

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

George P. Demopoulos*

Department of Mining and Materials Engineering, McGill University

[*george.demopoulos@mcgill.ca](mailto:george.demopoulos@mcgill.ca)

<https://www.mcgill.ca/materials/people/faculty/george-p-demopoulos>

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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)
- Mn removal by SO₂/O₂-patented process (1998-2001)
- Ni recovery from spent Cu electrolyte by crystallization (1998-2003)
- 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^{III} (not reviewed here; at McGill we have worked with H_2O_2 and SO_2/O_2 ; see new Barrick work with O_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?

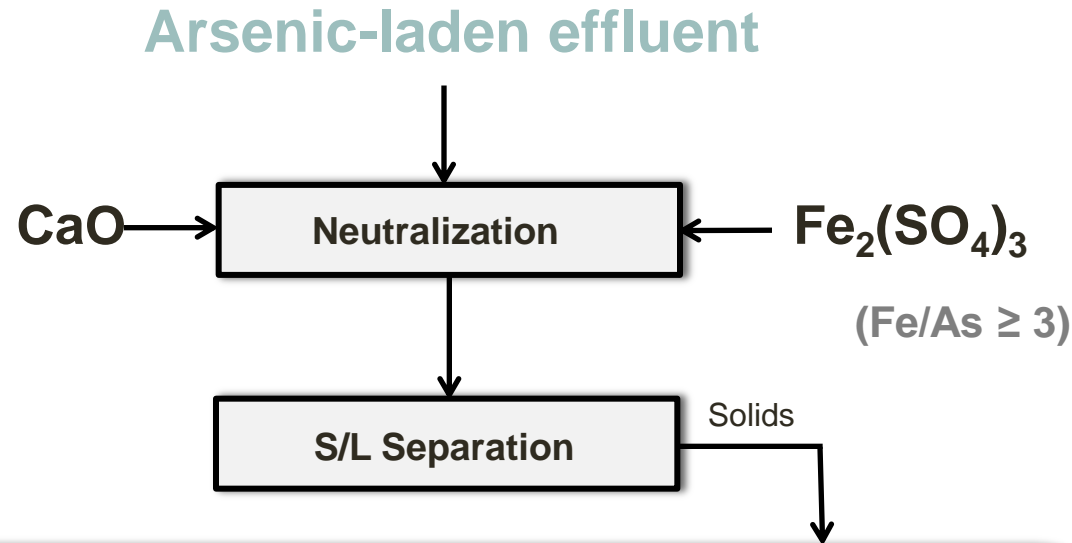
Arsenic Fixation Methods

*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 than 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

*See papers in *Chemosphere*, 151:318-323 (2016) and 138 (2015) 239–246; *Hydrometallurgy*, 151 (2015) 42–50 and 111-112 (2012) 65–72

Arsenic Fixation Methods: Co-precipitation with Fe(III)



Primary solid phases:

- $\text{AsO}_4\text{-FeOOH}$
- $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
- **$\text{FeAsO}_4\cdot x\text{H}_2\text{O}$, $x = 2-3$**

Insoluble Phase! Arsenic sink.

Long-term storage



Arsenic-bearing solids

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!

Arsenic Fixation Methods

Production of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$)

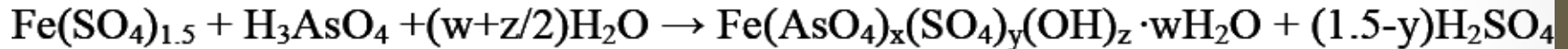
- Suitable for arsenic-rich solutions (e.g. acid plant effluents) or residues/flue dusts, e.g. As_2O_3 roaster-off flue dusts etc.
- Case study- Giant Mine As_2O_3 flue dust (>200kt) time-bomb (**\$1billion estimate...**)
- Review of methods of production and stability properties

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....)**

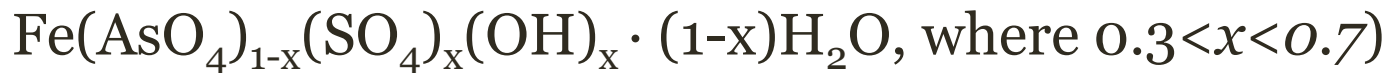
*J.F. Le Berre, R. Gauvin and G.P. Demopoulos, 2008, Colloids and Surfaces A, 131, 117–129.

Hydrothermal precipitation chemistry



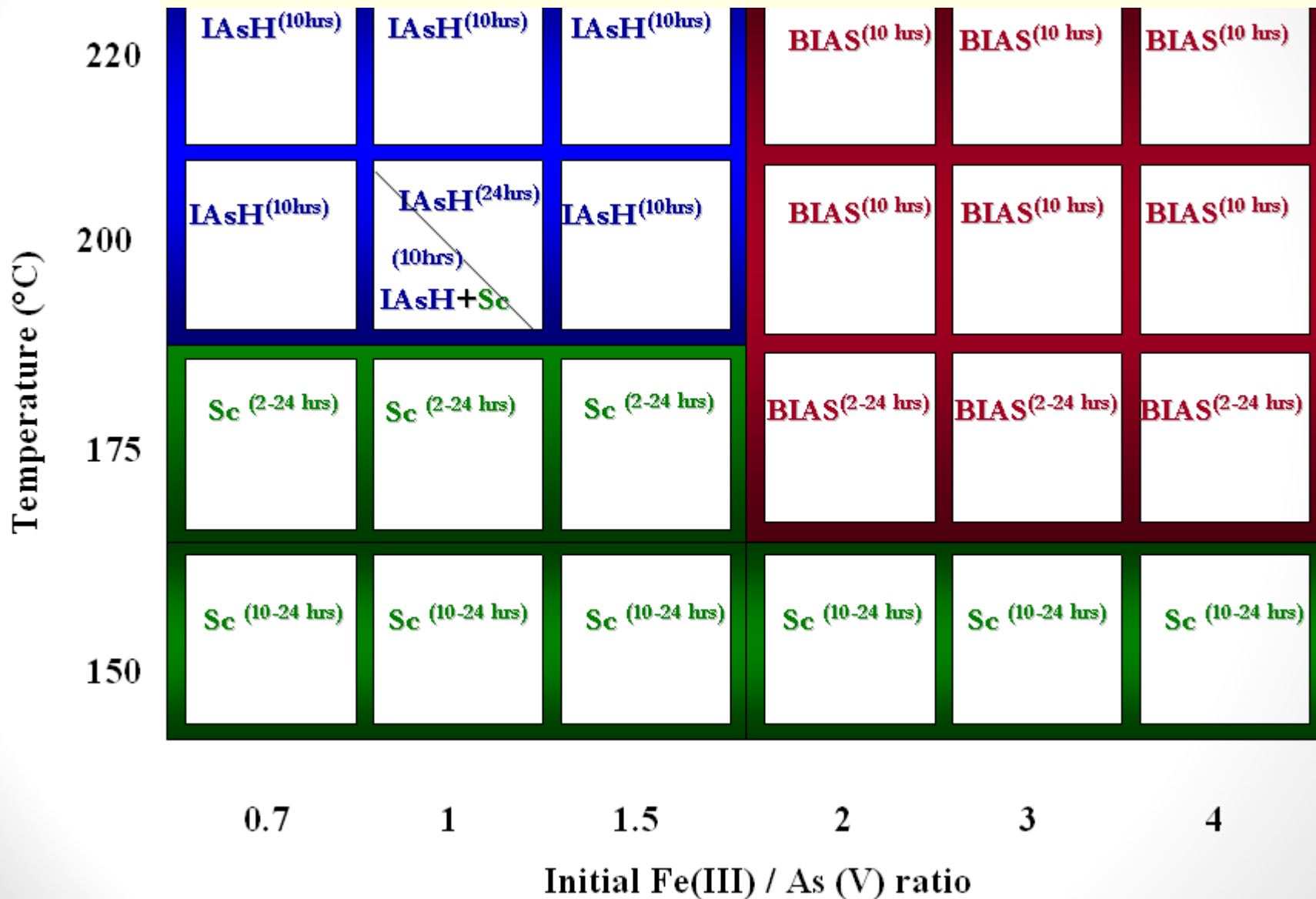
Depending on solution composition (mainly Fe(III)/As(V) ratio) and temperature three distinct crystalline phases may precipitate:

- **Scorodite** : $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$
- **Ferric Arsenate sub-Hydrate (FAsH)** : $\text{FeAsO}_4 \cdot 3/4\text{H}_2\text{O}$
- **Basic Ferric Arsenate-Sulphate (BFAS)**:



*M.A. Gomez, L. Becze, J. N. Cutler and G.P. Demopoulos, 2011, *Hydrometallurgy*, 107, 74–90.

The “G-B-D” Fe (III) - AsO₄ - SO₄ “Phase Diagram”

