La biolixiviation: apport des biotechnologies pour la valorisation des minerais et des déchets

A.G. Guezennec
BRGM (French Geological Survey), France
THE FRENCH GEOLOGICAL SURVEY

THE BRGM IS FRANCE’S LEADING PUBLIC INSTITUTION WORKING IN EARTH SCIENCE APPLICATIONS FOR THE MANAGEMENT OF SURFACE AND SUBSURFACE RESOURCES AND RISKS.

- State research institute.
- ~ 1000 people
- Department “Waste and Raw materials”:
  - Mineral processing (crushing, grinding, separation, concentration, L/S separation)
  - Hydrometallurgy □ Bioleaching
- Laboratories and over 2000 m² piloting hall
- What is Bioleaching? At the interface between Micro-Organisms (biology) and Minerals (geology)...

- Current status and case study (reprocessing of mine wastes)

- Some challenges and perspectives
What is « Bio-Hydrometallurgy »?

Hydrometallurgical reactions assisted with microbial activities:

- **Bio-flotation**: modification of mineral surfaces to enhance or depress flotation
- **Bio oxidation**: microbial catalyzed oxidation (especially of Fe\(^{2+}\) and S species)
- **Bio-complexation**: generation of organic compounds that favorably complex with metal species
- **Bio-sorption/ -accumulation**: incorporation of metal species from solution into biomass

Typical hydrometallurgical processes - Hayes, 1993
What is « Bioleaching »?

Microbially assisted leaching of certain minerals (Bio-oxidation/Bio-complexation):

- Bioleaching can be applied to various ore types through microbial generation of leach agents:
  - e.g.1: H\(^+\) and Fe\(^{3+}\) leaching mineral sulfides → Bio-oxidation
  - e.g.2: organic acids leaching oxides and laterites → Bio-complexation
  - e.g.3: biogenic cyanide for gold leaching → Bio-complexation

- Organic acid and cyanide bio-production remains at laboratory stage:
  - slow rates and low yields of metal extraction as well as the cost of microbial substrates (glucose, etc.) and the production of excess biomass have precluded these approaches being developed as commercial operations

- Most R&D has focused on BIO-OXIDATION which is the only bioleaching process to reach industrial implementation.
Bioleaching/Biooxidation

How does it work?

- **Bacterial degradation of the sulfide matrix:**
  - Oxidation of ferrous iron and sulfur = energy source

- **Liberation and/or solubilisation of the metals in acidic media**
  - $\text{H}_2\text{SO}_4 = \text{a product of the bacterial metabolism}$

- **Acidophilic, autotrophic bacteria** (heterotrophic), from 30°C to 80°C (mesophiles, moderate thermophiles, thermophiles)
  - $\text{Leptospirillum ferripilum, Acidithiobacillus caldus, Sulfolobus benefaciens, Sulfolobus sp...}$
  - aerobic

\[
\text{MS} + 2\text{Fe}^{3+} \rightarrow \text{M}^{2+} + 2\text{Fe}^{2+} + \text{S}^0 \\
2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \ (bact.) \\
\text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \ (bact.)
\]
Bioleaching/Biooxidation

Solubilisation of metals (associated to sulfide matrix) by bacteria, a natural phenomenon known and used since earliest Antiquity:

- Acid mine drainage
- Metals recovery, especially Cu

→ Rio Tinto: Cu exploitation from Phoenician times; 1st heap bioleaching attested in the 17th century

Rio Tinto, Spain (AMD)

Re Metallica – Georgius Agricola (1494-1555)
Bioleaching = an established technology and an industrial reality for ore processing

**Heap leaching**
- 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,...

**Stirred tank reactor**
- Mainly applied to refractory gold (Biox process) and some base metals (Co, Ni, Cu...)
- More than 15 plants in operation at industrial or demonstration scale
- Main operators: Newmont Mining, BHP Billiton, RioTinto, Codelco,...
KCC (Kasese Cobalt Company): An industrial project of cobalt recovery using bioleaching technology as an answer to an environmental issue

