Impurity Control in Mineral/Metal Processing/Extraction Processes: Technological Aspects

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Implementation of Sustainable Metallurgical Processes → Why?

- **Sustainability** is an imperative for the continuing exploitation and processing of minerals and metals
- **Green processing**: “It’s how you meet your environmental and economic goals simultaneously”! (P. Anastas, EPA, Uale U)
- Sustainable technologies can inspire the entry of new “blood” in the industry
- Not just small incremental steps; let’s be bold!
- Development of sustainable processes means innovation
- Innovation needs research collaborations
Sustainability Aspects of Impurity Control Technologies

• 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 or disposal
Sustainability Aspects of Impurity Control Technologies-2

• Consider recovery if there is demand of the impurity as by-product;
  ➢ Example: Se (Te) in Cu or Zn 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!)

• Consider: As, Sb, Se, Bi
Bi and Sb in Cu Refinery Electrolyte

- Bi and Sb removal from Cu electrolytes: IX process developed by UBC (D. Dreisinger), installed first at CCR (Montreal)
- Bi and Sb removal from Cu electrolytes: MRT process by IBC
- IBC reports at least 9 commercial Bi removal installations: >200 TPY Bi as bisulfate salt (picture below from IBC literature)
Impurity control studies at McGill

- Arsenic immobilization as scorodite plus (last 25 years)
- Antimony removal from acidic solutions by precipitation as stable ferric antimonate (2012-2015)
- Selenium(IV) elimination from acid plant effluents by reduction (1997-2011)
- New project launched on Se(VI) reduction/removal via designing of a nanocomposite filtration material (2017- )
- Impurity control by cementation in Zn plants (Co, Cd) (1996-2002)
- Bi removal from spent Cu electrolyte by SX (1984-85)
Arsenic in the Non-ferrous Industry

- Present in many non-ferrous sulphidic ores, such as Cu, Au, even U...
- 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!
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\text{III} (not reviewed here; at McGill we have worked with H\text{2}O\text{2} and SO\text{2}/O\text{2}; see new Barrick work with O\text{2}/C)

> Low concentration (<3 g/L As) sources as those found in most mineral processing / metal extraction plant effluents ➔ Ambient T co-precipitation with Fe(III)
- Arsenic-rich industrial solutions and solid wastes ➔ Scorodite!

- Other stabilization methods?
Arsenic Fixation Methods

Co-precipitation with Fe(III)*

- Combined with lime neutralization
- Areva’s Uranium Mill in Northern Saskatchewan—best example (strictly regulated by Canadian Nuclear Safety Commission); tailings are disposed (sub-aqueous) in open pit; consistently less that 0.5 ppm As in pore waters

- 10 years research at McGill focusing on circuit optimization, characterization of coprecipitated solids (“arsenical ferrihydrite”? “basic ferric arsenate”? ) and stability evaluation

**Ar嗜固方法**：共沉</p>  

![图解]

**砷 enquick effluent**

CaO → **中和** → Fe₂(SO₄)₃

(Fe/As ≥ 3)

**S/L分离**

**主要固相**：
- AsO₄⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-FeOOH
- CaSO₄·2H₂O
- FeAsO₄·xH₂O, x = 2-3

**不可溶相！**砷浸渍槽。

**长期储存**

**源**：
McGill Mini Co-precipitation Circuit
Arsenic Fixation Methods

Arsenic sulphide precipitation

- 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.
- Published stability/solubility data* indicate high soluble arsenic levels (~40 ppm at pH ~ 2-5 increasing significantly above this pH range)

- Not satisfactory for disposal!

*C. Young and R. G. Robins, paper in Minor Elements, C. Young Editor, SME, p381 (2000)
Arsenic Fixation Methods

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

- Suitable for arsenic-rich solutions (e.g. acid plant effluents) or residues/flue dusts, e.g. As$_2$O$_3$ roaster-off flue dusts etc.