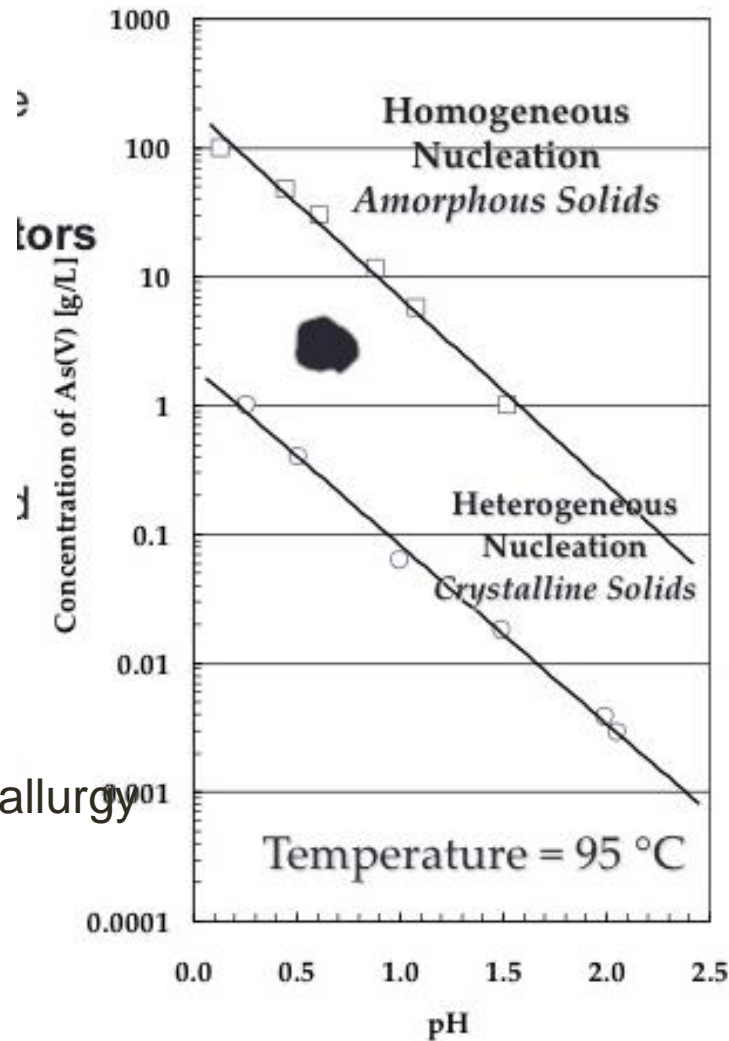


Scorodite Production - The Atmospheric Process

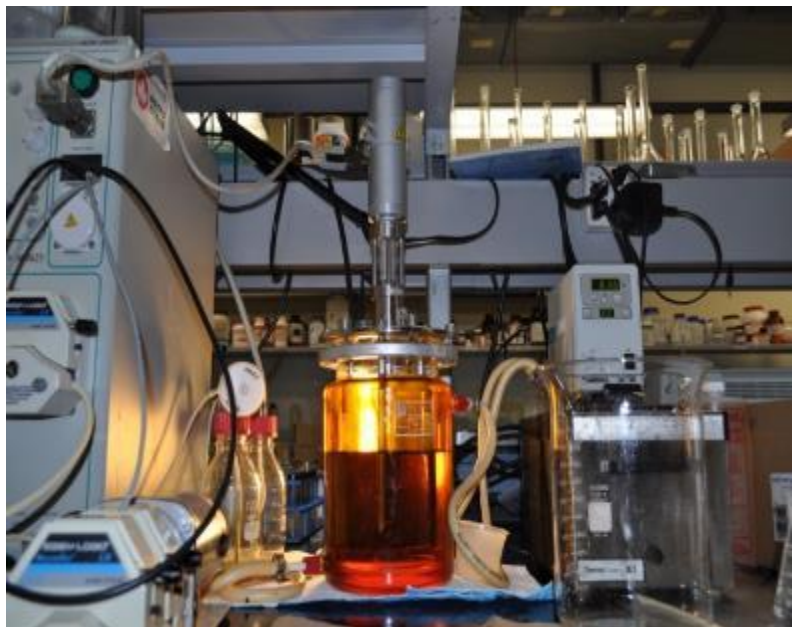
- Supersaturation-controlled process concept*
- Work within “heterogeneous” zone
- Self-seeded in continuous reactors
- “Self-corrected” in case of pH overshooting



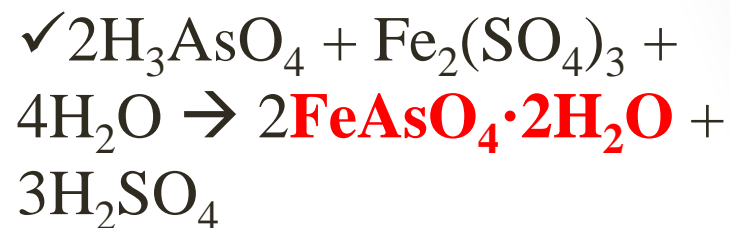
*Demopoulos, Hydrometallurgy
96 (2009) 199–214



Laboratory Crystallization



→ **NEW GEN
SCORODITE
FREE of GYPSUM!**

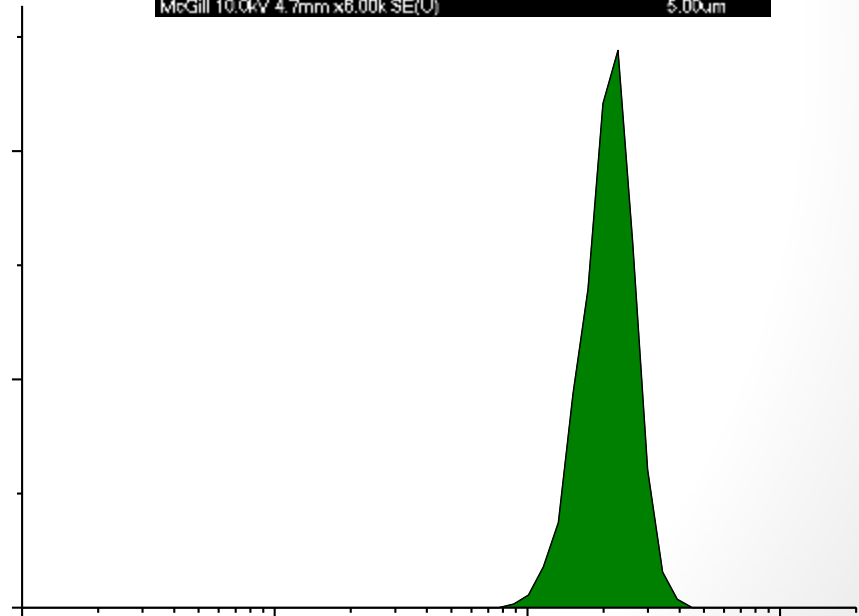


✓ 5 gr seed yields more than 100 g product; 12 hr at 95°C; 40 g/L As(V); pH<1

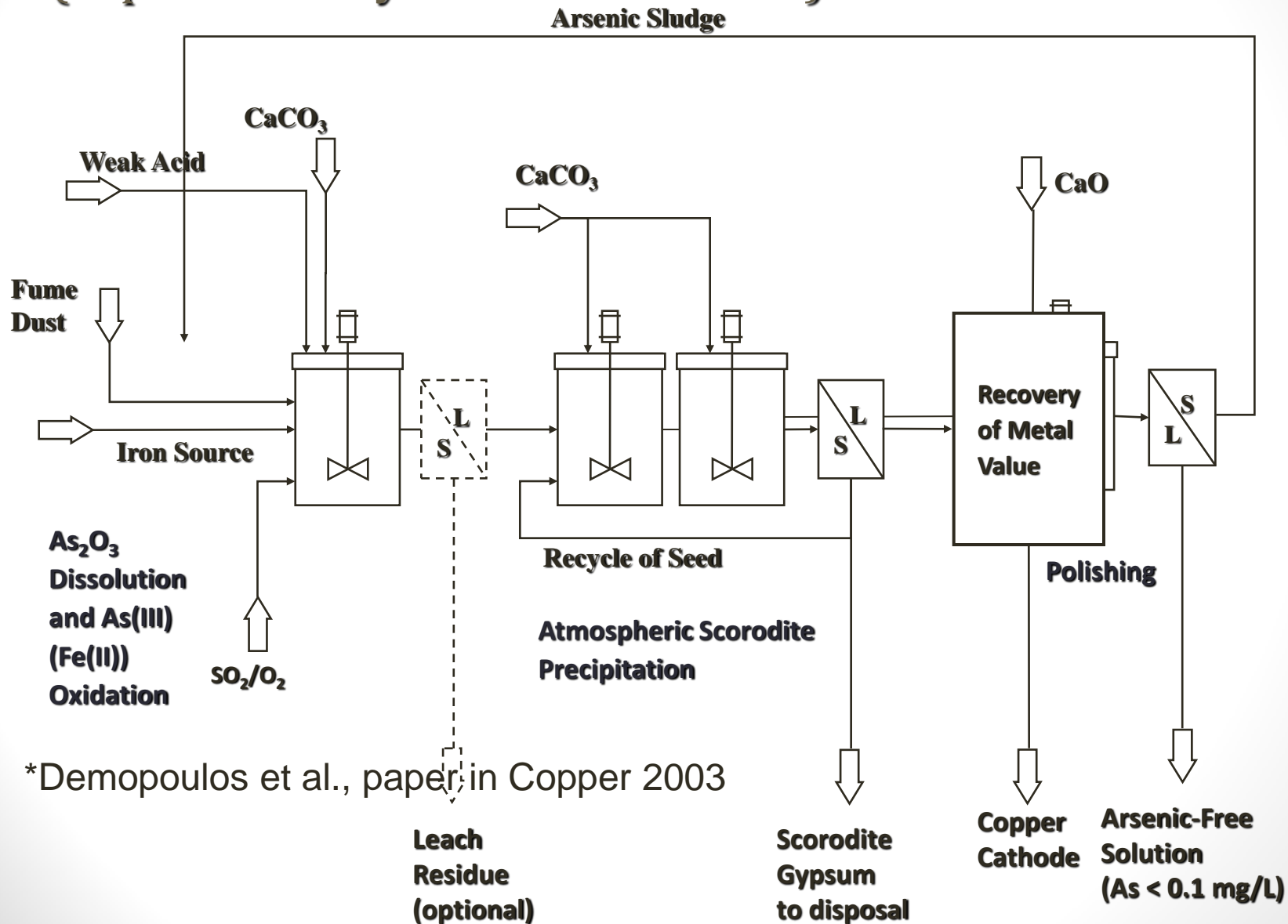


Atmospheric Precipitation of Scorodite

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



Atmospheric Scorodite Process Flowsheet* (implemented by Ecometales in Chile)



*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!**

Scorodite solubility data as a f(pH)