Context: Kilembe Mine - Kasese (Uganda)
- Former Cu mine -> 1.1 million tons of tailings
- Fine (<200µm) and heavy material (d ± 4.5)
- Pyrite FeS2: 80%
- 1.38% cobalt disseminated in the pyrite lattice

Biology:
- Identification of a biological activity around the stockpiles and in the drainage: natural bioleaching process
- Mesophile to moderate thermophile microbial consortium (Leptospirillum ferriphilum, Acidithiobacillus caldus, Sulfothiobacillus benefaciens...)
- Preliminary bioleach amenability tests in lab: more than 95% of Co recovery

A way to stop the discharge trail from the KASESE site to the Queen Elisabeth National Park due to runoff and natural bioleaching of the concentrate

An alternative to technologies which are air-polluting (roasting), or energy consuming (roasting and high-pressure leaching)
KCC project: a bioleach success story

- **1989-91: Pre-feasibility study**
  - Testwork on bioleaching at lab-scale (2L stirred tank reactor, batch)
  - Main operating parameters (temperature, pH) and microbial monitoring

  - Bioleaching pilot testwork in BRGM process hall (100L STR, 5 kg/d)
  - Residence time, solid load, mass transfer (pulp homogeneity, gas dispersion), energy transfer (thermal regulation), pH regulation...

- **1993-96: Feasibility step II and basic engineering**
  - Complementary testwork on bioleaching, zinc solvent extraction and electrowinning
  - Bioleaching pilot testwork: 1t per day in Uganda - 65 m3 tank
  - Environmental impact study & Power supply (hydroelectric)
  - Engineering and economic evaluation, feasibility report and auditing

- **1996-98: Detailed engineering**

- **1998-99: Construction and start-up**
  - First Co cathode in June 1999

- **2002: Monthly cobalt production reaches 67 tons (~2% of the world Co production)**

- **2014: End of the operation**
  - All the tailings stockpiles have been treated and the site environment has been restored!!!
How to improve process efficiency?

Process economy improvement

- **↑ revenues** by improving process efficiency
- **↓ operating costs**
- **↓ capital costs** = **↓ tank volume**

- **↓ Eh (< 420 mV)** better dissolution of chalcopyrite
- **↓ Agitation / aeration rates**
- **Reactor design**
- **↑ solids feed content > 20%**
- **↓ residence time < 6.5 days**

Cordoba et al. 2008; Pinches et al. 2000; Third et al 2002; Tshilombo et al 2002

Non-traditional operating conditions
Some challenges

The improvement of process efficiency (and economy):

- **Improvement of gas transfer:**
  - 2 kg of oxygen is needed to convert 1 kg of sulfide (for ex., the dissolution of 1 kg of pyrite requires 1 kg of oxygen)
  - The oxygen uptake rate (OUR) depends on the kinetics of the chemical and biological reactions and can vary with the type of micro-organisms. In optimal conditions, OUR varies between 800 and 2000 mg/L/h.
  - Main CAPEX: Agitator. Main OPEX: Energy to inject and to disperse the gas (air and CO2)
  - *Scientific challenges: impellers design, replacement of air by oxygen (microbial tolerance to increasing dissolved oxygen concentration)*

- **Increase of solid load:**
  - The solid load in the feeding pulp is comprised between 10% and 20%, and usually around 15%.
  - One of the main CAPEX for bioleaching processes is the cost of the tanks. Increasing solid load means decreasing the size and the number of tanks and thus their cost.
  - *Scientific challenges: oxygen transfer, metal tolerance, microbial resistance to shear stress*

- **Reactor design:**
  - In between heap and STR

The adaptation of the technology to new types of metals bearing targets:

- **Primary base metals resources (mainly Cu...)** -> Process economy
- **Oxyde ores (laterites)** -> reprocessing of untreated limonitic stockpiles (Ni, Co, Cu + REE, Sc...)
- **Secondary wastes (SAR, WEEE...)**
How to improve O₂ transfer?

