Centre for Innovation in Storage and Conversion of Energy

Immobilization of hazardous elements

via innovative crystallization and encapsulation processes

GEORGE P. DEMOPOULOS

MATERIALS ENGINEERING @ MCGILL UNIVERSITY

MONTREAL, CANADA

HTTPS://WWW.MCGILL.CA/MATERIALS/PERSONNES/FACULTY-STAFF/GEORGE-P-DEMOPOULOS/RESEARCH-INTERESTS

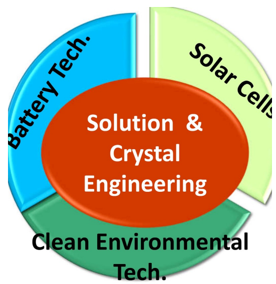
GEORGE.DEMOPOULOS@MCGILL.CA

1

INTRO to my HydroMET Odyssey!

"**Hydrothermal Materials for Environmental & Energy Technologies**"

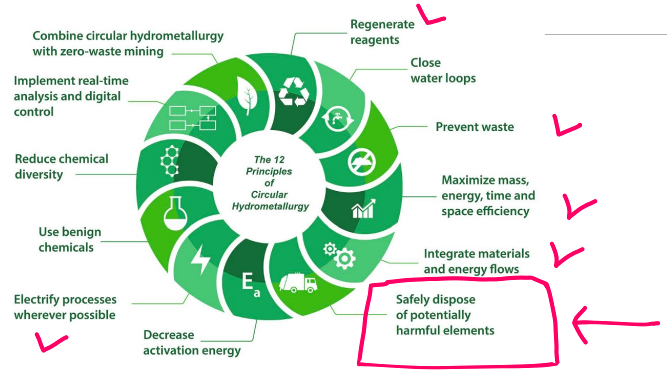
- This started as **HYDROMETALLURGY**: extraction and separation of metals from minerals using aqueous chemical solutions (1975-1990s)
- In mid 90s I started developing **environmental technologies** applied to mineral process effluents: from controlled neutralization processes to immobilization of elements-of-concern via crystallization
- Some 16 years ago I shifted my attention to **green** ENERGY MATERIALS (solar cells, Li-ion batteries, photocatalysis) having always crystallization as the foundation



→**Our mission: circular green materials-process innovations!**

2

Circular Hydrometallurgy Principles*



*Koen Binnemans and Peter Tom Jones, J. Sustainable Metallurgy, 9, 1-25 (2023).

3

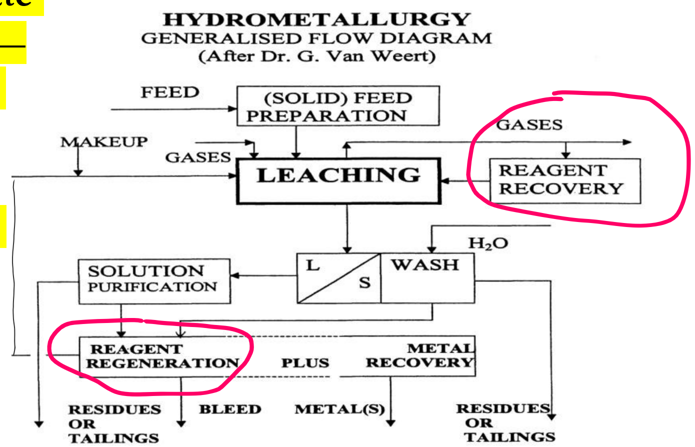
Circular Hydrometallurgy Principles→ Examples from my own research (see list of references at the end)

- **Principle 1-Regenerate reagents: HCl regeneration (2000-2016)**[1]
- **Principle 3-Prevent waste: Hematite and gypsum in Zinc industry (1997-2002)**[2]
- **Principle 4- Maximize mass, energy**…..: Pressure Hydrogen Stripping! (1978-1990)[3]
- **Principle 5- Integrate materials and energy flows**: Modelling of autothermal pressure oxidation of sulphides (1986-1996)[4]
- **Principle 6- Safely dispose harmful elements: This presentation (1992-present)**
- **Principle 7:-Decrease Activation Energy**: Activators in Co cementation (1998-2002)[5]
- **Principle 8-Electrify processes**: Iron production by electrolytic reduction (2022-present)[6]

Plus **Recycling of LIBs as of lately**[7]

4

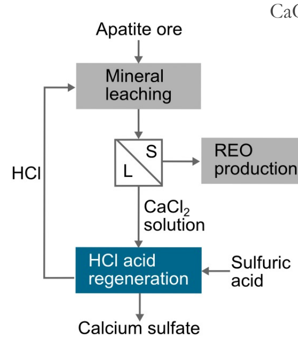
Regenerate reagents— a pioneer! Gus Van Weert @ TU Delft, 1992[8]