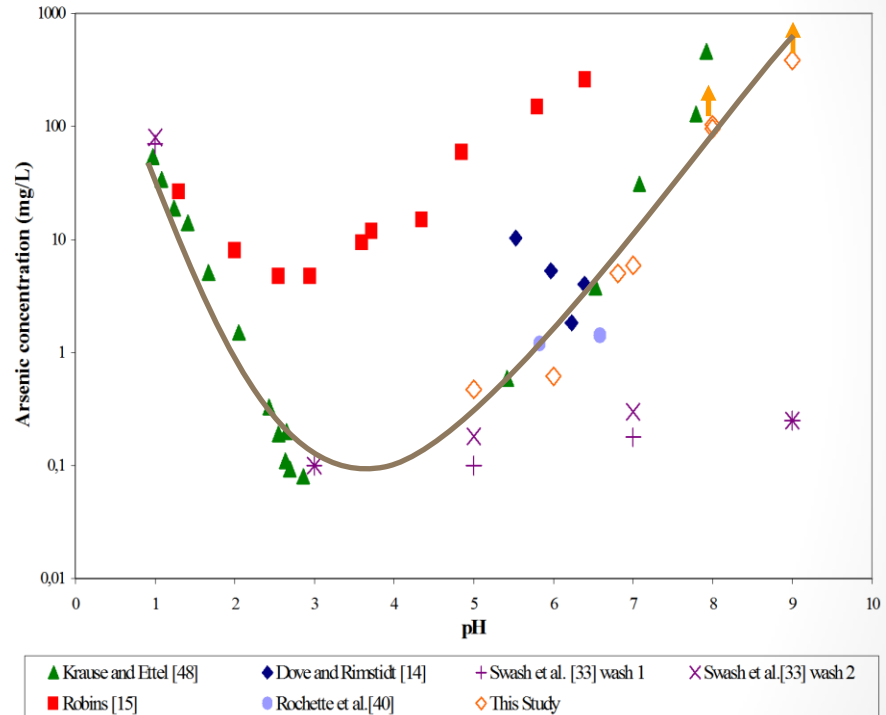
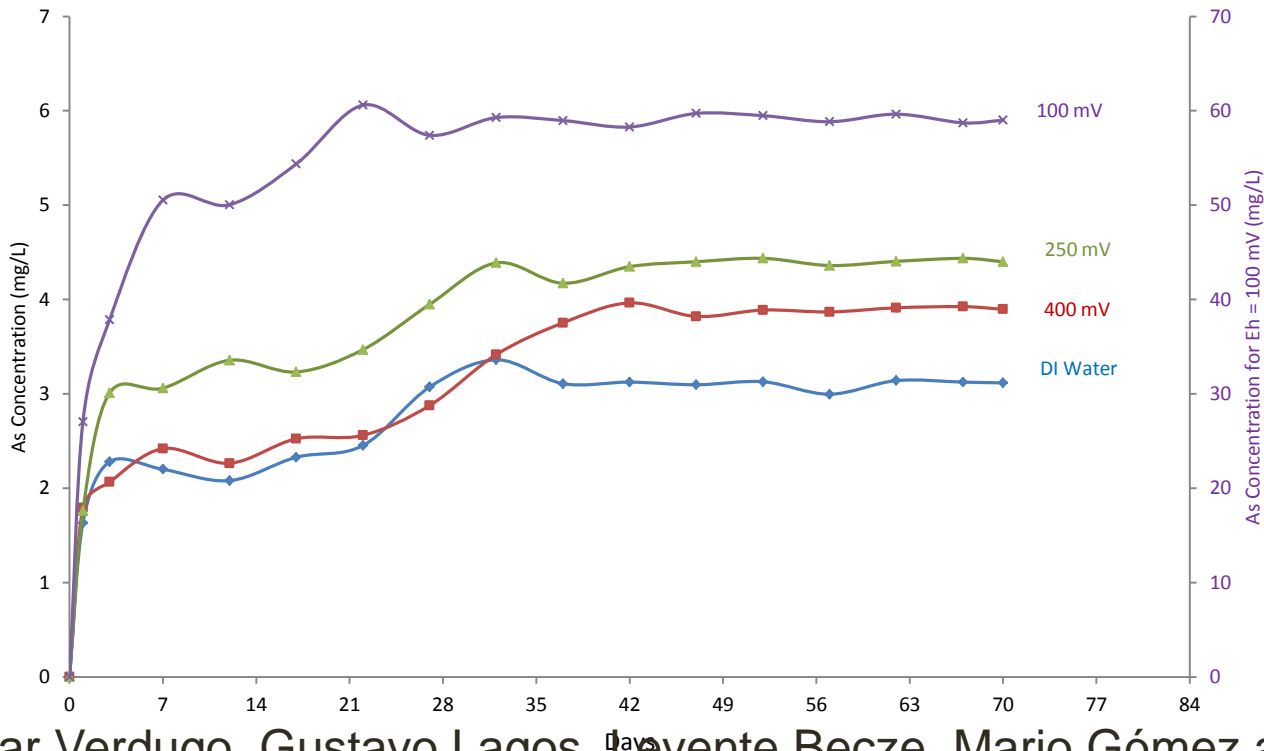


Figure from Bluteau & Demopoulos, Hydrometallurgy, 2007.

As release from atmospheric scorodite as a function of redox potential²⁸

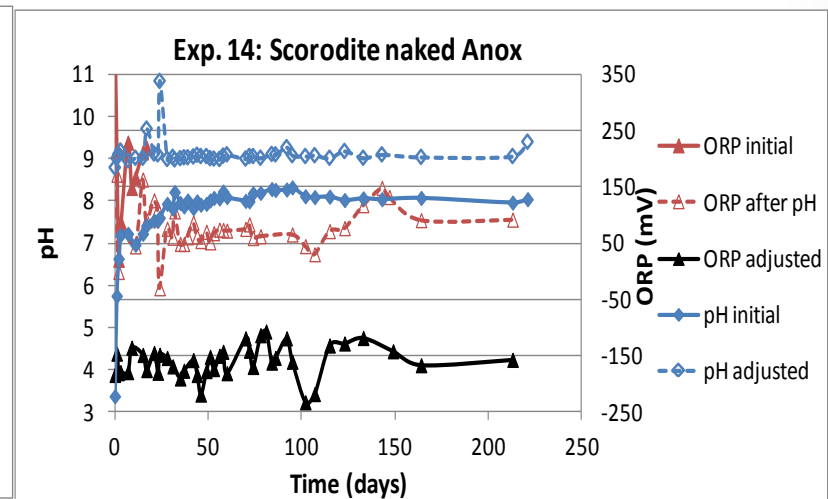
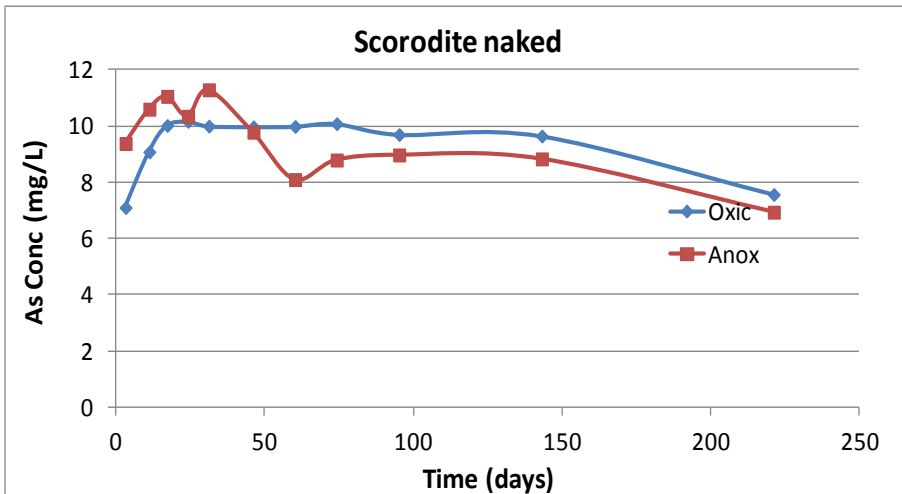
- pH 7 CaO and gypsum saturated
- Significant release when $E_h < 150\text{mV}$



28. Cesar Verdugo, Gustavo Lagos, Levente Becze, Mario Gómez and George Demopoulos, in Proceedings of HydroProcess 2012, Santiago, Chile

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

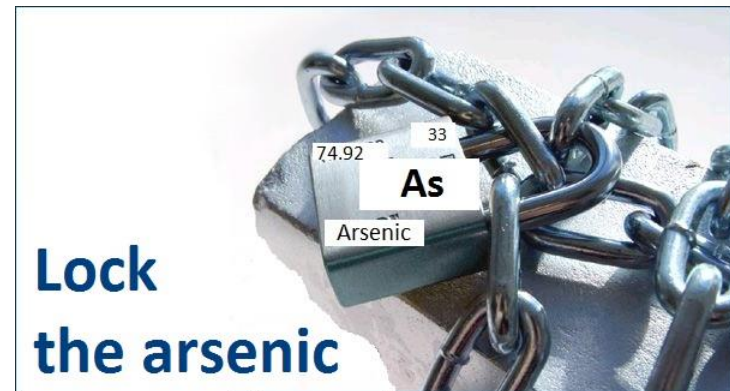


- Better stability than even that of hydrothermal scorodite (10 vs. 100 ppm As release)!

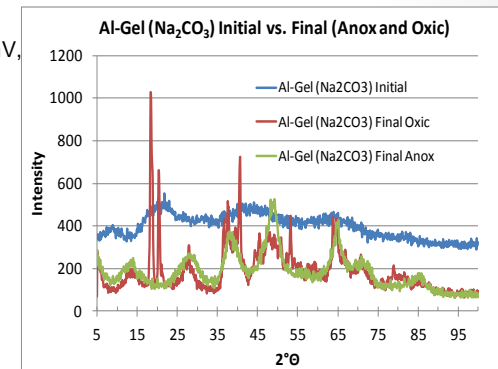
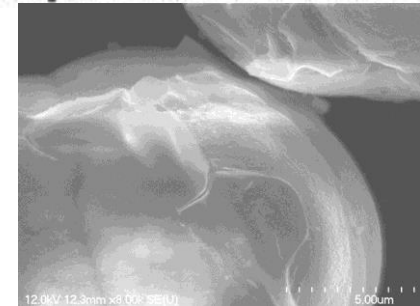
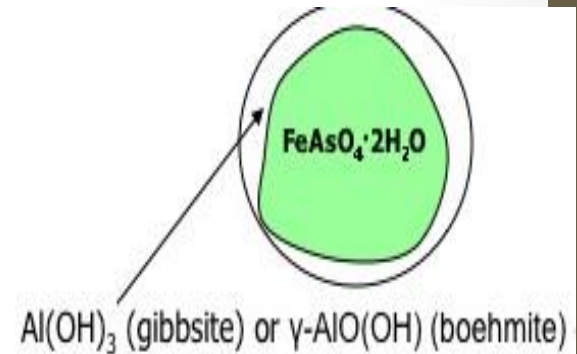
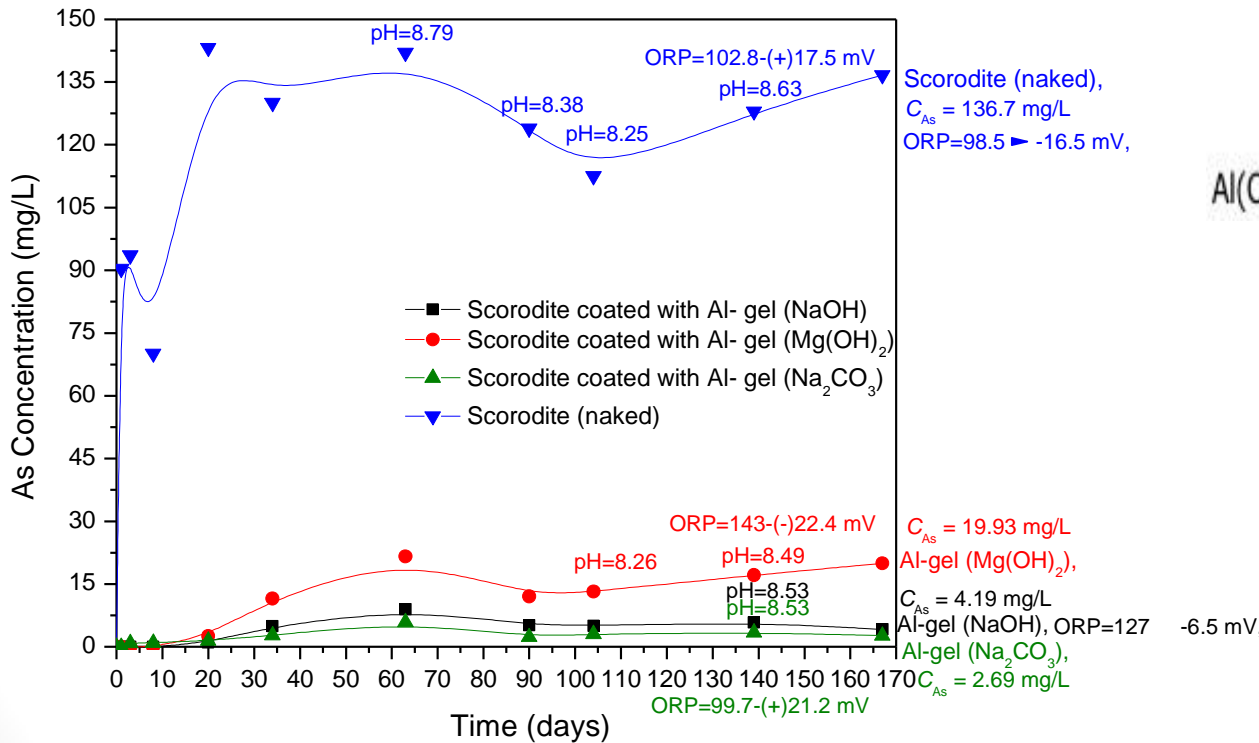
Development of scorodite **encapsulation** technology-the next generation!

