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

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AMD Treatment

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

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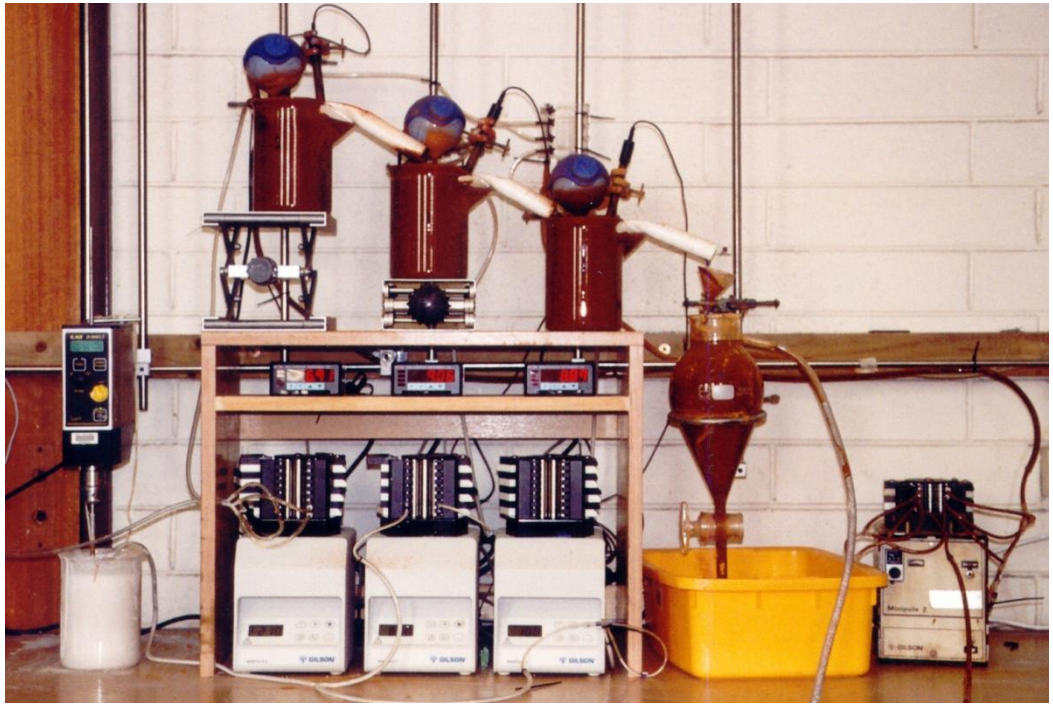
High Density Sludge (HDS)

Sludge recycle step

Recycled sludge acts an nucleation centre for new sludge precipitated



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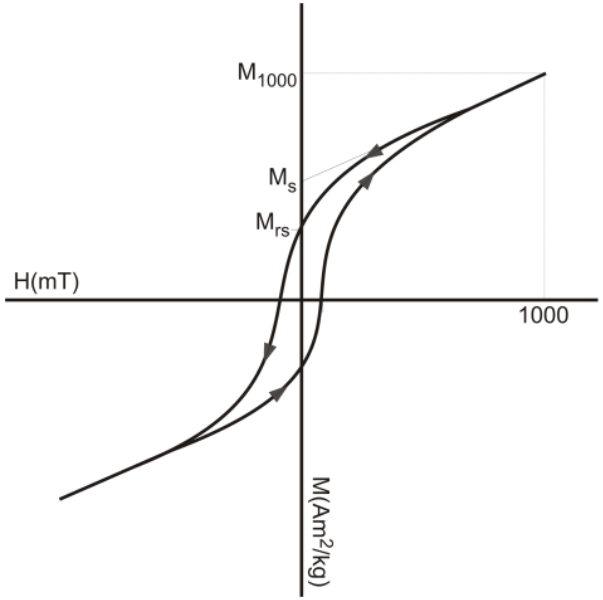
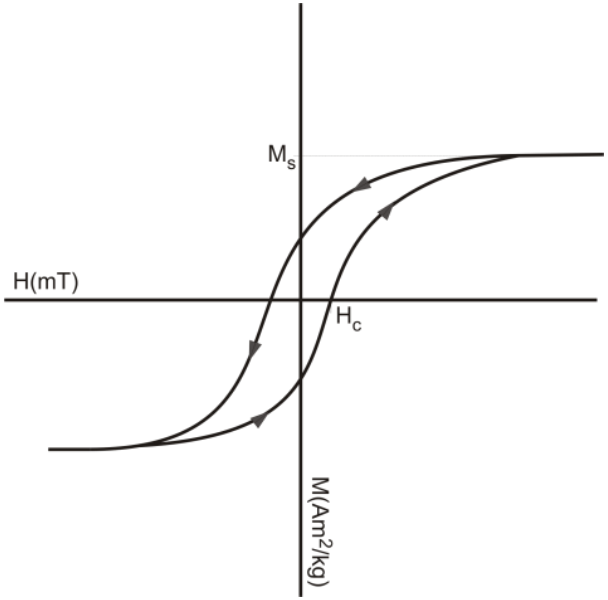
Magnetic Hysteresis

