Biological Treatment of Acid Wastewater for Selective Metal Recovery and Site Remediation

Commercial Case Studies

David Kratochvil, Michael Bratty
*BioteQ Environmental Technologies Inc, Canada*

Johannes Boonstra
*Paques BV, The Netherlands*
BioteQ and Paques have commercialized a high-rate H$_2$S generation biotechnology using sulphate and elemental sulphur for treatment of acid drainage, treatment of smelter and metal industry effluents, and recovery of metals as saleable concentrates.

4 Case studies:
- $S^0$ reduction upstream of an existing lime plant
- $S^0$ reduction to replace an existing lime plant
- $S^0$ reduction for metal recovery at a dump leach operation
- $SO_4$ reduction for groundwater remediation
Metal Sulphide Precipitation

Metal-contaminated effluent + H₂S → Metal Sulphide

- Metals can be removed selectively
- High grade, saleable products
Biological Sulphate Reduction

\[
3\text{SO}_4^{2-} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow 3\text{HS}^- + \text{CO}_2 + 3\text{H}_2\text{O} + 3\text{HCO}_3^- \\
\text{SO}_4^{2-} + 4\text{H}_2 + \text{H}^+ \rightarrow \text{HS}^- + 4\text{H}_2\text{O}
\]
Biological Sulphur Reduction

\[ 6S^\circ + C_2H_5OH + 3H_2O \rightarrow 6H_2S + 2CO_2 \]

- sulphur \( S^\circ \)
- anaerobic sulphur reducing bacteria
- sulphide \( H_2S \)
BioteQ and Paques have a Technology Cooperation Agreement and market the BioSulphide - Thiopaq technology for a number of industrial applications.

14 industrial plants for reduction of sulphur compounds marketed under trademark Thiopaq®.

BioteQ owns the patented BioSulphide Process™ concerned with the reduction of sulphur compounds and concurrent selective recovery of metals.

First industrial BioSulphide-Thiopaq plant built in Canada.
Why Sulphide for Water Treatment

- Better effluent water quality - metal sulphides have lower solubility than hydroxides - lower overall TDS
- Easier and less expensive solid-liquid separation - sulphide precipitates are crystalline and have higher density
- Metals not stored on site as hydroxide sludge
- Opportunities for revenue from recovered metals
- Stand-alone application or integrated with lime plant
- When integrated with lime plant:
  - Reduced chemical consumption
  - Reduced volumes and toxicity of sludge
  - Environmentally better solution - better quality water, metals recycled and sludge is more stable
Biogenic Sulphide Generation

- Sulphur reduction produces lowest cost sulphide
- Sulphide is produced on demand - more efficient dosing of reagent
- Increased safety - low inventory of sulphide
Case Study 1

S\textsuperscript{0} Reduction Upstream of Lime Plant

Caribou Mine, New Brunswick
Caribou Flowsheet

Bioreactor

Sulphur → Bioreactor → H₂S
Nutrients → Bioreactor

Mine Water → Contactor

Soda Ash → Clarifier

Lime (reduced consumption) → Lime Reactor

Sludge (reduced volume and toxicity) → Clarifier

Effluent (high quality)

Design
700 m³/day
450 mg/L Zn
30 mg/L Cu
pH 2.7

Bioteq
Benefits of BioteQ Plant at Caribou

Incorporating high-rate biotechnology at Caribou has resulted in the following benefits (Stage 1):

- ~100% removal of zinc, copper, cadmium and lead from the mine water
- Zinc product recovered for sale (est. 215 tonnes per year)
- Projected lime savings of 24%
- Volume of lime sludge production reduced by estimated 35%
- Estimated reduction of heavy metal content of sludge from 125 tonnes/year to less than 0.1 tonnes/year
Caribou Project Facts

- Started Engineering: June 1, 2001
- Start up / inoculation: November 23, 2001
- Commissioning complete: February 2002
- Budget CAPEX: $550,000
- Actual CAPEX: $523,000

- Metal concentrations in feed water exceeded design by 1.5 to 2 times
- Sulphide generation rate 0.26 to 0.43 kg/m³ mine water - exceeded design expectations
- Plant availability 98%
- Zn concentrate (+ Cd, Cu, Pb) sold to Noranda Brunswick
Caribou Expansion Under Review

- **Tailings**
- **Mine Water**
- **Bioreactor**
  - **H₂S**
  - **Sulphur**
  - **Reductant**
- **Lime**
- **Zinc Concentrate**
- **Copper Concentrate**
- **Lime Reactor**
- **Clarifier**
- **Wash**
- **To Tailings Pond**
- **Thickener**
- **Leach**

