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Technological Options for Arsenic Stabilization and Management in the Copper Industry

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GLENCORE

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XPS Expert Process Solutions is an Engineering and Technology Development Facility with +50 Professionals

Main areas of expertise:

- Geology, mineralogy, mineral processing and metal accounting
- Process control/artificial intelligence (AI), expert control systems
- Materials/maintenance/asset integrity management
- Pyro/Hydro/Electro metallurgy development and optimisation
- Process modelling and simulation

XPS serves the mineral and metals industry worldwide
(Glencore and non-Glencore assets, various metals)

Testing and Piloting Facilities

XPS has a network (external consultants and piloting facilities) to evaluate technologies
(due diligence)/develop/scale up/implementation

Goals of this Presentation

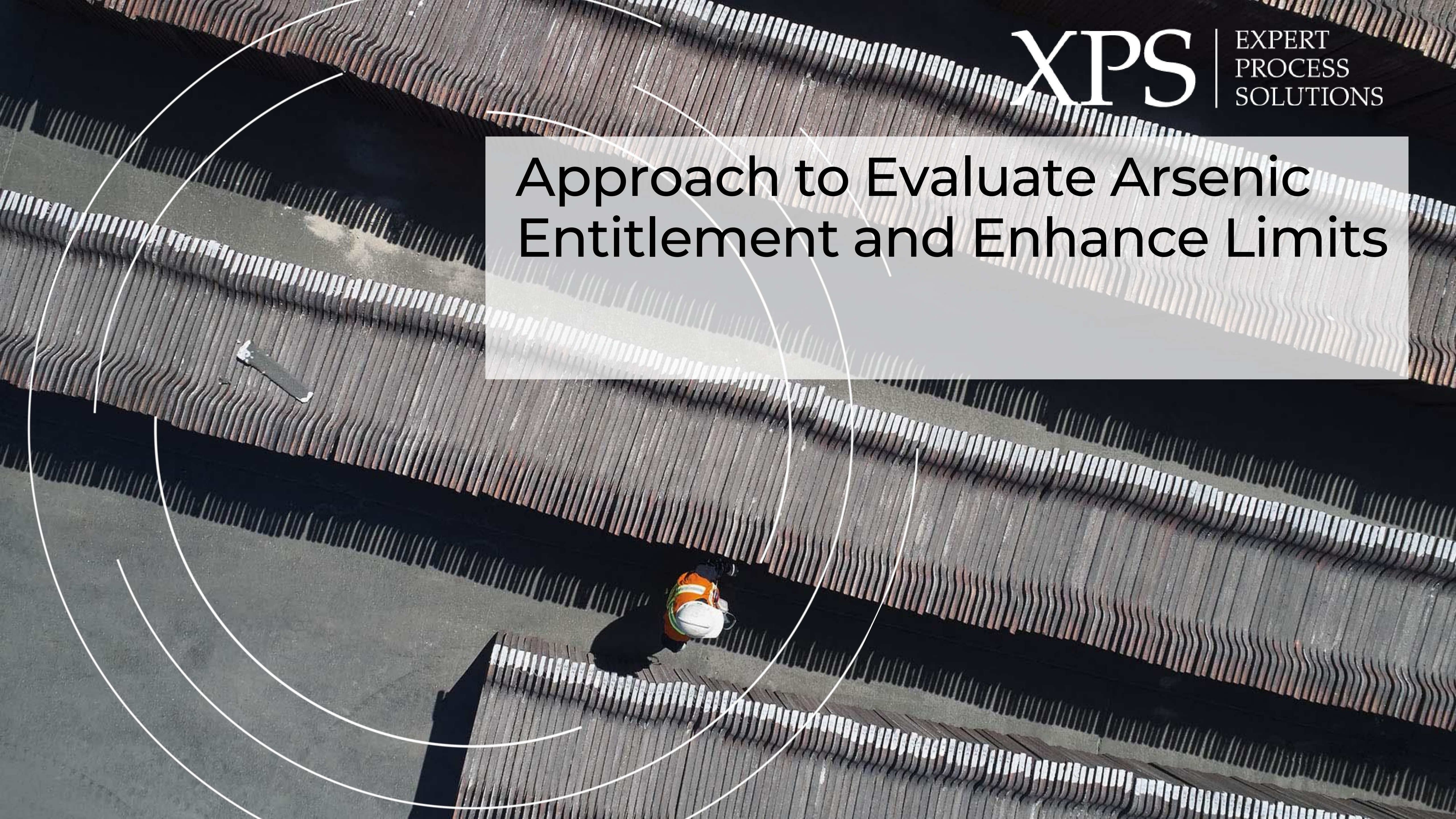
- Participate in this seminar held in honour of **Professor George Demopoulos**. Prof Demopoulos has proven to be a tremendous leader in hydrometallurgy: Well done George !!!
  - Outstanding academic career
  - Made his academic work intimately connected to real life problems
  - Has trained engineers/scientists/process developers working worldwide throughout the industry

- Share views on arsenic management in the copper industry based upon information from the public domain (non asset specific).

- Present a high level approach, as holistic as possible, for continuous improvement of arsenic management in the copper industry.

