TECHNISCHE UNIVERSITÄT
BERGAKADEMIE FREIBERG
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Bioremediation and phytoremediation 2021/22

Topic 6: Biological mine water treatment

Jun.-Prof. Dr. Sabrina Hedrich
TU Bergakademie Freiberg

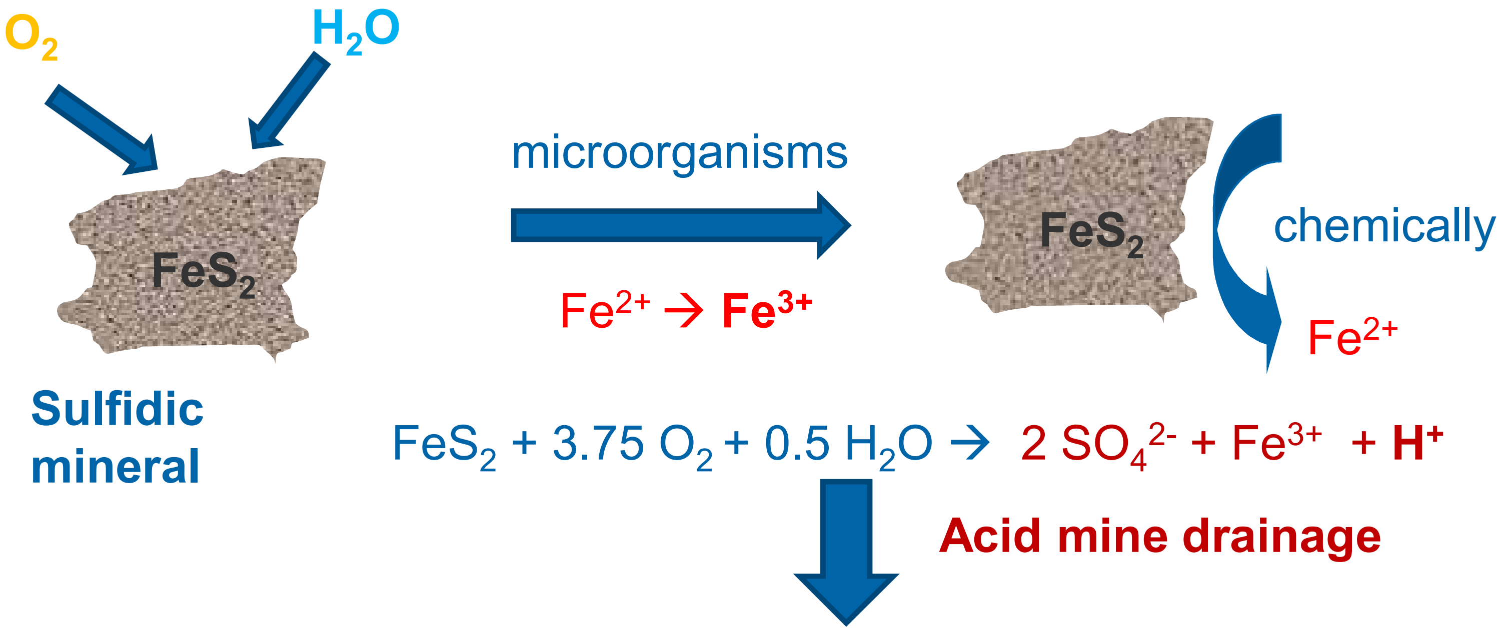
Acid mine/rock drainage is a global environmental issue

Citronen Fjord, High Arctic

Bor copper mine, Serbia

El Dollar mine, High Andes, Peru

Acid mine drainage formation



O_2

H_2O

FeS_2

Sulfidic mineral

microorganisms

$Fe^{2+} \rightarrow \mathbf{Fe^{3+}}$

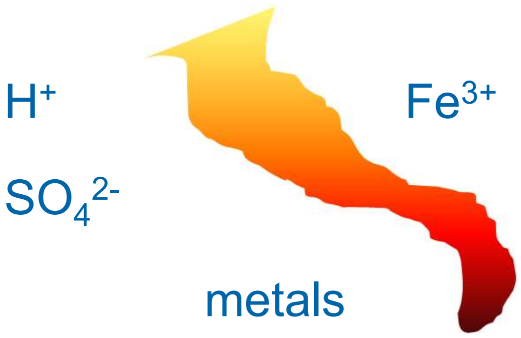
FeS_2

chemically

Fe^{2+}

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

Acid mine drainage



H^+

SO_4^{2-}

Fe^{3+}

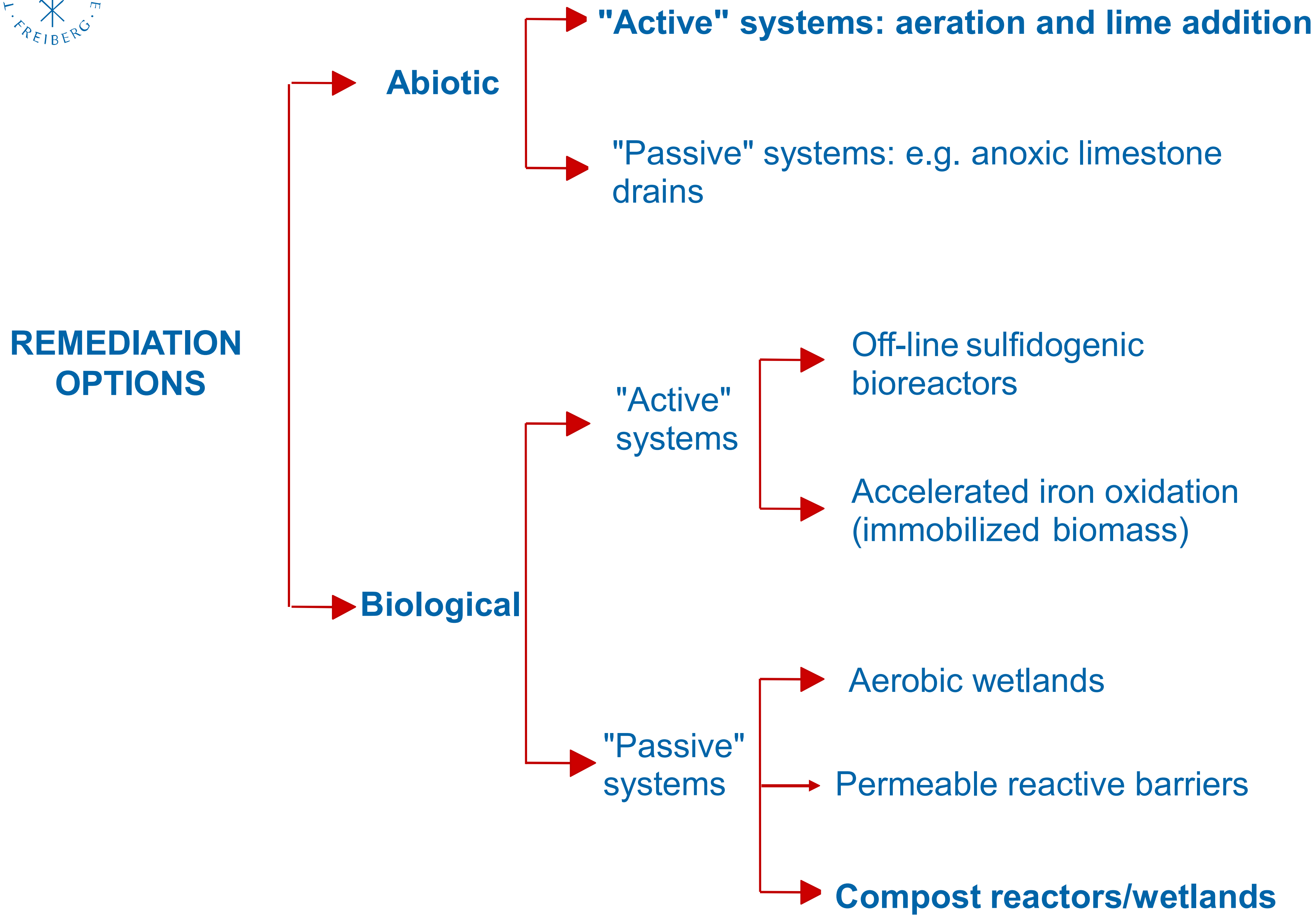
metals

Perceived issues with AMD/ARD

- Acidity (proton and mineral; <5.0 but mostly <3.0)
- 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



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**

Groundwater is pumped
to the surface & aerated

Chemical oxidation of ferrous
iron in a surface lagoon

Iron flocs are filtered out
in a constructed wetland

Active chemical remediation of AMD (HDS* approach)

Appropriate for net acidic AMD, that contain dissolved Al and heavy metals, other than Fe:

1. Addition of lime (CaO) slurry to increase pH
2. Active aeration to (chemically) oxidise Fe^{2+}
3. Addition of a chemical flocculant to coagulate ferric precipitates into a sludge
4. Dewatering of the sludge to reduce its bulk (→80% solids)

