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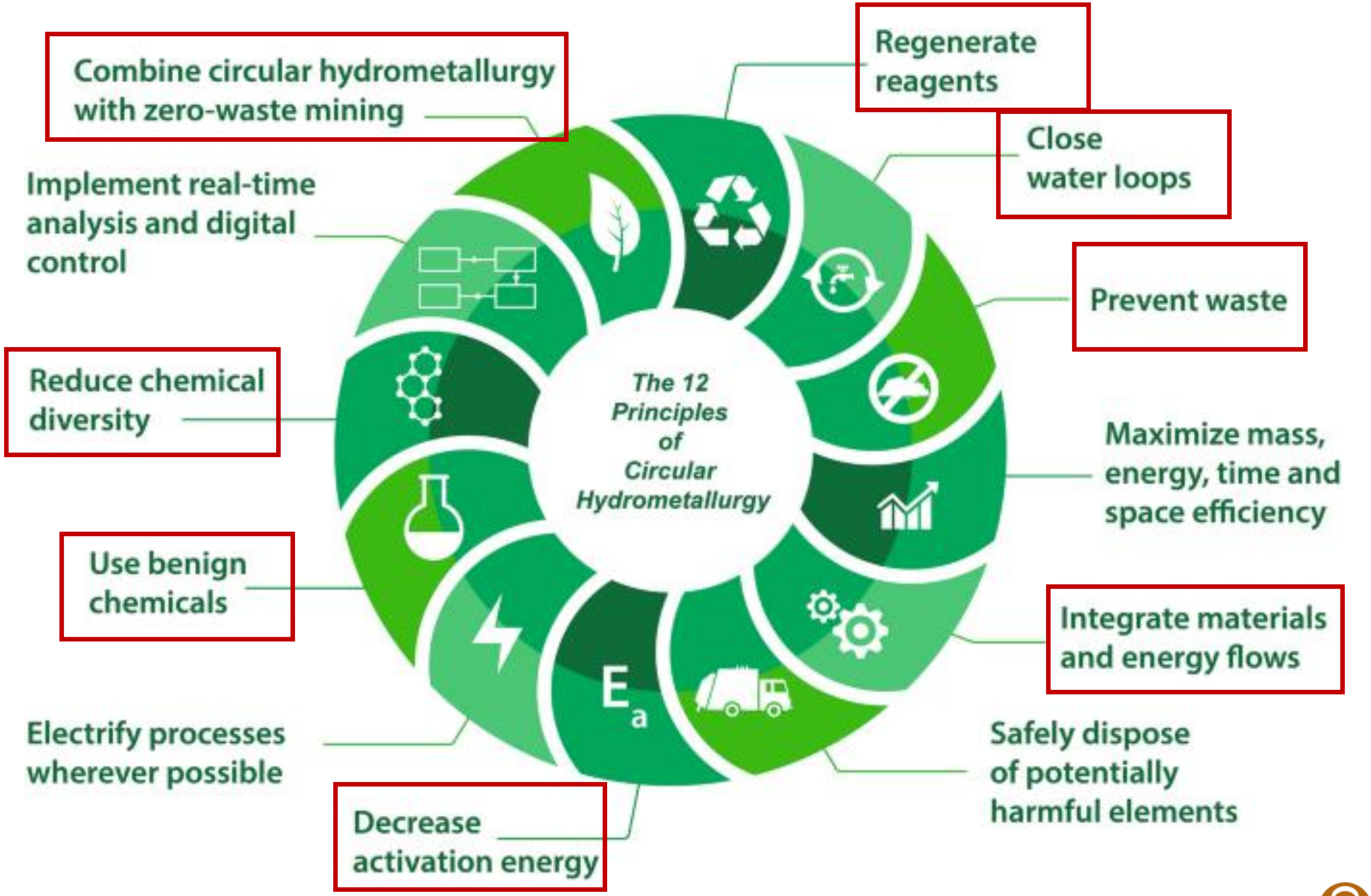
BIOHYDROMETALLURGY AND CIRCULARITY, A LONG STORY

International Circular Hydrometallurgy Symposium

Anne-Gwénaëlle Guezennec

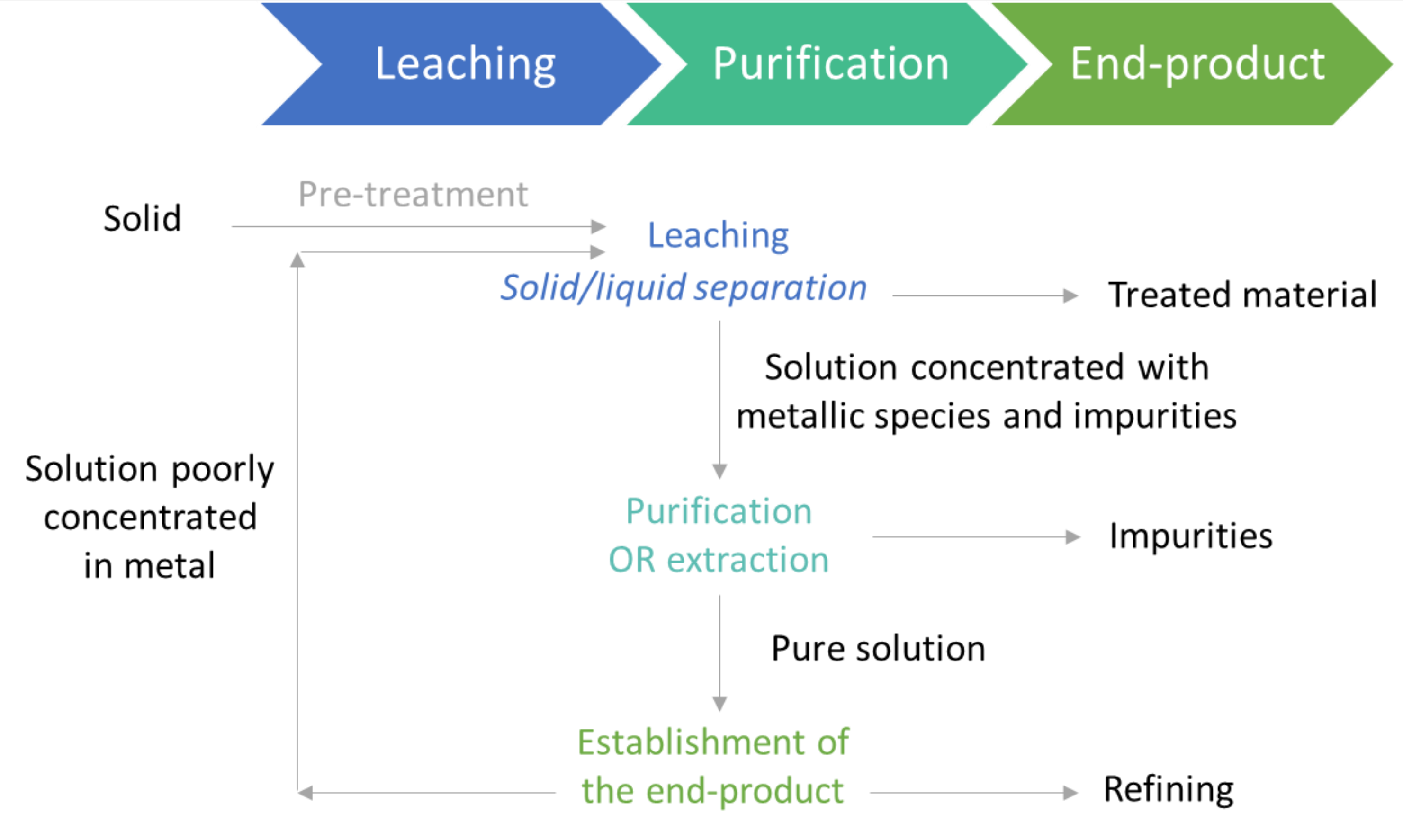
September 11^{th}, 2024



Binnemans & Jones, 2023

#01 WHAT IS BIOHYDROMETALLURGY?

DEFINITION



(from Techniques de l'Ingénieur, Rizet et Charpentier, 2000)

Biohydrometallurgy - also called **biomining** - is a portfolio of hydrometallurgical processes that use **microorganisms** (bacteria, archaea or fungi) to extract metals from mineral matrixes.

