Development and application of novel low pH sulfidogenic bioreactors for mitigating mine waters

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• also Guest Professor at Exeter University (UK) and Changsha University (China)

• research going research collaboration with groups (universities, research organisation and industries) throughout the world (Chile, China, South Africa, Germany, France…..)
Synopsis:

- Background: the environmental threat of acid mine/rock drainage waters
- Deficiencies of commonly-used mitigation strategies and advantages of generating hydrogen sulfide at low pH
- Evolution of the development of acidic sulfidogenic bioreactors
- Some examples of applications of the technology
Acid mine/rock drainage is a global environmental issue

Citronen Fjord, High Arctic

Bor copper mine, Serbia

El Dollar mine, High Andes, Peru
Catastrophic incidents grab the headlines.........

Wheal Jane, 1992

Aznalcollar, 1998

Baia Mare, 2000
but continuous, on-going release is more pernicious

Water draining Mynydd Parys (the largest copper mine in the 18th – early 19th century)

- still the largest source of pollution of the Irish Sea
• Although the process of AMD genesis may be entirely chemical, it is greatly accelerated by certain (mostly lithotrophic) bacteria and archaea in the presence of both **air** and **water**

![Pyrite (FeS$_2$)](image)

(i) at pH < ~2.5:

$$FeS_2 + 3.75 O_2 + 0.5 H_2O \rightarrow Fe^{3+} + H^+ + 2 SO_4^{2-}$$

(ii) at pH ~2.5 – 4.5:

$$8 FeS_2 + 30 O_2 + 18 H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 30 H^+ + 15 SO_4^{2-}$$

(schwertmannite)

• AMD may form in mine waste dumps impacted with surface water, or in underground workings (groundwater)

• Mine closure results in pumps being switched off, which results in rebound of the water table

• production of AMD may continue long after mines are decommissioned
Perceived issues with AMD/ARD:

- Acidity (proton and mineral)
- Concentration of (toxic) transition metals, and metalloids such as As
- High osmotic potential
- Elevated sulfate concentrations
Arsenic is occasionally the most significant pollutant in mine waters e.g. Carnoulès, France
However, mine water effluents may be **net acidic** or **net alkaline**

**Acidity:**
- proton acidity (\([H^+]\))
- mineral acidity (\([Fe/Al/Mn]\)), as:

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+
\]

**Alkalinity:**
- chiefly bicarbonate, as:

\[
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2
\]

This dictates which remediation process is most appropriate
REMEDIATION OPTIONS

Abiotic

"Active" systems: aeration and lime addition

"Passive" systems: e.g. anoxic limestone drains

Biological

"Active" systems

Off-line sulfidogenic bioreactors

Accelerated iron oxidation (immobilized biomass)

"Passive" systems

Aerobic wetlands

Permeable reactive barriers

Compost reactors/wetlands
Mitigation strategies:

• The most frequently used method for remediating acidic metal-rich waste waters is a chemical approach, whereby an alkaline material (very often lime, CaO) is added, aeration used to promote the oxidation of (ferrous) iron and the sludge generated is collected and disposed of in landfill sites.

• Generally perceived as a reliable approach, though it has significant drawbacks:
  - high CAPEX and OPEX
  - no recovery of potentially valuable resources in mine waters
  - toxic materials (e.g. As) can be remobilised from stored sludge products

Chemical ("high density sludge") treatment of mine water at the former Wheal Jane tin mine, south-west England. OPEX ~$3 million/annum.
A radical departure from this convention arose from the observation by Robert Kleinmann and others (in the early 1980s) that the chemistry of mine waters was moderated as it flowed through a natural wetland.