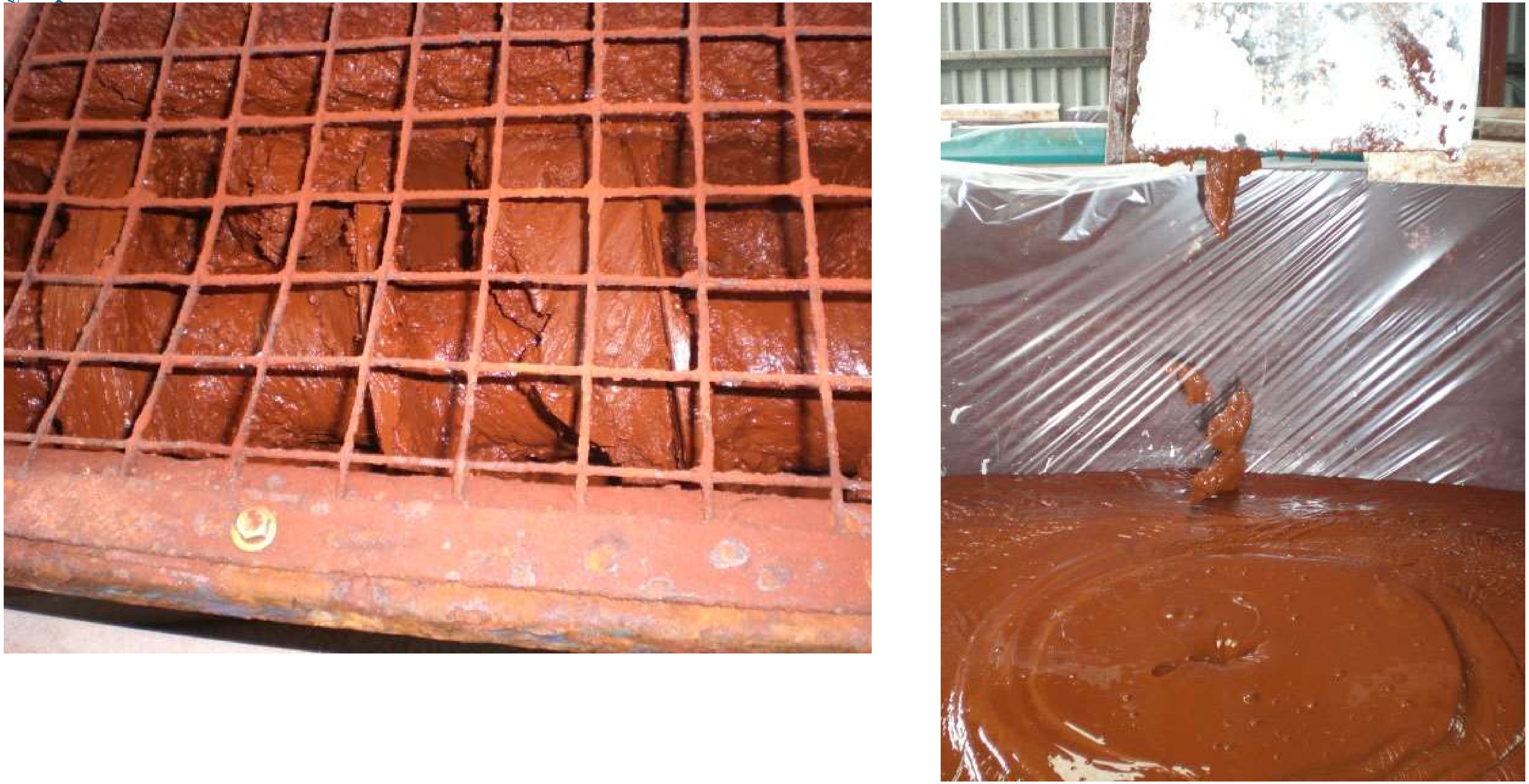
* this approach also some removal of the sulfate present in AMD, as gypsum ($CaSO_4$)

*High Density Sludge

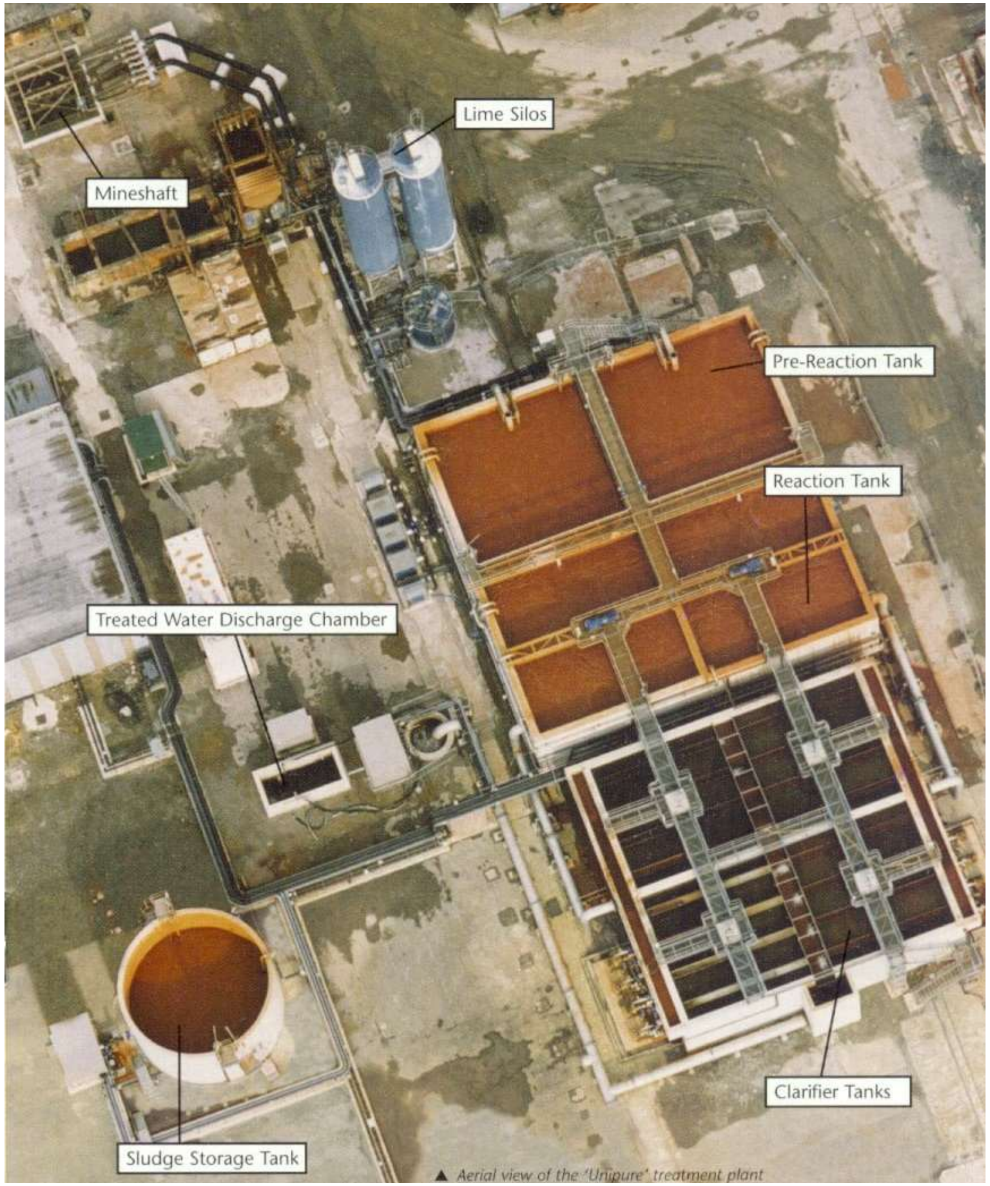
Addition of lime

pH control/aeration

Addition of flocculant



Dewatering and formation of HDS



▲ *Aerial view of the 'Unipure' treatment plant*

Generally considered a high cost option, e.g. ~$3 million/annum to treat AMD at the former Wheal Jane tin mine, south-west England

Passive Bioremediation Systems

- natural and constructed aerobic and compost wetlands
- permeable reactive barriers

Advantages:

- low maintenance costs
- use natural biological processes

Disadvantages:

- construction costs
- requirement of land area (“footprint”)
- can be unreliability and inefficient
- disposal of spent composts

Functions:

- removal of iron (aerobic wetlands)
- removal of other chalcophilic metals (as sulfides; anaerobic systems)
- Addition of alkalinity (e.g. RAPS)

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

Rather than considering AMD/ARD as a waste material, we should consider it as a potential resource of:

- heat
- minerals
- metals

Learn from and adapt "natural" systems that exhibit attenuation of mine waters………