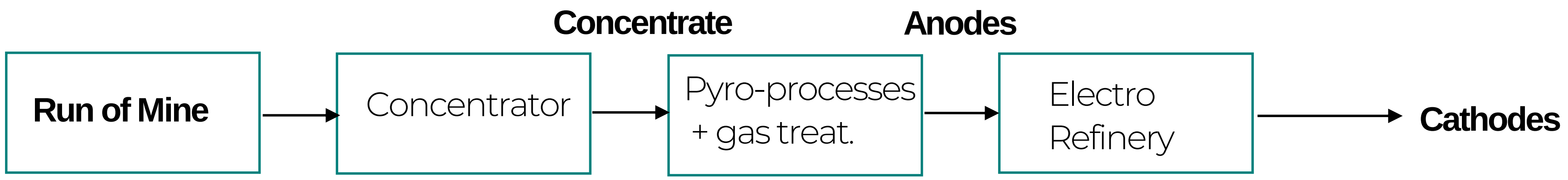
- While respecting clients' proprietary information (not in the public domain), participate in panel discussions aimed toward improving arsenic management/stabilisation in the copper industry.

Approach to Evaluate Arsenic Entitlement and Enhance Limits



Considerations for the Smelting/Roasting Approach

- In heap leach (copper oxide) operations the contained arsenic is generally sequestered within the heaps; however, in copper sulphide operations arsenic is often harder to separate and reports with copper to the sulphide concentrate.
- The block diagram shows the typical flow of materials in copper sulphide processing operations:



Arsenic outlets:	*Waste rocks*	*Tailings*	*Slag/dust/gas treatment by-products*	*Electrolytic sludge*
Relative As removal:	(low)	(low)	(high)	(medium)

We will focus mainly upon the most relevant As removal opportunity (pyro-processes/dust/off gas).

Natural Entitlement for a Smelter/Refinery Complex

- A substantial fraction of the arsenic in concentrate will deport to slag and water treatment within the smelter/refinery complex, along with a permissible arsenic level within anodes sent for electro-refining. The precise limits are specific to the technologies utilised at each metallurgical complex as well as internal recycle practices. Within these limits the marginal cost for processing arsenic is not prohibitive.

- Once the arsenic "entitlement" is exceeded, additional technologies are required to maintain limits in the various stages (smelter feed, anode composition, arsenic in electrolyte/liberators). At this point, the incremental cost of treating arsenic becomes significant, warranting higher discounts to compensate for additional OPEX and CAPEX requirements.

- Generally, the engineering approach to increase arsenic capacity at a given complex is the following:
  - Define/maximise natural entitlement (experience, minor element balance, minor element model).
  - Optimise the smelter/refinery complex with existing equipment (fill the window).
  - Evaluate technologies to increase the plant entitlement considering sustainability and costs.
  - Execute selected capital projects.

Considerations with the Hydrometallurgical Approach

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- Hydrometallurgical approaches are also available for concentrate treatment

Run of Mine → Concentrator → (**Concentrate**) → Hydro processes → (**Cu solution**) → Electro winning → **Cathodes**

	Run of Mine	Concentrator	Hydro processes	Electro winning
Arsenic outlets :	*Waste rocks*	*Tailings*	*Leach & As precipitation residues*	*Electrolytic sludges*
Relative As Removal:	(low)	(low)	(high)	(low)

- Generally speaking, full blown hydro-processes for concentrate treatment are more CAPEX and OPEX intensive and are more technically challenging for PM/PGM recovery.
- Hydro processes are generally easier to permit, and by design should aim at producing stable arsenic by-products.

Technology Highlights

Slide 1 of 3

Mining

- Copper and Arsenic are generally encountered as admixtures of chalcopyrite ($CuFeS_2$), Enargite (Cu_3AsS_4), Tennantite ($Cu_{12}As_4S_{13}$) and Arsenopyrite (FeAsS). Mine-site ore sorting for arsenic rejection is not easily feasible due to high copper losses.

Mineral Processing

- Separation of chalcopyrite from enargite and tennantite can produce low-arsenic and high-arsenic copper concentrates for appropriate treatments. Similarly it is possible to depress arsenopyrite into flotation tailings for reduction of As in concentrate.

Concentrate Blending

- Blending is an effective solution to adjust smelter feeds to their arsenic entitlement level (see slide 5).

Roasting

- Partial roasting (Codelco Mina Ministro Hales Roaster approach) segregates arsenic into an off-gas stream for further treatment, producing an arsenic-depleted calcine which can be autogenously smelted.

Smelting

- Top fed bath smelting technologies are the most effective at eliminating arsenic at the smelting stage.

Technology Highlights
Slide 2 of 3

Converting

- Pierce Smith Converters (PSCs) (batch converting) have an intrinsic advantage over continuous converting furnaces for arsenic elimination (fayalite slag). For continuous converting, Ca-ferrite slag is preferred.

Fire refining

- Lime, soda and sulphate fluxing are known technologies for arsenic control in anode furnaces. With respect to refractory wear, slag fluidity and achieving an appropriate level of arsenic in anode copper the sulfate approach is considered most effective. (Author is one developer of this technology)

Dust treatment from smelting and converting furnaces

- Dust treatment by various methods is an effective way of controlling the arsenic balance of a smelting/refining complex. Ideally, the arsenic precipitate meets high stability standards.

Smelter weak acid treatment plants

- Smelter water treatment plants are complex and designed base on several considerations (H_2SO_4 neutralisation, Cu recovery, As,Hg,Pb,Cd stabilisation). Lime-based processes (Ca arsenite/arsenate) and iron-based processes (Fe arsenates and scorodite) are used to produce relatively stable waste streams at a bearable cost. Landfill practices are adapted.