- Increase transfer coefficient
  - Mixing system

- Increase the driving force
  - To replace air by O₂ enriched gas or pure O₂

**Main issue:** the DO concentration will increase, which might affect bacterial activity. See the recent work of Wang et al. (2015) who observed a decrease of bacterial activity for DO > 5 mg/L
Improvement of gas transfer

To study bioleaching efficiency vs. DO concentration

Bioleaching rate and sulfide dissolution yields

Wide range of DO concentration (below and above 6ppm)

Oxygen transfer

Biomass
Improvement of gas transfer

To study bioleaching efficiency vs. DO concentration

Agitator design:
- BROGIM® turbine
- Floating agitator

Oxygen transfer

Bioleaching rate and sulfide dissolution yields

Biomass

Wide range of DO concentration (below and above 6ppm)

Economic assessment

Source: UMICORE

Bioleaching rate and sulfide dissolution yields

Wide range of DO concentration (below and above 6ppm)
Improvement of gas transfer

To study bioleaching efficiency vs. DO concentration

Wide range of DO concentration (below and above 6ppm)

Agitator design:
- BROGIM® turbine
- Floating agitator

Oxygen transfer

Bioleaching rate and sulfide dissolution yields

Biomass

Experimental design: bioleaching in continuous mode (20L STR, 20% solid, 5kg/d, 2 days residence time, 4 months of operation, 5kg/d)

- Time and HR consuming
- Numerous failures (pumps, plugging...)
- Few tested conditions
- Exhausts operators’patience

- Enables to operate at steady state -> avoids DO variation due to changes in O₂ demand
- Reliable analysis of the gas phase -> reliable OTR quantification
Improvement of gas transfer

<table>
<thead>
<tr>
<th>Condition</th>
<th>measured DO concentration (ppm)</th>
<th>Residence time (Day)</th>
<th>Sulfide dissolution yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Condition 1</strong></td>
<td>4,7</td>
<td>2,5</td>
<td>63%</td>
</tr>
<tr>
<td><strong>Condition 2</strong></td>
<td>5,0</td>
<td>2,2</td>
<td>56%</td>
</tr>
<tr>
<td><strong>Condition 3</strong></td>
<td>9,5</td>
<td>2,2</td>
<td>61%</td>
</tr>
<tr>
<td><strong>Condition 4</strong></td>
<td>12,9</td>
<td>2,2</td>
<td>77%</td>
</tr>
<tr>
<td><strong>Condition 5</strong></td>
<td>17,7</td>
<td>2,4</td>
<td>29%</td>
</tr>
</tbody>
</table>

pyrite dissolution rate 57% O2  × pyrite dissolution rate 71% O2  ○ OUR 57% O2

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**Pulp**

- L. ferriphilum
- Sb. benefaciens
- At. caldus
- Total

**Liquid phase**

- L. ferriphilum
- Sb. benefaciens
- At. caldus
A new bioleaching concept:

- Floating 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
- Use of oxygen-enriched air instead of air
  - Temperature regulation by varying gas flow and $O_2$ partial pressure
  - Improving gas to liquid transfer
Technologie Readiness Level

Step 1: 1st feasibility level
- Influence of $O_2$ on bacteria
- Compatibility between the floating agitation device and the pyrite rich pulp

Preparatory step

Optimization step

Step 2: 2nd feasibility level
- Compatibility between the floating agitation device and the bacteria
- Effect of out-range temperature levels on process operation (overheating or under-temperature operation)

Industrial demonstrator (1 agitator; scale 1:200)

Industrial pilot (scale 1:10)

Optimization of bioleaching $\rightarrow$ Optimized operating parameters

Pre-Optimization of gas transfer $\rightarrow$ OPEX preliminary evaluation

Pre-Optimization of agitation $\rightarrow$ Agitator design

Bioreactor modeling $\rightarrow$ Dedicated model


AL/BRGM/MRM Phase I and II

AL/BRGM/MRM Phase II (2016-2017)

Optimization of bioleaching $\rightarrow$ Optimized operating parameters

Pre-Optimization of gas transfer $\rightarrow$ OPEX preliminary evaluation

Pre-Optimization of agitation $\rightarrow$ Agitator design

Design of a dedicated experimental device

Feasibility study (ProMine)