→ Production of **chemicals**

→ **Catalysis** of chemical reaction

Bioleaching is the oldest application:

→ Applied at **industrial level** since the end of the seventies

→ **Cu, Au, Ni, Co, U…**

A LONG STORY…

Early biominers…

Re Metallica – Georgius Agricola (1494-1555)

Current bioleach plant…

BIOX, Runruno Philippines

A LONG STORY…

Early biominers…

Re Metallica – Georgius Agricola (1494-1555)

Current bioleach plant…

To produce and to recycle *in situ* chemical such as acids, oxidising agents, complexing agents

BIOX, Runruno Philippines

→ Principles 1, 9 & 10

#02

A FOCUS ON BIOLEACHING

HOW DOES IT WORK?

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TWO APPROACHES

Bio-oxydation:

- Production of sulfuric acid and ferric iron
- Oxidation of reduced metal bearing minerals (sulfides or metals in zero-valent state)
- Applied at industrial scale for primary resources (ores and tailings)
- At pilot scale for secondary resources

Bio-complexation:

- Production of complexing molecules (organic acids, cyanide, siderophores…)
- Complexation of metals in different resources (oxides, laterites, urban wastes…)
- No commercial application: slow rates, low yields, cost of microbial substrates, production of excess biomass

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MAIN MECHANISMS

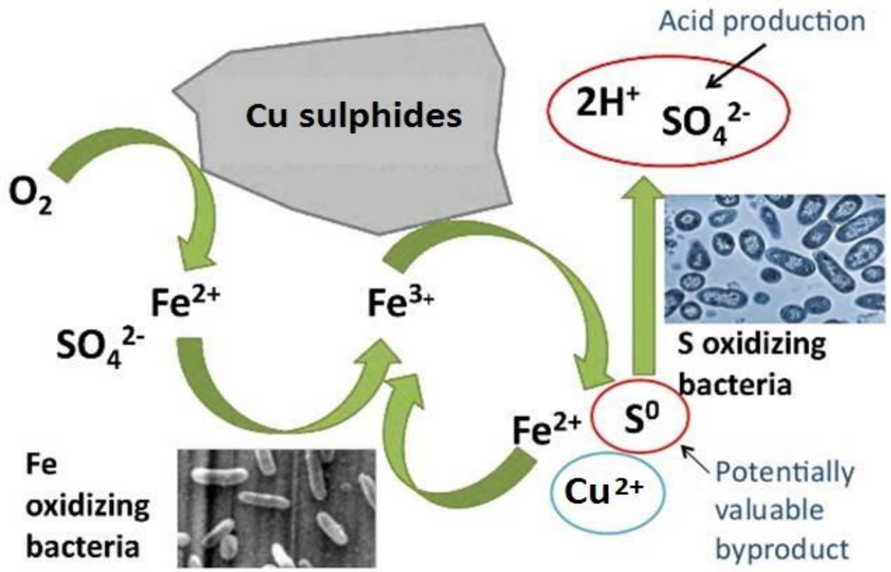
Bioleaching can be defined as the microbially assisted dissolution of certain minerals containing metals in reduced form (**mainly sulfides**). It relies on a combination of **chemical and microbial oxydation reactions**.

Oxidation and dissolution of the sulfide matrix:

- Liberation and/or solubilisation of the metals associated to the matrix -> **Chemical process.**
- Reactants: ferric iron (Fe^{3+}), sulfuric acid (H_2SO_4), oxygen (O2)
- Production of FeII and reduced sulfur compounds

Bio-Oxidation of ferrous iron and sulfur compounds:

- Production of FeIII and sulfuric acid.
- This process is **catalysed by the microorganisms.**



$$MS + 2Fe^{3+} \xrightarrow{chemical} M^{2+} + 2Fe^{2+} + S^0$$

$$MS + 2H^+ + 0.5O_2 \xrightarrow{chemical} M^{2+} + S^0 + H_2O$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{biological} 2Fe^{3+} + H_2O$$

$$S^0 + 1.5O_2 + H_2O \xrightarrow{biological} 2H^+ + SO_4^{2-}$$

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Guezennec, 2019. In: Copper Hydrometallurgy: Principles and Practice. Publisher: B. Wassink & E. Asselin (Eds). METSOC, West Westmount, Québec, Canada. https://store.cim.org/copper-hydrometallurgy-principles-and-practice-electronic-handbook.

KEY FEATURES

The microorganisms:

- *Leptospirillum ferriphilum, Acidithiobacillus caldus, Sulfobacillus benefaciens , Sulfolobus* sp…
- Mining and geothermal environments
- Main characteristics: a**cidophile**, mostly **autotroph** (they use CO_2 as source of carbon), **aerobe**
- They are classified according to the **temperature** (from ambiant temperature up to 80°C) **:** mesophiles, moderate thermophiles, thermophiles

Main advantages compared to conventional processes:

- **Mild operating conditions** (ambient pressure, low temperature, pH>1)
- **Less chemicals and energy consumption**
- **Lower CO_2 emissions**
- **Lower CAPEX and OPEX**
- **Easy to operate**

Main drawback:

- **The kinetics:** slower than conventional processes!!!
- **Large flow of Fe** to manage

#03

INDUSTRIAL APPLICATIONS

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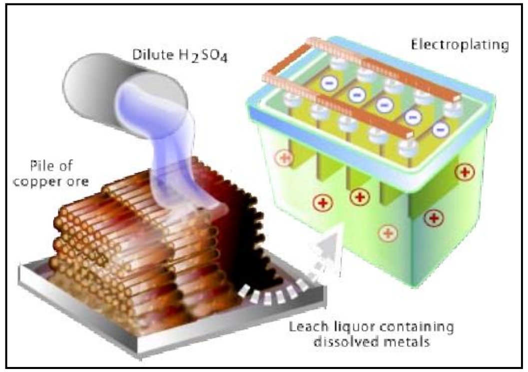
CURRENT STATUS

Heap leaching

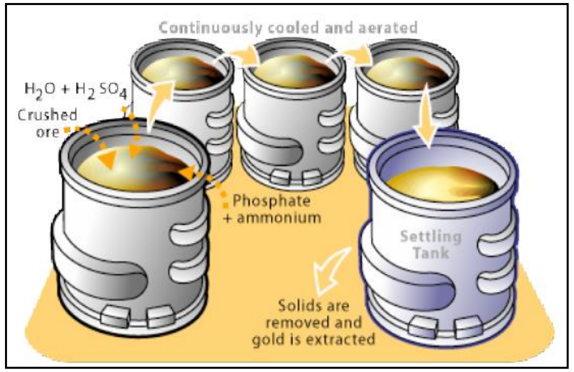


Current status

- Mainly applied for the treatment of Cu ores
- Many bioheap processes have targeted extraction of marginal ores not suitable for concentration and smelting
- Main operators : Newmont Mining, BHP Billiton, RioTinto, Codelco,…

Cu 15 %

Stirred tank reactor (STR)



Current status

- Mainly applied to refractory gold (Biox process) and some base metals (Co, Ni, Cu…)
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Au 6 %

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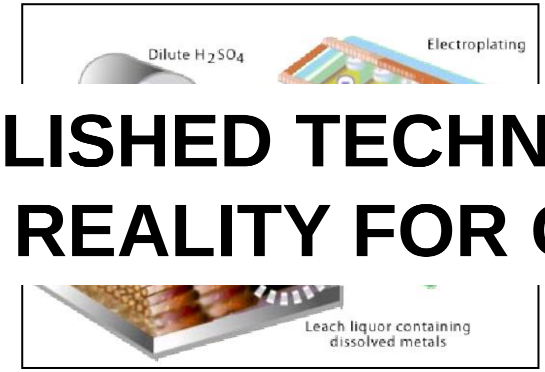

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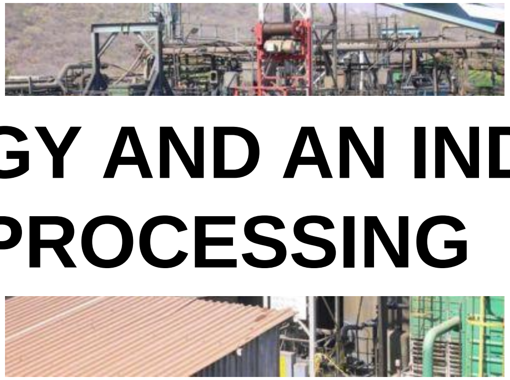