- Case study- Giant Mine As$_2$O$_3$ flue dust (>200kt) time-bomb ($1billion estimate...$)

- Review of methods of production and stability properties
Scorodite Production Methods

- Crystalline scorodite can be produced in autoclaves (i.e. 140°C < T < 180°C; use of autoclaves is capital intensive)

- Research at McGill based on the concept of supersaturation control proved that crystalline scorodite can be produced also at atmospheric pressure (i.e. T < 100°C)-The Atmospheric Process; this became a commercial reality first here in Chile in 2012!

- A variation of atmospheric precipitation based on oxidation forms the basis of the Dowa Metal Scorodite Process

- Also it can be produced by conversion of amFA to scorodite; this concept* constitutes the basis of the new Outotec Scorodite Process

- Other (Bioscorodite....)

Hydrothermal precipitation chemistry

Depending on solution composition (mainly Fe(III)/As(V) ratio) and temperature three distinct crystalline phases may precipitate:

- **Scorodite**: \( \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} \)
- **Ferric Arsenate sub-Hydrate (FASH)**: \( \text{FeAsO}_4 \cdot \frac{3}{4}\text{H}_2\text{O} \)
- **Basic Ferric Arsenate-Sulphate (BFAS)**:
  \[ \text{Fe(AsO}_4\)_{1-x}(\text{SO}_4\)_{x}(\text{OH}\)_{x} \cdot (1-x)\text{H}_2\text{O}, \text{ where } 0.3<x<0.7 \]

# The “G-B-D” Fe (III) - AsO$_4$ - SO$_4$ “Phase Diagram”

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Initial Fe(III) / As (V) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>IAsH$^{(10\text{hrs})}$</td>
</tr>
<tr>
<td></td>
<td>IAsH$^{(24\text{hrs})}$</td>
</tr>
<tr>
<td></td>
<td>IAsH$^{(10\text{hrs})}$</td>
</tr>
<tr>
<td>200</td>
<td>BIAS$^{(10\text{ hrs})}$</td>
</tr>
<tr>
<td>175</td>
<td>Sc$^{(2-24 \text{ hrs})}$</td>
</tr>
<tr>
<td></td>
<td>BIAS$^{(2-24 \text{ hrs})}$</td>
</tr>
<tr>
<td>150</td>
<td>Sc$^{(10-24 \text{ hrs})}$</td>
</tr>
<tr>
<td></td>
<td>Sc$^{(10-24 \text{ hrs})}$</td>
</tr>
<tr>
<td></td>
<td>Sc$^{(10-24 \text{ hrs})}$</td>
</tr>
</tbody>
</table>

*Details: IAsH, BIAS, and Sc indicate different phases or conditions.*
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

✓ $2H_3AsO_4 + Fe_2(SO_4)_3 + 4H_2O \rightarrow 2FeAsO_4 \cdot 2H_2O + 3H_2SO_4$

✓ 5 gr seed yields more than 100 g product; 12 hr at 95°C; 40 g/L As(V); pH<1

→ NEW GEN SCORODITE FREE of GYPSUM!
Atmospheric Precipitation of Scorodite

- Well grown solids (20-30 μm)
- Excellent S/L separation & washing characteristics
Polishing Arsenic Sludge

As$_2$O$_3$ Dissolution and As(III) (Fe(II)) Oxidation

Fume Dust

Iron Source

Weak Acid

CaCO$_3$

As$_2$O$_3$ Dissolution and As(III) (Fe(II)) Oxidation

SO$_2$/O$_2$

Leach Residue (optional)

Scorodite Gypsum to disposal

Copper Cathode

Arsenic-Free Solution (As < 0.1 mg/L)

Recovery of Metal Value

Polishing

Recycle of Seed

Atmospheric Scorodite Precipitation

*Demopoulos et al., paper in Copper 2003
**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!