**Flowchart:**
- Tailings and Mine Water enter the system.
- Flow through **Leach**,
- then **Thickener**,
- then **Wash**,
- then **Bioreactor** with **H₂S**,
- then **Sulphur** and **Reductant**,
- then **Lime** to **Lime Reactor**,
- then **Clarifier**,
- then **Copper Concentrate** and **Zinc Concentrate**
- to **Sludge** and **Effluent**.
Case Study 2

$S^o$ Reduction to Replace Lime Plant

Raglan Mine, Quebec
Raglan Flowsheet

Bioreactor

\[ \text{Sulphur} \rightarrow \text{H}_2\text{S} \rightarrow \text{Soda Ash} \]

\[ \text{Nutrients} \rightarrow \text{Sulphur} \rightarrow \text{H}_2\text{S} \rightarrow \text{Soda Ash} \]

Contaminated Water

\[ \text{Contaminated Water} \rightarrow \text{Bioreactor} \rightarrow \text{Clarifier} \rightarrow \text{Contactor} \rightarrow \text{Nickel Sulphide Product} \rightarrow \text{Treated Water Discharge} \]

Design

5000 m³/day
30 mg/L Ni
pH 6.5

5000 m³/day
<0.5 mg/L Ni
pH 7.5

(NO SLUDGE)
Advantage to SMRQ-Falconbridge

- No sludge disposal and storage
- Better quality treated water (TDS)
- Nickel recovery from wastewater
- More reliable treatment process for cold weather operation
- Reduced water treatment costs
Raglan Facts

- Piloting on site complete
- Engineering in progress
- Mine life +30 years

- Projected capital cost: CDN $1.1 million
- Net operating cost: $0.05 per m³ (after nickel revenue)
- Current operating cost: $0.45 per m³
Case Study 3

$S^0$ reduction for Metal Recovery in Dump Leach Operation
Bisbee, Arizona
Bisbee Flowsheet

**Design**
- 10,300 m³/day
- 390 mg/L Cu
- 860 mg/L Fe (III)
- pH 2.4
Bisbee Facts

- Detailed engineering in progress
- Planned startup 3Q 2003
- 3.2 million lb Cu /year
- 3,500 tonnes Cu concentrate/year @>45% Cu
- Reduced environmental liability

Projected capital cost: CDN $2.56 million
Operating cost: $0.20 per lb Cu
Capital payback: < 2 years
Case Study 4

SO$_4^-$ Reduction for Groundwater Remediation

Budel Zink, Netherlands
Sulphate Reduction at Budelco

- 200,000 tonnes/y zinc refinery
- Original plant commissioned in 1992
- UASB bioreactor
- Metal sulphide and sulphur returned to smelter

Diagram:

- Groundwater
  - Flow 300 m³/h
  - Zn 100 mg/L
  - SO₄ 1000 mg/L

- HS⁻

- Anaerobic
  - Reductant

- Aerobic
  - Air

- Sulphur
  - Zn <0.3 mg/L
  - SO₄ <200 mg/L

- Effluent

Zinc product to smelter
Thiopaq® Bioreactor at Budelco

- Hydrogen-fed Thiopaq® bioreactor commissioned in 1999
- 2 streams are treated...
  - Wash tower acid (0.5 g/L Zn, 10 g/L H₂SO₄, 1 g/L HCl, 0.5 g/L HF)
  - Electrolyte bleed (15 g/L Mg, 300 g/L SO₄)
- Streams previously treated with lime

**Diagram:**
- Calcine, ZnO
- Wash Tower Acid
- Crystalactor
- Electrolyte bleed
- Bioreactor
- Hydrogen
- CaF₂ pellets
- Zinc product to smelter
- Effluent to groundwater plant
# Budel Plant Data

<table>
<thead>
<tr>
<th>Design Capacity</th>
<th>H$_2$S Influent</th>
<th>Production</th>
<th>Water Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3,200 kg/day</td>
<td>ZnS</td>
<td>In</td>
</tr>
<tr>
<td></td>
<td>40 m3/h</td>
<td>CaF$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**BiOTEQ**
Conclusions

- High-rate, engineered bioreactor systems offer many possibilities for application in mining and related industries.

- Commercially proven, safe and robust biological processes remove sulphur compounds and recover metals for sale.

- Current and potential applications include:
  - Treatment of ARD
  - Low cost $\text{H}_2\text{S}$ production
  - Selective metal removal from metallurgical and waste streams
  - Sulphate reduction for environmental compliance
  - Sulphate reduction for industrial water control
  - $\text{SO}_2$ removal