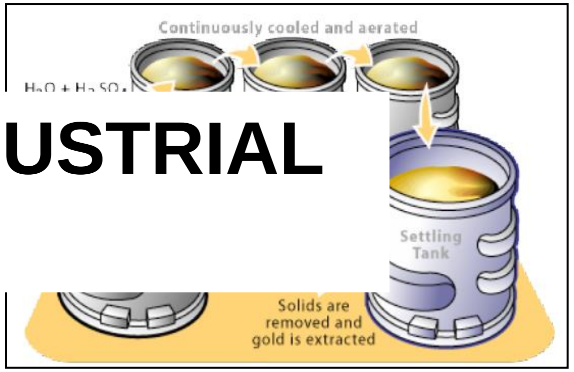

AN ESTABLISHED TECHNOLOGY AND AN INDUSTRIAL REALITY FOR ORE PROCESSING

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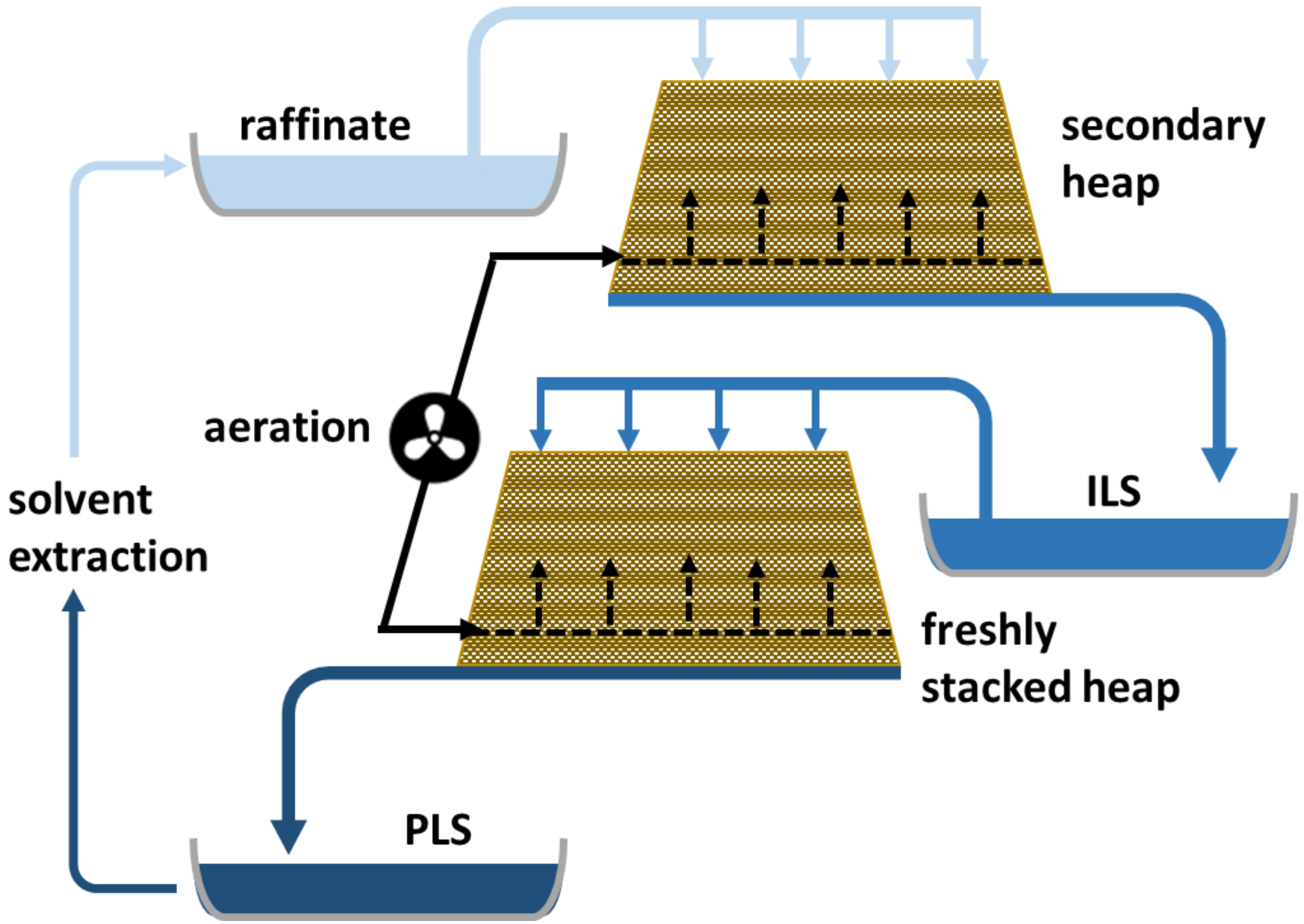
HEAP LEACHING



Main drawbacks:

- Large areas are required
- A slow process:

→ one month residence time for the primary heap

→ 200 days residence time for the secondary heap

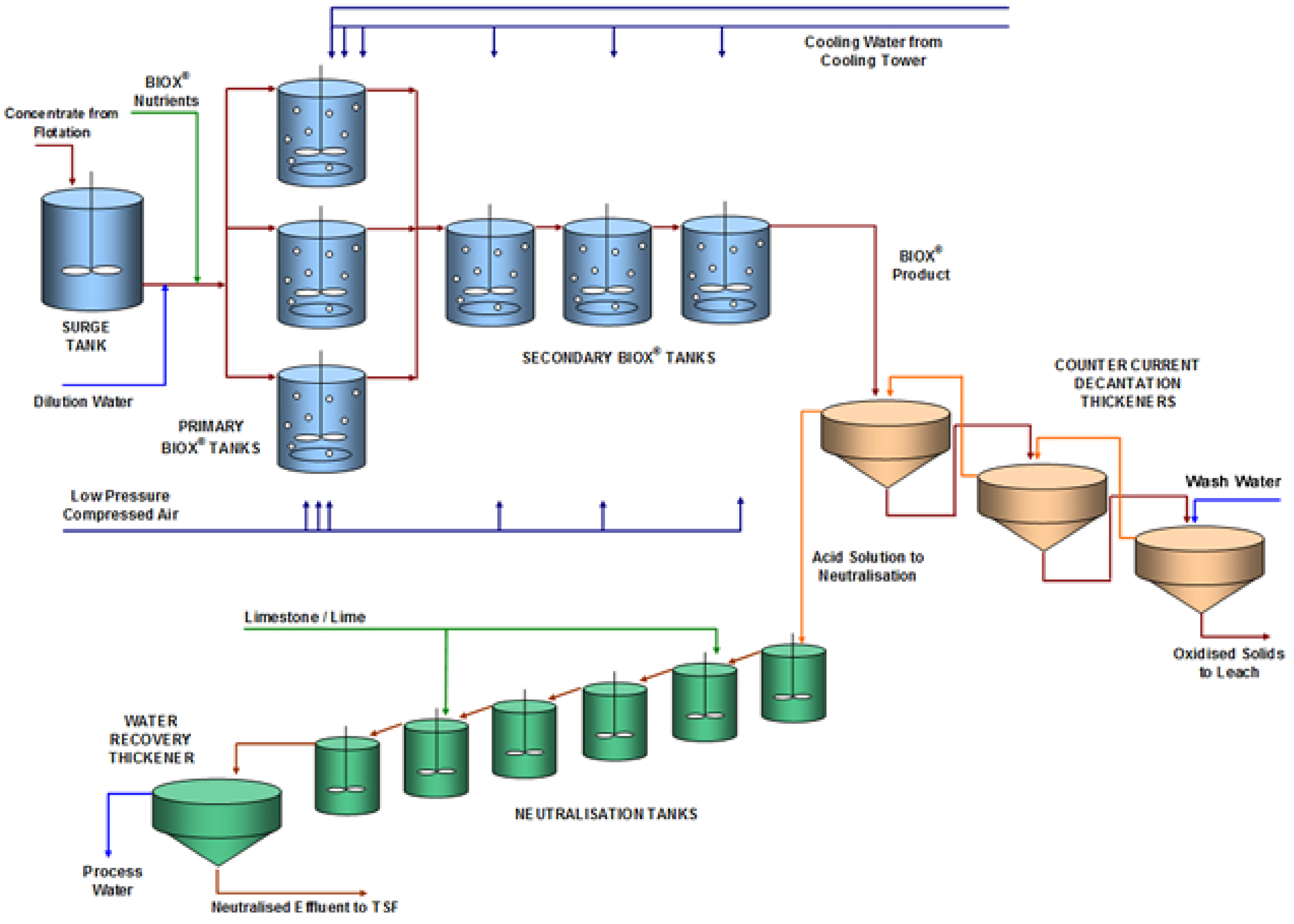
Main advantages:

- Cheap
- Easy to operate
- Low environmental footprint

1kg of $NiSO_4$ produced at **Terrafame** plant is **1.75 kg CO_2-equivalent**, compared to the industry average of **5.4 kg CO_2-equivalent***.