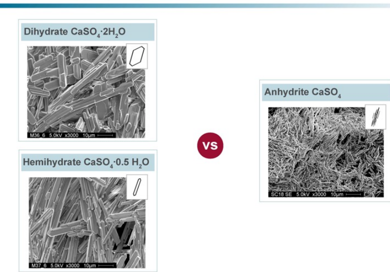
5

Principle 1-Regenerate reagents: HCl regeneration (<100 °C) by reactive crystallization

$$CaCl_2 + H_2SO_4 + x\ H_2O \rightarrow 2\ HCl + CaSO_4.xH_2O\downarrow$$



Calcium sulfate phases have different size, morphology, properties and value

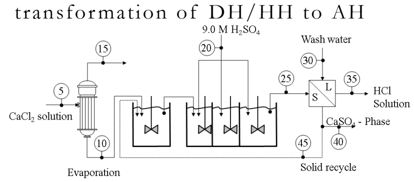


6

Crystallization circuit design*: in-series (staged) vs. single-stage (in-parallel tanks)!

→ **Initial design**[#]: supersaturation control by staged acid addition (in-series tanks)

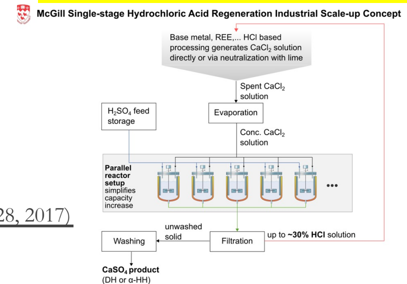
→ Pilot-plant testing failed due to transformation of DH/HH to AH



*Patented (United States Patent No. 9,783,428, 2017) and licensed to a REE company

[#] 1(a): A. Al-Othman and G.P. Demopoulos, 2009, *Hydrometallurgy*, 96, 95-102.

→ **Single Stage (In-parallel)**[+] avoids long exposure of crystals to high-acid environment so no Transformation to undesirable AH Phase!



[+] 1(b): Thomas Feldmann and G. P. Demopoulos, *Hydrometallurgy,* 155 (2015) 20-28.

10-09-2024 ICHS 2024, MECHELEN, BE 7

7

Principle 3-Prevent waste: Hematite and gypsum in Zinc industry

- Japanese metallurgical industry – a global leader in sustainable material and energy usage, practicing circularity since the 70s!
- Full integration of operations promoting comprehensive processing of all streams* to recover all valuable elements while minimizing waste generation

- My experience from collaboration with Akita Zinc on the Hematite Process[2]

Hydrometallurgy 2003 Fifth International Conference in Honor of Professor Ian Ritchie
Volume 2: Electrometallurgy and Environmental Hydrometallurgy
Edited by C.A. Young, A.M. Alfantazi, C.G. Anderson, D.B. Dreisinger, B. Harris and A. James
TMS (The Minerals, Metals & Materials Society), 2003

THE PRECIPITATION CHEMISTRY AND PERFORMANCE OF THE AKITA HEMATITE PROCESS — AN INTEGRATED LABORATORY AND INDUSTRIAL SCALE STUDY

Terry C. Cheng[1], George P. Demopoulos[1], Yutaka Shibachi[2], and Hitoshi Masuda[2]

[1.]Department of Mining, Metals, and Materials Engineering, McGill University, 3610 University, Montreal, Canada H3A 2B2
terry.cheng@mail.mcgill.ca, george.demopoulos@mcgill.ca
[2.]Iijima Zinc Refinery, Akita Zinc Co. Ltd. 217-9 Shimo-Kawabata, Furumichi, Iijima, Akita 011-0911, Japan

* Ex. Processing of Cu_3As residue generated in Zn plant at Cu smelter

10-09-2024 ICHS 2024, MECHELEN, BE 8

8

Iron-the good, the bad and the ugly in hydrometallurgy

GOOD: Removal of impurities during Neutral Leach; Acts as catalyst in direct/pressure leaching of zinc cons.

BAD: Huge volumes of iron residues; environmental stability?

UGLY:

Colorado mine spill spews metallic discharge into waterways
Aug 10, 2015
Thomson Reuters

9

Process	Hematite	Goethite	Jarosite
Compound formula	α-Fe_2O_3	α-FeOOH	$MFe_3(SO_4)_2(OH)_6$
%Fe content			
theoretical	69.9	62.9	30–35
actual [17, 18, 19]	50–60	40–45	25–30
%S content [18, 20]	2–5	5–8	10
%Zn content [17, 18, 21]	0.5–1	8	4–6
amount (wet basis)			
(t/t Zn slab) [17, 19]	0.22	0.64	1.0

Iron precipitation in Zn Industry

Jarosite Leachability, mg/L: Cd >10, Cu>30, Zn>2000 mg/L

10

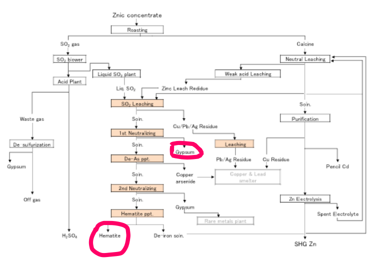
The JAROFIX process[9] - a temporary civil eng solution: Not sustainable!

