BIO-REMEDIATION OF MINE WATER

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Introduction

Mining History in South Africa

- Gold Mining started in the late 1880's on the farm Langlaagte, west of Johannesburg
- Soon thereafter coal mining started in the Witbank Area as well as in Northern Natal
- Diamond mining in Kimberley

Chinese coal miners in an illustration of the *Tiangong Kaiwu* Ming Dynasty encyclopedia, published in 1637 by Song Yingxing.
Coal fields in South Africa
Wealth versus environment

- SA is 5th largest coal producer in the world
- SA is third largest coal exporter
- South Africa gains economic prosperity from the act of mining

- The mining industry contributes negatively to the pollution of the water environment by producing Acid Mine Drainage.
Impact of mining

By act of mining: AMD is formed

Arises from oxidation of pyrite, due to exposure to air and water.

\[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \]

Characteristics of AMD:

High SO4: Salinity

High acidity: low pH

High metal content
Environmental impact:
Water pollution

AMD
Water Pollution trough mining in South Africa

Statistics

• Mpumalanga coal field produces 40-50ML/d, may increase to 120ML AMD/d

• Gauteng mining area produces 300-400 ML AMD/d

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Mine water remediation

- Biological treatment
- Chemical treatment
- Physical treatment

Possible ground water contamination
**Chemical treatment**

**CSIR Limestone/Lime Neutralisation**

The integrated limestone/lime process is used for treating acid, iron and sulphate-rich water with powder calcium carbonate.

- Acidic mine effluents are neutralised
- Sulphate is removed from 20 g/ℓ to less than 2 g/ℓ
- Metal removal (Ca, Mg), using lime
Full scale implementation of CSIR neutralisation technology

**South Africa:**
- Ticor, Limestone/lime
- Navigation and Kromdraai mines, Anglo coal (both Limestone)
- Namaqua Sands Limestone/lime
- Zincor (limestone)
- Optimum (limestone)

**Botswana**
- BCL (limestone)

**Australia**
- Iluka resources (limestone/lime)
Biological Sulphate (SO$_4$) removal

- Requires Sulphate Reducing Bacteria (SRB)
- Requires a carbon and energy source
- Requires SO$_4$
- Requires anaerobic conditions
CSIR developed biological treatment

Biological AMD treatment using alternative carbon and energy sources

- Degradation products of cellulose occurring in grass
- Volatile Fatty Acids (VFA) and hydrogen ($H_2$) production
- VFA and $H_2$ can function as C+E source for SRB
Biological degradation of cellulose

Polymers
Cellulose; Protein; Carbohydrates; Lipids; etc

→ Hydrolysis

Monomeres
Sugar; Amino acids; etc

→ Fermentation

Volatile Fatty Acids (VFA)
Acetic, Propionic, Butyric, Valeric
Microorganisms produce VFA and $H_2$

Use of natural occurring microorganisms

- Rumen fluid from ruminant
- SRB participate in the degradation of the polymers and monomers to produce VFA
Polymers, as cellulose and hemicellulose

Dissolved monomers / sugars

Hydrolysis

Butyrate
Propionate
Acetate
Hydrogen

Energy supply and growth of Rumen

Grass

CO₂, H₂O

Methane

Waste VFA
SRB

CO₂, H₂O

Energy supply and growth of SRB

S²⁻
SO₄²⁻
Benefits of biological $SO_4$ removal

- Sulphate removal to <200 mg/L
- Alkalinity production to increase pH
- Sulphide is the reduction product of sulphate
- Metal removal due to Metal-sulphide precipitation
Biological SO$_4$ reduction using grass-cellulose as the carbon and energy source

Aim of study

To remove biologically:

- Sulphate from AMD
- Sulphide after sulphate reduction
Materials and Methods

Feed water

• Pre-treated AMD

• Mix 1 part AMD with 1 part of reactor effluent

Purpose

• Metal removal

• pH increase of AMD
Reactor: Hybrid Reactor System

Schematic overview of HFS reactor system.
Laboratory study: continuous operation of hybrid reactor