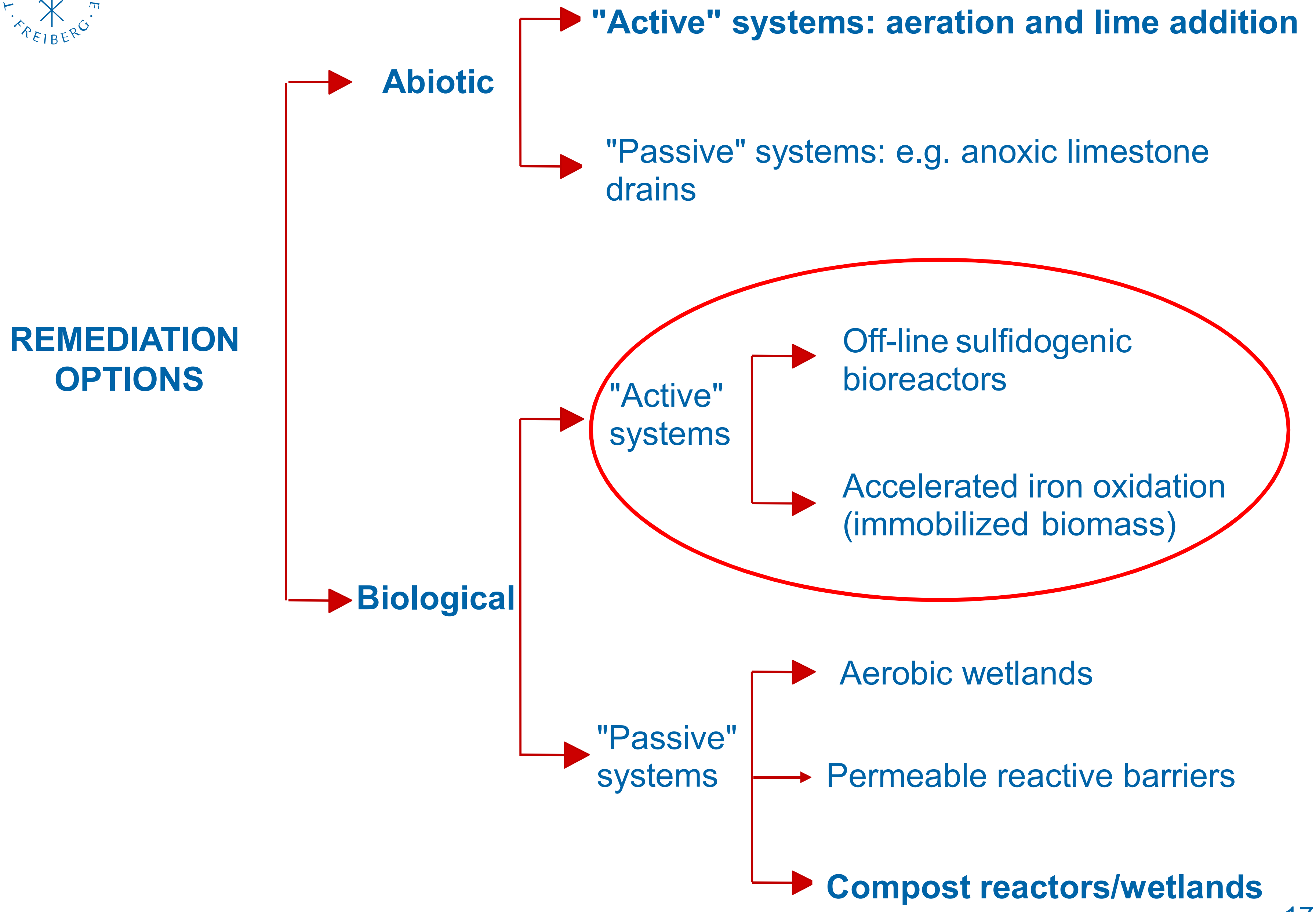
"*Ferrovum*"-dominated biomass in a AMD stream draining the San Telmo mine, Spain

$Fe^{2+} \rightarrow Fe^{3+}$

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

- $CO_2 \rightarrow$ organic C (algae)
- organic C + $SO_4^{2-} + Cu^{2+} \rightarrow CuS + CO_2$
  (sulfate reducing bacteria)

…and to combine this with chemical constraints and opportunities



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    - **Compost reactors/wetlands**

Development of new biological process options

- metals are selectively removed from mine waters, forming “clean” precipitates that can be re-used
- mine waters are considered as resources, rather than wastes
- technology also applicable to mine process waters (e.g. pregnant leach solutions)

Fe

Zn

Cu

Ni

SO_4^{2-}

H^+

Selective removal of iron from Mynydd Parys AMD

Analyte	Concentration (mg/L)
SO_4^{2-}-S	917
Fe^{2+}	280
Al^{3+}	90
Mg^{2+}	80
Zn^{2+}	70
Cu^{2+}	45
Ca^{2+}	42
Na^{+}	15
Mn^{2+}	10
NH_4^{+}	1.8
(pH	2.1)

Mine water treatment plant – Iron recovery

pilot-scale plant at Nochten, Germany*, where acidic iron-rich ground-water at a lignite mine is being remediated

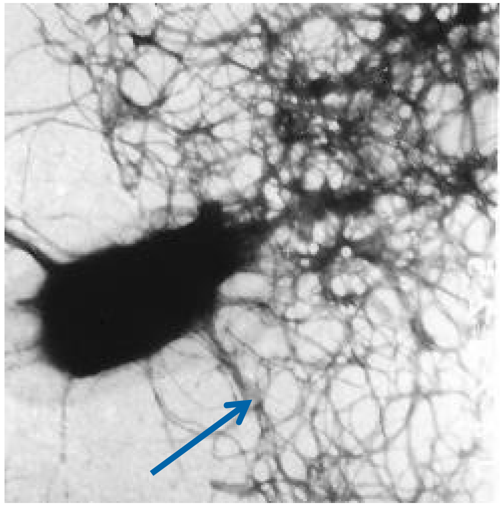
- plant contains naturally enriched bacteria
- Schwertmannite is a valuable product
- can be utilized as dye
- removal of As etc. from acidic waters

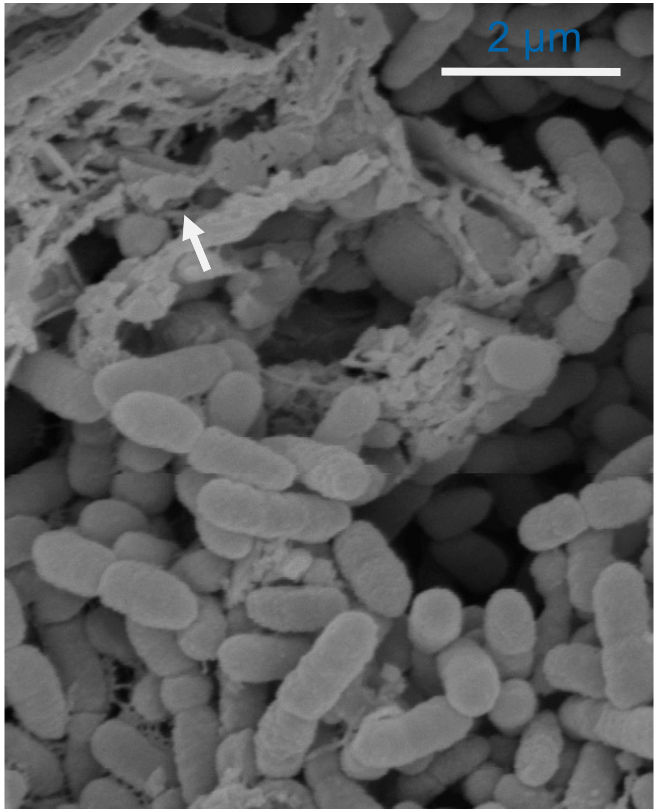
*operated by G.E.O.S.