* Value from Ni Institute. More recent and accurate data: 49 kg CO_2-eq for HPAL (A. Mas-Fons PhD)

STIRRED TANK REACTOR



Typical BIOX® process flow sheet

Main drawbacks:

- More expensive than heap (but less than pressure leaching)
- Faster than heap leaching but slower than pressure leaching

~2 and 5 days residence time depending on the temperature and the operation time (adaptation of the microorganisms)

Main advantages:

- Robust and reliable
- Easy to operate
- Less chemicals and energy consumption than conventional metallurgical processes

Dew & Guezennec. In: Biomining Technologies. Springer International Publishing, pp. 41–65. https://doi.org/10.1007/978-3-031-05382-5_3

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FROM TAILINGS TO RESOURCE

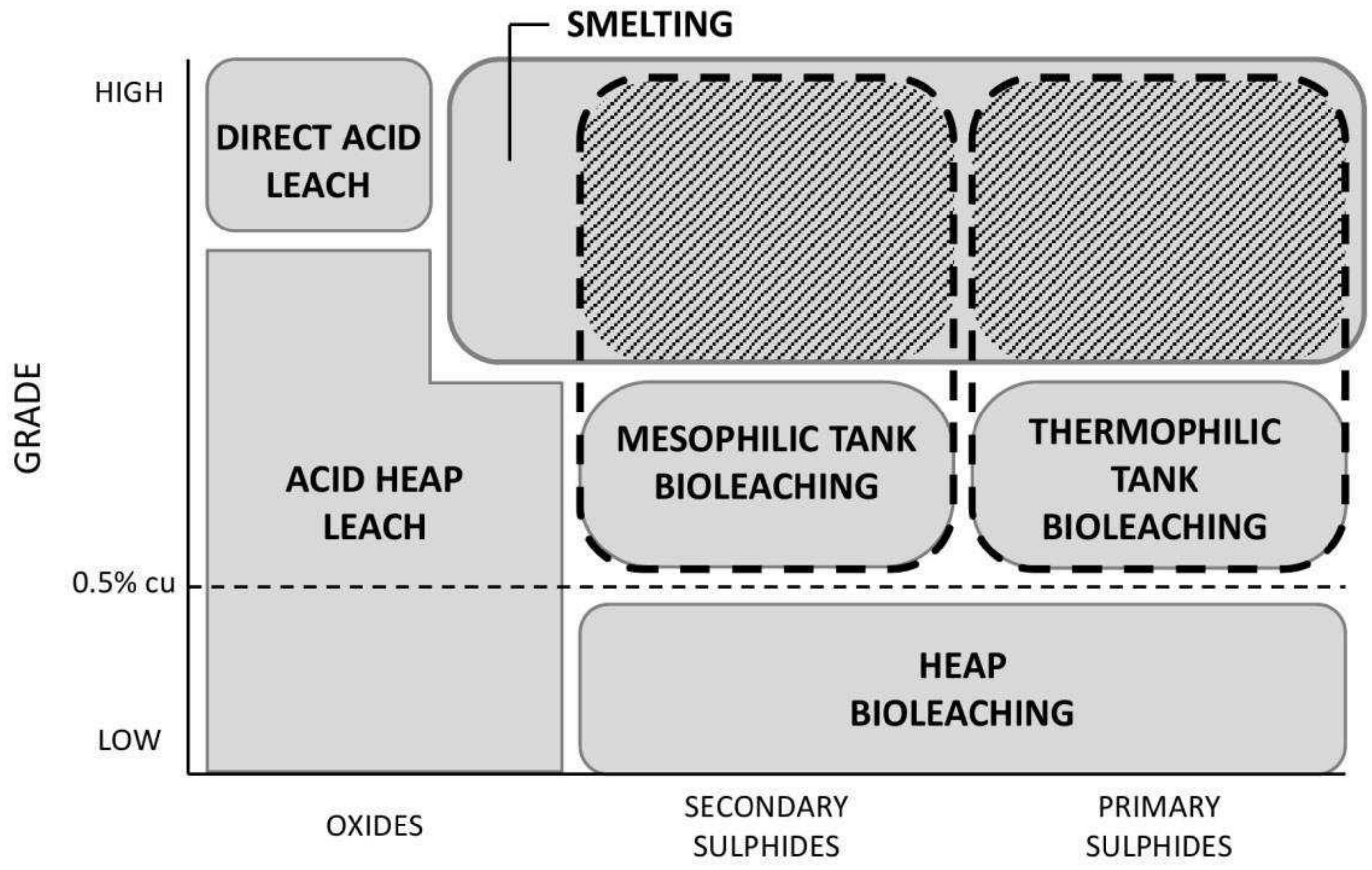
- Some examples of industrial case studies around the world:
  - **Kasese** (former Cu mine, Uganda): production of **Co** from 2000 to 2014 (2% of world wide Co production)
  - **Vuonos** (active talc mine, Finland): production of **Ni** and **Co** from high-grade sulfide flotation tail

➔ **Bio-Hydrometallurgy** is a core technology for mine waste reprocessing

→ *Principle 12*

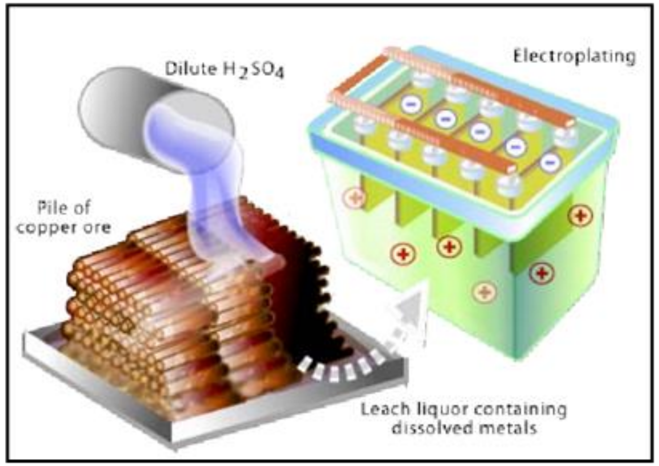
Joulian et al., 2023. Research in Microbiology 104112. https://doi.org/10.1016/j.resmic.2023.104112.
Beylote at al., 2022. Resources, Conservation and Recycling 183, 106347. https://doi.org/10.1016/j.resconrec.2022.106347
Morin & d'Hugues, 2007. In: Biomining. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-540-34911-2_2