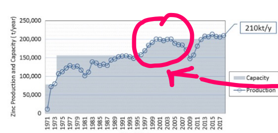
- After filtration & washing the jarosite residue is subjected to solidification/stabilization by mixing it with lime and cement
- Used in Canada, Spain, India and elsewhere
- 3 Million TPY of jarosite residue treated globally
- **Passes TCLP but long-term???**

Element	TCLP 2000	
Al	<0.1–0.2	ppm
As	0.02–0.06	
Be	<0.01	
Cd	<0.005	
Co	0.09	
Mn	0.02–0.03	
Ni	<0.01	
Pb	<0.05	
Zn	0.01–0.03	

11

The Akita Zinc Hematite Process



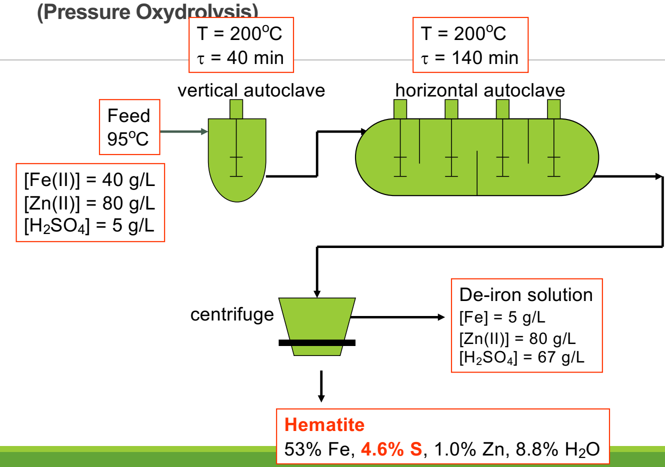


- **This is "waste-free" technology as the hematite precipitate (but also gypsum!) is used in various construction applications**
- Capital cost is high but it allows for easier recovery of high value minor metals (In, Ga, Ag)
- Operated for a while in Germany but shut down due to cost….
- Technology is used now also in China
- McGill-Akita Collaborative Work in 1997-2004 led to cleaner hematite production and increased throughput

Figures from: Dai Matsuura et al., Recent Operational Improvements of Hematite Plant at Akita Zinc Co., Ltd., A. Siegmund et al. (eds.), PbZn 2020: TMS Series, https://doi.org/10.1007/978-3-030-37070-1_76

12

Industrial Hematite Process (Akita, Japan)
(Pressure Oxydrolysis)



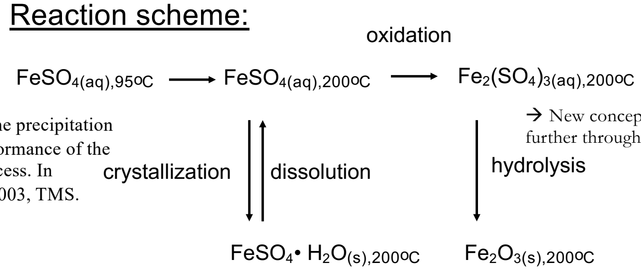
13

Hematite Process Chemistry (at 200°C)*

Overall reaction:

$$4\,FeSO_4(aq) + O_2(g) + 4\,H_2O \longrightarrow 2\,Fe_2O_3(s) + 4\,H_2SO_4(aq)$$

Reaction scheme:



* 2. Cheng et al, The precipitation chemistry and performance of the Akita hematite process. In Hydrometallurgy 2003, TMS.

→ New conceptual design can increase further throughput and product purity@

@Cheng & Demopoulos in Pressure Hydrometallurgy 2004.

→Further complexity: Formation of basic ferric sulfate and transformation to Fe_2O_3

→Hematite product contains only ~58% Fe (vs. 70% theoretical) (~10% SO_4)

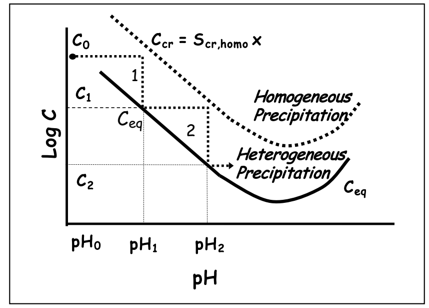
14

Production of Well Grown and Clean Crystalline Compounds[10]

- Avoid homogeneous nucleation-operate at low S
- Use seed/product recycling
- The above lead to avoidance of the formation of undesired metastable phases (Stranski's Rule) and minimization of impurity uptake (suppression of surface adsorption)

Supersaturation Control by Step-wise Neutralization

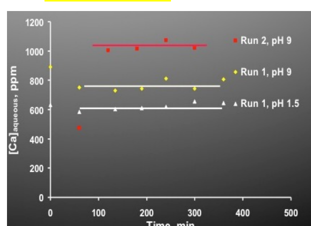
(method developed at McGill)



15

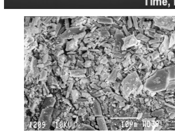
Production of Clean Gypsum: Crystallization in Zinc plant Wastewater Treatment*