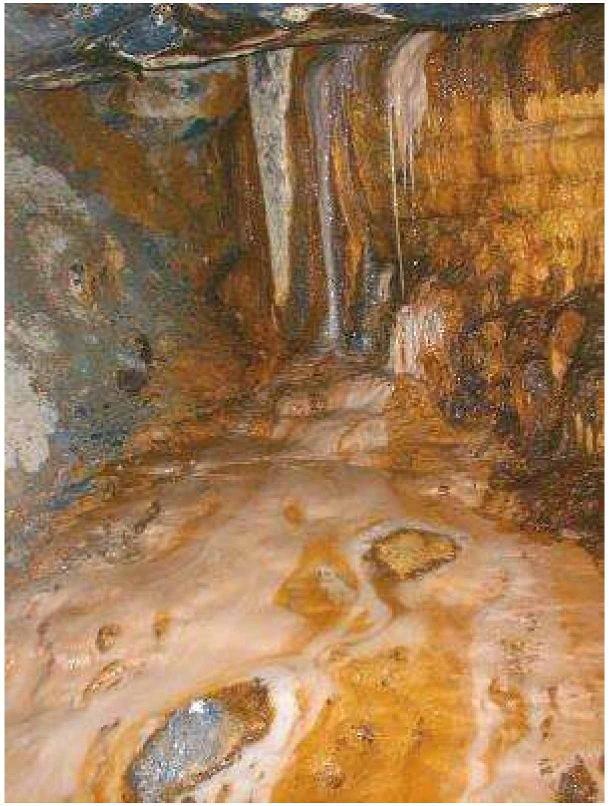
Heinzel et al., 2009, Hedrich et al., 201, Janneck et al., 2012

“*Fv. myxofaciens*” produces copious amounts of extracellular polymeric substances (EPS)

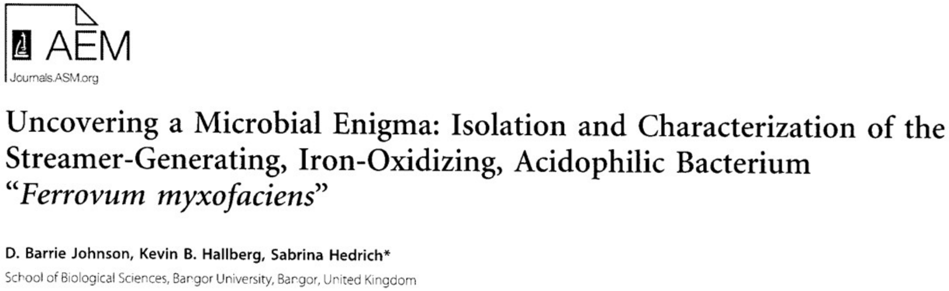
Micrographs of “*Fv. myxofaciens*”
Arrows indicate dehydrated EPS







Acid streamer growths (dominated by “*Fv. myxofaciens*” and *At. ferrivorans*)

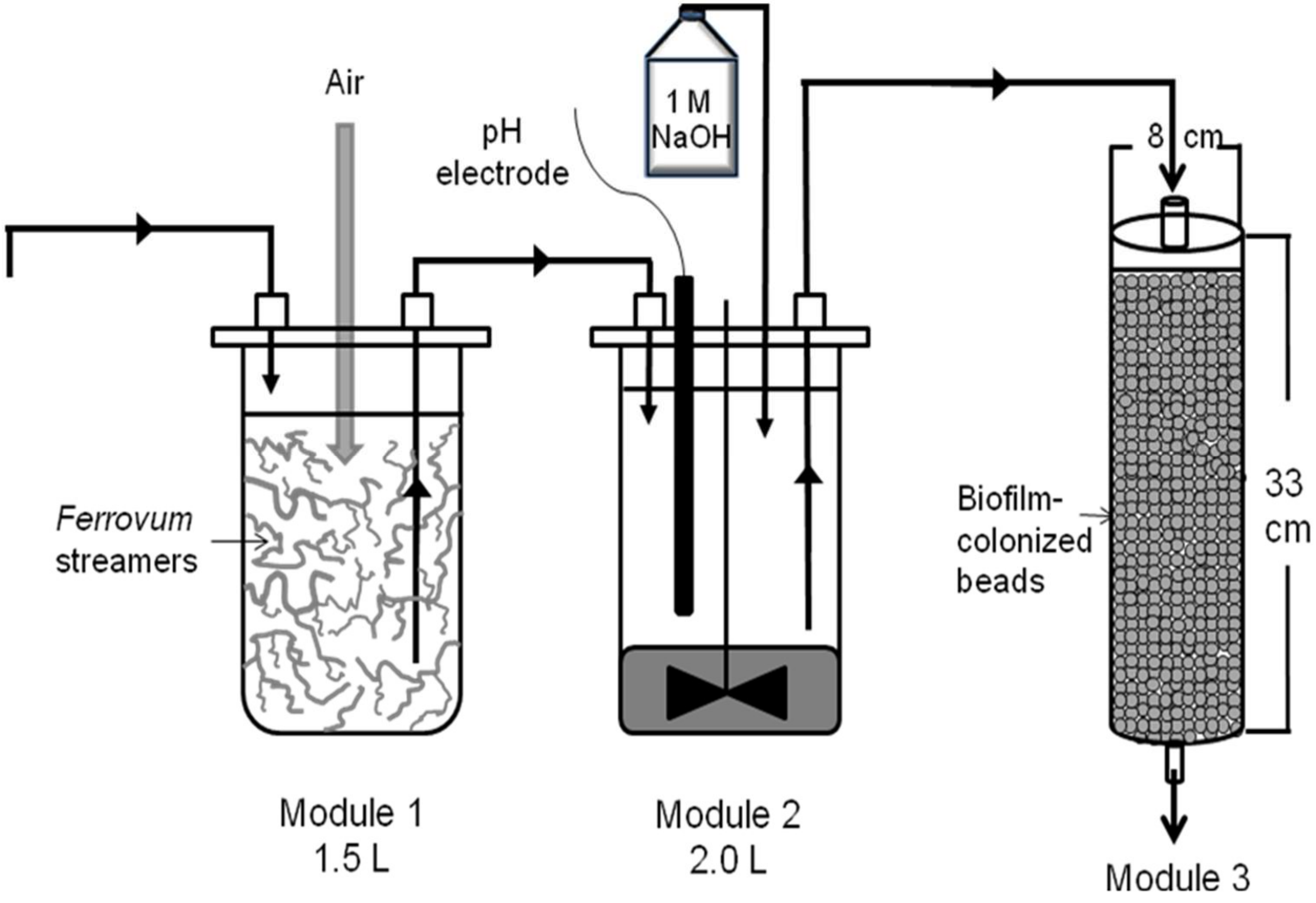


AEM
Journals.ASM.org

Uncovering a Microbial Enigma: Isolation and Characterization of the Streamer-Generating, Iron-Oxidizing, Acidophilic Bacterium “*Ferrovum myxofaciens*”

D. Barrie Johnson, Kevin B. Hallberg, Sabrina Hedrich*
School of Biological Sciences, Bangor University, Bangor, United Kingdom

Three connected modules
that operate in continuous flow mode



Module 1
1.5 L

Module 2
2.0 L

Module 3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journal homepage: www.elsevier.com/locate/biortech

ELSEVIER

A modular continuous flow reactor system for the selective bio-oxidation of iron and precipitation of schwertmannite from mine-impacted waters

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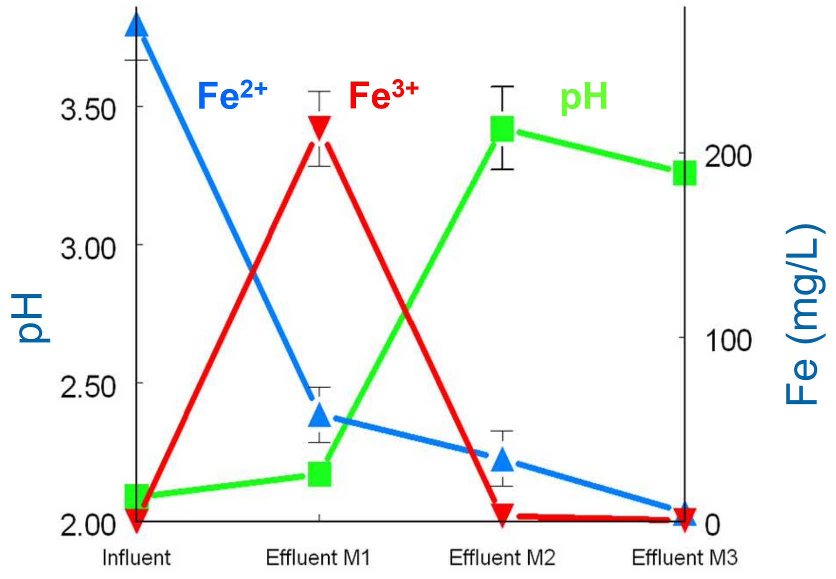
School of Biological Sciences, Bangor University, Bangor LL57 2UW, UK

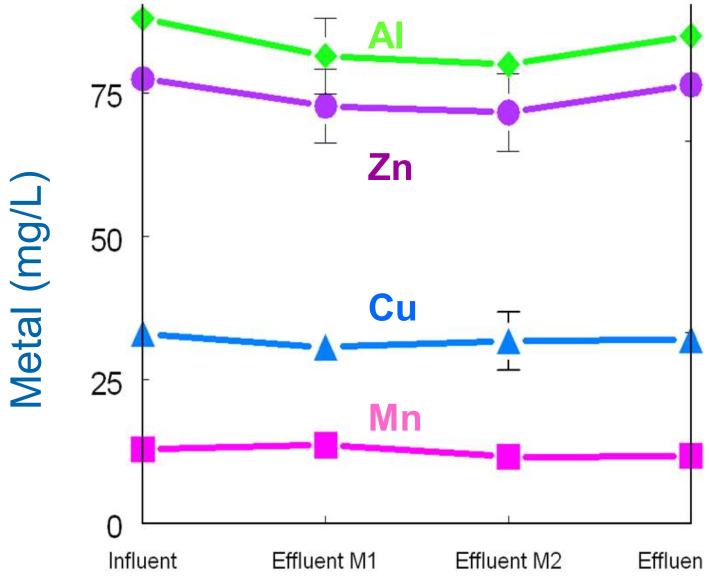
Ferrous iron is microbially oxidised in reactor 1