- this is an example of “natural attenuation”: natural processes that decrease or “attenuate” concentrations of contaminants in soil and groundwater (EPA)

- from this arose the concept of using constructed wetlands, that were specifically engineered to optimise the benign chemical processes occurring in a natural wetland, to remediate mine waters

- widespread use, especially in the USA and UK
constructed aerobic wetland
(coal mine drainage, north-east England)

anaerobic compost “reactor” construction
(metal mine drainage, south-west England)

RAPS
(coal mine drainage, south Wales)
Both active chemical and passive (compost-based) remediation systems are either expensive to set up or to operate, and produce hazardous wastes (metal-rich sludge or metal-rich spent compost) which:

- require storage in landfill sites designated for hazardous waste
- have the potential for metal (and As) re-mobilisation
- do not allow the recovery and recycling of metals

Both these remediation systems have major drawbacks, and should be considered only as intermediary solutions to the problem until more environmentally-acceptable solutions have been developed and validated.
The BART philosophy is also learn from and adapt “natural” systems that exhibit attenuation of mine waters, but to optimise engineering designs for microbial communities that can both mitigate mine waters and recover (metal) resources

“Ferrovum”-dominated biomass in a AMD stream draining the San Telmo mine, Spain

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

Selective removal of Cu in AMD draining the Cantareras mine, Spain

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{organic C (algae)} \\
\text{organic C} + \text{SO}_4^{2-} + \text{Cu}^{2+} & \rightarrow \text{CuS} + \text{CO}_2
\end{align*}
\]
**Remediation Options**

**Abiotic**
- "Active" systems: aeration and lime addition
- "Passive" systems: e.g. anoxic limestone drains
- Off-line sulfidogenic bioreactors
- Accelerated iron oxidation (immobilized biomass)

**Biological**
- "Active" systems
- Aerobic wetlands
- "Passive" systems
- Permeable reactive barriers
- Compost reactors/wetlands
Biosulfidogenic processes for remediation mine waters/sulfate-rich water already exist:

- Thiopaq process (Paques, the Netherlands), based on sulfate reduction
- BioteQ process (BioteQ corp, Canada), based on sulfur reduction

- both biotechnologies utilise neutrophilic bacteria

BART has developed novel modular low pH sulfidogenic (sulfate- and sulfur-reducing) bioreactors that operate as continuous-flow modular units
Advantages of operating a sulfidogenic bioreactor at low pH:

- Acidic waters can be treated within the bioreactor module, reducing engineering complexity
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- Acidic waters can be treated within the bioreactor module, reducing engineering complexity

- The main product is a gas (H\textsubscript{2}S), which is more readily transferred to off-line reactor vessels than soluble HS\textsuperscript{-}

\[
\begin{align*}
H_2S & \leftrightarrow HS^- & \leftrightarrow S^{2-} \\
pK_a & 6.9 & pK_a & 14.2
\end{align*}
\]

→ at pH 4.0, H\textsubscript{2}S accounts for 99% of the sulfide product

→ at pH 7.0, HS\textsuperscript{-} accounts for 56% of the sulfide product
Advantages of operating a sulfidogenic bioreactor at low pH:

• Acidic waters can be treated within the bioreactor module, reducing engineering complexity

• The main product is a gas (H₂S), which is more readily transferred to off-line reactor vessels than soluble HS⁻

• Biosulfidogenesis can neutralise acidity when carried out at low pH (since the main metabolic waste products are H₂S and H₂CO₃, rather than HS⁻ and HCO₃⁻):

  \[
  4 \text{C}_3\text{H}_8\text{O}_3^* + 7 \text{SO}_4^{2-} + 14 \text{H}^+ \rightarrow 12 \text{CO}_2 + 7 \text{H}_2\text{S} + 16 \text{H}_2\text{O} \quad \text{(pH 4)}
  \]

  \[
  4 \text{C}_3\text{H}_8\text{O}_3^* + 7 \text{SO}_4^{2-} + 1.4 \text{H}^+ \rightarrow 3 \text{CO}_2 + 9 \text{HCO}_3^- + 3.4 \text{H}_2\text{S} + 3.6 \text{HS}^- + 7 \text{H}_2\text{O} \quad \text{(pH 7)}
  \]