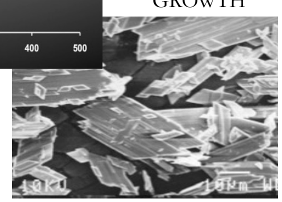
LOW SUPERSATURATION BY STAGING



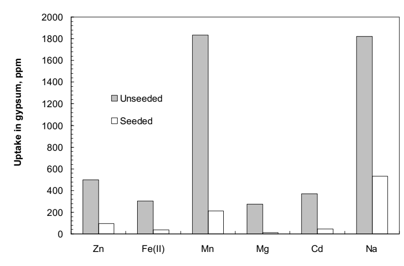
Run 2: No staging
Run 1: With staging

CRYSTAL GROWTH





IMPACT OF SEEDING/*S* ON IMPURITY UPTAKE



* 11. **C. Verbaan, S. Omelon** and G.P. Demopoulos, in *Solid-Liquid Separation in Hydrometallurgy*,, CIM (1999)

16

Let's now discuss Principle 6

17

Principle 6: Safely dispose harmful elements→ the case of As + Sb, Se

1. Conventional practice: aiming at REMOVAL from spent solutions/effluents is NOT adequate
2. The result: voluminous tailings mixed with other wastes or disposed in "temporary" storage facilities
3. Not proper environmental standard in evaluating stability: 24-hr TCLP
4. WE SHOULD: Fix these elements into highly insoluble compounds that have a long-term stability (tested thermodynamically, kinetically, mineralogically, geochemically)

→Combine with Recovery of Valuable Minor Elements and….

→DESIGN FOR 1000 YEARS!

18

Development of clean environmental technologies-our research

- Controlled aqueous crystallization of well grown and highly insoluble synthetic minerals as carriers for the **immobilization of inorganic pollutants (e.g. As or Sb*)**

*As tripuhyite $FeSbO_4$, R. Multani, T. Feldmann, G.P. Demopoulos, *Hydrometallurgy* 169 (2017) 263–274

- Development of encapsulation technologies for enhanced stabilization of hazardous solids (As, Hg)

- Nano/Photocatalytic adsorptive deposition & recovery (Se)/Not covered

Arsenic Fixation[12] -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 process 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!

*See papers in *Chemosphere*, 151:318-323 (2016) and138 (2015) 239–246; *Hydrometallurgy*, 151 (2015) 42–50 and 111-112 (2012) 65–72

CRYSTALLINE SCORODITE ($FeAsO_4.2H_2O$) PRODUCTION –

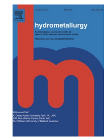
Atmospheric Precipitation Process → enabled by supersaturation control*

I. By step-wise pH control→ Commercialized by EcoMetales in Chile and recently Zijin Co in China !

II. By oxidation→ Piloted by DOWA; plus Bio-scorodite by PAQUES (low [As])

III. By transformation/redissolution→ Patented by Outotec

IV. By dissolution→ Patent filed by McGill



* 10. Demopoulos, Hydrometallurgy, 2009, 96, 199–214

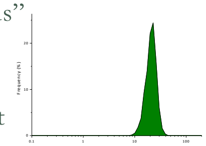
Low solubility[#] at 4<pH<7

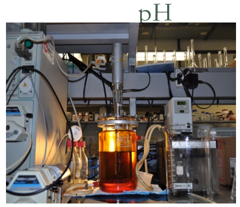
[#]Bluteau and Demopoulos, 2007, Hydrometallurgy , 87, 163-177.

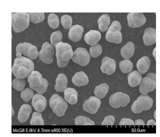
21

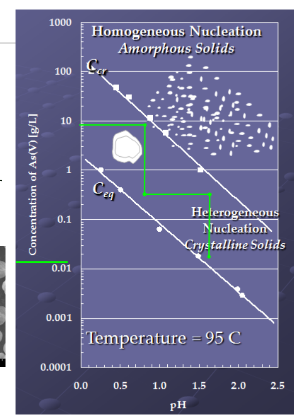
Scorodite Production: promote crystal growth by Supersaturation Control[13,14]

- Work within "heterogeneous" zone
- Translation to multi-tank circuit operating at different pH