TECHNOLOGY SELECTION FOR METAL EXTRACTION



NEW DESIGN OF BIOREACTOR

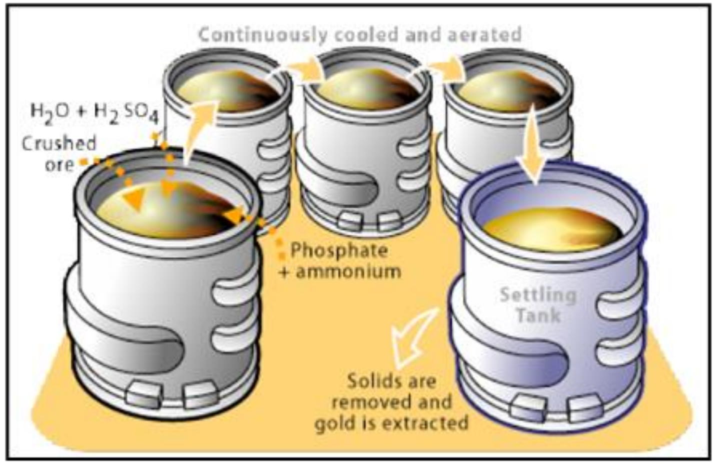
Heap leaching



- Low CAPEX and OPEX
- Suitable for low grade ores

- Low kinetics and recovery yields
- Large foot print

Stirred tank reactor



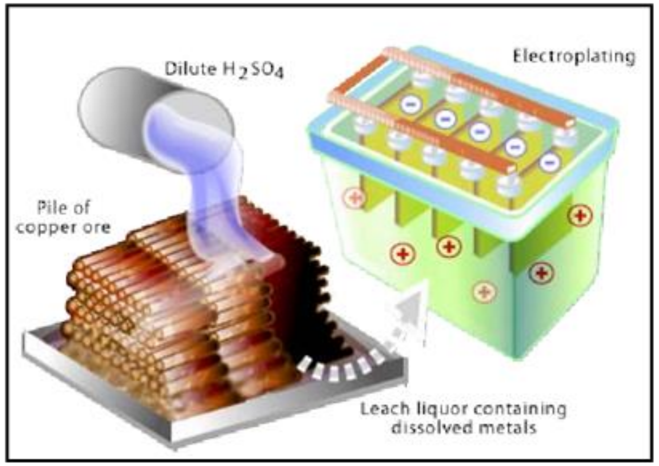
- Robustness and reliability
- High recovery yields

- High CAPEX and OPEX
- Costly mineral processing

NEW DESIGN OF BIOREACTOR

Heap leaching	New Bioreactor for Bioleaching An in-between pathway	Stirred tank reactor

Heap leaching



New Bioreactor for Bioleaching
An in-between pathway

Low CAPEX

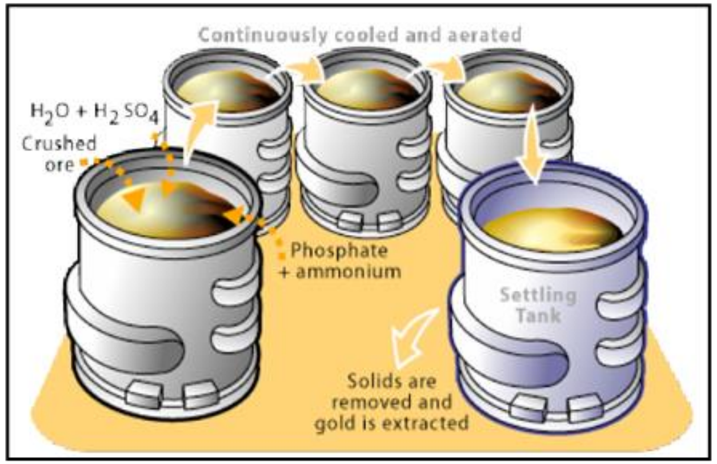
Easy maintenance

Continuous service

Flexible operation

Highly profitable

Stirred tank reactor



Heap leaching:

- Low CAPEX and OPEX
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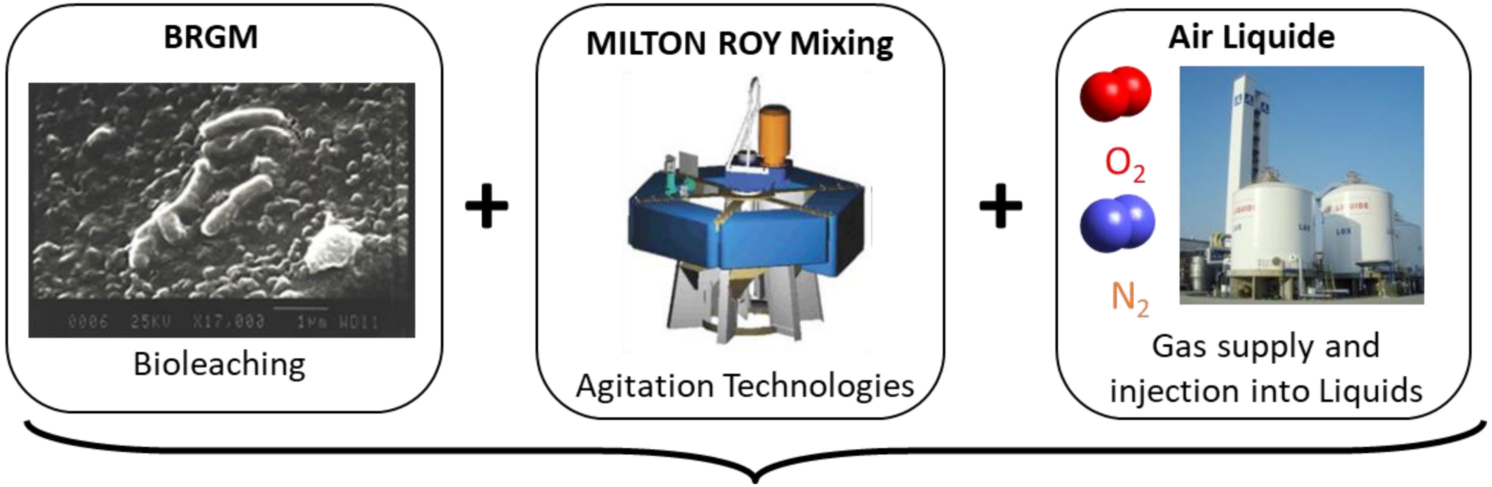
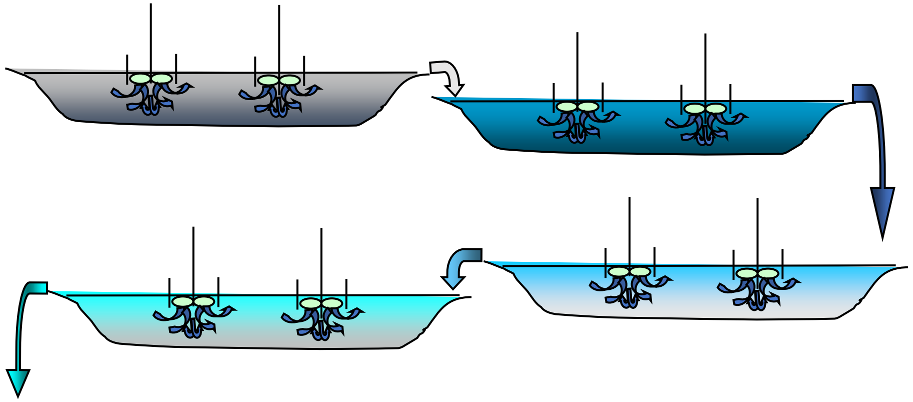


A new bioleaching concept:

- **Floatting agitators to inject gases and to mix solids:**
  - higher solid load (up to 40%) than in conventional stirred tank bioreactor;
  - lagoons or ponds instead of costly tanks
- **No heat exchanger**