Technology Highlights
Slide 3 of 3

Electro-refining and related electro-winning cells (liberators)

- Arsenic can be concentrated within refinery streams. These streams (refinery sludge, black acid and liberator sludge) contain only a small proportion of the smelter arsenic inlet. Opportunities for arsenic stabilisation are limited.

Concentrate leaching

- Technological developments are ongoing. High pressure concentrate leaching is a technically viable option for transforming arsenic into a stable form while extracting Cu. Atmospheric leaching after fine grinding (Albion Process) is also an option. Other options include chloride leach, Galvanox. Challenges lie in overall CAPEX/OPEX and PM recoveries.

Co-deposition

- When engineered properly, mixtures of components (blended or layered) can enhance overall stability and reduce risks of dispersion and perpetual costs. For example, if one component or by-product is stable on the short term, but could partially decompose on the long run, another component could be used as a scavenger. Regulators allow for this approach in many jurisdictions as long as there is a benefit.

Vitrification technologies

- There is an emerging and interesting technology for transforming As_2O_3 in a stable glass product. (TBR)

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Arsenic Stabilisation
Some Highlights and Examples

Relative Stability of Arsenic Precipitates

Ichimura et al, 2007

Arsenic compound	Chemical formula	Solubility by TCLP test*	Reaction pH	Reaction temperature	Arsenic content
Crystalline scorodite	$FeAsO_4 \cdot 2H_2O$	0.2 mg/L	1	95 °C	28.8%
Amorphous ferric arsenate	$FeAsO_4 \cdot XH_2O$	0.9 mg/L	1.5	Room temperature	23.9%
Ferric co-precipitation		1 mg/L	5	Room temperature	17.2%
Calcium arsenate	$Ca_3(AsO_4)_2$	430 mg/L	12	Room temperature	12.6%
Arsenic sulfide	As_2S_3	25 mg/L	2	Room temperature	41.5%

*Definition of TCLP: *Toxicity Characteristic Leaching Procedure EPA Method 1311*

Solids leached (agitated vessel) in appropriate solution with 20x the mass of the dry sample for 18h, followed by analysis of the solution.
Arsenic compounds generally deemed disposable at <5mg/l extract concentration by TCLP

Impact of Fe and As and Related Oxidation States

From literature As^{5+} is preferred to As^{3+} for enhanced stability. Generally, arsenic is present as As^{3+} in smelter off-gas and roaster gases and is resistant to oxidation. Effective conversion to As^{5+} requires the use of peroxide, high pressure/temperature, SO_2-Air, ozone, or other higher cost oxidation technologies.

Literature recommends Fe/As ratios (molar) of between 1,5 and 5 to produce stable hydrometallurgical precipitated, depending on compounds/crystallinity. This is approximately: 1-3 MT of Fe per MT of As and represents a significant cost.

If Fe-sulphates (Fe^{2+} or Fe^{3+}) are utilized as a source of iron the sulphate needs to be neutralized to gypsum, leading to additional costs and volume for the final residue. Oxidation of Fe from Fe^{2+} to Fe^{3+} is also preferable in principle.

A low cost Fe source would be an enabler for cost effective arsenic stabilization. This could include acid mine drainage water, concentrator tailings, Fe in concentrate, FeS, FeS_2, or magnetite from slag. The cost would also be reduced if no expensive means of Arsenic oxidation was required. Some technologies are available but more development is required.

Ecometales: Dust Leaching Plant (Stage 1)