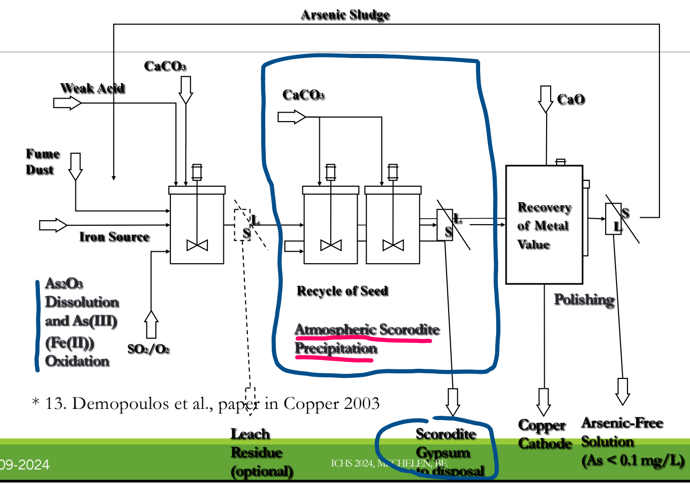






22

Atmospheric Scorodite Process Flowsheet*

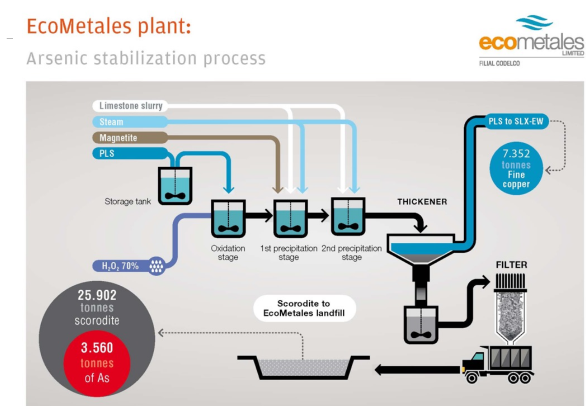


Anecdote: The concept was criticized in the 90s as non-feasible chemeng process!

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

23

EcoMetales Commercial Plant*



* The atmospheric scorodite process became an industrial reality after 20 yrs research in 2012!

- Product: scorodite (1/3) gypsum (2/3) mixture

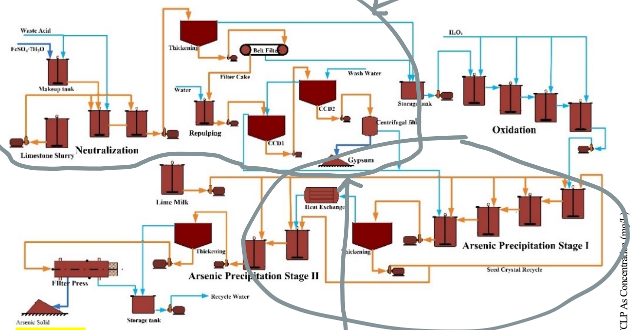
24

Ceremony at Ecometales scorodite plant, April 2022

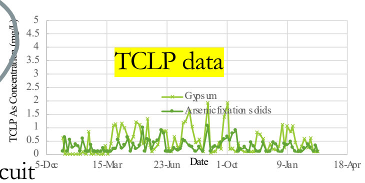
25

Gypsum circuit

Recent industrial developments: Scorodite in China (Zijin Mining Corporation) *



- Bulk of acid neutralized prior to Sc precipitation
- Produced gypsum is clean (0.01% As); used in cement making
- TCLP < 1.2 ppm As



Q. Wang et al., paper in Arsenic Symposium @ COM2024 Proceedings (Springer) in press.

Scorodite circuit

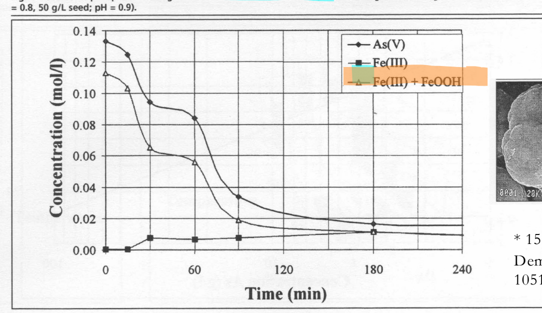
26

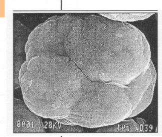
IV. Scorodite formation via dissolution of iron solids (proof of concept)*

Iron solids like (oxy)hydroxides, carbonates, scrap iron etc.

$$H_3AsO_4\,(aq) + FeOOH(s) \rightarrow FeAsO_4 \bullet 2H_2O\,(\downarrow)..$$

Fig. 11. Scorodite precipitation using FeOOH as iron source and base (T = 95°C, 10 g/L As(V), 10 g/L FeOOH, Fe(III)/As(V) = 0.8, 50 g/L seed; pH = 0.9).





* 15. Dabekaussen, Droppert & Demopoulos, *CIM Bulletin*, Vol. 94 (No. 1051), pp. 116-122 (2000)

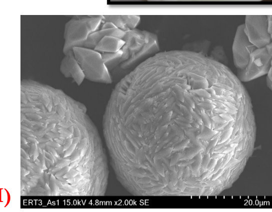
10-09-2024 ICHS 2024, MECHELEN, BE 27

27

New Gypsum-free Process: Use FeOOH or other iron source-patent pending[16,*]

- Iron (hydro)-oxides as **source of iron(III) and base**
- Supersaturation control by iron dissolution
- Fast kinetics

Reaction time (hours)	0	1	2	3	4
[As] (g/L)	14.60	7.98	4.09	2.04	1.29
As removal %					91.1
[Fe] (g/L)	2.22	7.50	6.73	5.87	5.34
Fe removal %					74.49
pH	0.62	0.74	0.73	0.98	1.06