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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 $E_h < 150\text{mV}$

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 $\rightarrow$ 70mV vs. SHE or -150mV ORP) with 0.125 M Na$_2$S

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

![Graphs showing As concentration over time for oxic and anoxic conditions for scorodite and pH and ORP changes over time for Exp. 14: Scorodite naked Anox]
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!
New robust encapsulation system\(\rightarrow\) provides stability under oxic & anoxic conditions\(\rightarrow\) patent pending
Industrial scorodite developments

- First industrial plant in Chile (Ecometales)
- Demonstration plant in Japan (Dowa)
- Patent activity and great industrial interest

- Ecometales - subsidiary of CODELCO - operates a 5,000 t/yr As fixation plant in Northern Chile since 2012
Arsenic stabilization via Scorodite Production in CHILE!

• The atmospheric scorodite process became an industrial reality after 20 yrs research in 2012!
• ECOMETALLES – a subsidiary of Codelco – operates a 5,000 TPY As fixation plant in Northern Chile-to visit tomorrow!
Ecometales’ demo plant results

- Feed: 10 g/L As, 20-30 g/L Cu, Fe3O4 as Fe source
- Product: scorodite/gypsum
- Excellent stability!

As-produced scorodite; Final pH 7.2

Consecutive TCLP-like tests on as-produced scorodite

Industrial developments: Scorodite in Japan

Dowa Metals & Mining Corporation developed and tested an atmospheric scorodite process which involves precipitation via oxidation (with sparged O2)* of an acidic FeSO₄/As(V) solution at 95 °C.

Precipitation occurs within the heterogeneous zone reported here: Filippou and Demopoulos, 1997, JOM, Vol. 49, pp. 52-55.


The process was tested at a demonstration plant (30 t/month of As fixed as scorodite) in their copper smelter site located in Kosaka.
DMSP® flowsheet*

Bioscorodite and Outotec Process

**BIOSCORODITE**

- Being developed in the Netherlands by Paques Bio-systems and Wageningen Institute
- Similar to Dowa’s process. Here oxidation is done using air and thermophilic (80 °C) bacteria instead oxygen.
- Slow kinetics...suitable for low As concentrations?
- Stability?

**OUTOTEC SP**

1. S/L problems?
2. Metal losses?
3. Stability of scorodite?
Removal of antimony from aqueous process solutions as stable crystalline $\text{FeSbO}_4$ (Tripuhyte)*

Antimony in the environment: Tripuhyite ($\text{FeSbO}_4$) very stable!

Pourbaix diagram of Fe – Sb – H$_2$O system$^2$ (25°C, 10$^{-6}$ M Sb and Fe).

- Tripuhyite ($\text{FeSbO}_4$)

$\text{Fe}^{\text{III}}$  $\text{Sb}^{\text{V}}$

$^2$ Reproduced from Leverett et al., 2012, Mineralogical Magazine.
Methodology: Aqueous oxidative precipitation with treatment

Antimony(III) salt
\[\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2\cdot\text{xH}_2\text{O}\] + Iron(II) salt
\[\text{FeSO}_4\cdot7\text{H}_2\text{O}\]

\[
\begin{align*}
\text{Sb}^{\text{III}} & \rightarrow \text{Sb}^{\text{V}} \\
\text{Fe}^{\text{II}} & \rightarrow \text{Fe}^{\text{III}} \\
\text{(co–oxidation)}
\end{align*}
\]

1. Filtered precipitate
2. Hydrothermal treatment
3. Calcination treatment
4. FeSbO$_4$ (Reference)

Stability tests
Hydrothermal treatment of precipitate to induce full crystallization/stabilization of tripuhite

Hydrothermal Treatment (Autoclave) → 200°C, 12 hrs

<table>
<thead>
<tr>
<th>Sample type</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unadjusted pH</td>
</tr>
<tr>
<td>Precipitate</td>
<td>87</td>
</tr>
<tr>
<td>Autoclave</td>
<td>0.5</td>
</tr>
<tr>
<td>Reference</td>
<td>0.5</td>
</tr>
</tbody>
</table>

⇒ Excellent stability!
Selenium Elimination

• In 1998, CEZinc developed and implemented a 2-step process to precipitate Se and Hg from weak sulphuric acid stream*.