https://patents.google.com/patent/US20170175223A1/en

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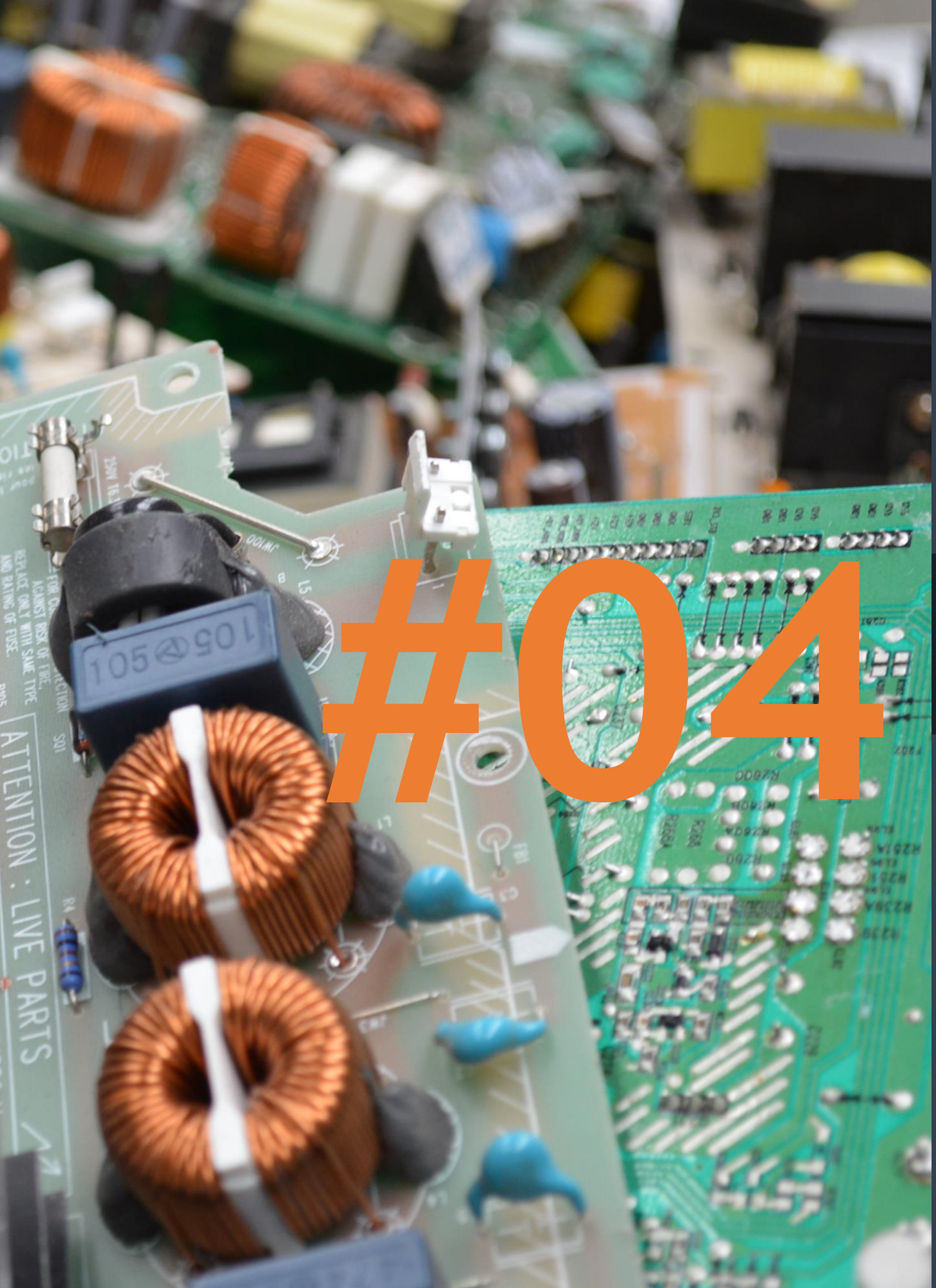

#04

WHAT ELSE?

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BIOLOGICAL SULFATE REDUCTION

- Production of **H_2S** or **sulfur** with sulfate reducing bacteria (SRB)
- H_2S can be used **to precipitate metal sulfide**
- Sulfur can be used **to produce sulfuric acid** (with bacteria) or other sulfur compound (MSA)
- Already applied at industrial scale for effluent treatment (PACQUES)

→ *Principles 1, 2 & 5*

- **Pueblo Viejo gold mine** in the Caribbean: recovery of **Cu** contained in the mine effluent (10kt/y)
- **Landau Colliery** mine in South Africa: sulfate removal as sulfur to produce sulfuric acid
- **Nyrstar zinc refinery** (Netherlands): zinc recovery from acid wash water as Zn sulfides which are reused in the Zn process (300 t/y)

Battaglia-Brunet, et al. 2024. In: Advances in Biochemical Engineering/Biotechnology. Springer, Berlin, Heidelberg.
https://doi.org/10.1007/10_2024_264

E-WASTE RECYCLING: recovery of metals in PCBs

Dissolution of M^0 metals by chemical oxidation

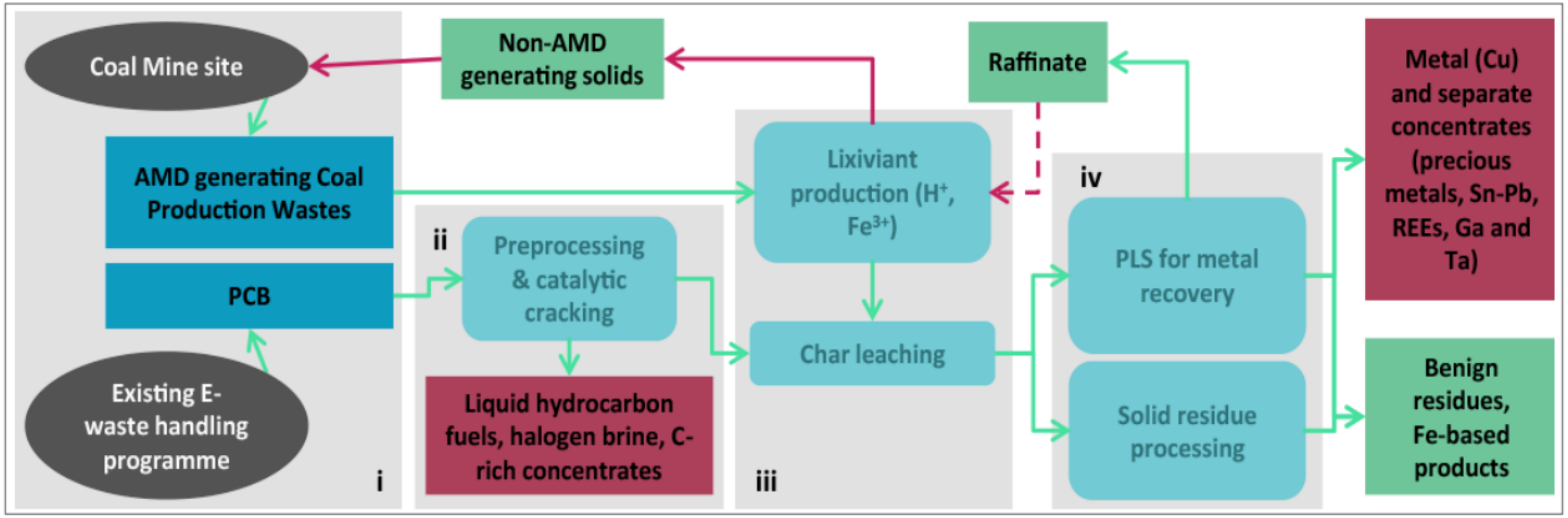
$$M^0 + 2Fe^{3+} \longrightarrow M^{2+} + 2Fe^{2+}$$

$$2Fe^{2+} + 0{,}5O_2 + 2H^+ \xrightarrow{\text{Bacteria}} 2Fe^{3+} + H_2O$$

Regeneration of Fe^{3+} : microbial catalysis of Fe^{2+} oxidation

M^0 = base metals (Cu, Ni, Co, Zn, Sn…)
Precious metals are liberated but not dissolved.

pH < 2 – 30 to 40°C
CO_2 as carbon supply
No sterile conditions



→ *Principles 1, 5 & 12*

➔ **MAIN CHALLENGE: metal toxicity!!!**

Anaya et al., 2021. Frontiers in Microbiology 12. https://doi.org/10.3389/fmicb.2021.669738.
Bryan et al., 2020. Hydrometallurgy 105444. https://doi.org/10.1016/j.hydromet.2020.105444
Hubau et al., 2020. Separation and Purification Technology 238, 116481. https://doi.org/10.1016/j.seppur.2019.116481
Guezennec et al., 2015. Minerals Engineering 75, 45–53. https://doi.org/10.1016/j.mineng.2014.12.033

REDUCTIVE BIOLEACHING

Oxidative bioleaching

$$MS + 2Fe^{3+} \xrightarrow{chemical} M^{2+} + 2Fe^{2+} + S^0$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{biological} 2Fe^{3+} + H_2O$$

- Applied at industrial scale
- For sulfidic ores or wastes

Reductive bioleaching (or bioleaching in « reverse gear »)

$$6Fe^{3+} + S^0 + 4H_2O \xrightarrow{bacteria} 6Fe^{2+} + SO_4^{2-} + 8H^+$$

$$FeOOH \rightleftarrows Fe^{3+} \xrightarrow{bacteria} Fe^{2+}$$

$$MnO_2 + Fe(II) \rightarrow Mn(II) + Fe(III)$$

- Oxidized ores
- Low TRL

Same micro-organisms and same operating conditions as oxidative acidophilic bioleaching: pH 1-2 ; 30°C – 50°C ; CO_2; but absence of O_2