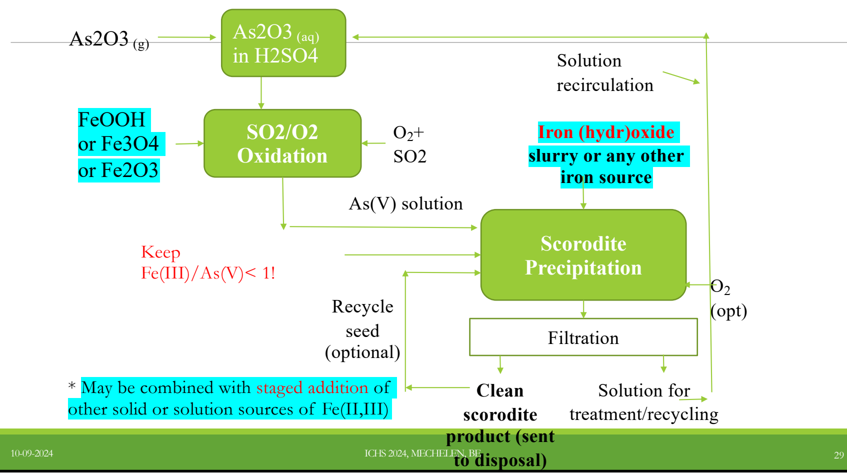


* WO/2020/237361 **Gypsum-free scorodite (<5% unreacted FeOOH)**

10-09-2024 ICHS 2024, MECHELEN, BE 28

28

As_2O_3 oxidation in solution and precipitation of scorodite with Fe oxides*

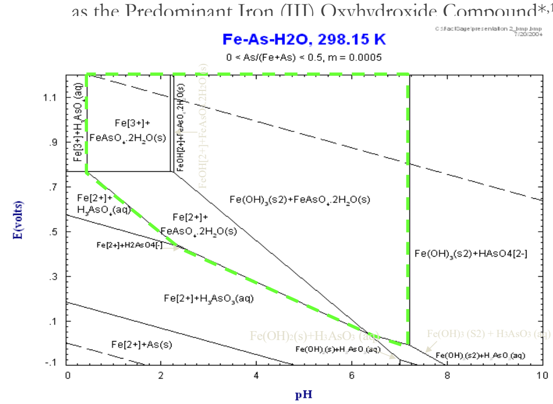


* May be combined with staged addition of other solid or solution sources of Fe(II,III)

29

Scorodite stability: Thermodynamics

E_h-pH Diagram for Fe-As-H_2O at 25°C (0.0005 *m*), with Ferric Hydroxide (K_{SP}=-38.6) as the Predominant Iron (III) Oxyhydroxide Compound*,[14]



*M-C. Bluteau and G.P. Demopoulos, 2004, "Fixation of Arsenic in the Form of Scorodite – A Solubility Study", in Waste Processing and Recycling in Mineral and Metallurgical Industrials V, R. Rao et al. Eds., CIM, Montreal, pp.439-451

30

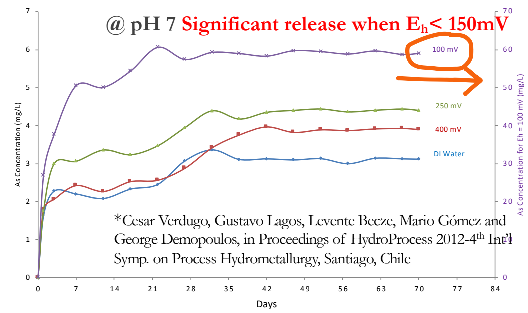
Scorodite stability: pH and E_h dependent

- Scorodite passes **TCLP test** involving testing @ pH 5 for 20 hr
- Stable (long term >1 year dissolution tests#) at 4 < pH < 7
- Also note that not all scorodites are equal!

#Bluteau and Demopoulos, 2007, Hydrometallurgy , 87, 163-177.

AS RELEASE AS A FUNCTION OF REDOX POTENTIAL*

@ pH 7 Significant release when E_h < 150mV



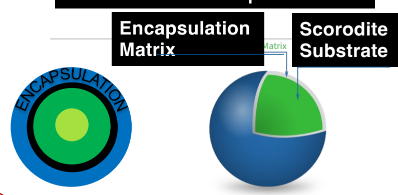
*Cesar Verdugo, Gustavo Lagos, Levente Becze, Mario Gómez and George Demopoulos, in Proceedings of HydroProcess 2012-4th Int'l Symp. on Process Hydrometallurgy, Santiago, Chile

31

Enhance stability of scorodite by encapsulation

McGill UNIVERSITY

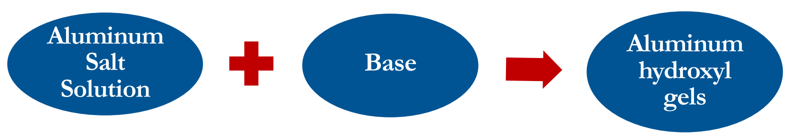
Stabilization technology based on encapsulation