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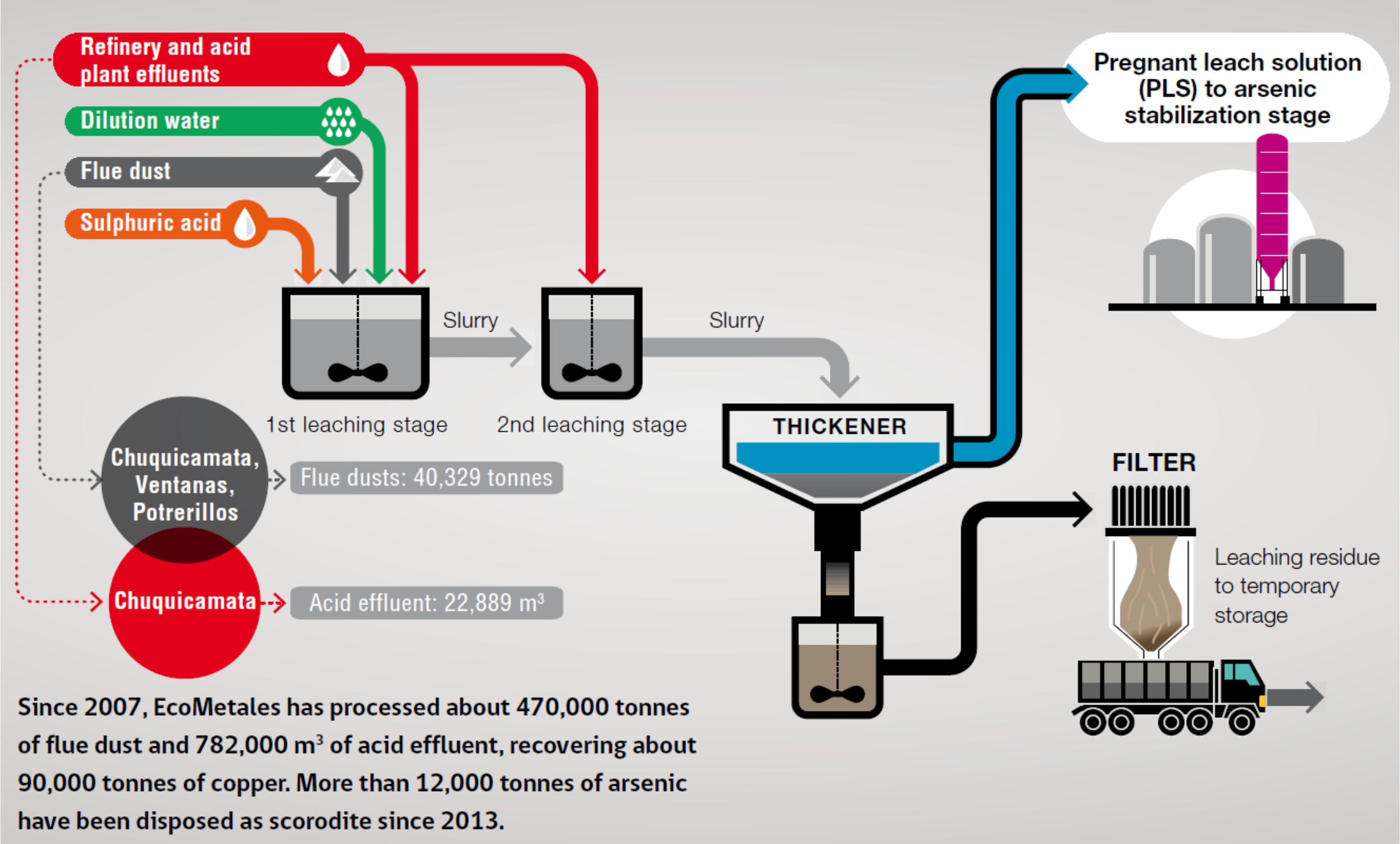
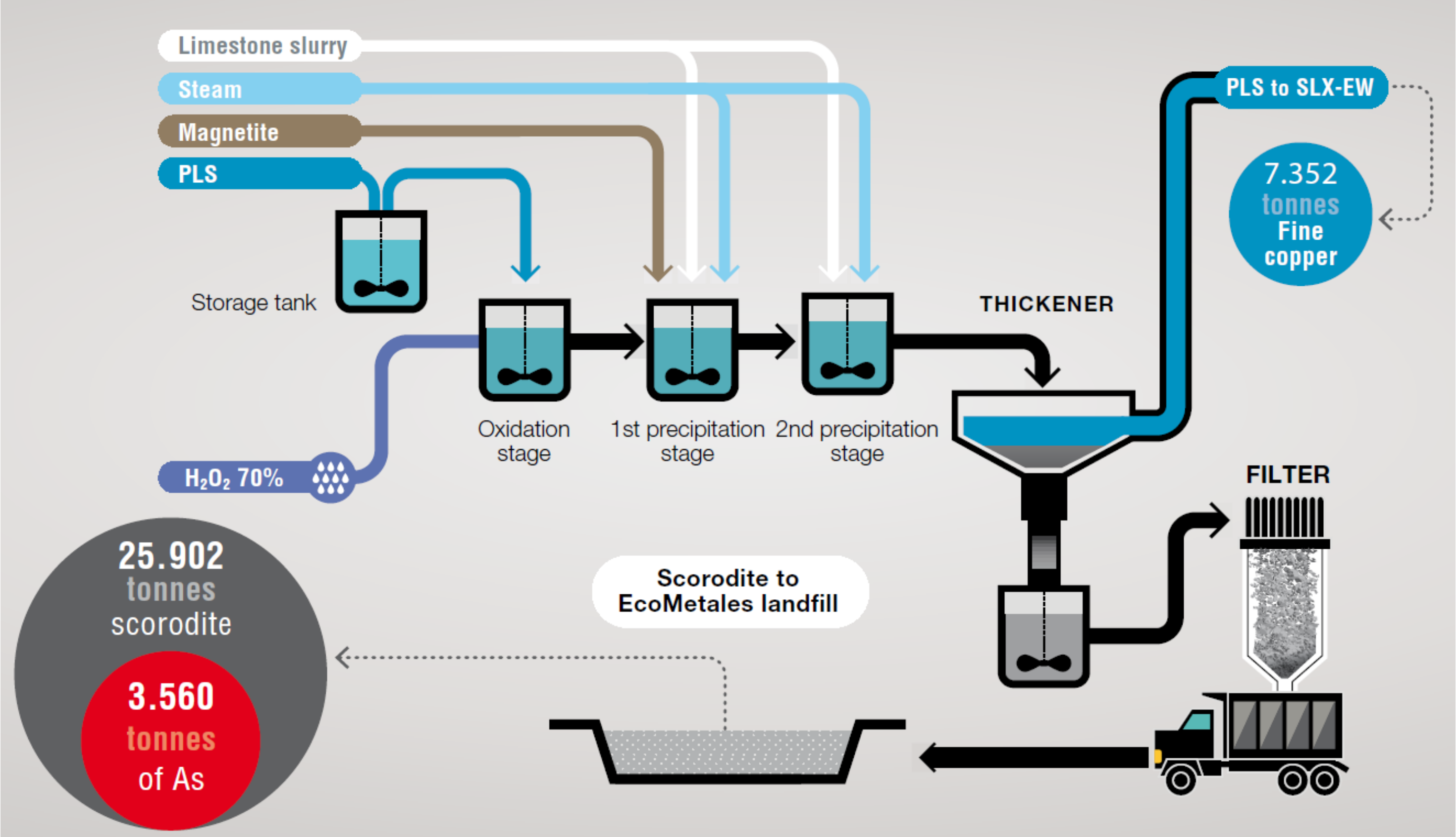
- Ecometales operates an atmospheric dust leaching plant
  - Atmospheric leach at 95°C
  - Combines weak acid and refinery and effluents from Chuquicamata.
  - High dissolution of copper and arsenic. Arsenic subsequently precipitated as scorodite (Stage 2 overleaf) with copper recovered in a neighboring facility.