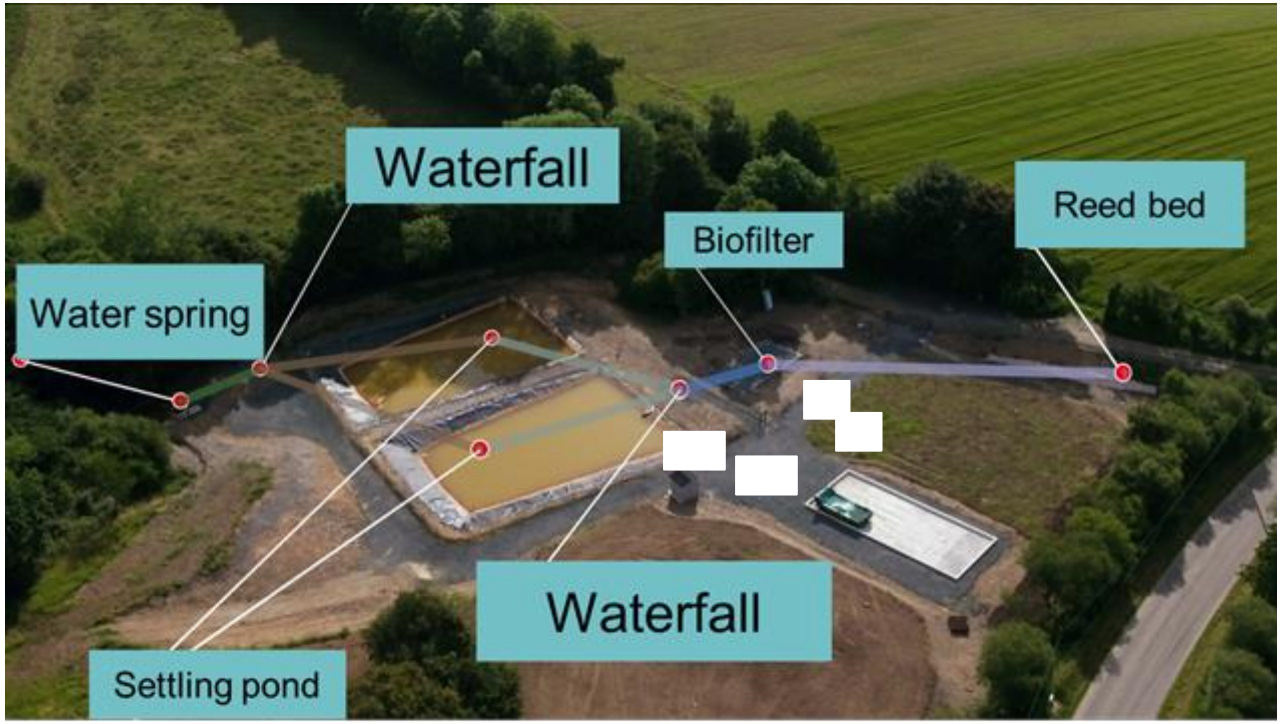
Control of FeII/FeIII, and redox potential

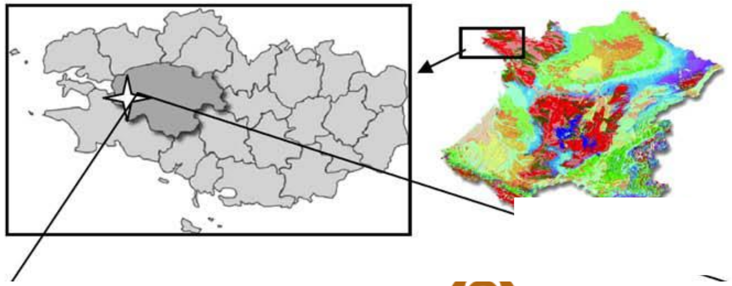
Hubau et al., 2024.Front. Microbiol. 15:1358788. doi: 10.3389/fmicb.2024.1358788

ARSENIC BIO-OXYDATION

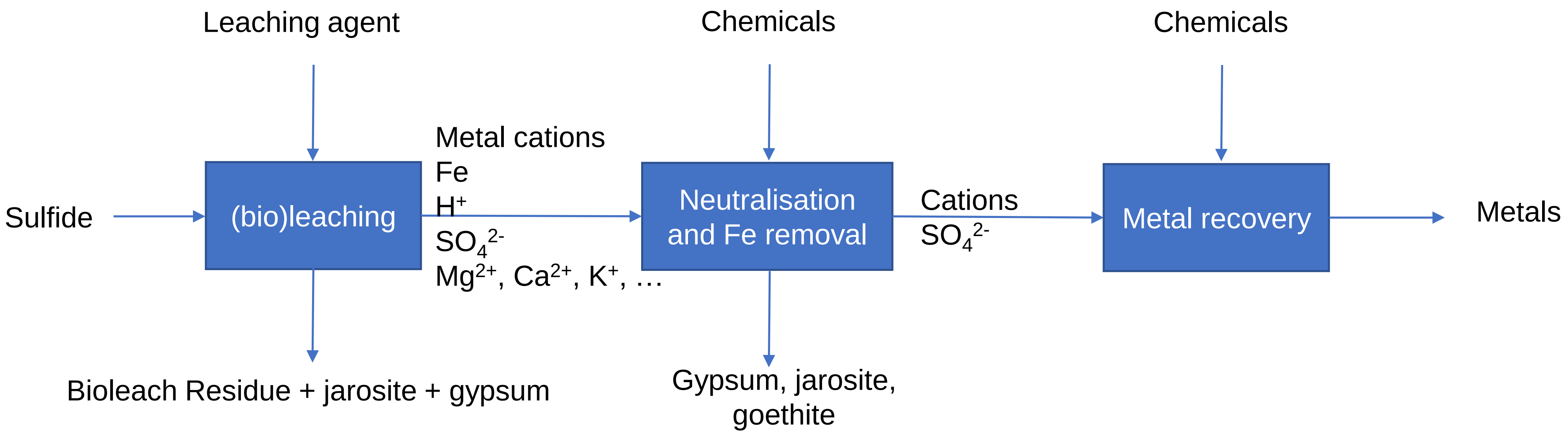
- Classical treatments of arsenic contaminated mining waters:
  - Filtration, ion exchange, lime softening, adsorption → **efficient for As(V)**
  - Need a **preliminary oxidation step for As(III)**: addition of strong oxidants (potassium permanganate, hydrogen peroxide, ozone, …)
    - → **High consumption and cost of reagents, potentially toxic by-products generation, …**
- Alternative way: biological treatments using As(III)-oxidizing bacteria
  - Use of process naturally occurring in the environment

Loperec former Au mine (France)





Guezennec et al., 2012. https://brgm.hal.science/hal-00691189/
Diaz-Vanegas et al., 2023. FEMS Microbiology Ecology 99 https://doi.org/10.1093/femsec/fiad089