*glycerol
Advantages of operating a sulfidogenic bioreactor at low pH:

• Acidic waters can be treated within the bioreactor module, reducing engineering complexity

• The main product is a gas (H$_2$S), which is more readily transferred to off-line reactor vessels than soluble HS$^-$

• Biosulfidogenesis can neutralise acidity when carried out at low pH (since the main metabolic waste products are H$_2$S and H$_2$CO$_3$, rather than HS$^-$ and HCO$_3^-$)

• Allows transition metals to be selectively precipitated *in situ*
Log $K_{sp}$ (solubility products, at 25°C) of metals commonly found in AMD

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydroxide</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>-33.5</td>
<td>-</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-19.8</td>
<td>-35.9</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-16.3</td>
<td>-18.8</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>-38.6</td>
<td>-</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>-12.7</td>
<td>-13.3</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-16.1</td>
<td>-24.5</td>
</tr>
</tbody>
</table>

- for any particular metal (Me$^{2+}$) sulfide to precipitate, $[\text{Me}^{2+}] [\text{S}^{2-}] > K_{sp}$
- this is dictated by $[\text{S}^{2-}]$, which varies with pH; e.g. for $10^{-2}$ M total sulfide:

<table>
<thead>
<tr>
<th>pH</th>
<th>$H_{2}S$ (M)</th>
<th>$\text{HS}^{-}$ (M)</th>
<th>$\text{S}^{2-}$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>$4.9 \times 10^{-3}$</td>
<td>$5.1 \times 10^{-3}$</td>
<td>$5 \times 10^{-10}$</td>
</tr>
<tr>
<td>4</td>
<td>$9.99 \times 10^{-3}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$1 \times 10^{-15}$</td>
</tr>
<tr>
<td>2</td>
<td>$10 \times 10^{-3}$</td>
<td>$1 \times 10^{-7}$</td>
<td>$1 \times 10^{-19}$</td>
</tr>
</tbody>
</table>
The implication for metals that form sulfide phases:

<table>
<thead>
<tr>
<th></th>
<th>pH 2</th>
<th>pH 4</th>
<th>pH 7</th>
</tr>
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<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-</td>
<td>-</td>
<td>↓</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

i.e. by operating at low pH (<~5.5), Fe (usually present in large concentrations in AMD) flows through the reactor and does not precipitate
Advantages of operating a sulfidogenic bioreactor at low pH:

- Greater potential for acid consumption (pH amelioration; metabolic waste products are $\text{H}_2\text{S}$ and $\text{H}_2\text{CO}_3$, rather than $\text{HS}^-$ and $\text{HCO}_3^-$)

- Acidic waters can be treated within the bioreactor module, reducing engineering complexity

- $\text{H}_2\text{S}$ (gas) is more readily transferred to off-line reactor vessels than is soluble $\text{HS}^-$

- Allows selective precipitation of transition metals \textit{in situ}

- Fe (usually present in large concentrations in AMD) flows through the reactor and does not precipitate

Major requirement: acidophilic/acid-tolerant strains and species of sulfate- and sulfur-reducing bacteria (SRB)
By the mid-1990’s acidophilic bacteria had been characterised that catalyse the dissimilatory oxidation of iron and sulfur, and the dissimilatory reduction of iron, but no acidophilic sulfate reducing bacteria (SRB) had been described, even though there were reports of sulfate reduction in environments impacted with acidic mine waters.

- our first attempts to isolate acidophilic SRB (aSRB) was during a visit to the volcanic island of Montserrat (WI)
- it was apparent that techniques used to enrich for and to isolate neutrophilic SRB were inappropriate for acidophiles, e.g. using lactate as a potential substrate
The problem with organic acids
(for acidophiles)

Acetic acid: \( \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \); \( pK_a \) 4.75

(i.e., at pH 4.75, the dissociated and non-dissociated forms of the acid occur at equimolar concentrations).