Schwertmannite is precipitated in reactor 2

Final traces of soluble iron are removed in reactor 3

Data from experimental tests





- Efficient removal of Fe
- clean schwertmannite precipitate → valuable product
- low operation costs
- no waste products
- effluent can be fed into other metal removal units
- removal of iron from synthetic Parys AMD water was >99%

Option 2: reductive biomineralisation

- Bacterial sulfate reduction can have three important roles in mitigating mine waters:

- precipitating transition metals and As (CuS, ZnS, As_2S_3 etc.);

$$H_2S + Me^{2+} \rightarrow MeS\downarrow + 2\ H^+$$

- lowering sulfate concentrations

- removing protons (increasing pH) but only significant if carried out at low pH:

$$4\ C_3H_8O_3^{*} + 7\ SO_4^{2-} + 14\ H^+ \rightarrow 12\ CO_2 + 7\ H_2S + 16\ H_2O \qquad \text{(pH 4)}$$

$$4\ C_3H_8O_3^{*} + 7\ SO_4^{2-} + 1.5\ H^+ \rightarrow 3\ CO_2 + 9\ HCO_3^- + 3.5\ H_2S + 3.5\ HS^- + 7\ H_2O \qquad \text{(pH 7)}$$

*glycerol

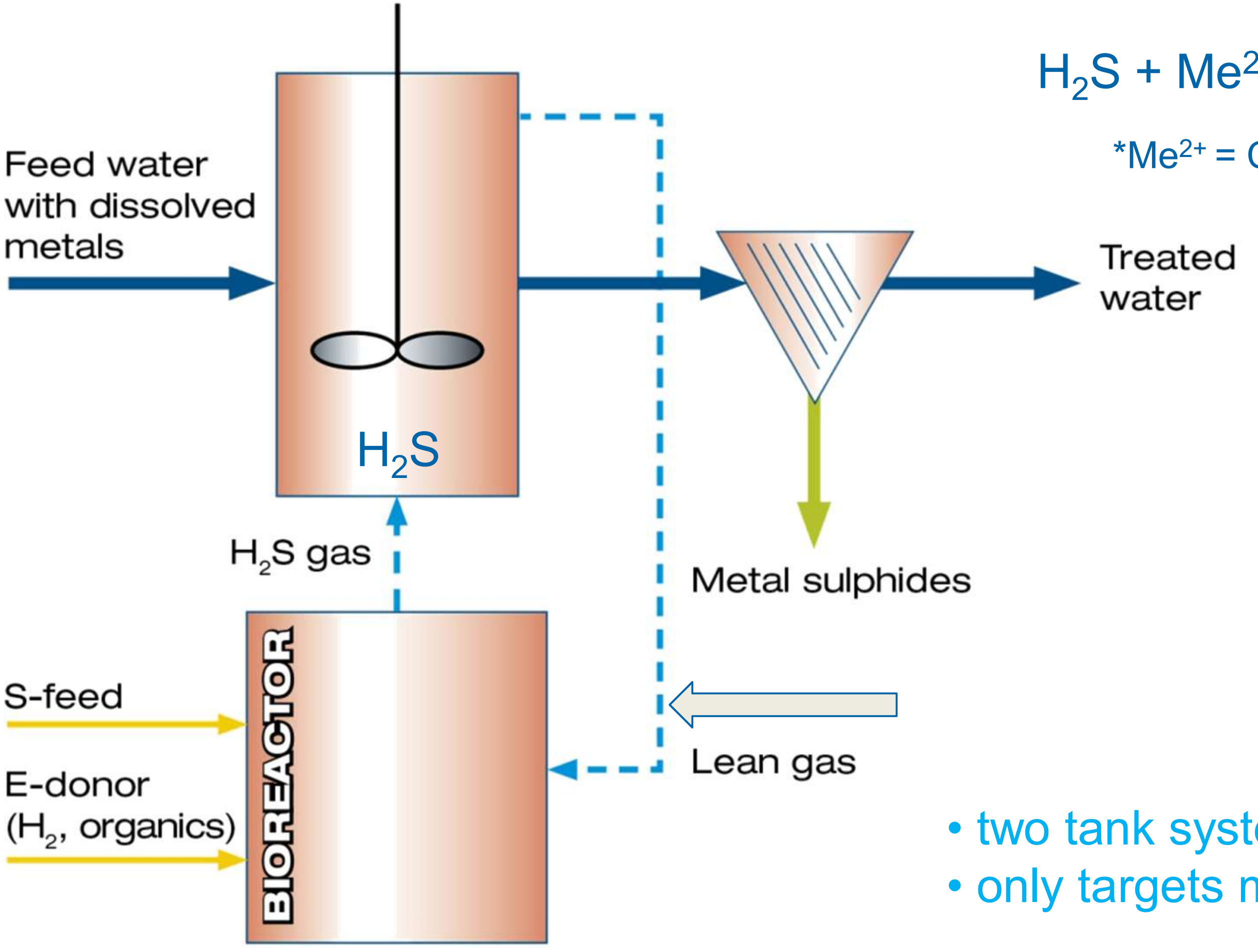
Biosulfidogenic processes for remediation mine waters/sulfate-rich water already exist:

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

both biotechnologies utilise neutrophilic bacteria

Biological H_2S production and metal sulfide precipitation

Thioteq®Process (Paques, NL)



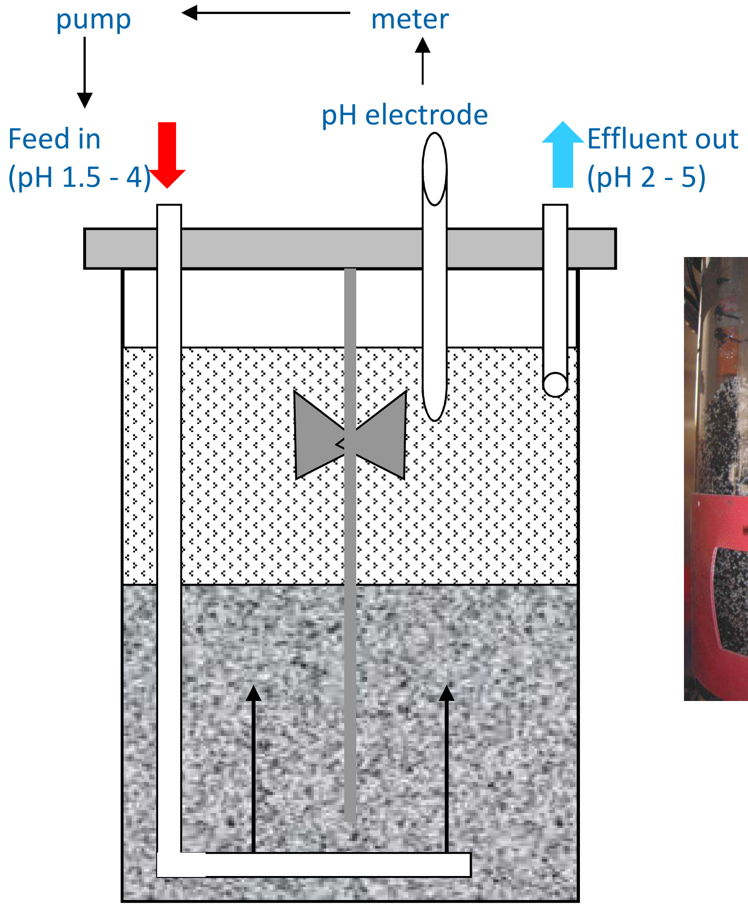
Neutrophilic sulfate-reducing bacteria (SRB)

$H_2S + Me^{2+*} \rightarrow MeS\downarrow + 2\ H^+$

$^*Me^{2+} = Cu^{2+}, Zn^{2+}, Co^{2+}$

- two tank system
- only targets metal precipitation

Novel modular low pH sulfidogenic bioreactors that also operate as continuous flow modular units



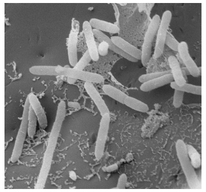
pump

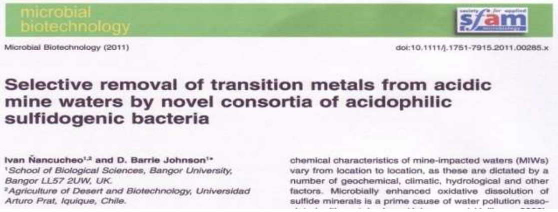
meter

Feed in
(pH 1.5 - 4)

pH electrode

Effluent out
(pH 2 - 5)





microbial
biotechnology

Microbial Biotechnology (2011)

doi:10.1111/j.1751-7915.2011.00285.x

Selective removal of transition metals from acidic mine waters by novel consortia of acidophilic sulfidogenic bacteria