Patent (2013)
**Batch tests** in 1.5 m³ tank with a mini TURBOXAL scale ¼

**Tested parameters:** solid load and gas composition (oxygen enrichment), bacterial tolerance towards agitation device, gas transfer

**Materials:** sulfide rich tailings (60% pyrite, 600 ppm Co)

### Experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Test 0</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid load</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td>O₂ partial pressure</td>
<td>air</td>
<td>30%</td>
<td>50%</td>
<td>70%</td>
<td>70%</td>
</tr>
<tr>
<td>Maximum gas flow rate (m³/h)</td>
<td>6</td>
<td>2</td>
<td>1,2</td>
<td>0,9</td>
<td>0,9</td>
</tr>
<tr>
<td>Mean DO concentration (ppm)</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

### Leaching rate (mgCo/L/d)

<table>
<thead>
<tr>
<th></th>
<th>Test 0</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching rate</td>
<td>9 (± 1)</td>
<td>13 (± 1)</td>
<td>12 (± 1)</td>
<td>11 (± 1)</td>
<td>12 (± 1)</td>
</tr>
</tbody>
</table>

![Graph showing leaching rates for different tests](image-url)
Development of new bioleaching approaches for the processing of kupferschiefer ores

Kupferschiefer deposits:
- Largest known Cu reserve in Europe
- Black shale type ores
- Polymineral: chalcocite, bornite, covellite, chalcopyrite...
- Presence of carbonate, organic C and As
  - Low quality concentrate
  - Operating and environmental issues in pyro operations

Development of a dedicated bioleaching process as an alternative and complementary route to the conventional smelting methods

Borg et al., 2012
Cu ore bioleaching

Selected technology = stirred tank reactor, due to high levels of carbonates in the concentrate

Main challenges:

1. Selection and adaptation of microbial consortia
   - Autotrophic/heterotrophic
   - Mesophile (40-45°C) / thermophile (70-80°C)
   - Metal tolerant (Cu and As, mainly...)

2. Chalcopyrite recalcitrance to leaching at low T°
   - Leaching at reduced redox level

3. Optimisation of process operating parameters
   - Increase of solid load
   - Decrease of tank volume, lower investments

Experimental studies from lab scale to pilot scale:

- Bioleaching tests in shake flasks, lab stirred reactors (2L, batch mode) and pilot stirred tank reactors (110L, continuous mode)
- Mineralogical analysis, determination of kinetics and mass balances

Design of process options and economic assessment


<table>
<thead>
<tr>
<th>Conc. and nutrients</th>
<th>H$_2$SO$_4$ (20% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50L</td>
<td>20L</td>
</tr>
<tr>
<td>20L</td>
<td>20L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eh (mV)</td>
<td>601</td>
</tr>
<tr>
<td>$O_2$ (mg/L)</td>
<td>1.9</td>
</tr>
<tr>
<td>OUR (mg/L/h)</td>
<td>115</td>
</tr>
</tbody>
</table>

Cu concentrate (%)

<table>
<thead>
<tr>
<th>Ag</th>
<th>As</th>
<th>Cmin</th>
<th>Corg</th>
<th>Cu</th>
<th>Fe</th>
<th>S=</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.1</td>
<td>1.9</td>
<td>8.2</td>
<td>14.6</td>
<td>7.5</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Low O2 demand!!!

No mixing or transfer issues
High copper tolerance (> 40 g/L)

Operating at 25% solid load requires 2.3 less tank volume than operating at 15% solid load for the same Cu recovery and the same residence time.
Bioleaching and WEEE recycling?

**Objective**
- Metal recovery in “atmospheric conditions” with lower environmental impacts

**Targets**
- Mainly focused on “Low-grade” Printed Circuit Board, but can be applied to any type of metal rich wastes

**Current status**
- Lab-scale to piloting scale

**Two types of bacteria**
- **Heterotrophic bacteria:** production of biogenic acids for base metals solubilisation or production of cyanide for noble metals recovery
  - Aseptic growth conditions → not suitable for large scale application
  - Consumption of cyanide by Cu
- **Autotrophic bacteria:** bacteria act as catalyzers that promote the recycling (re-oxidation) of FeII in FeIII and the production of H$_2$SO$_4$ (similar to bioleaching of sulfidic minerals) which are used to solubilize metals
  - PCBs toxicity (metal tolerance)
  - Chemicals consumption: PCBs are highly acid-consuming...