Source: EcoMetales at JOGMEC 2018

Ecometales: Atmospheric Scorodite

- Ecometales operates an atmospheric scorodite precipitation process
- Arsenical solution enters a 3-stage reactor series
  - Stage #1 arsenic oxidation with H_2O_2
  - Stage #2 adds Fe as an iron sulfate source (Fe:As ~1.5:1)
  - Stages #2, #3 raises the pH gradually with lime
  - Scorodite forms gradually as the magnetite dissolves in the presence of As^{5+}



Source: EcoMetales at JOGMEC 2018

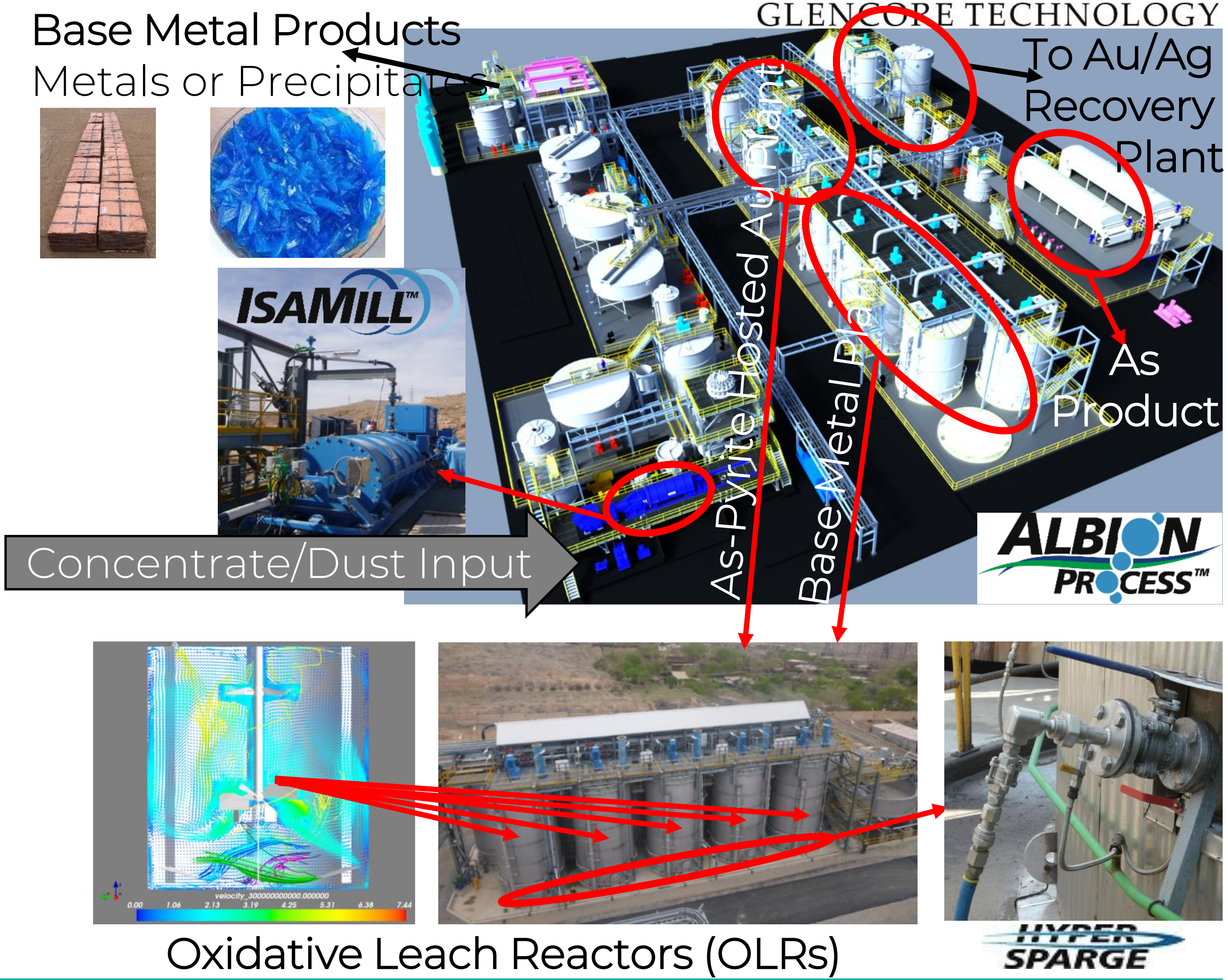
Albion Process™ – Plant Operation

The Albion leach features:

- Fine grinding of solids (ie.. pyrite and/or high arsenic concentrates)
- Atmospheric leach with oxygen injection (HyperSparge™)
- Safe As stabilization in leach residues given an appropriate Fe/As ratio and O_2 efficiency.
- Used in Mount Isa CuSm plant

Albion technology is relevant:

- Utilize the iron units from concentrate to stabilize arsenic.
- Reducing cost of Arsenic oxidation for stabilization (O_2)



Combination of ISASMELT™ with Albion Process™ Mount Isa Copper Smelter

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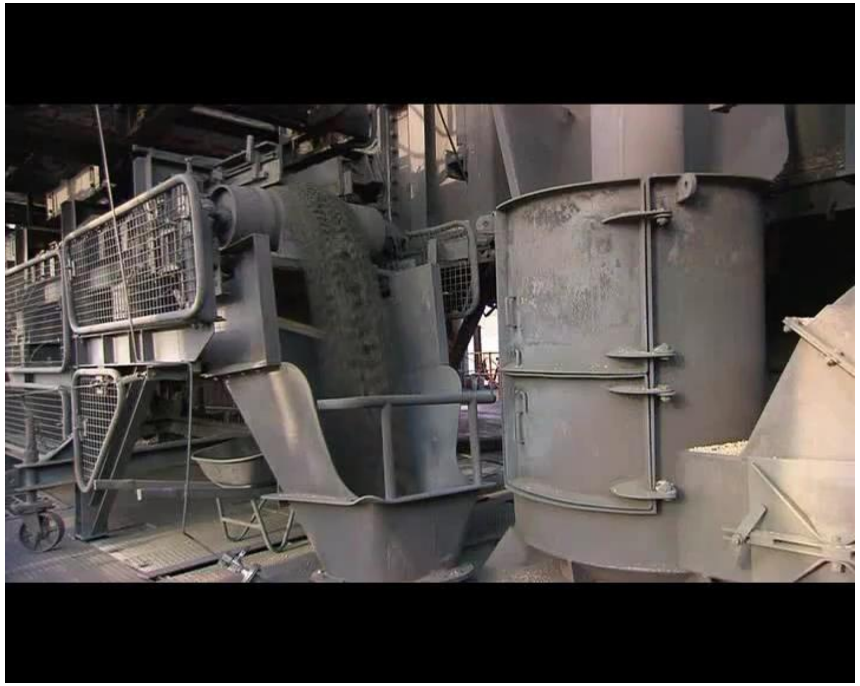
ISASMELT™