- 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 → provides stability under oxic & anoxic conditions → **patent pending**

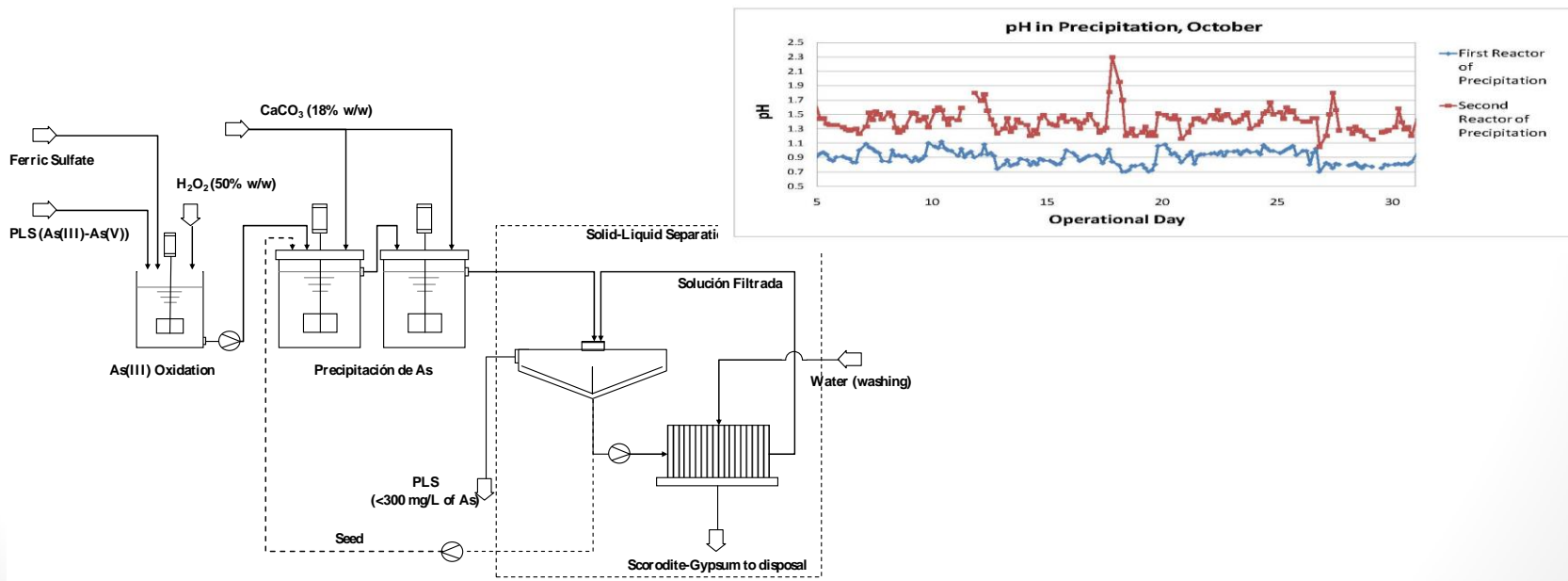


Industrial scorodite developments

- 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

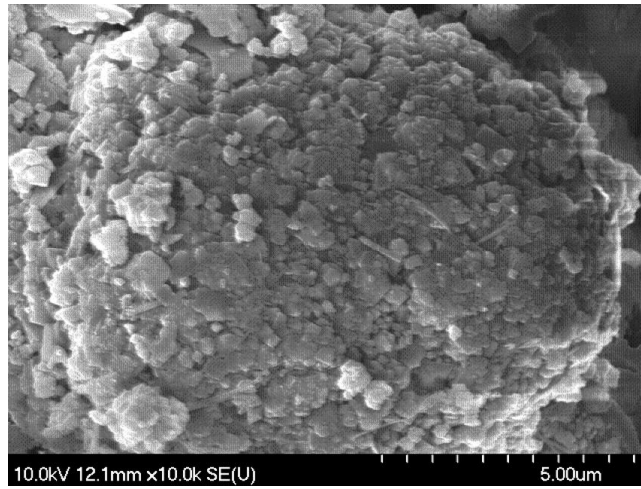
Arsenic stabilization via Scorodite Production in CHILE!

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



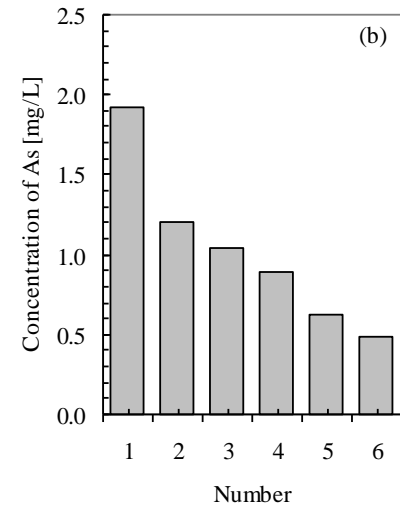
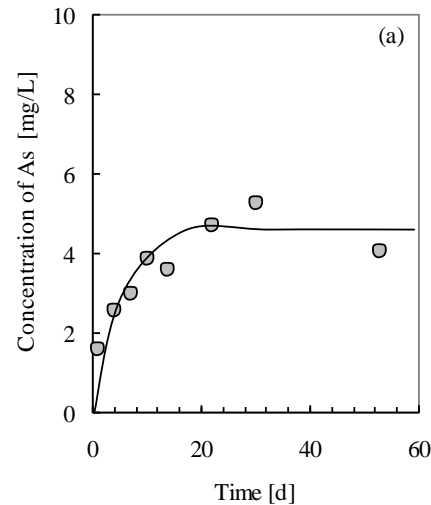
Ecometales' demo plant results¹²

- 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

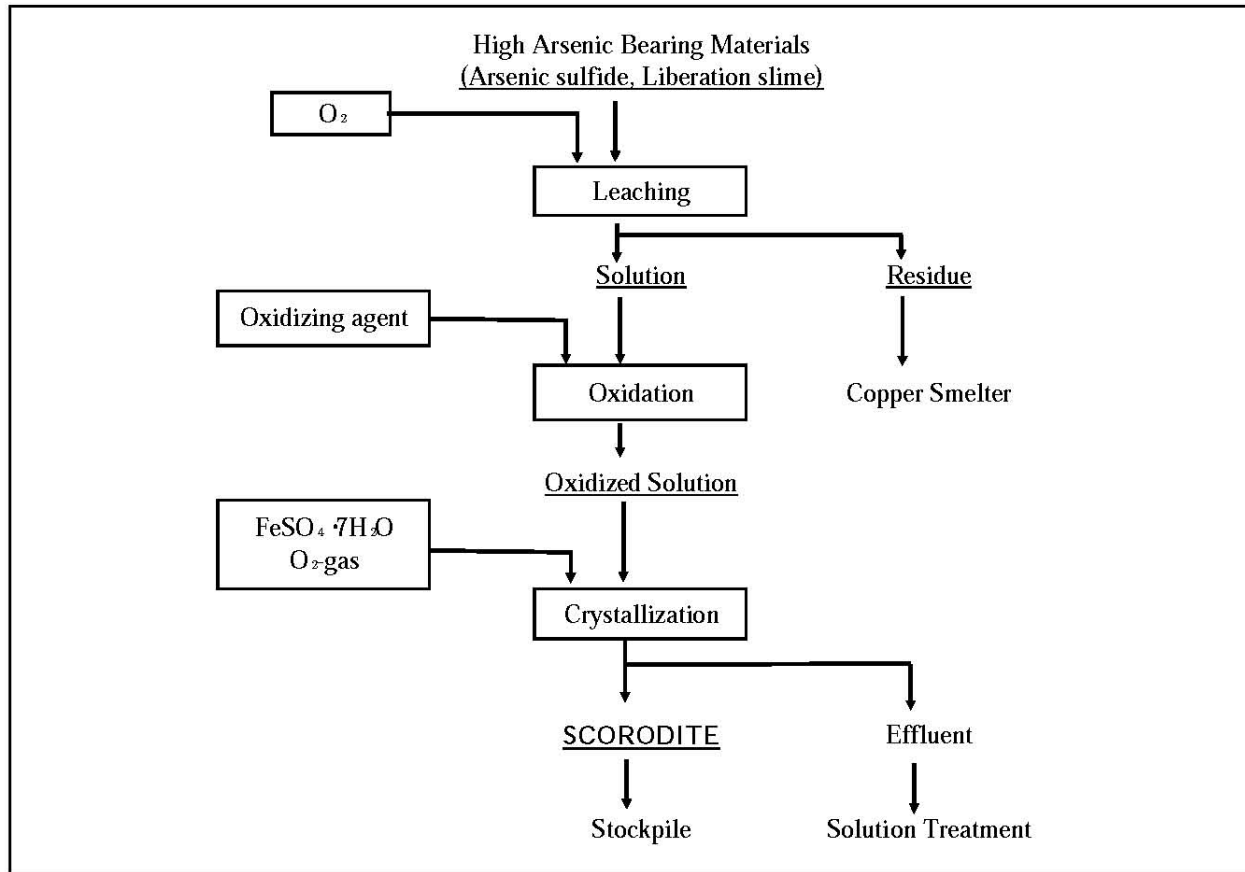


12. F. Lagno, .I. Garcia, C. Ledesma, A. Reghezza, G. P. Demopoulos, L. Becze, M. Gomez and L. Katsarou, paper presented at the HYDROCOPPER 2009