• The process was difficult to control
• A CEZinc-McGill project was launched in 2007

Dithionite precipitation of Se(IV)*

- Precipitation reaction:
  \[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 2\text{S}_2\text{O}_4^{2-} \rightarrow \text{Se} + 4\text{SO}_2 + 3\text{H}_2\text{O} \]
- Goes to completion (<0.5 μg/L) in less than 1 min
- Formation of red amorphous Se

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The McGill research project solved the mystery of Se leaking!

- Se precipitate resolubilization in contact with mother liquor!

- This led to redesigning of the precipitation/filtration circuit at CEZinc* and the problem solved!

Final words

- A lot of challenges remaining
- 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.)
Acknowledgments

• All past and current graduate students and postdocs whose work was highlighted here
• NSERC: The Canadian Research Funding Agency
• The many companies over the years that supported our research
• Ecometales and the organizers of this seminar!

THANK YOU!
From the Zinc Industry:
- Cobalt/Cadmium Cementation
- Mn removal

From the Cu ER Industry:
- Ni Removal From Spent Electrolyte

APPENDIX: Additional Impurity Control Systems
CEZinc flowsheet
Cobalt cementation

- Zn EW is a “thermodynamic anomaly” as we can deposit Zn in high acid solution with minimum H$_2$ evolution!
- We have to thank the H$_2$ overpotential for that!
- But H$_2$ overpotential can be easily altered (lowered) by the action of minor impurities (electrocatalysts) causing havoc to CE!
Cobalt Cementation

- The CEZinc-sponsored project* considered the effect (on cobalt removal and zinc dust consumption) of different solution constituents and novel activators

An important discovery-the role of Cd

- Small amounts of Cd & Cl in addition to the activators (Cu/Sb) were found to increase the amount of cobalt removed and reduce Zn consumption.
- Optimum results with 15 mg/L Cu, 10 mg/L Cd, 2 mg/L Sb, 3.5 g/L zinc dust, and 85°C.
- CEZinc modified filtration of the first cementation stage (Cd/Cu) to permit a small amount (~10 ppm) of Cd to pass into the 2\textsuperscript{nd} stage hence ensuring optimum results.
The role of activators explained -
the case of Sb

Cobalt removal activity correlated
with $\log K_{OH}$ of activator

Sb/Co cementation mechanism

- Graph showing the correlation between cobalt removal activity and $\log K_{OH}$ for various activators, with a linear trend line and $R^2 = 0.83$.
- Diagram illustrating the Sb/Co cementation mechanism.
Mn Removal

- Important for the treatment Mn-rich Zn concentrates
- Joint CEZinc-McGill research (Q. Wang) led to a patented process making use of SO2/O2*
- \[ \text{Mn}^{2+} + \text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ \]
- Process piloted at CEZinc (work led by Y. Choi of NTC)
- Follow up work at McGill (MEng Vincent Menard) focused on process optimization

Mn precipitation circuit
Process optimization*

- Proper design of the gas/liquid transfer mixer (mass-transfer control) and applied ORP and pH controls are critical for optimum results.

SOLVENT DISPLACEMENT CRYSTALLISATION:

Nickel Sulfate Removal from Cu ER Spent Electrolyte as an energy-efficient alternative to evaporative crystallization*

CONCEPTUAL FLOWSHEET OF SDC TECHNIQUE

Organic Solvent

Recovered Organic Solvent

SDC Reactor

Crystalliser

S/L Separation (Filtration)

Low-temp. Distillation

Aqueous Solution

Wash

Crystallised Product

Dilute Aqueous Phase
SDC vs. EC: NICKEL SULFATE PRODUCT PURITY

- EC final product: NiSO$_4$$\cdot$2H$_2$O with high impurity content;
- SDC can produce electroplating quality crystals (as NiSO$_4$$\cdot$6H$_2$O).

![Graph showing comparison of impurity types and concentrations between EC and SDC.](image-url)
Solvent Displacement Crystallisation:
- NiSO$_4$·6H$_2$O
- Tetragonal, compact crystals
- avg. size: ~ 100 μm

Evaporative Crystallisation
- NiSO$_4$·2H$_2$O
- Irregular, porous particles
- avg. size: ~ 10μm
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)
The End!