\( pK_a \)'s of some other organic acids:

Lactic acid - 3.86
Pyruvic acid - 2.50
Formic acid - 3.75
Citric acid - 3.68, 4.74 & 5.39
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<td>1. Organic acid “substrates” are toxic to aSRB</td>
<td>Cultures are killed</td>
<td>Use non-acid substrates, e.g. glycerol</td>
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Desulfosporosinus M1 – the first acidophilic SRB to be described (in 1999)

Acidophilic sulphate-reducing bacteria: candidates for bioremediation of acid mine drainage

A.M. Sen and B. Johnson

School of Biological Sciences, University of Wales, Bangor, Gwynedd, Wales, UK, LL57 2UW
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<td>2. pH increases during enrichment</td>
<td>Neutrophilic strains increasingly dominate</td>
<td>Include Zn$^{2+}$ to re-generate acidity</td>
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$$4\text{C}_3\text{H}_8\text{O}_3^* + 7\text{SO}_4^{2-} + 7\text{Zn}^{2+} \rightarrow 12\text{CO}_2 + 7\text{ZnS} + 16\text{H}_2\text{O}$$

*Desulfosporosinus acididurans*<sup>T</sup> grown at pH 4.0 in a bioreactor with Zn$^{2+}$

Colonies of *Desulfosporosinus acididurans*<sup>T</sup> grown on an overlay plate containing Zn$^{2+}$
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<td>Include Zn$^{2+}$ to re-generate acidity</td>
</tr>
<tr>
<td>3. <em>Desulfosporosinus</em> M1 is an “incomplete” oxidiser, and generates acetic acid</td>
<td>Poor growth at low pH as a pure culture</td>
<td>Grow in co-culture with <em>Acidocella aromatica</em></td>
</tr>
</tbody>
</table>

$$4 \text{C}_3\text{H}_8\text{O}_3^* + 3 \text{SO}_4^{2-} + 6 \text{H}^+ \rightarrow 4 \text{CH}_3\text{COOH} + 4 \text{CO}_2 + 3 \text{H}_2\text{S} + 8 \text{H}_2\text{O}$$
The syntrophic association between *Ac. aromatica* and aSRB is used in overlay media for directly isolating the latter.
Since then, we have established a consortium of sulfate-reducing and non-sulfidogenic acidophiles isolated from sites in Spain, Monserrat (WI) and Wales

- the consortium is robust and adaptable (continuous operation for >7 years)
- pH range 2.5 – 5.5; T range 15 - 45ºC
- the composition of the consortium changes with varying operational parameters
Phylogenetic affiliations of novel acidophilic & acid-tolerant SRB present in BART’s low pH sulfate reducing bioreactors

Desulfosporosinus genus

Desulfosporosinus acididurans\textsuperscript{T}

Desulfosporosinus acidiphilus\textsuperscript{T}

Desulfosporosinus orientis\textsuperscript{T}

Desulfosporosinus auripigmentii\textsuperscript{T}

Desulfosporosinus hippei\textsuperscript{T}

Desulfosporosinus meridiei\textsuperscript{T}

Desulfosporosinus youngiae\textsuperscript{T}

Desulfosporosinus lacus\textsuperscript{T}

YNP hot spring clone pCOF 65.7 B6

ethanol AMD enrichment culture clone CL4

Peptococcaceae bacterium MCF108

CeB3

Rio Tinto sediment clone la

copper AMD clone ORCL4.20

Desulfitobacterium genus

Desulfitobacterium dehalogenans\textsuperscript{T}

Desulfitobacterium hafniense\textsuperscript{T}

Desulfitobacterium chlororespirans\textsuperscript{T}
The most recent addition to the low pH sulfidogenic bioreactor is a cold-tolerant acidophilic SRB (strain AC9-9-1*)
Setting up and operating laboratory-scale (2 – 5 L) low pH sulfidogenic bioreactors