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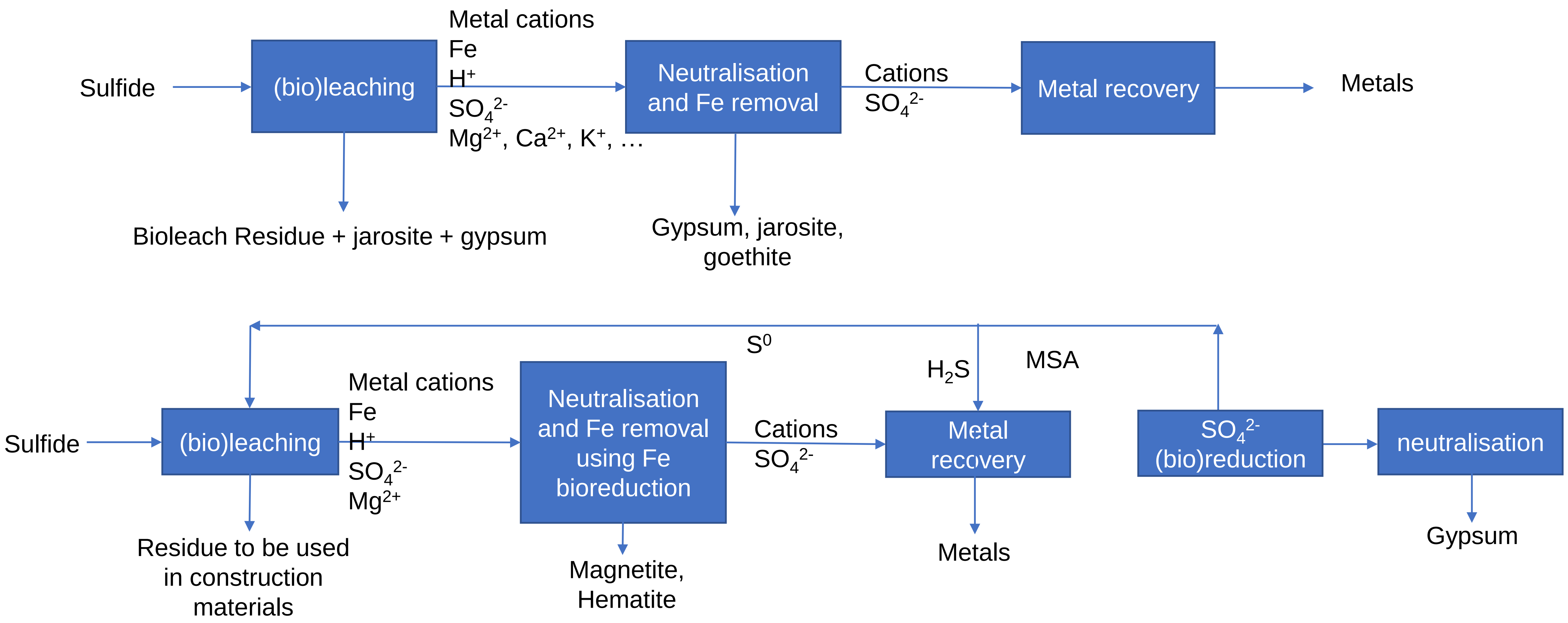

Sulfide
(bio)leaching
Metal cations
Fe
H^+
SO_4^{2-}
Mg^{2+}, Ca^{2+}, K^+, …
Neutralisation and Fe removal
Cations
SO_4^{2-}
Metal recovery
Metals
Bioleach Residue + jarosite + gypsum
Gypsum, jarosite, goethite
S^0
H_2S
MSA
Sulfide
(bio)leaching
Metal cations
Fe
H^+
SO_4^{2-}
Mg^{2+}
Neutralisation and Fe removal using Fe bioreduction
Cations
SO_4^{2-}
Metal recovery
SO_4^{2-} (bio)reduction
neutralisation
Residue to be used in construction materials
Magnetite, Hematite
Metals
Gypsum

CONCLUSIONS

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CONCLUSIONS

- Biohydrometallurgy is slower than conventional hydrometallurgy but is also a proven technology in the field of primary resources
  - Robust, easy to operate
  - Low emission, low energy and chemicals consumption…
  - Flexible (lower CAPEX & OPEX than conventional processes)
- Intense research activity is on-going to adapt this process for recycling purposes (recovery of metals in industrial waste or urban mine)
  - Production of metals from waste (PCBs)
  - Making new products from waste (Pd/Au catalysts)

« It is abundantly clear that future advances in all aspects of bioleaching and mineral biooxidation depend on continued and balanced dialogue among scientists and engineers in disparate disciplinary areas » (Brierley, 2008).

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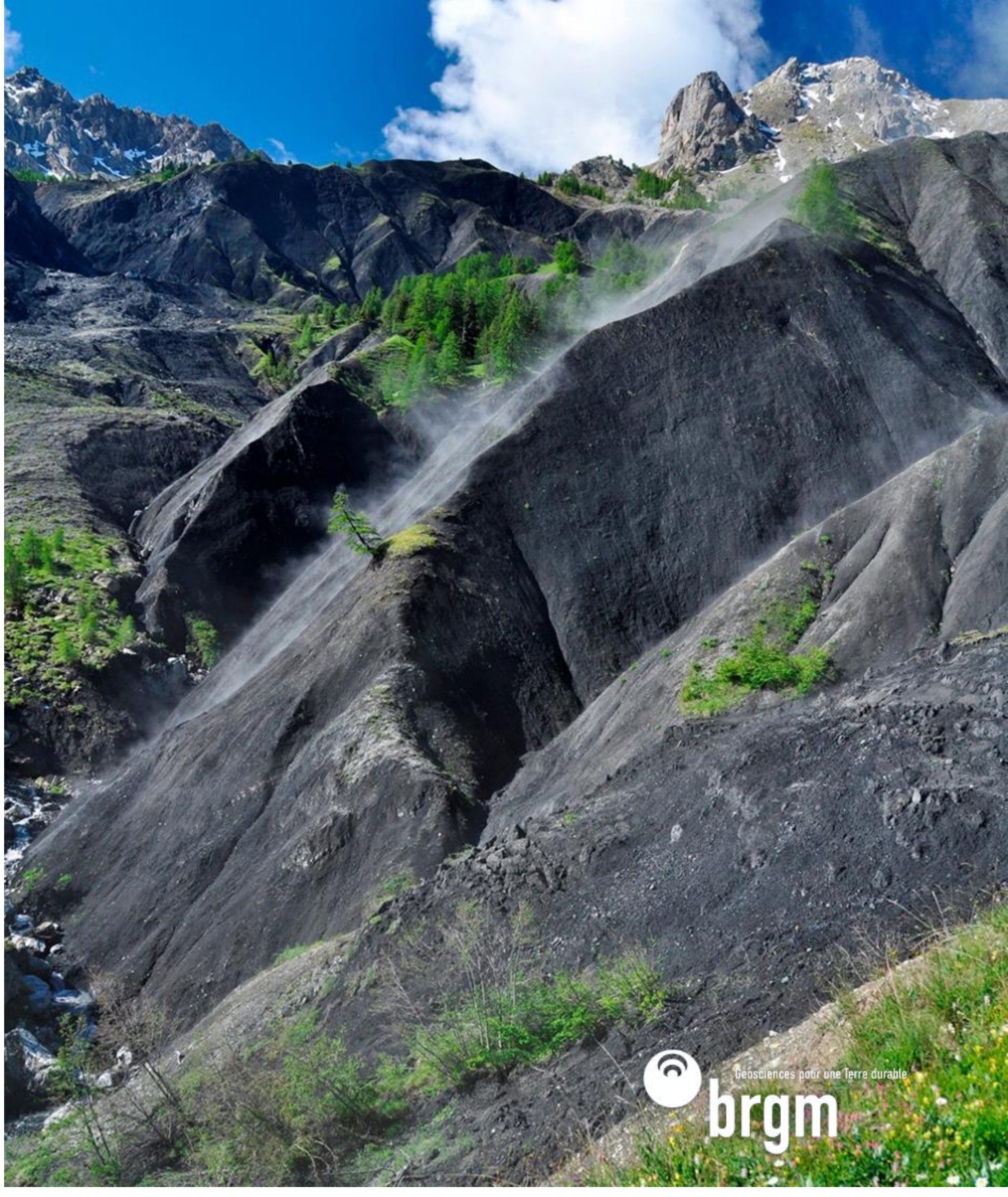
ACKNOWLEDGEMENTS:

- All my colleagues who take or took part in bioleaching experimental and modelling activities:, Douglas Pino-Herrera, Agathe Hubau, Mickaël Beaulieu, Jérémy Engevin, Camille Becquet, Marion Erard, Françoise Bodénan, Jérôme Jacob, Catherine Joulian, Hafida Tris, Mickaël Charron, Clément Duval, Samir Daniel, Jonathan Chéron, Céline Loubière, Juan Anaya, Adeline Po, Simon Chapron, Patrick D'Hugues, Stephane Touzelet, Marine Respaut Monet, Mohamed Djemil, Benoit Henry, Yannick Menard …
- Our partners in European and national projects, especially our colleagues at the University of Lorraine, Eric Olmos, for the collaboration with CFD simulations, and at GEOS, Boliden, Terrafame, KGHM, Milton Roy Mixing, Air Liquide, VALEO…
- Projects: CICERO (HE 10113756), NEMO (H2020 776846), RAWMINA (H2020 958252), CROCODILE (H2020 776473), ANR ECOMETALS, ANR BIOMECALIX, PEPR Sous-Sol Bien Commun…



Thank you for your attention!!!

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BIOLEACHING: main bio-chemical reactions (oxidation process)

The electron shuttle: a mechanism that maintains the **pH neutral** inside the cell.