Encapsulation materials

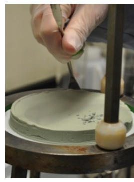
- Metal phosphates (AlPO4·1.5H2O, and Ca5(PO4)3OH,F)
- Aluminum hydroxyl gels

Aluminum hydroxyl gels



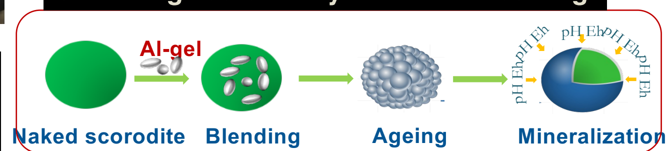
32

Development of Al-gel encapsulation technology-the next generation*

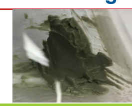


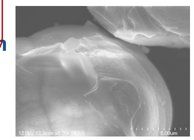
- Enhance scorodite stability by encapsulation;
- Perfect for integration with gypsum-free scorodite

*Patents in several countries granted



Low gel/scorodite ratio (Al:As = 0.1)

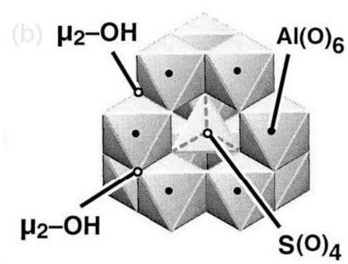




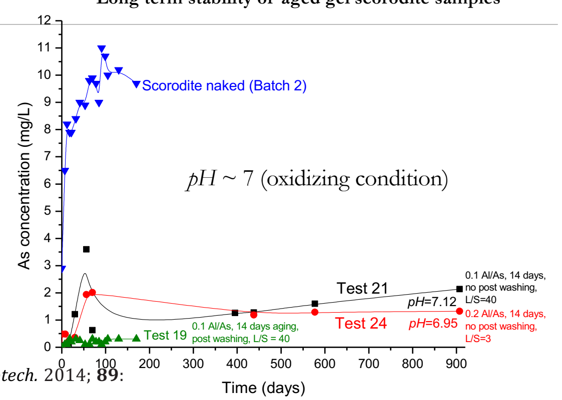
33

Al-gel structure and Stability testing[17]

SO_4-stabilized Keggin Al_{13} structure
$AlO_4Al_{12}(OH)_{24}(SO_4)_{3.5}(H_2O)_{12}$



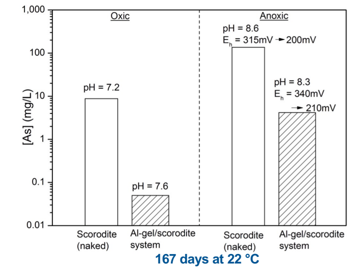
Long term stability of aged gel scorodite samples

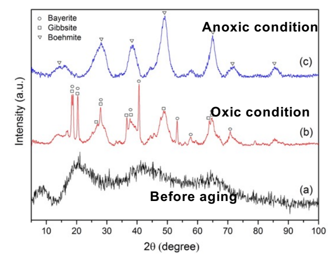


17. **Karl Leetmaa et al.,** *J. Chem. Technol. Biotech.* 2014; **89**: 206–213; and 2016, **91**: 408–415

34

➢Wide pH and oxic-anoxic stability via formation of AlOOH mineralized coatings*

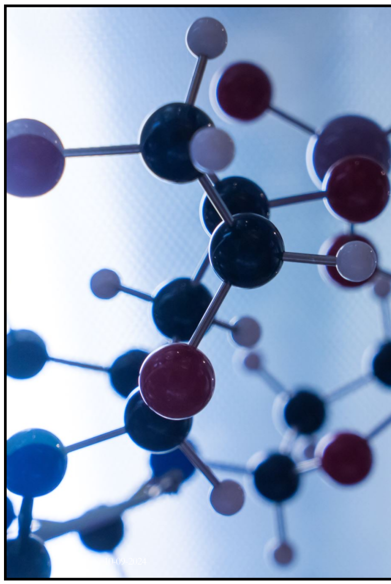




STABILITY OF GEL MINERALIZED SCORODITE:
33 times reduced As release!

* 17(c). Fuqiang Guo and G.P. Demopoulos, 2018, in *Extraction 2018*, TMS, 1411-1420.

35



Concluding remarks

- ➢Hazardous element control: think first value-recovery options; in case of disposal, link process selection and design to stability; enhance long-term stability by encapsulation
- ➢Crystallization but also encapsulation and new nanomaterial-based technologies (e.g. photocatalysis) very important in our pursuit of circular hydrometallurgy solutions
- ➢National and international collaboration as well as creation of research consortia with industry as done in Japan by JOGMEC is the way forward!
- ➢We need to advance "Benign by Design" paradigms!