1. Continuous flow systems: need to immobilise bacteria to prevent washout

   porous beads made from recycled glass (Poraver, Germany)

2. Requirement for simple automated operation: controlled by setting pH
The bioreactor allows both in-line removal of metals (and sulfate) and off-line metal precipitation.
(i) Biosulfidogenesis via sulfate reduction

- Bacterial sulfate reduction can have three important roles in mitigating mine waters:
  - precipitating transition metals and As (CuS, ZnS, As$_2$S$_3$ etc.);
    \[ \text{H}_2\text{S} + \text{Me}^{2+} \rightarrow \text{MeS} \downarrow + 2 \text{H}^+ \]
  - removing protons (increasing pH) but only significant if carried out at low pH
  - lowering sulfate concentrations

- However, the reduction of sulfate to sulfide requires 8 electrons and is therefore requires more electron donor than many other respiration modes, e.g. 1 mole of glycerol can reduce:
  - 14 moles of Fe$^{3+}$
  - 3.5 moles of O$_2$
  - 1.75 moles of SO$_4^{2-}$
Application #1: selective in-line removal of Zn from AMD (mid-Wales)

- Zn was removed selectively within the bioreactor vessel
- other major metals (Fe & Al) flowed through the bioreactor

<table>
<thead>
<tr>
<th></th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$-S</td>
<td>387</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>167</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>13</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>196</td>
</tr>
</tbody>
</table>

(pH 2.5)
Application #2: selective in-line removal of Cu from AMD (north-Wales)

- by “fine tuning” the pH and concentration of glycerol, it was possible to selectively precipitate Cu in-line
- however, when the bioreactor was operated at pH 2, HRTs were very long
Application #3: sequential removal of metals from mine water (Brazil)

- the pH of this mine water was too high for injecting directly into the bioreactor
- a combined off-line (for Cu) and in-line (for Zn, Ni & Co) approach was used to recover these transition metals and remediate the mine water

<table>
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<th>Ion</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$-S</td>
<td>660</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zn$^{2+}$/Ni$^{2+}$/Co$^{2+}$</td>
<td>20</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>476</td>
</tr>
</tbody>
</table>

(pH 5.0)
• preliminary off-line removal of CuS lowered the pH from 5.0 to 2.1
  \[(\text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow \text{CuS} + 2 \text{H}^+)\]

• the part-treated mine water was dosed with glycerol and used as influent liquor for the bioreactor, which was operated at pH 5, causing >99% of the Zn/Ni/Co to be removed
• The economics of the proposed process are encouraging (vary with commodity prices):

• The copper value of \( \sim \$3.5 \) (US)/m\(^3\) AMD more than offsets the cost of the main consumable (glycerol; \( \sim \$0.43/m^3 \))

• Recovery of Co, Ni and Zn adds some further value to the process

• When compared against alternative treatment systems where no metals are recovered and recycled, the economics look even more attractive
Application #4: removal of sulfate from acidic groundwater (Germany)

- it was possible to remove up to 99% of the sulfate, exceeding the target discharge (30 mg/L)
- the H$_2$S produced was converted (biologically) to S$^0$ (off-line)

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<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>670</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>110</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>nd</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

(pH 1.8 – 3.0)
(i) Biomineralisation via sulfur reduction

• bacterial sulfur reduction also generates H₂S and can therefore be used for the selective removal of transition metals present in AMD:
  \[ \text{H}_2\text{S} + \text{Me}^{2+} \rightarrow \text{MeS}↓ + 2 \text{ H}^+ \]

• sulfate concentrations are not lowered, and the cost of sulfur needs to be added to OPEX

• reduction of sulfur does not consume or generate protons at low pH
  \[ \text{C}_3\text{H}_8\text{O}_3^* + 7 \text{ S}^0 + 3 \text{ H}_2\text{O} \rightarrow 3 \text{ CO}_2 + 7 \text{ H}_2\text{S} \]

