scorodite → Blending → Ageing → Mineralization

Scorodite → GEL → After blending → After ageing → Mineralized AlOOH coated SCORO
• Enhanced stability!
• Mineralized coatings: Gibbsite, bayerite, and boehmite

**STABILITY OF GEL MINERALIZED SCORODITE:**

33 times reduced As release!
Process flow diagram for industrial application

Atmospheric production of crystalline scorodite

Preparation of amorphous aluminum hydroxyl gel
Final words

- Process selection and design is linked to stability.
- Pay equal attention to method of removal and disposal.
- Encapsulation is expected to provide an additional layer of protection-stability to disposed hazardous impurity compounds.
- Intensify efforts for recovery of impurities that can be sold to other industries (re. Bi, Se, Te etc.).
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THANK YOU!
Atmospheric scorodite stability—recent data

- Scorodite produced at 85°C from 40 g/L As(V) solution
- pH adjusted at 9 with 0.5 M Ca(OH)₂ (avoid NaOH!)
- ORP adjusted (anoxic→70mV vs. SHE or -150mV ORP) with 0.125 M Na₂S

Better stability than even that of hydrothermal scorodite (10 vs. 100 ppm As release)!