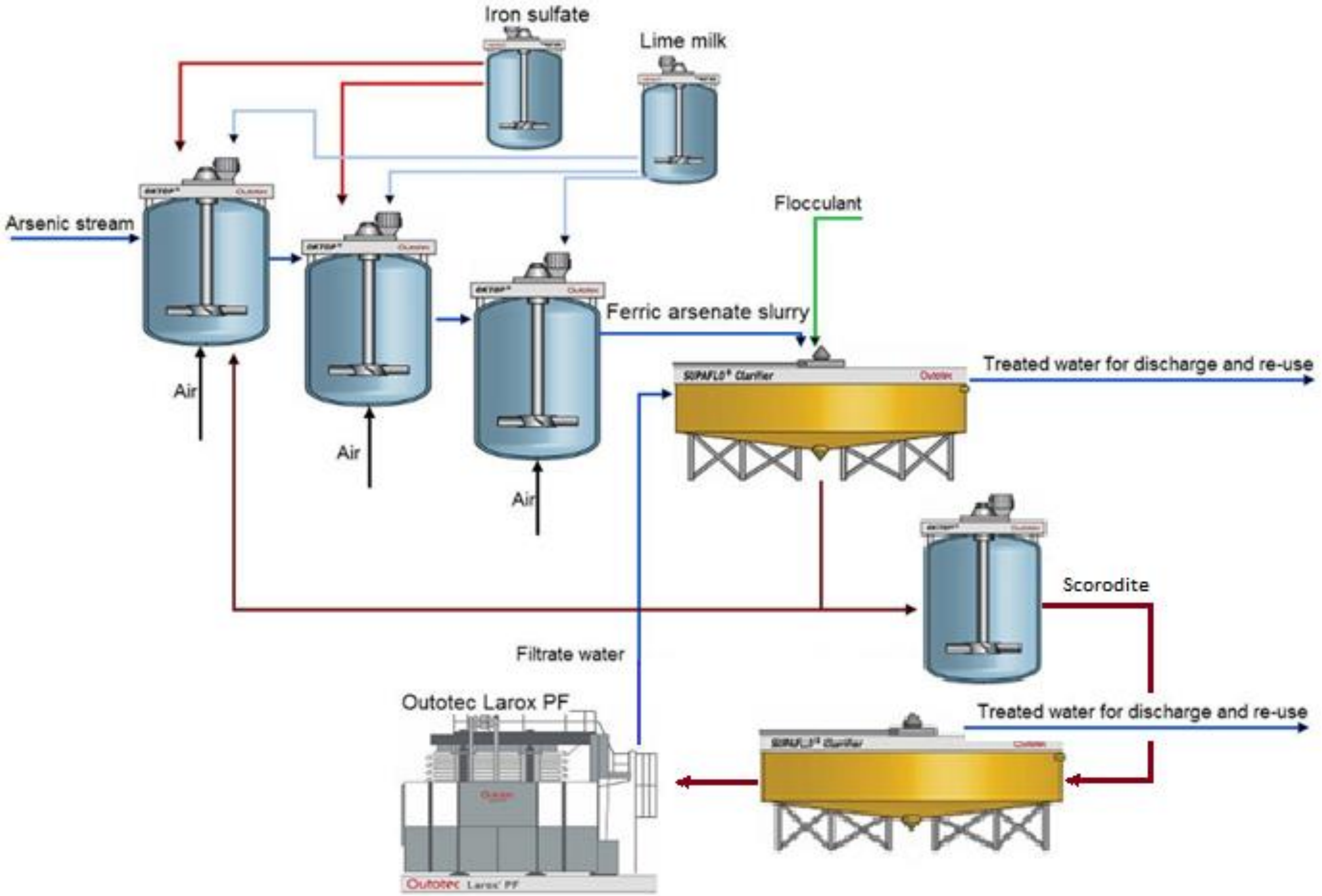


Parameter	Unit	Value
ISASMELT™ Plant		
Normal target Concs rate	t/h (dry)	175
Average Cu in Feed	%	22.4
Average Silica feed rate	t/h (dry)	3.7
Average Coal feed rate	t/h (dry)	1.2
Average Reverts feed rate	t/h (dry)	3.0
Oxygen Enrichment	%	60
Smelter Product Analysis		
Cu in Matte	%	59.5
Slag SiO_2/Fe	Ratio	0.85

Parameter	Unit	Value
Albion Process™ Plant		
Treatment rate – dry solids	t/a	27,200
Availability	%	90
Instantaneous rate	t/y (dry)	3.45
Smelter Dust Analysis		
Cu	%	17.3
As	%	6.70
Fe	%	20.49
S	%	10.27
Cu recovery	%	>99

ALBION PROCESS™

Outotec Hydrothermal Scorodite



Outotec describes a hybrid process for arsenic removal

- Arsenical solution enters a 3-stage reactor series
  - atmospheric oxidation/precipitation at 95°C; air added to all tanks
  - ferric sulphate (reagent) is added to the first two tanks (Fe:As ~ 1.5 molar)
  - the pH is gradually raised with lime
- Precipitate is an amorphous ferric arsenate

Hydrothermal transformation to scorodite can be done in an autoclave

- Amorphous ferric arsenate autoclaved @ 150-175°C to produce scorodite

Mina Ministro Hales Roasting Plant (Codelco)

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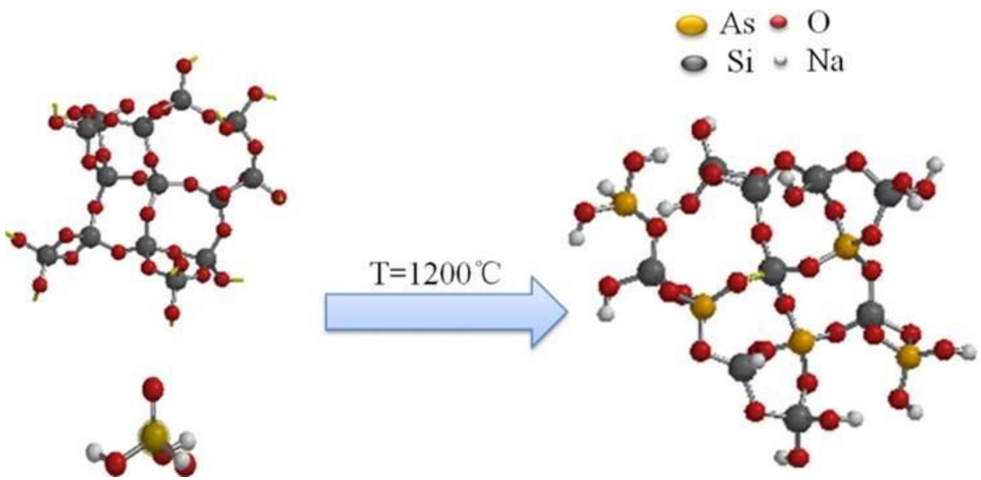
- Autogenous roasting of high arsenic (and Sb) Concentrate
- Fuming of As and Sb (as sulphides and oxides)
  - Arsenic stabilised in subsequent stages
- Calcine (still containing sulphur and heat value) is subsequently smelted autogenously.

	CONCENTRATE	CALCINE
Cu	30%	35%
Fe	21%	23%
S	35%	20%
As	4%	0.3%
Sb	1%	0.2%
Zn	0.4%	0.4%

Source: Wood Mackenzie, Mina Ministro Hales (MMH) copper mine

Source: Concepcion University, Codelco

Dundee Sustainable Technology Glasslock™ Vitrification Process



DUNDEE SUSTAINABLE TECHNOLOGIES

GLASSLOCK PROCESS™

- Patented process in which arsenic gets stabilized in a glass matrix (>10% As) composed of silica, sodium carbonate, hematite and arsenic trioxide.
- Passes TCLP.
- DST developed this technology at the bench scale and has now proceeded with piloting of their technology at a Copper Smelting Facility (pictures overleaf).
- This innovative approach has a chance of being an enabling technology for stabilization of arsenic.

Glasslock Process

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Pilot Plant installed which produced several hundred metric tonnes of arsenical glass.

Dundee designing an industrial scale plant capable of immobilizing much larger quantities of arsenic.