Industrial developments: Scorodite in Japan

- Dow Chemicals & 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.
- * Essentially here supersaturation is controlled via oxidation as demonstrated here: S. Singhania, Q. Wang, D. Filippou and G.P. Demopoulos, 2006, *Metall. Mater. Trans. B*, 37B, 189-197.
- 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*



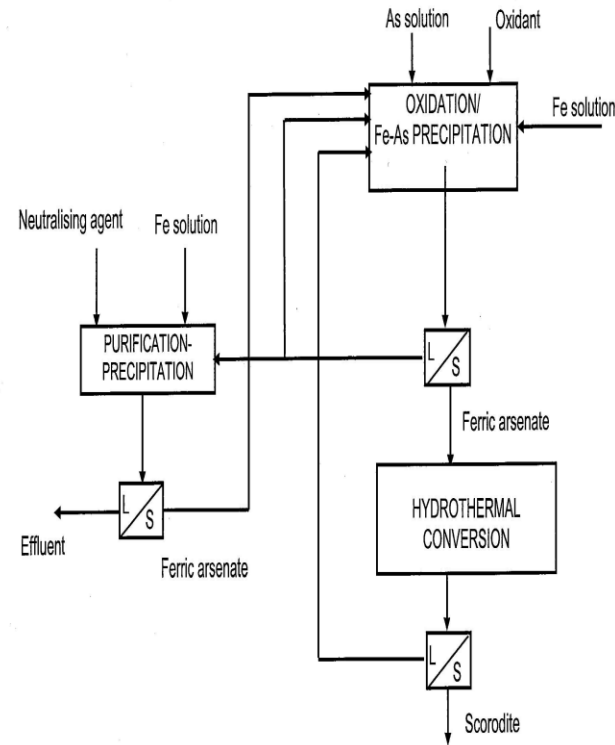
*Kubo et al, paper in Proceedings of Copper 2010, Vol 7-2.

Bioscorodite and Outotec Process

BIOSCORODITE

- Being developed in the Netherlands by Paques Bio-systems and Wageningen Institute
- Similar to Dow'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?

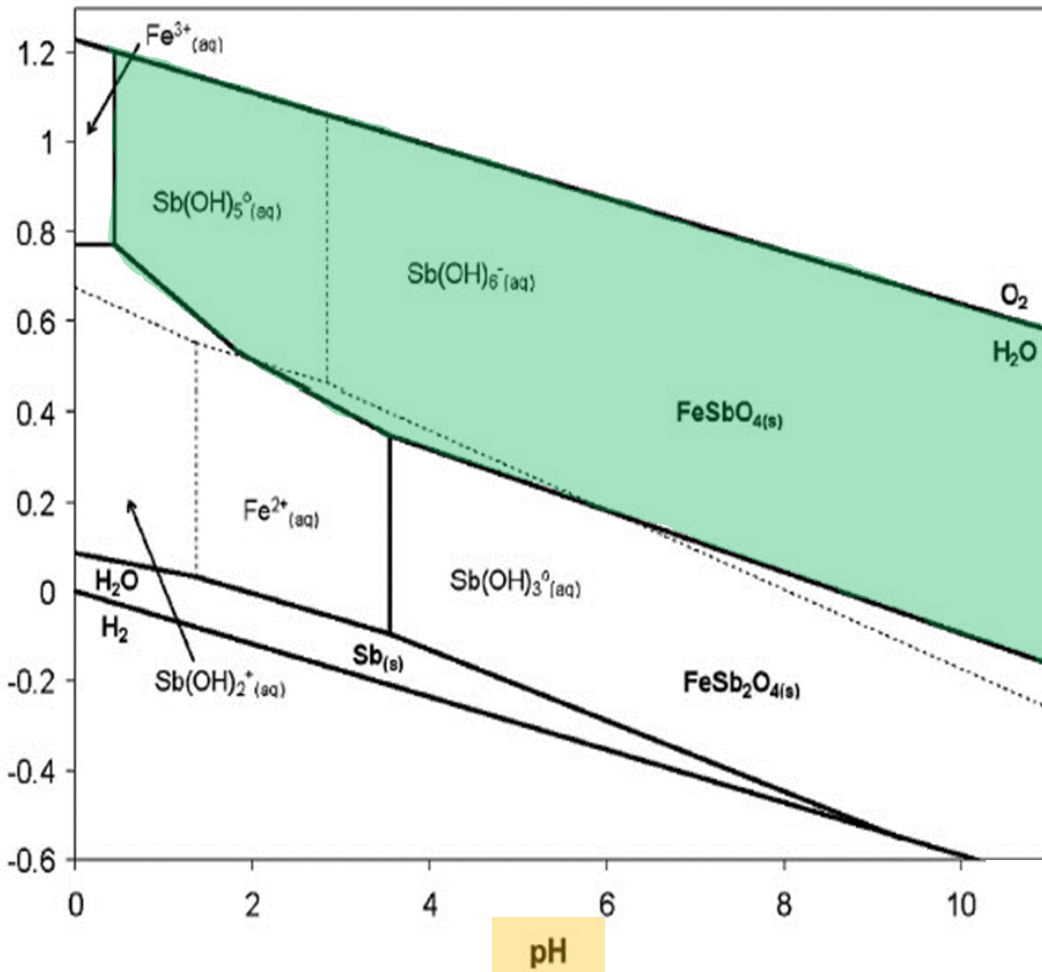
Removal of antimony from aqueous process solutions as stable crystalline FeSbO_4 (Tripuhyite)*

*R. Multani, T. Feldmann, G.P. Demopoulos,
Hydrometallurgy 169 (2017) 263–274



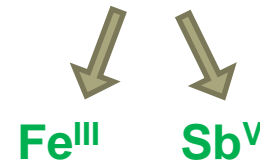
Department of Mining and
Materials Engineering

Antimony in the environment: Tripuhyte (FeSbO_4) very stable!



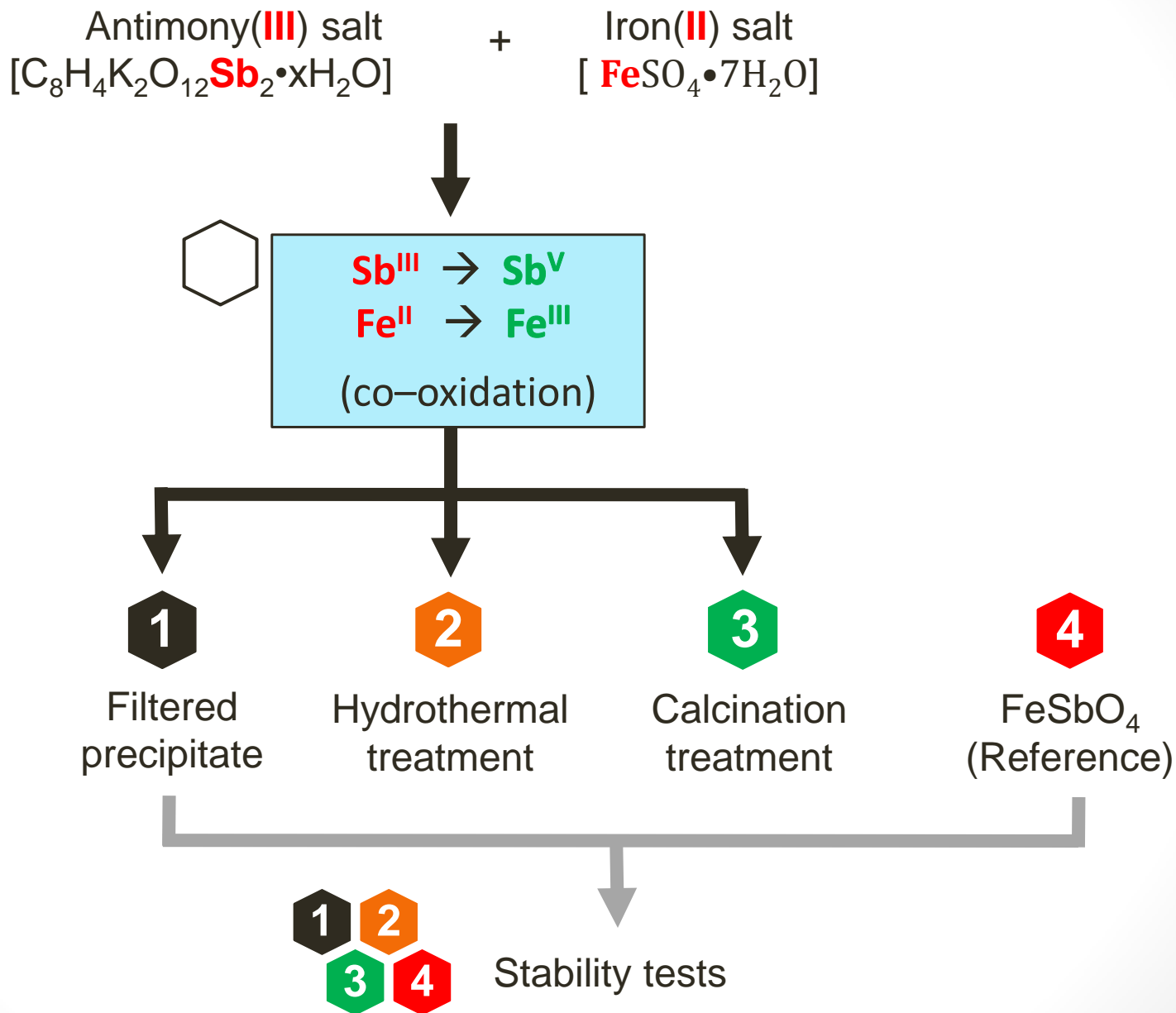
Pourbaix diagram of Fe – Sb – H₂O system² (25°C, 10⁻⁶ M Sb and Fe).