• the stoichiometry of electron donor use to H₂S generated (1:7, in the case of glycerol) is superior to sulfate reduction

• potential use for remediating circum-neutral pH and alkaline AMD

*glycerol
BART has developed a low pH “hybrid” sulfidogenic that combines dissimilatory sulfate- and sulfur-reduction.
- the bacteria used in the hybrid bioreactor include those present in the low pH sulfate-reducing module, plus a novel acidophile that catalyses the dissimilatory reduction of sulfur but not of sulfate.

- the novel isolate is a *Firmicute*, very distantly related to all currently known bacteria (~ 92% 16S rRNA gene similarity to *Alicyclobacillus*).

- it is more acidophilic than the sulfate-reducers (grows at pH 2 and above) and can grow via nitrate respiration as well as by reducing S⁰.
Application #5: removal of zinc from non acidic mine water (England)

<table>
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<tr>
<th></th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SO}_4^{2-})-S</td>
<td>12</td>
</tr>
<tr>
<td>(\text{Fe}^{2+})</td>
<td>0.3</td>
</tr>
<tr>
<td>(\text{Mn}^{2+})</td>
<td>0.6</td>
</tr>
<tr>
<td>(\text{Zn}^{2+})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{HCO}_3^-)</td>
<td>26</td>
</tr>
</tbody>
</table>

(pH 6.9 – 7.2)

- A passive remediation system installed at the site (right side image) had caused severe short-term pollution due to the BOD of drainage waters.

- Both in-line and off-line approaches were tested to remove Zn.
both configurations resulted in rapid & effective removal of Zn
the water alkalinity neutralised acid generation from ZnS formation
due to the large discharge from the mine (~1,400 m³/day) off-line treatment is more feasible
Proposed active biological treatment of Force Crag mine water

Discharge/day: 1,400 m$^3$
Zinc value/day: ~$14$
Consumable cost/day: ~$9$

Hybrid sulfidogenic bioreactor
(10 m$^3$)
30$^\circ$C

Contact tank
(750 m$^3$)
(x 2)
Ambient T
6-12$^\circ$C

H$_2$S

ZnS

Mine water (3 mg Zn$^{2+}$/L)
A non-biological alternative?

- several years ago, we were investigating the possibility of using *Acidithiobacillus ferrooxidans* to generate H$_2$S, by catalysing the reduction of sulfur using hydrogen as an electron donor

- zero-valent iron (ZVI) was used as the source of hydrogen (Fe$^0$ + 2 H$^+$ → Fe$^{2+}$ + H$_2$)

- unexpectedly, sterile controls were also found to generate H$_2$S

- more recently we have confirmed these findings, which represent an alternative way of safely generating H$_2$S, without any biological constraints

- the process appears to involve initial formation of iron sulfide (mackinawite?), followed by acid dissolution:

  \[
  \begin{align*}
  \text{(i)} & \quad \text{Fe}^0 + S^0 \rightarrow \text{FeS} + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S} \\
  \text{(ii)} &
  \end{align*}
  \]
• Although reaction (i) is exothermic, it has a large activation energy and does not occur spontaneously below ~ 200°C

• The reason we believe it happens at 30 - 40°C in our acidic bioreactors is due to the creation of highly reactive Fe⁰ surfaces as a consequence of acid attack

• Total reagent (ZVI, S⁰ and acid) costs are ~$13/kmole H₂S, but the FeSO₄ generated also has a value of ~$13/kmole
Take home messages:

(i) mine waters should be considered as potential resources rather than only wastes

(ii) recover and recycle metals, rather than dump in land fill sites

(iii) biotechnologies are available for doing this

20th century

mixed metal sludge or contaminated compost

21st century

copper    zinc    iron
Key members of BART involved in pure and applied research in sulfidogenesis at low pH

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