Horne Smelter Effluent Treatment Plant

Published Glencore Horne Smelter's dust treatment, arsenic precipitation and slag concentrator flow diagram (high level, 1995, Godbehere et al.)

Highlights:

- Fe was supplied from acid mine drainage water pumped from two closed mines (Remnor and Gallen).
- Co-deposition of slag flotation tailings (high Fe) and the waste water precipitate are co-deposited.

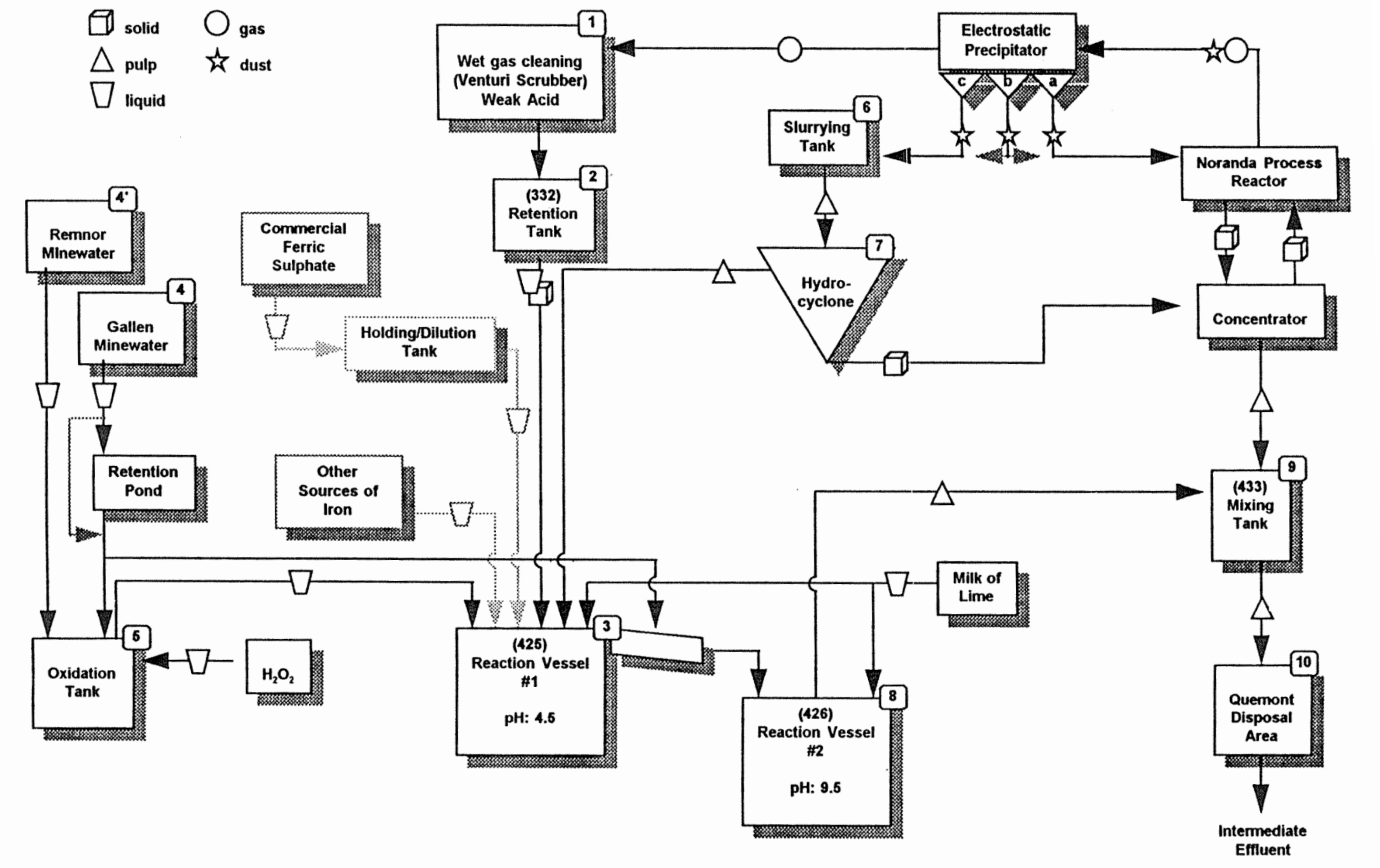

Figure 1 - Process flowsheet

Summary/Conclusions

Summary/Conclusions

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Setting an Industry Objective

- The copper market will expand in the coming years, with more arsenic in copper concentrates expected. Primary producers/equipment manufacturers/universities need to continue working together to ensure we extract copper from these orebodies with the lowest impact on environment.

Technologies for Arsenic Processing/Stabilisation

- Arsenic processing and stabilisation technologies are relatively well know with high potential for further developments, especially on the hydrometallurgical side. Technology selection is highly dependant on regional attributes (overall costs, other impurities, water availability, rainfall, legislative framework). As an industry, we need to support further technology development.

Some noticeable advancements in Chile

- Codelco/Ecometales have advanced the state of the art during the last 15 years. The Mina Ministro Hales roasting plant and the scorodite arsenic stabilisation plant (AAA) are two examples of this progression.

Contributions from Professor Demopoulos

- Professor Demopoulos' commitment to the scorodite process and other hydrometallurgical advancements and his training of highly qualified engineers has certainly contributed to Ecometales' , Codelco's and Industry's successes.: Thanks George for your contributions !

Questions

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