- Tripuhyte (FeSbO_4)



² Reproduced from Leverett et al., 2012, Mineralogical Magazine.

Methodology: Aqueous oxidative precipitation with treatment



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

2

Hydrothermal Treatment
(Autoclave)

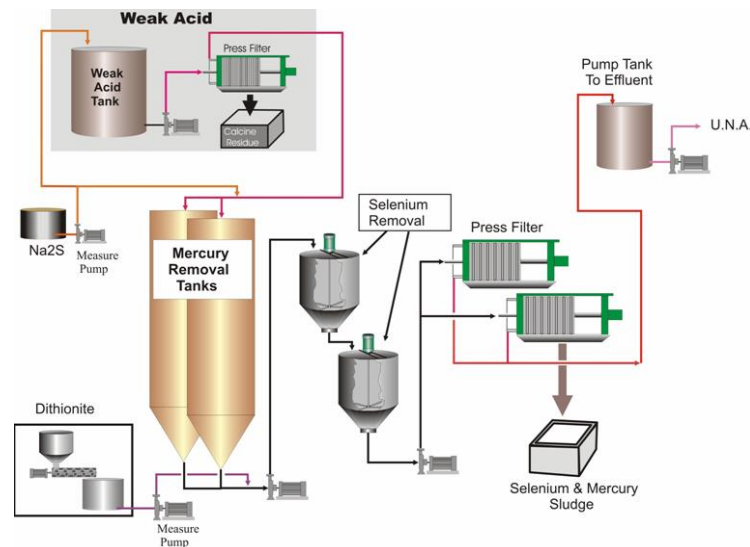
→ 200°C, 12 hrs

Sample type	pH			
	Unadjusted pH	6	7	8
Precipitate	87	114	117	171
Autoclave	0.5	0.2	0.3	0.3
Reference	0.5	0.3	0.4	0.6

➤ Excellent stability!

Selenium Elimination

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

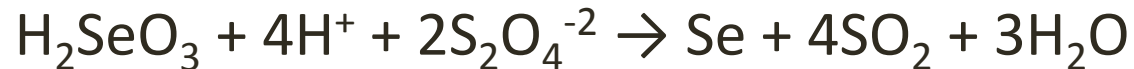


- The process was difficult to control
- A CEZinc-McGill project was launched in 2007

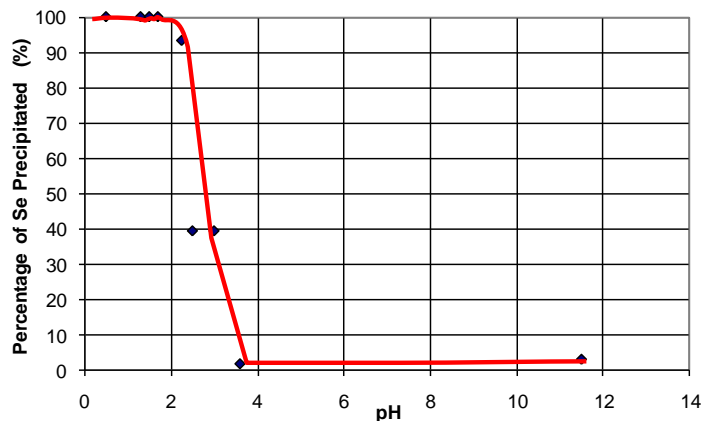
*G. Houlachi, G. Monteith, and L. Rosato, *US Patent*, No, 6,228,270, 2001.

Dithionite precipitation of Se(IV)*

- Precipitation reaction:



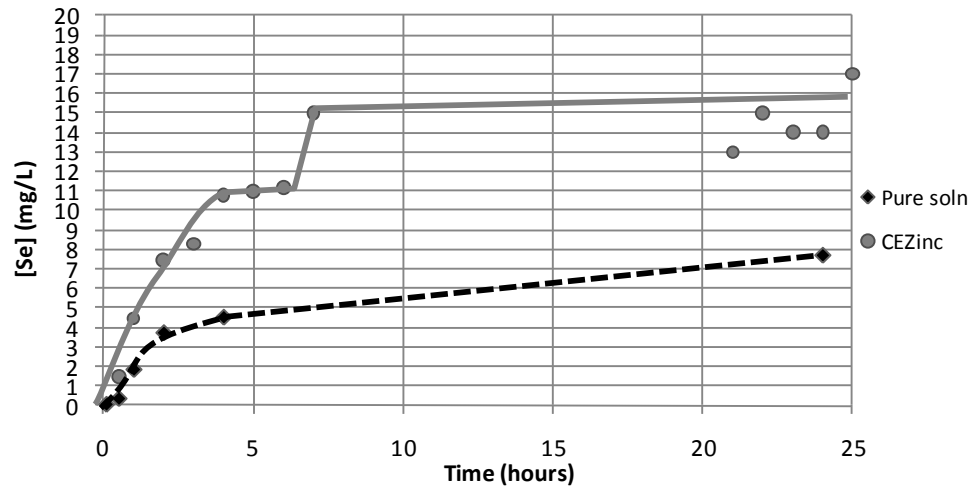
- Goes to completion (<0.5 µg/L) in less than 1 min
- Formation of red amorphous Se



*N. Geoffroy and G. P. Demopoulos, *Ind. Eng. Chem. Res.*, 48 (2009), 10240–10246.

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!

***E. Benguerel**, S. Seyer, **N. Geoffroy**, A. Le Regent, Upgrading the Selenium Removal Process for CEZinc's Acid Plant Effluents, *in Lead-Zinc 2010*, CIM, 2010.

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!

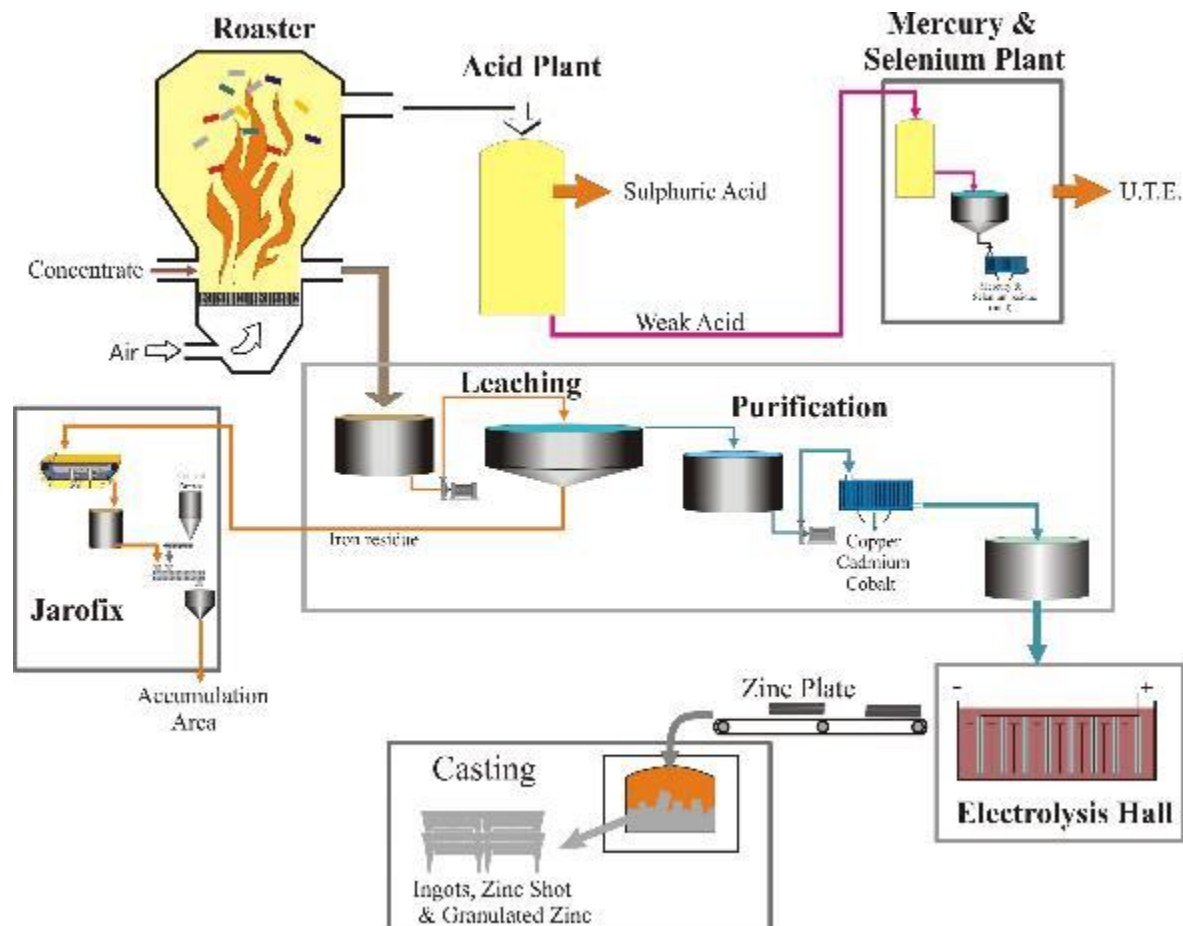
THANK YOU!



