The Magnetic Sludge Process

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The Magnetic Sludge Process: A Potential New Method for Active Neutralisation of AMD

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Acid and Metalliferous Drainage

Formed by oxidation of naturally occurring minerals

> Usually pyrite, but can be any metal sulfide
> Often after large scale disturbance

Legacy impact for hundreds to thousands of years
Widely regarded as the major environmental and economic issue facing worldwide mining operations
Best practice is to reduce AMD formation
Usually neutralised with hydrated lime
Produces a voluminous metal hydroxide sludge
Part 1: Chemical Stability of AMD Treatment Sludges
150L synthetic AMD

- 1200 mg/L Fe
- 110 mg/L Al
- 100 mg/L Cu
- 100 mg/L Zn

Stirred, aerated reactor

Treat with

- Ca(OH)$_2$,
- CaCO$_3$ then Ca(OH)$_2$
- KB-1
- Bauxsol
- HDS process
High Density Sludge (HDS)

Sludge recycle step
Recycled sludge acts as a nucleation centre for new sludge precipitated
Magnetic Hysteresis

Crystallite size in AMD treatment sludges often too small for XRD analysis
Magnetic field applied
Hysteresis response measured
XANES

X-ray Absorption Near Edge Spectroscopy
Australian National Beamline Facility (beamline 20b),
2.5 GeV Photon Factory, (KEK, Tsukuba, Japan)
Information on nearest-neighbour and next-nearest-neighbour chemical bonding
Composition

Sludges dominated by XRD amorphous ferric oxyhydroxide (ferrihydrite) and gypsum
Magnetic hysteresis parameters indicate very small goethite in some samples
Unreacted materials from reagents
Cu and Zn are surface adsorbed
High volume and low density
Strong Acid Leach Test (SALT)

Results from TCLP dependent on final pH which is determined by neutralisation efficiency
SALT tests the strength of chemical bonding
Designed to simulate disposal at a mine
Several extractions performed, each with a different amount of $\text{H}_2\text{SO}_4$
Most acidic solution pH $<$ 2.5
% Leached = 330000e^{-4.10pH}

R^2 = 0.96
% leached – Aluminium

% Leached = 1100^{1.19x}

R^2 = 0.92
% leached – Copper

% Leached = -5.2x^2 + 9.1x + 100
R^2 = 0.94
% leached – Zinc

$y = -3.8x^2 + 12x + 82$

$R^2 = 0.75$
Summary

Typically high volume & low density
Often disposed into an acidic environment
Manufactures of proprietary treatment reagents claim increased chemical stability – not observed
Treatment sludges will re-release metals to environment when stored in acidic environment
In general, current sludge management practices do not address long-term storage or stability
Improved neutralisation treatment sludges are required, that will resist leaching under low pH conditions
Part 2: Magnetic Sludge Process
AMD treatment sludge management is an escalating concern.
Results to date show that known reagents unable to form a more chemically stable treatment sludge.
Preliminary experiments showed that particular conditions can produce a brown partly crystalline sludge:
- Higher density / Lower volume
- Increase chemical stability
- Cheap – still uses hydrated lime reagent
Laboratory Batch Reactor
Treated Synthetic ARD
A,B – strongly magnetic maghemite/magnetite sludges;
C-E - non-magnetic poorly crystalline sludges
In most experiments, neutralisation was largely complete at an endpoint of pH ~8
Settling rates

Volume of Sludge (ml) vs. Time (mins)

- Magnetic sludge
- Non-magnetic sludge
Drop in pH during aeration due to release of sulphate and acidity during conversion of green rust (ferrous hydroxide-sulphate) to ferric oxide/hydroxide
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Affect of Aeration Rate

Slow oxidation (aeration) allows crystal structures to reform to maghemite.
Affect of Aluminium and Seeding

With Aluminium

With Aluminium & Seeding

Seeding assists magnetite/maghemite formation
Leachability of Crystalline Sludges

Data from phase 1 sludges
- Fe(OH)2 ppt
- Fe(OH)2 ppt
- Fe(OH)3 ppt
- Fe(OH)3 ppt
- Fe(OH)2 Al-free (a)
- Fe(OH)2 Al-free (b)

% Zn leached

Time (minutes)

18 hours
After neutralisation and aeration, levels of metals in the treated AMD were very low – successfully treated water.

Initial sludge was dark green ("green rust" - ferrous hydroxide-sulphate)

Aeration oxidised it to a ferric hydroxide phase (releasing sulphate and acidity)

Results Summary

- Aeration during neutralisation a XRD-amorphous orange-brown sludge
- Rapid aeration post neutralisation produced a poorly crystalline light brown sludge
- Slow aeration post neutralisation generally formed a crystalline, strongly magnetic dark brown sludge (maghemite/magnetite)
High treatment pH (10-11) needed to produce crystalline sludges
Copper and zinc did not affect sludge mineralogy
  > Incorporated into maghemite/magnetite crystal structure and therefore resistant to leaching
  > Also demonstrated for Cr and Co (by others)
Crystalline sludges greatly enhance chemical stability
Calcium and aluminium reduce maghemite formation
Seeding with sludge from previous runs increases mineral formation
  > More work required to optimize process
Potential Advantages

Magnetic minerals easily separated from other constituents, e.g. gypsum
May produce economic by-product
Chemical stability of trace metals increased
Produces less volume of sludge (higher density)
Next Steps

Continue seeding experiments (as in HDS process)
  > Magnetite from natural samples
  > Magnetite/maghemite from previous runs
  > Reduce inhibitory effects of calcium and aluminium
  > Increase crystal size and density of sludges

2 stage neutralisation process
  > Initial neutralisation to ~5 to produce Al hydroxide sludge,
  > Second neutralisation to form maghemite/magnetite sludge
  > Potentially seeded process

Seek Australian Research Council Industry linkage funding
  > Need industry partner
References


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