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[1] *School of Biological Sciences, Bangor University, Bangor LL57 2UW, UK.*

[2] *Agriculture of Desert and Biotechnology, Universidad Arturo Prat, Iquique, Chile.*

chemical characteristics of mine-impacted waters (MIWs) vary from location to location, as these are dictated by a number of geochemical, climatic, hydrological and other factors. Microbially enhanced oxidative dissolution of sulfide minerals is a prime cause of water pollution asso-

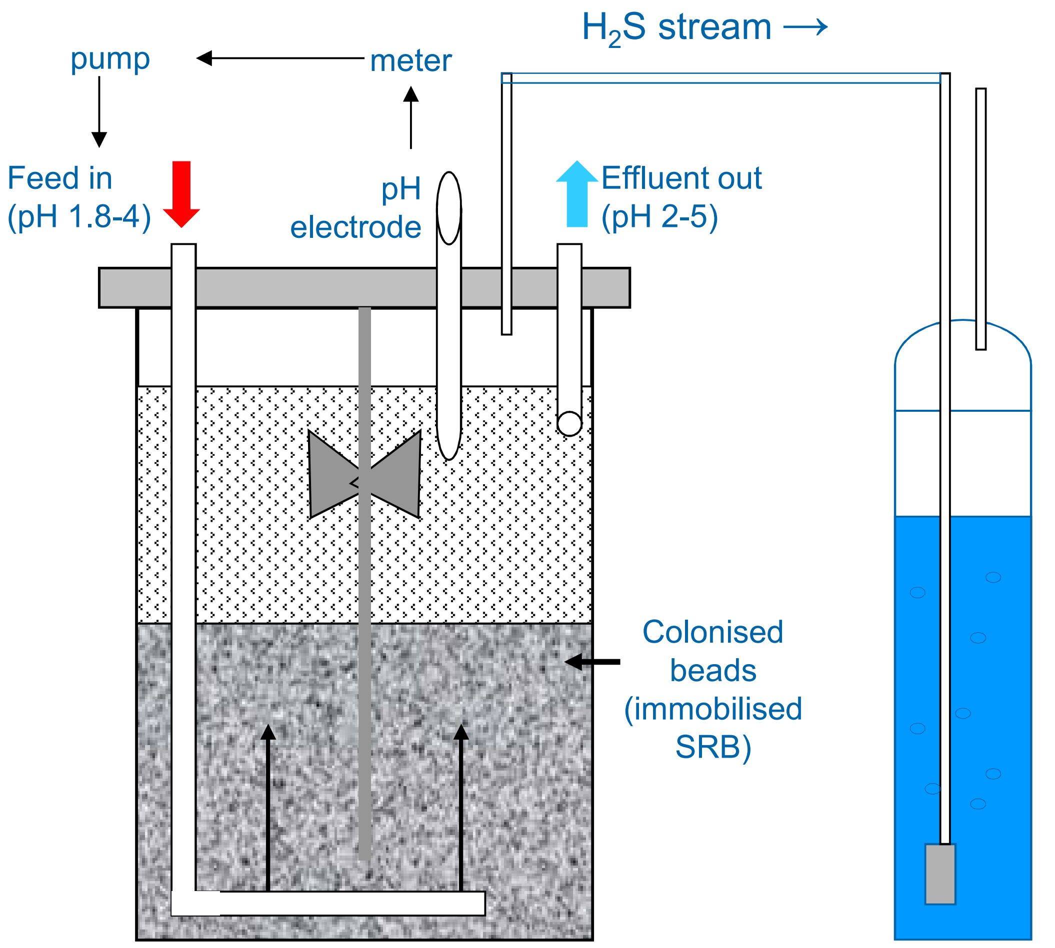
- many transition metals can be highly effectively removed from mine waters as reduced sulfide minerals

- again the challenge is to make a “clean” products, i.e, free of other metal suflides and other minerals such as gibbsite ($Al(OH)_3$)

Selective recovery of transition metals based on the different solubilities of their sulfide phases

	pH 2	pH 4	pH 7
Fe^{2+}	Fe^{2+}	Fe^{2+}	$FeS\downarrow$
Zn^{2+}	Zn^{2+}	$ZnS\downarrow$	
Cu^{2+}	$CuS\downarrow$		

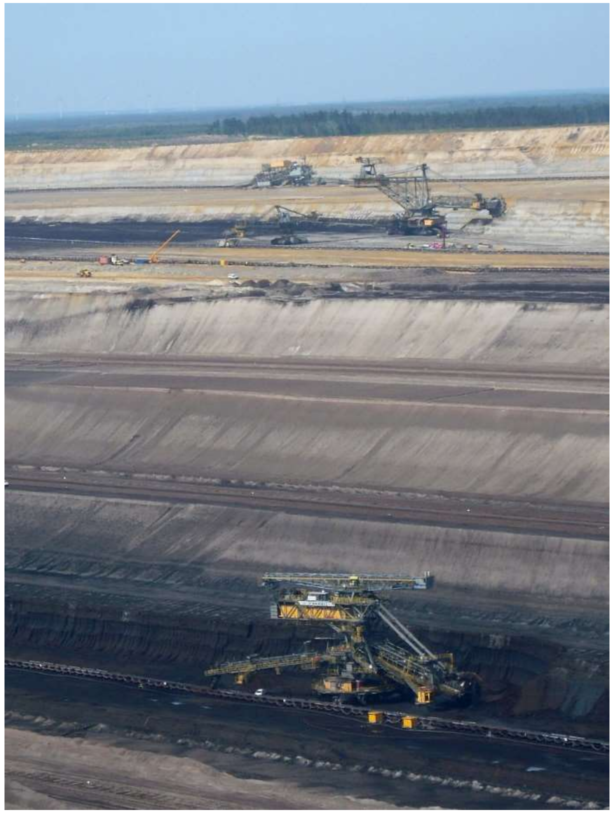
The modular units can be used to precipitate metals both off-line and within the bioreactor itself



In-line metal precipitation bioreactor

Off-line metal precipitation vessel

Remediation example 1: removal of sulfate, Nochten lignite mine, Germany

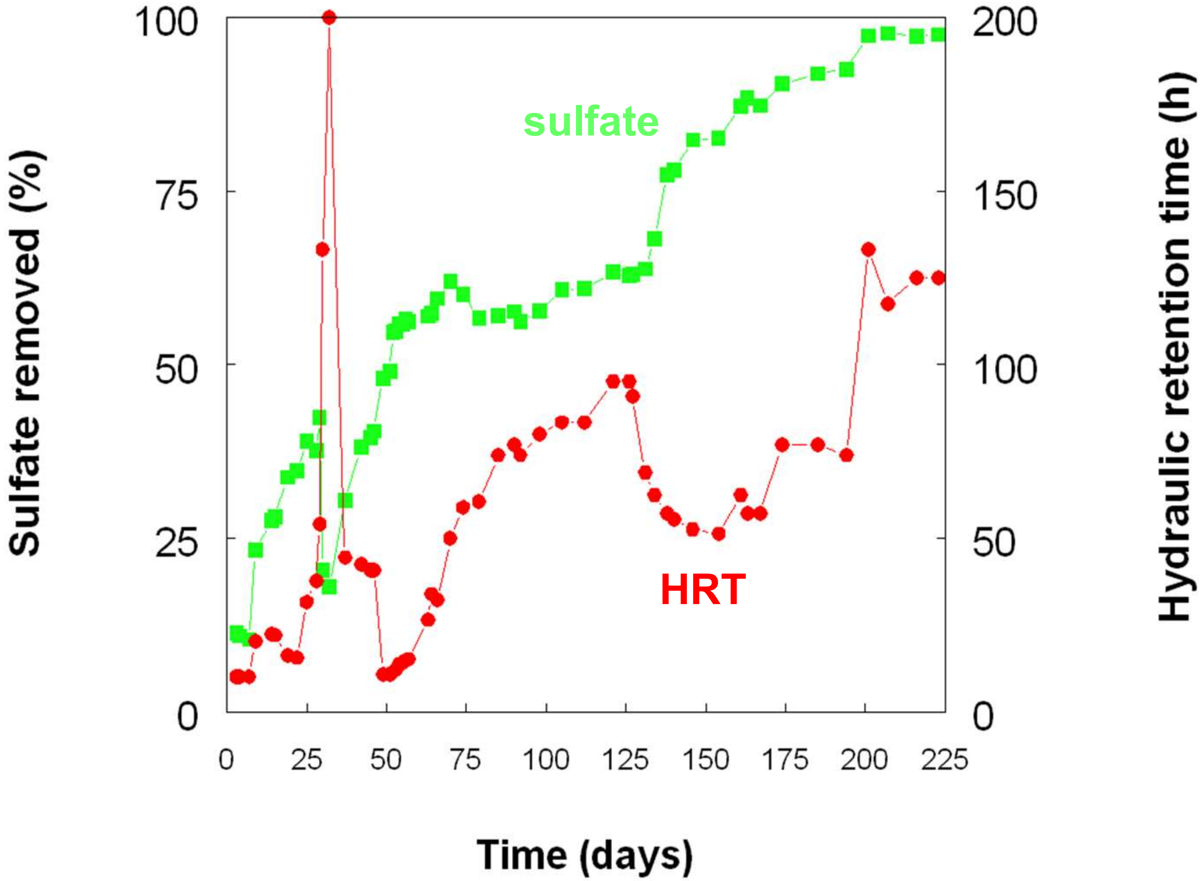


Chemical composition of synthetic mine water

Analyte	mg/L)
Mg	360
Ca	120
Na	23
Fe	110
SO_4-S	670
pH	1.8 – 3.0

Objectives:

- to lower [SO_4-S] to <30 mg/L
- to increase water pH



- $[SO_4\text{-}S]$ was lowered to <20 mg/L
- the H_2S generated was converted (off-line) to elemental S
- pH of the processed water was between 4 and 5

Combined bioremediation and resource recovery from a highly complex mine water (Maurliden mine, Sweden)

Discharge rate: 10 L/s

component	mg/L
Fe	403
Zn	464
Al	132
Cu	7.72
As	1.33
Cd	1.02
Co	0.4
Cr	< 90 µg/l
Mn	49
Ni	0.3
Ca	271
K	4.01
Mg	123
Na	13.8
Hg	< 0.02 µg/l
Pb	0.08

Objectives:

- removal of As and Cd
- recovery of Cu and Zn
- production of schwertmannite

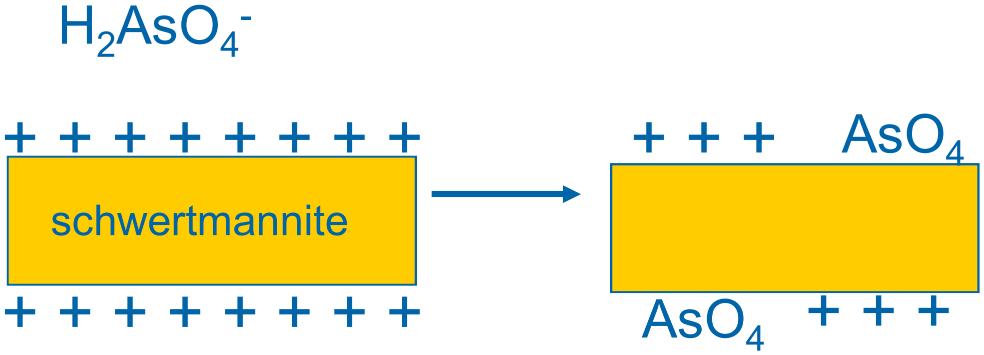
Hedrich & Johnson (2014)

Arsenic exists as both As (III) and As (V) (H_3AsO_3 and $H_2AsO_4^-$ at pH 2)

As (III) can be precipitated as a sulfide (As_2S_3) by, e.g. *Desulfotomaculum* spp.

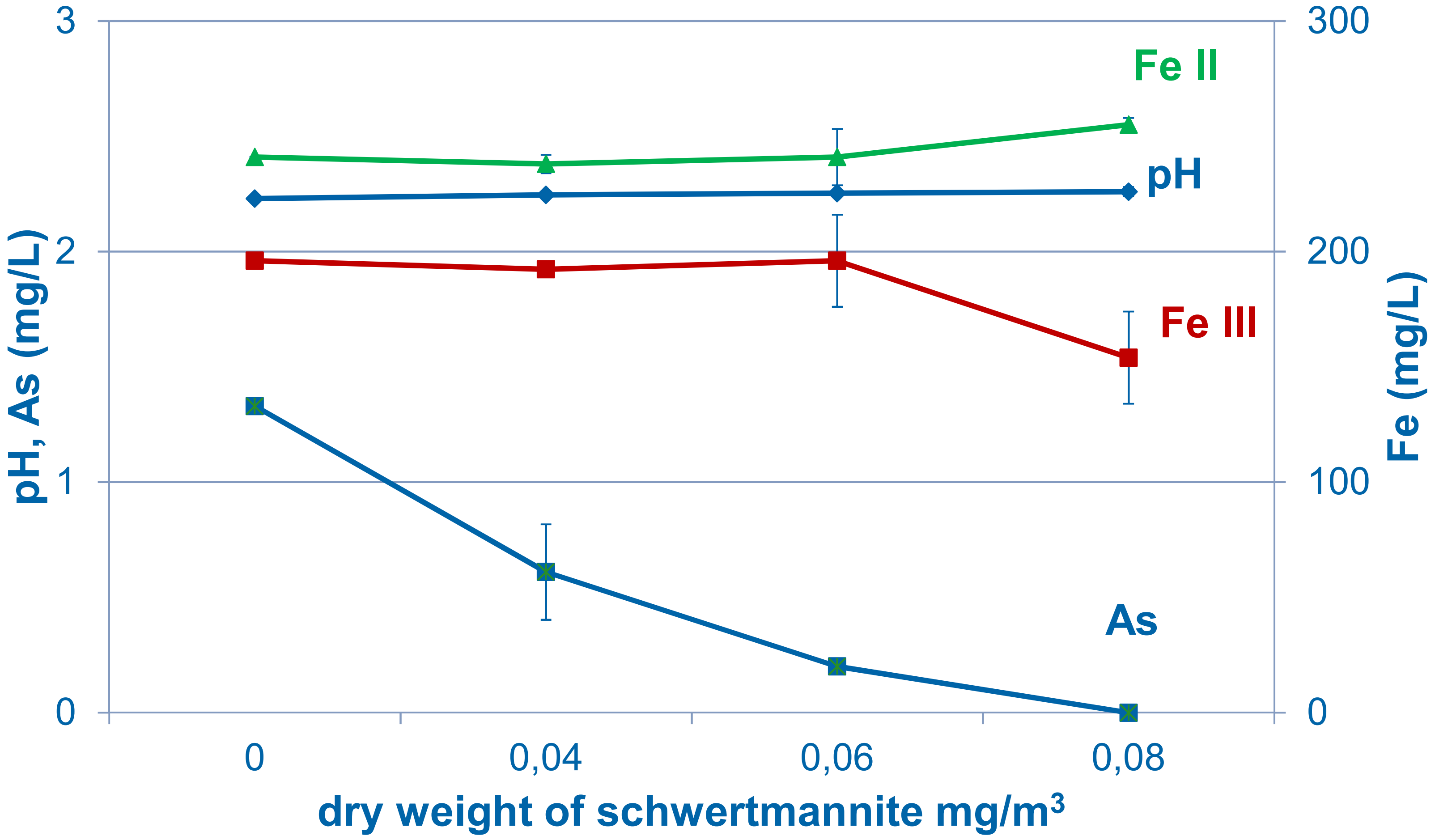
(and oxidized to As (V) by some acidophiles)