- **From the Zinc Industry:**
- Cobalt/Cadmium Cementation
- Mn removal
- **From the Cu ER Industry:**
Ni Removal From Spent Electrolyte

➤ APPENDIX: Additional Impurity Control Systems

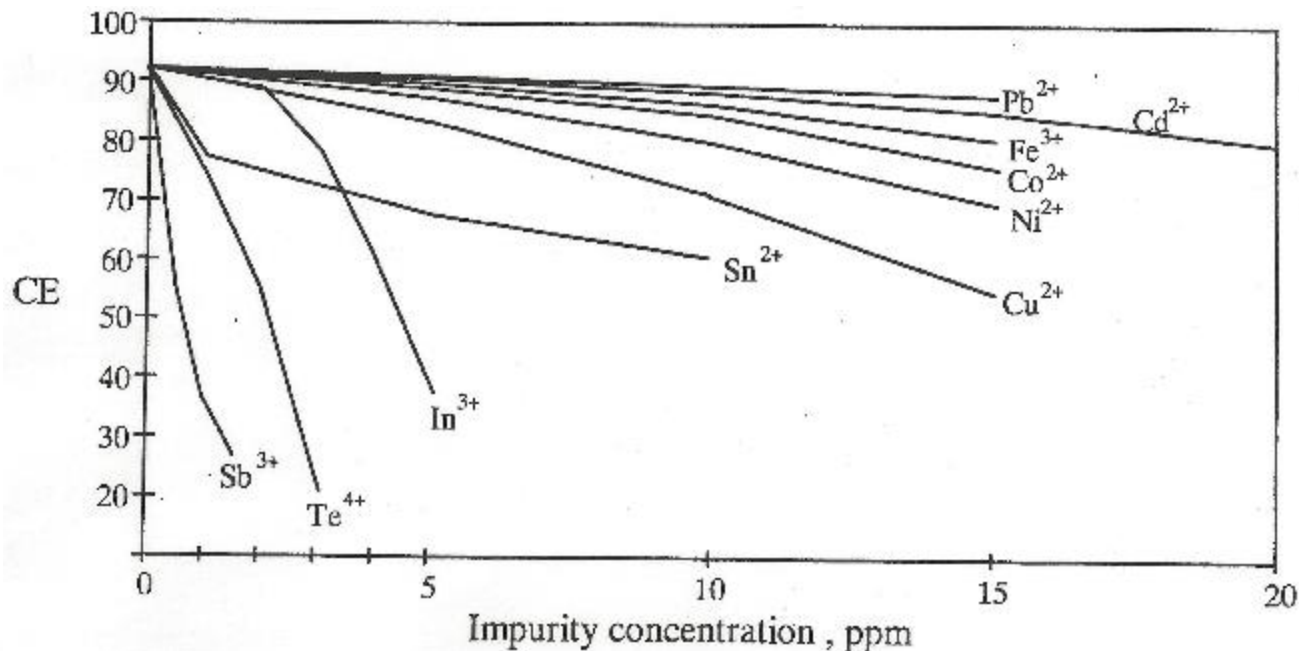
CEZinc flowsheet



Original dans: U:\Ingenierie Publie\Schema de Procede\Usine Generale\Procede General_1 (Anglais) (2013-07-29)

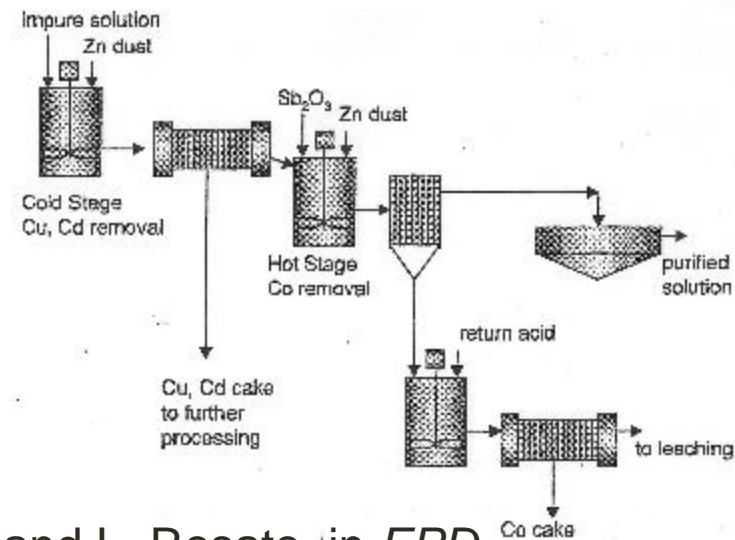
Cobalt cementation

- 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



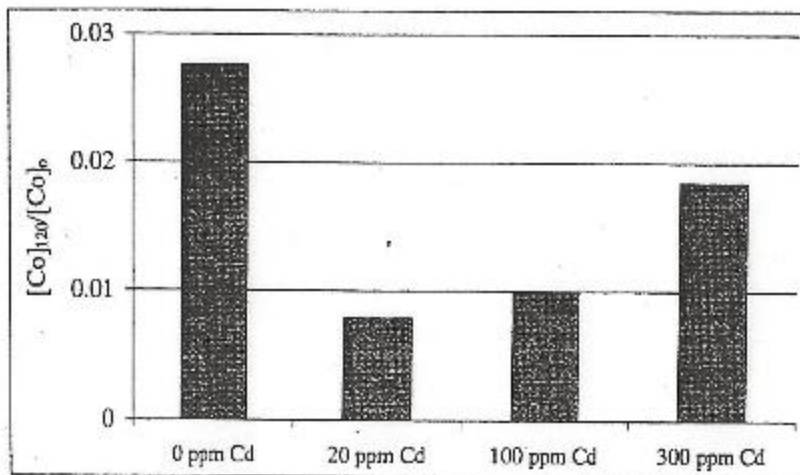
*A. Nelson, G.P. Demopoulos, G. Houlachi and L. Rosato, in *EPD Congress 1998*, TMS.

A. Nelson, G.P. Demopoulos and G. Houlachi, *Can. Metall. Q.*, 39 (2), (2000).

T. Dreher, A. Nelson, G.P. Demopoulos and D. Filippou, *Hydrometallurgy*, Vol. 60, 105-116 (2001).

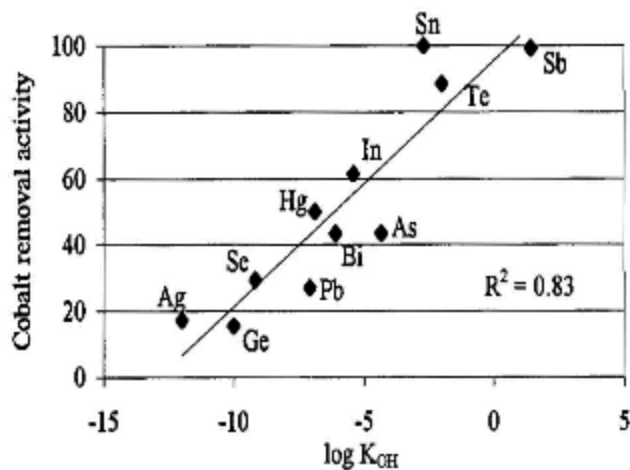
An important discovery-the role of Cd

- 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 2nd stage hence ensuring optimum results.

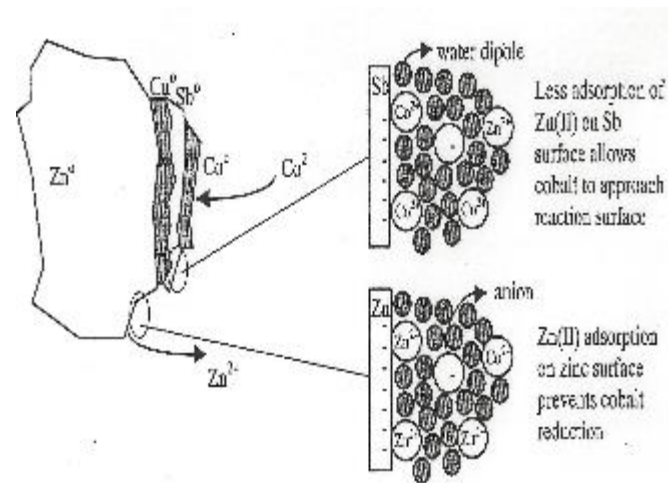


The role of activators explained- the case of Sb

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



Sb/Co cementation mechanism



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

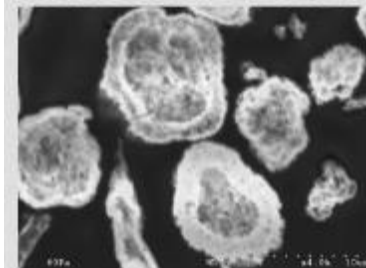
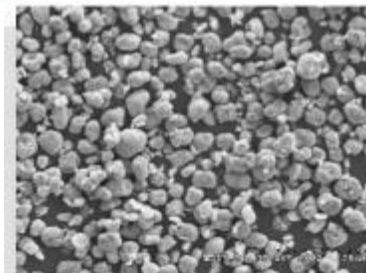
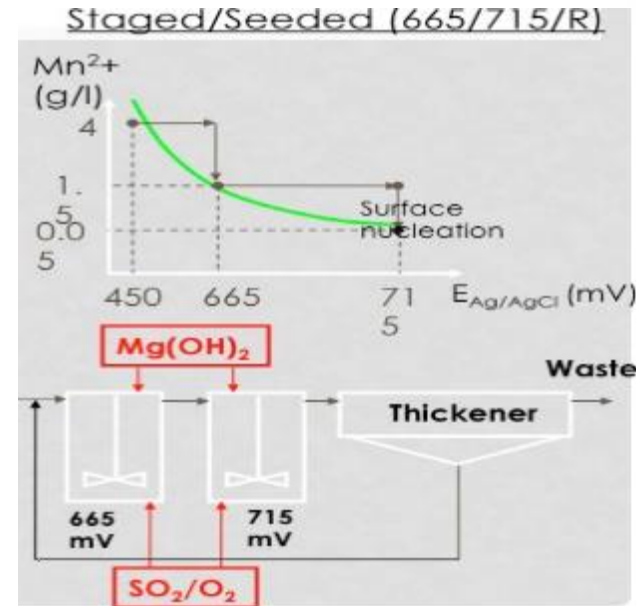
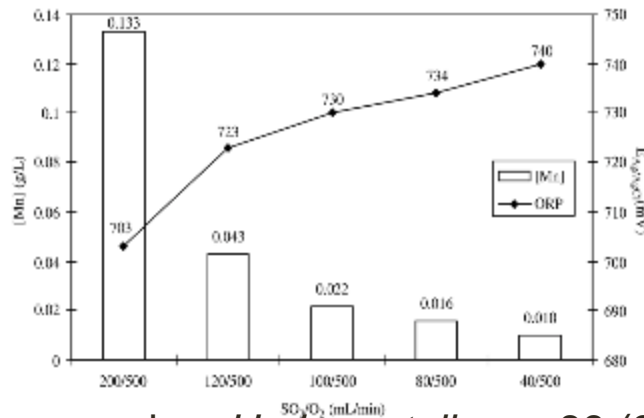
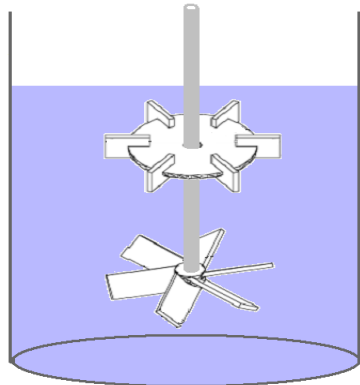
*G.P. Demopoulos, Q. Wang and L. Rosato, A Method for Recovering Manganese from Acidic Sulphate Solutions, *U.S. Pat. No. 6,391,270*, May 21, 2002.