36

Acknowledgements

NSERC CRSNG

- My HydroMET group members: past and present
- My collaborators and sponsors

McGill Sustainability Systems Initiative | Initiative Systémique de McGill sur la Durabilité

McGill | Centre for Innovation in Storage and Conversion of Energy

37

References

1. (a) A. Al-Othman and G.P. Demopoulos, 2009, *Hydrometallurgy*, 96, 95-102. (b) Thomas Feldmann and G. P. Demopoulos, *Hydrometallurgy,* 155 (2015) 20-28.
2. T.C. Cheng, G.P. Demopoulos, Y. Shibachi, and H. Masuda , The precipitation chemistry and performance of the Akita hematite process. In Hydrometallurgy 2003, C. Young. Ed., TMS,, pp. 1657-1674. .
3. G.P. Demopoulos and P.A. Distin, 1985, "Pressure Hydrogen Stripping in Solvent Extraction", *Journal of Metals*, 37(7), pp. 46-52.
4. V.G. Papangelakis and G.P. Demopoulos, 1992, "On the Attainment of Autothermal Operation in Continuous Pressure Leaching Reactors", *Hydrometallurgy*, 29, pp. 297-318.
5. (a) T. Dreher, A. Nelson, G.P. Demopoulos and D. Filippou*, 2001, "The Kinetics of Cobalt Cementation in an Industrial Electrolyte Using a Combination of Additives", *Hydrometallurgy*, Vol. 60, pp. 105-116; (b) A. Nelson, G.P. Demopoulos and G. Houlachi*, 2000, "The Effect of Solution Constituents and Novel Activators in the Cementation of Cobalt", *Can. Metall. Q.,* Vol. 39 (No. 2), pp. 175-186.
6. Philip Gamboa, A. Norouzi, K. Waters*, G.P. Demopoulos, 2024, Direct electrolytic conversion of hematite to metallic iron in a caustic solution at 50 °C, Electrometallurgy Symposium, COM 2024 Proceedings, Springer (in press) August 2024.
7. (a) Krystal Davis and George P. Demopoulos, 2024, Effective upcycling of NMC 111 to NMC 622 cathodes by hydrothermal relithiation and Ni-enriching annealing, *Next Energy*, 4 (2024) 100122; (b) **François Larouche**, Kamyab Amouzegar*, Georges Houlachi, Patrick Bouchard, G. P. Demopoulos, 2022, Conversion of LiFePO4 to FePO4 via selective lithium bicarbonation – A direct pathway towards battery recycling, *J. Electrochem. Soc.* 169, 073509

38

References-2

8. G. Van Weert and E.M.L. Peek, Reagent recovery in chloride hydrometallurgy —some missing links, Hydrometallurgy, Volume 29, Issues 1–3, June 1992, 513-526.
9. George. P. Demopoulos, 2015, Sustainability-driven R&D in Zinc Hydrometallurgy: Remembering Lucy Rosato, *COM 2015, The Conference of Metallurgists*, Toronto, CIM, Proceedings, 19p.
10. G.P. Demopoulos. 2009, Aqueous Precipitation and Crystallization for the Production of Particulate Solids with Desired Properties. Hydrometallurgy, 96, 199–214.
11. N. Verbaan, S. Omelon and G.P. Demopoulos, 1999, “The Effect of Staging and Seeding/Recycling in the Production of High Density and Clean Gypsum from Zinc Process Waste Waters”, in Solid-Liquid Separation in Hydrometallurgy, G.B. Harris and S. Omelon, Eds., CIM, 251-264.
12. George P. Demopoulos, 2014, Arsenic Immobilization Research Advances: Past, Present and Future, in *Proceedings of Arsenic Metallurgy & the Environment* symposium, A. Barnes et al, Editors, COM2014 (paper no 8560, 13p) MetSoc of CIM, Vancouver, B.C., Sept. 2014
13. G.P. Demopoulos, F. Lagno, Q. Wang and S. Singhania, 2003, “The Atmospheric Scorodite Process”, in Copper 2003, P.A. Riveros et al. Eds., Vol. IV., pp. 597-616.
14. G.P. Demopoulos, 2005, “Preparation and Stability of Scorodite”, in Arsenic Metallurgy, R.G. Reddy and V. Ramachandran, Eds., TMS, Warrendale, PA, pp. 25-50.
15. R. Dabekaussen, D. Droppert and G.P. Demopoulos, 2001, “Ambient Pressure Hydrometallurgical Conversion of Arsenic Trioxide to Crystalline Scorodite”, *CIM Bulletin*, Vol. 94 (No. 1051), pp. 116-122
16. G.P. Demopoulos, 2024, Scorodite 3.0: Production of gypsum-free scorodite by iron dissolution, Arsenic/Minor Element Symposium, COM 2024 Proceedings, Springer (in press) August 2024.
17. (a) Karl Leetmaa et al., *J. Chem. Technol. Biotech.* 2014; 89: 206–213; and (b) 2016, 91: 408–415; (c) Fuqiang Guo and G.P. Demopoulos, 2018, Development of an Encapsulation Process to Extend the Stability of Scorodite under Wide pH and Redox Potential Range Conditions, in B. Davis et al. (eds.), *Extraction 2018*, TMS Series, 1411-1420; https://doi.org/10.1007/978-3-319-95022-8_115

39

THANK YOU!

40