As (V) can be adsorbed onto positively-charged colloids

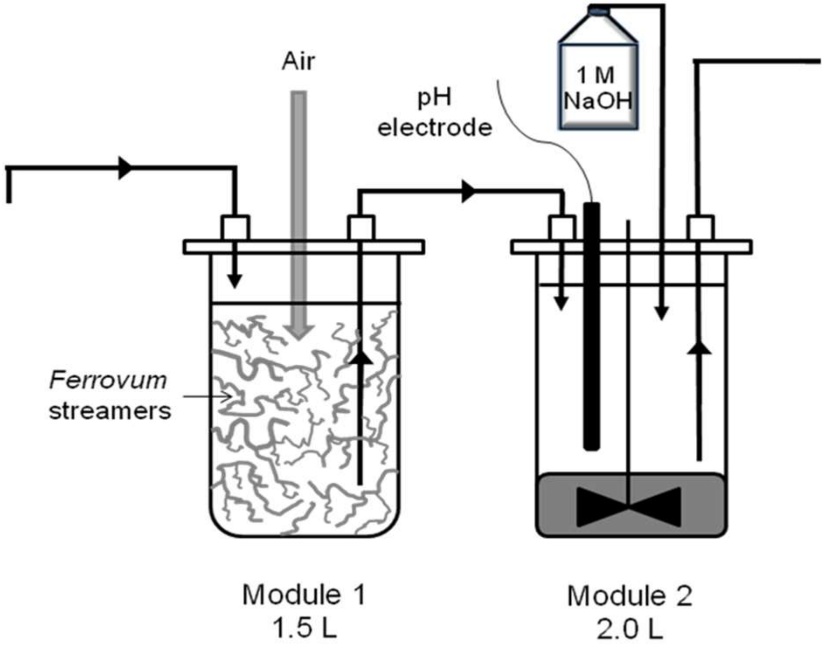


Stage I: Removal of As (V) by biological-produced schwertmannite

Schwertmannnite used for As removal is produced in **Stage II** of the process



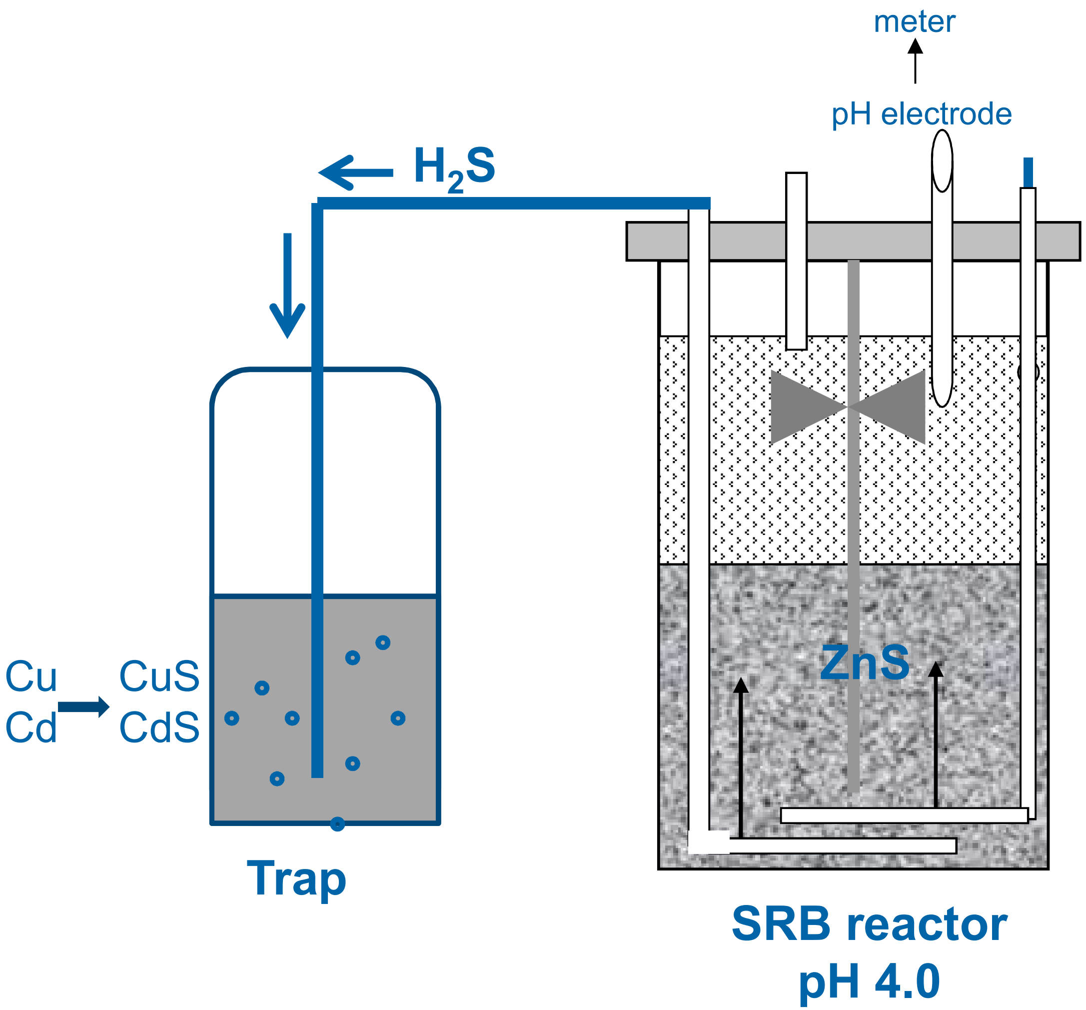
Stage II: Iron recovery – oxidative process



- modular iron oxidation/precipitation system
- acidophilic iron-oxidizer *Ferrovum myxofaciens*
- recovery of iron as schwertmannite

Hedrich & Johnson (2012) Bioresource Technol., 106, 44-49

Stage III and IV: Removal of chalcophilic metals

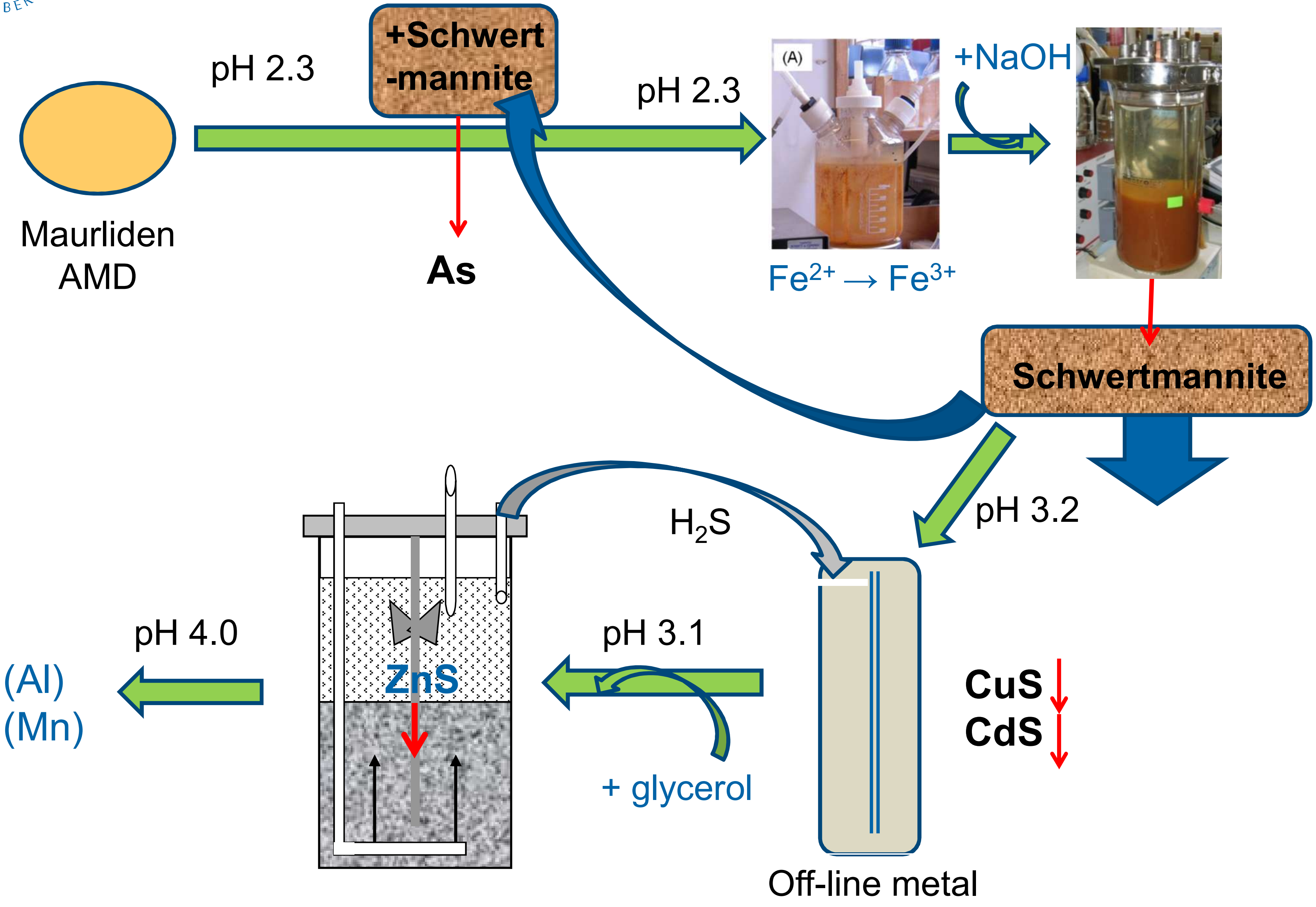


Metal	log K_{sp}
Cu^{2+}	-35.9
Cd^{2+}	-28.9
Zn^{2+}	-24.5
Co^{2+}	-22.1
Ni^{2+}	-21.0
Fe^{2+}	-18.8
Mn^{2+}	-13.3

$$7\ C_3H_8O_3 + 7\ Zn^{2+} + 14\ H^+ + 14\ SO_4^{2-} \longrightarrow 21\ CO_2 + 7\ ZnS + 7\ H_2S + 32\ H_2O$$

Ñancucheo & Johnson (2012)
Microb. Biotechnol. 5, 34-44

Flow sheet



Maurliden
AMD

pH 2.3

+Schwert
-mannite

As

pH 2.3

(A)

$Fe^{2+} \rightarrow Fe^{3+}$

+NaOH

Schwertmannite

pH 3.2

H_2S

CuS
CdS

Off-line metal
precipitation

pH 3.1

+ glycerol

ZnS

sulfidogenic bioreactor

pH 4.0

(Al)
(Mn)

Hedrich & Johnson, 2012

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

Thank you for your attention!

Glück auf!