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



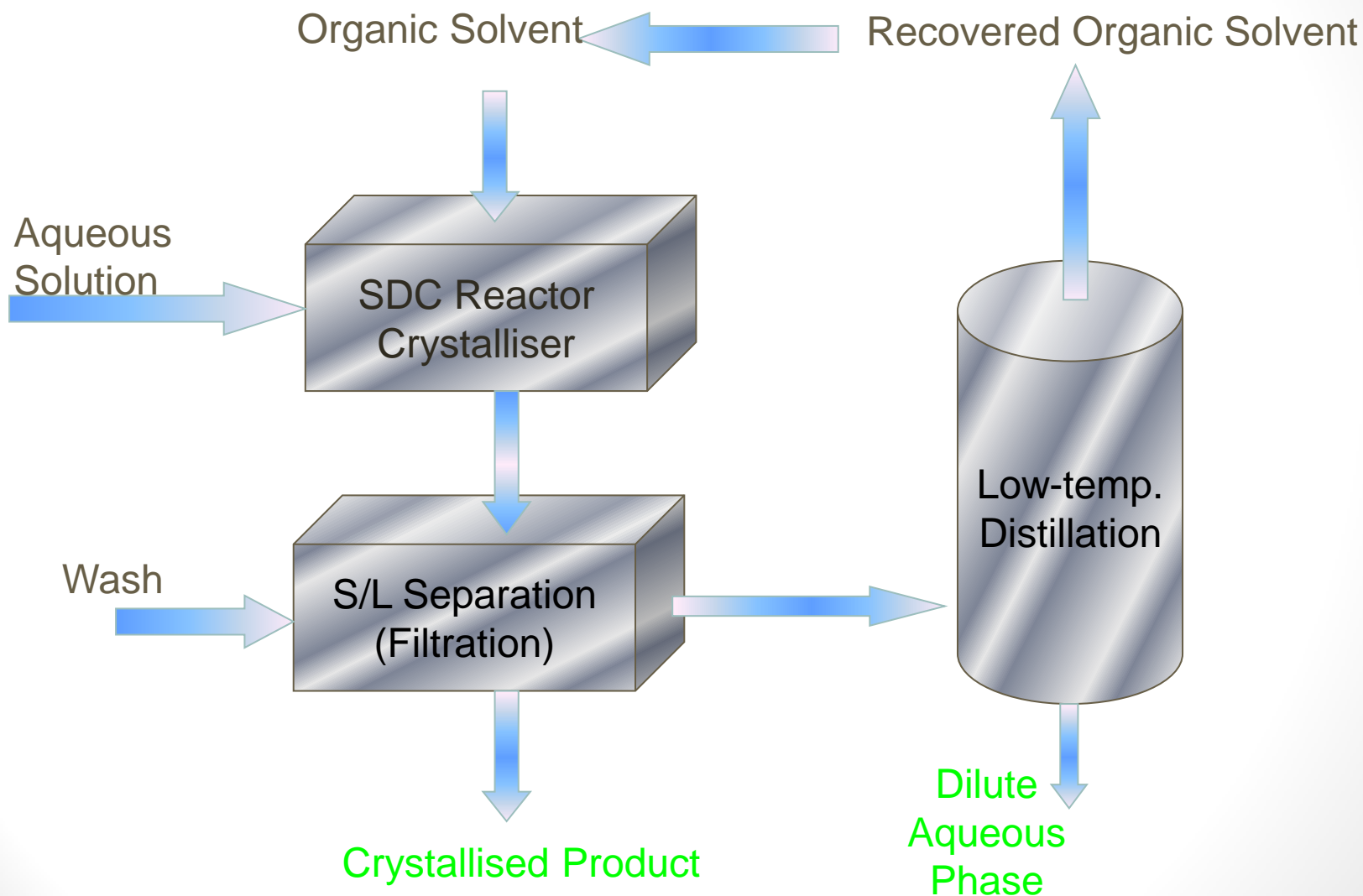
*V. Menard and G.P. Demopoulos, *Hydrometallurgy*, 89 (2007)

SOLVENT DISPLACEMENT CRYSTALLISATION:

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

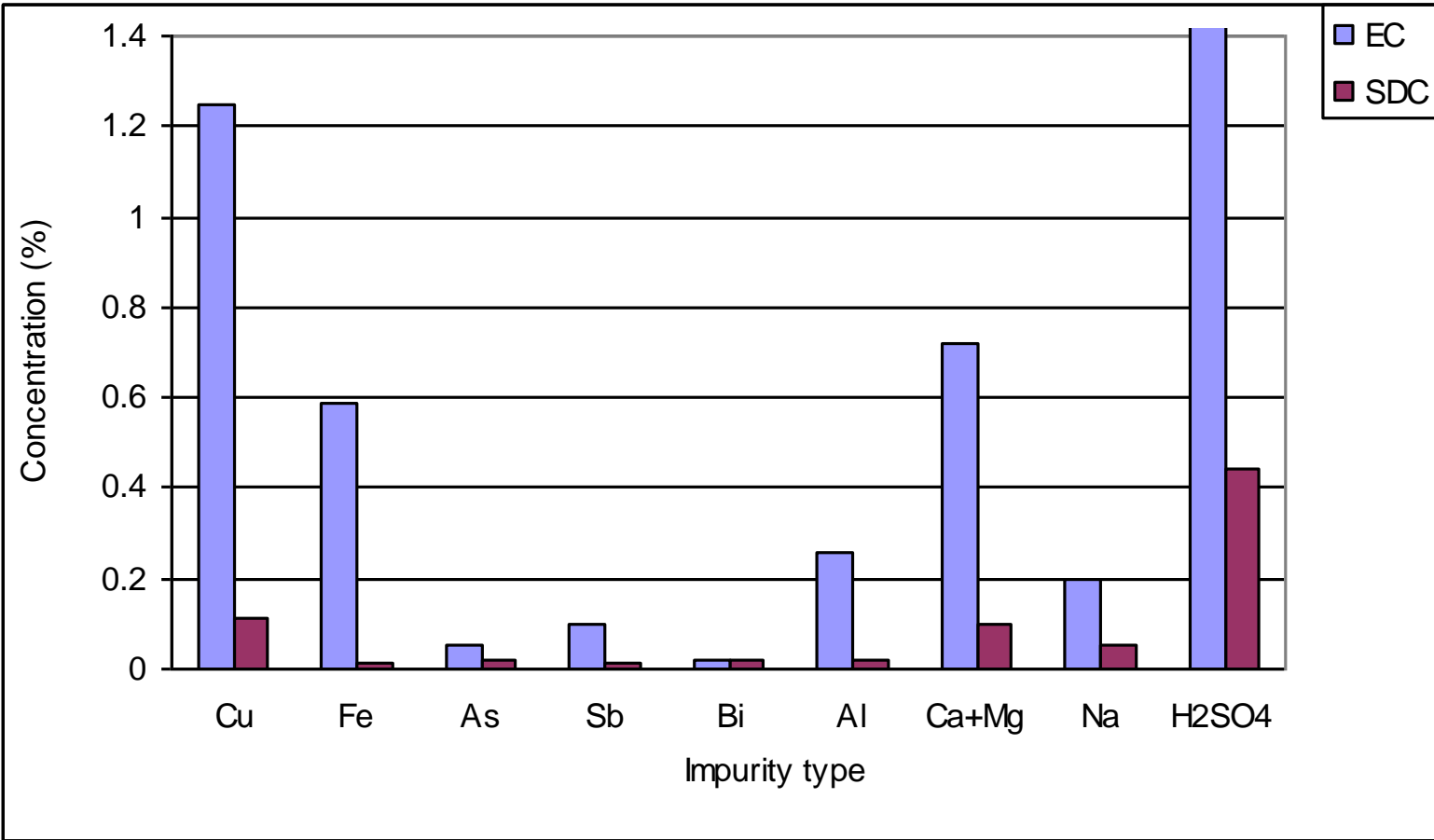
G. Moldoveanu and G.P. Demopoulos, 2002,
JOM, Vol. 54, No. 1, pp. 49-54

CONCEPTUAL FLOWSHEET OF SDC TECHNIQUE

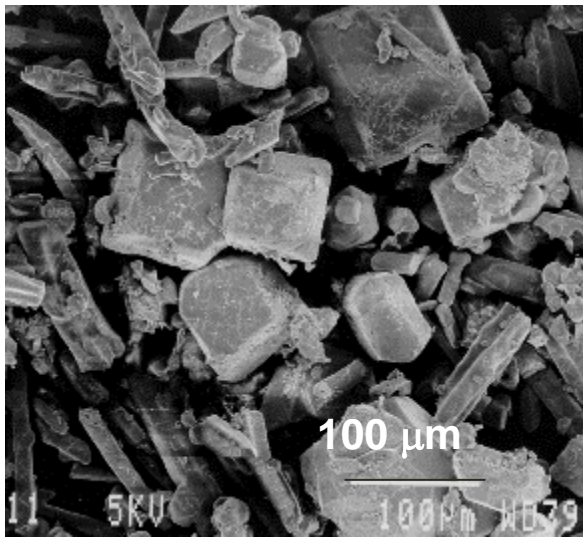


SDC vs. EC: NICKEL SULFATE PRODUCT PURITY

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

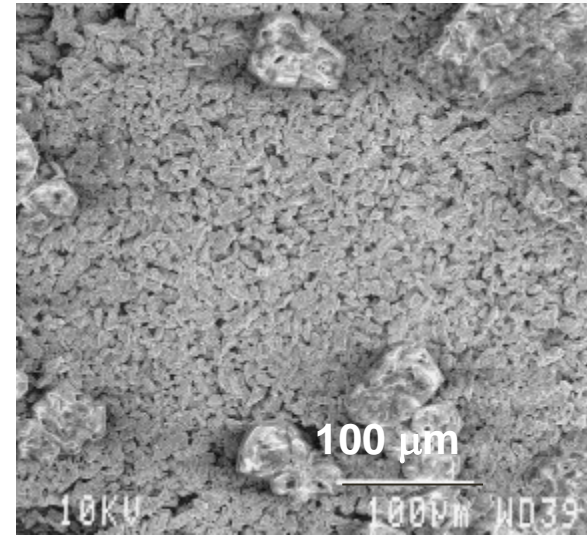


SDC vs. EC: CRYSTAL QUALITY/SIZE



Solvent Displacement Crystallisation:

- $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- Tetragonal, compact crystals
- avg. size: $\sim 100 \mu\text{m}$



Evaporative Crystallisation

- $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$
- Irregular, porous particles
- avg. size: $\sim 10 \mu\text{m}$

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!