Fractionation and leachability of Fe, Zn, Cu and Ni in the sludge from a sulphate-reducing bioreactor treating metal-bearing wastewater

P. Kousi, E. Remoundaki, A. Hatzikioseyian, V. Korkovelou & M. Tsezos

Laboratory of Environmental Science and Engineering
School of Mining and Metallurgical Engineering
National Technical University of Athens (NTUA)

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Process:
Microbially mediated sulphate reduction

- by sulphate-reducing bacteria (SRB)
- under anaerobic conditions

Process benefit:
simultaneous removal of
- sulphate
- metal ions
- acidity
- organic carbon

acidity neutralisation
precipitation of metal sulphides
Metal ion sequestering - Sludge formation

Prevailing mechanism:
bioprecipitation of metal sulphides

• A key aspect of the sustainability of the process, besides its effectiveness, is the management of the generated sludge
• Potential scenarios range from disposal via landfilling to further treatment for metal recovery
Bioreactor

Upflow, packed-bed reactor
Biofilm established on porous ceramic pipes 1 cm long
(Cermec®, JBL Germany)

Operation: batch mode for 6 years at room temperature

1. Sulphate- and metal-bearing substrate solution
2. Sulphate-reducing bioreactor
3. Peristaltic pump
Issue addressed:
Propose sludge management options for overall process sustainability

Relevant questions:

1. Is the sludge safe for disposal via landfilling?
2. Is the metal content of the sludge recoverable?
Issue addressed: sludge management for overall process sustainability

Formation mechanism
- mineral phases

Sludge stability

Other factors (temp, pH, sulphide)
- crystallinity
- particle size

Metal mobility
Methodology

Sludge samples from the bottom of the reactor → low redox and neutral pH conditions

Physical, chemical, mineralogical characterisation

- Laser Diffraction - Low Angle Laser Light Scattering
- X-Ray Diffraction
- Thermogravimetry-Differential Scanning Calorimetry
- Scanning Electron Microscopy / Energy Dispersive X-ray Spectrometry
Methodology

Metal fractionation
Sequential extraction method (Tessier)

Metal leachability and environmental stability
- EN 12457-2
- TCLP
- pH-time effect
RESULTS

Particle size distribution

\[ D_{90} = 45.73 \mu m \]

\[ D_{50} = 8.31 \mu m \]

\[ D_{10} = 0.20 \mu m \]
## Sludge composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (wt. %, dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>14.80</td>
</tr>
<tr>
<td>Zinc</td>
<td>18.73</td>
</tr>
<tr>
<td>Copper</td>
<td>18.24</td>
</tr>
<tr>
<td>Nickel</td>
<td>17.71</td>
</tr>
<tr>
<td>Total metal content</td>
<td><strong>69.48</strong></td>
</tr>
<tr>
<td>Sulphur (total)</td>
<td>31.22</td>
</tr>
<tr>
<td>Carbon (total)</td>
<td>5.00</td>
</tr>
<tr>
<td>Volatile solids</td>
<td>14.70</td>
</tr>
</tbody>
</table>
### Mineralogy - XRD

<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeS₂</td>
<td>pyrite</td>
</tr>
<tr>
<td>2</td>
<td>FeCO₃</td>
<td>siderite</td>
</tr>
<tr>
<td>3</td>
<td>CuS</td>
<td>covellite</td>
</tr>
<tr>
<td>4</td>
<td>Zn₅S₅</td>
<td>wurtzite</td>
</tr>
<tr>
<td>5</td>
<td>ZnS</td>
<td>sphalerite</td>
</tr>
<tr>
<td>6</td>
<td>NiS</td>
<td>millerite</td>
</tr>
<tr>
<td>7</td>
<td>Ni₃S₂</td>
<td>heazlewoodite</td>
</tr>
<tr>
<td>8</td>
<td>Cu₄Fe₅S₈</td>
<td>haycockite</td>
</tr>
<tr>
<td>9</td>
<td>Cu₂FeS₂</td>
<td>bornite</td>
</tr>
<tr>
<td>10</td>
<td>CuFe₂S₃</td>
<td>cubanite</td>
</tr>
<tr>
<td>11</td>
<td>CuFeS₂</td>
<td>chalcopryite</td>
</tr>
</tbody>
</table>
Mineralogy - SEM/EDS

![SEM/EDS Image]

- Energy-dispersive X-ray spectroscopy (EDS) spectrum showing peaks for elements such as Zn, Ni, and Cu.
- The sample was imaged at 15 kV, X3,500 magnification, with a scale of 5 µm.
- The date and time of the imaging session are 14 50 SEI.
Metal fractionation

![Metal fractionation diagram]

- **Fe**
  - water-soluble: 20%
  - exchangeable: 10%
  - Fe/Mn oxides: 30%
  - carbonate: 20%
  - organic/sulphide: 20%

- **Zn**
  - water-soluble: 10%
  - exchangeable: 10%
  - Fe/Mn oxides: 10%
  - carbonate: 40%
  - organic/sulphide: 20%

- **Ni**
  - water-soluble: 10%
  - exchangeable: 10%
  - Fe/Mn oxides: 30%
  - carbonate: 10%
  - organic/sulphide: 30%

- **Cu**
  - water-soluble: 10%
  - exchangeable: 10%
  - Fe/Mn oxides: 10%
  - carbonate: 20%
  - organic/sulphide: 30%
Environmental stability

Initial water pH=2

Metal concentration (mg/L) vs. Time (h)

- Fe
- Zn
- Ni
- Cu
- pH

Fe (mg/L) vs. Time (h)
Environmental stability (long-term)

Leached (%) vs. pH for different elements:
- Fe
- Zn
- Ni
- Cu
- S-SO$_4^{2-}$

Legend:
- pH=2
- pH=4
- pH=6
- pH=9
90% of the particles are smaller than 47 μm, 50% of the particles are smaller than 8.5 μm

Amorphous or poorly crystalline phases and aggregates of Fe, Zn, Cu, Ni sulphides

Metal content adds to 70% dw:
Fe (14.8%), Zn (18.7%), Ni (17.7%), Cu (18.2%)

Main metal sulphides determined:
pyrite, covellite, wurtzite/sphalerite and millerite/heazlewoodite
The sludge is characterised as hazardous and inappropriate for disposal via landfilling without any prior treatment.

The sludge fine grain size and poorly crystalline structure, as well as the direct oxidation of sulphide upon exposure to water/air, render the high metal content (70 % dw) of the sludge recoverable.