→ **Autotrophic bacterial leaching remains the most promising way but requires further improvement...**

→ **Similar technology applied at industrial pilot scale for metal recovery for automotive shredded residues (Phoenix project, Comet, Belgium)**
## Bioleaching and WEEE recycling?

![Periodic Table](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB content (g.L⁻¹)</td>
<td>20</td>
<td>10</td>
<td>100</td>
<td>7.8</td>
<td>8</td>
</tr>
<tr>
<td>time (day)</td>
<td>16</td>
<td>18</td>
<td>12</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>% diss. Cu</td>
<td>95%</td>
<td>74%</td>
<td>90%</td>
<td>70%</td>
<td>92.9%</td>
</tr>
</tbody>
</table>
Bioleaching and WEEE recycling: BRGM recent work

Context:
∇ At least 5000 Km of Europe’s rivers are contaminated with acid mine drainage (AMD) which is formed by microbiological weathering of sulfidic mine waste
∇ AMD = acidic, ferric iron-rich run off
∇ Regular major accidents caused by AMD (Aznacolar, Baia Mare...) → environmental and health impacts

Purpose:
∇ to develop a novel bioleaching process based on a co-processing approach for the recovery of metals contained in waste PCBs using sulfidic mining wastes as a source of lixiviant

Objectives:
∇ Enhancing metal recovery in both wastes
∇ Decreasing environmental impacts linked to mining wastes (AMD)

Treatment principles (2-steps process):
∇ Biological oxidation of the sulfidic wastes using acidophilic bacteria → production of a ferric iron-sulfuric acid leaching solution
∇ PCBs leaching → solubilisation of base metals (Cu + Zn, Ni, Sn, Co, Ga...)
Bioleaching and WEEE recycling: BRGM recent work

Biotic tests:
- 82% of Cu extraction after 5h
- 92% of Cu extraction after 24h
- No addition of H₂SO₄

Abiotic tests:
- 58% of Cu extraction after 5h
- 78% of Cu extraction after 24h
- Addition of H₂SO₄ to maintain the pH below 2

⇒ The use of biological leaching solution improves the leaching efficiency...
Bioleaching and WEEE recycling: BRGM recent work

\[ M^0 + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} \text{ (fast)} \]
\[ 2M^0 + 4H^+ + O_2 \rightarrow 2M^{2+} + 2H_2O \text{ (slow)} \]
\[ 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \text{ (bact.)} \]

The bacterial recycling of FeIII improves leaching kinetics...

<table>
<thead>
<tr>
<th></th>
<th>One-step leaching</th>
<th>Two-steps leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB content (g.L⁻¹)</td>
<td>20</td>
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<td>95%</td>
<td>74%</td>
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</table>
Some perspectives

**Improvement of gas transfer:**
- Modelling of oxygen transfer
- Assessment of DO micro-heterogeneity in the reactor
- Investigation of oxygen toxicity mechanisms

**Reactor design:**
- Pilot demonstration with a copper sulfidic ore -> technical and economic assessment of the technology
  - *ECOMETALS (German and French ANR project)*

**WEEE recycling:**
- PhD to investigate:
  - Leaching mechanisms
  - Microbial tolerance toward metals
  - *Chaire Paris Tech “Mines Urbaines” - EcoSystemes*
- Demonstration of the co-processing concept (sulfidic wastes + PCBs) at pilot scale (Polish coal waste)
  - *CERES EU project (RFCS call)*

**Beyond BRGM work:**
- MUNDO bioleach plant (Finland): reprocessing of tailings produced by talc ore treatment for the recovery of Co and Ni
- Acquisition of BIOX process by OUTOTEC -> OKTOP® reactor plant for gold ore pre-treatment
- PHOENIX project launch in Belgium: bioleach process to recover metals in automotive shredded residues