Reactor contains
1. Grass cuttings as cellulose source
2. Cellulose degrading microorganisms
3. SRB

Feed water:
Pre-treated AMD for pH increase and metal precipitation

Principle
VFA and $H_2$ production and utilisation in reactor for biological sulphate removal
Reactions using VFA and $H_2$ for $SO_4$ removal

Propionate$^-$ + $\frac{3}{4} SO_4^{2-}$ → Acetate$^-$ + $HCO_3^-$ + $\frac{3}{4}$ HS$^-$ + $\frac{1}{4}$ H$^+$

Butyrate$^-$ + $\frac{1}{2} SO_4^{2-}$ → 2 Acetate$^-$ + $\frac{1}{2}$ HS$^-$ + $\frac{1}{2}$ H$^+$

$8H_2 + 2SO_4^{2-} + 2H^+$ → 2 HS$^-$ + 8$H_2$O
Results

Sulphate removal (mg/L)

Sulphate removal as function of COD
Percentage Sulphate removal efficiency

Average sulphate removal was 85%
Results scanning electron microscope
# Metal removal

<table>
<thead>
<tr>
<th>Metal</th>
<th>AMD</th>
<th>Pre-treated AMD</th>
<th>Effluent HFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>24</td>
<td>14</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Iron</td>
<td>851</td>
<td>102</td>
<td>0.21</td>
</tr>
<tr>
<td>Lead</td>
<td>0.15</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Manganese</td>
<td>48</td>
<td>27</td>
<td>5.9</td>
</tr>
<tr>
<td>Nickel</td>
<td>11</td>
<td>4.3</td>
<td>0.04</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.4</td>
<td>0.94</td>
<td>&lt;0.06</td>
</tr>
</tbody>
</table>

All units in mg/L
Sulphide oxidation after sulphate reduction

Biological sulphide oxidation using air

• By *Thiobacillus* Species
  - *Thiobacillus thioparus*,
  - *Thiobacillus denitrificans* and
  - *Thiobacillus ferroxidans* (Chung et al., 1996).

• Producing sulphur or sulphate

  - $\text{HS}^- + \frac{1}{2} \text{O}_2 \rightarrow S + \text{OH}^-$
  - $\text{HS}^- + 2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$
Experimental conditions of a continuous laboratory study

<table>
<thead>
<tr>
<th>Period (days)</th>
<th>Air supply to reactor (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-43</td>
<td>0.2</td>
</tr>
<tr>
<td>44-59</td>
<td>0.4</td>
</tr>
<tr>
<td>62-81</td>
<td>0.6</td>
</tr>
<tr>
<td>83-97</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Results of biological sulphide oxidation after continuous laboratory studies

<table>
<thead>
<tr>
<th>Air supply (L/min)</th>
<th>S(^2)-removed (g/d)</th>
<th>Sulphur produced (g/d)</th>
<th>%SO(_4) increase in reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5.13</td>
<td>1.98</td>
<td>8</td>
</tr>
<tr>
<td>0.4</td>
<td>4.45</td>
<td>1.96</td>
<td>28</td>
</tr>
<tr>
<td>0.6</td>
<td>4.62</td>
<td>2.06</td>
<td>47</td>
</tr>
<tr>
<td>0.8</td>
<td>5.77</td>
<td>1.28</td>
<td>57</td>
</tr>
</tbody>
</table>
Conclusions continuous operation
SO$_4$/grass/rumen reactor and biological sulphide oxidation

• Efficient sulphate removal (Average 85%)

• Metal removal, especially iron

• Biological sulphide oxidation achieved, at low air concentration, otherwise SO$_4$ is end product rather than Sulphur

• Based on obtained results, pilot scale reactor will be constructed
For more information

www.csir.co.za

Thank You