Crystallite size in AMD treatment sludges often too small for XRD analysis

Magnetic field applied

Hysteresis response measured





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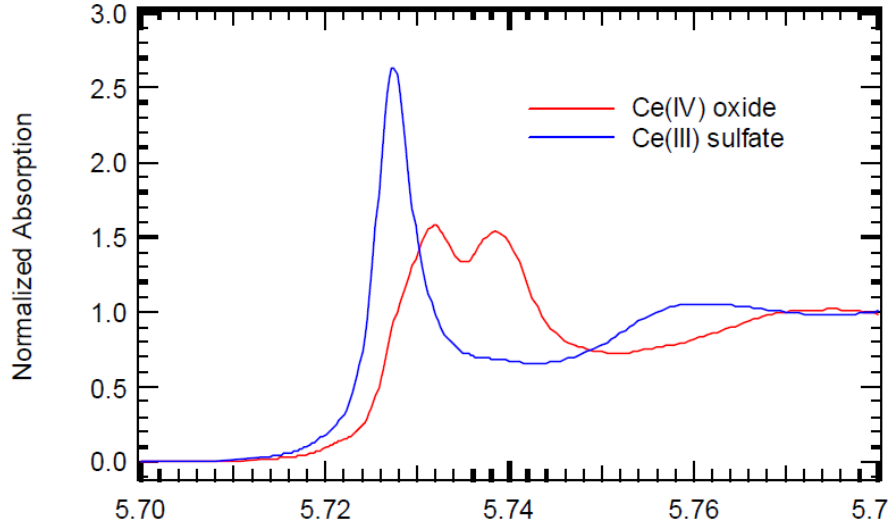
XANES

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



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Composition

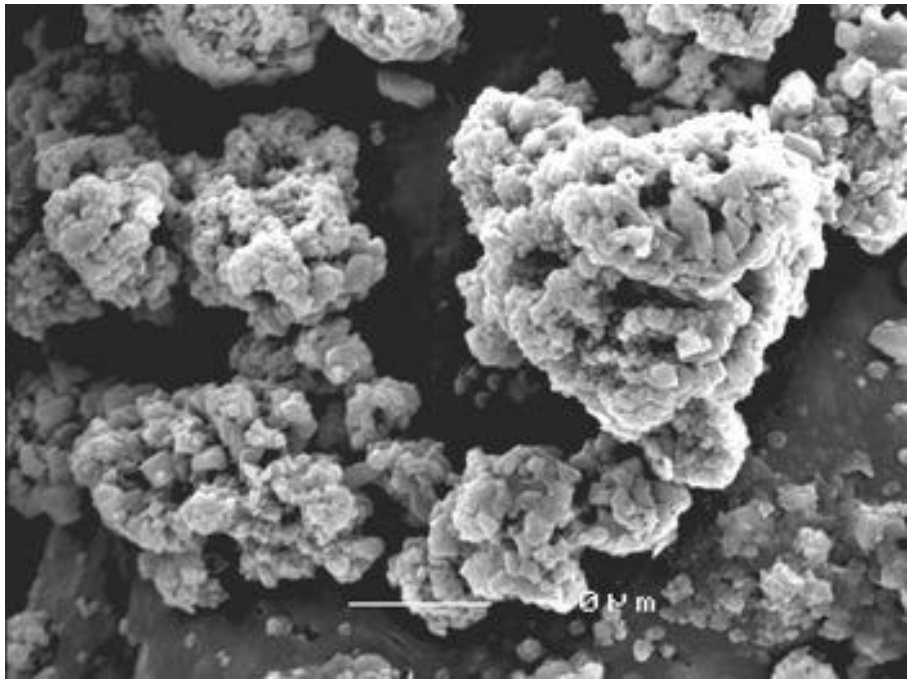
Sludges dominated by XRD amorphous ferric oxy-hydroxide (ferrihydrite) and gypsum

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

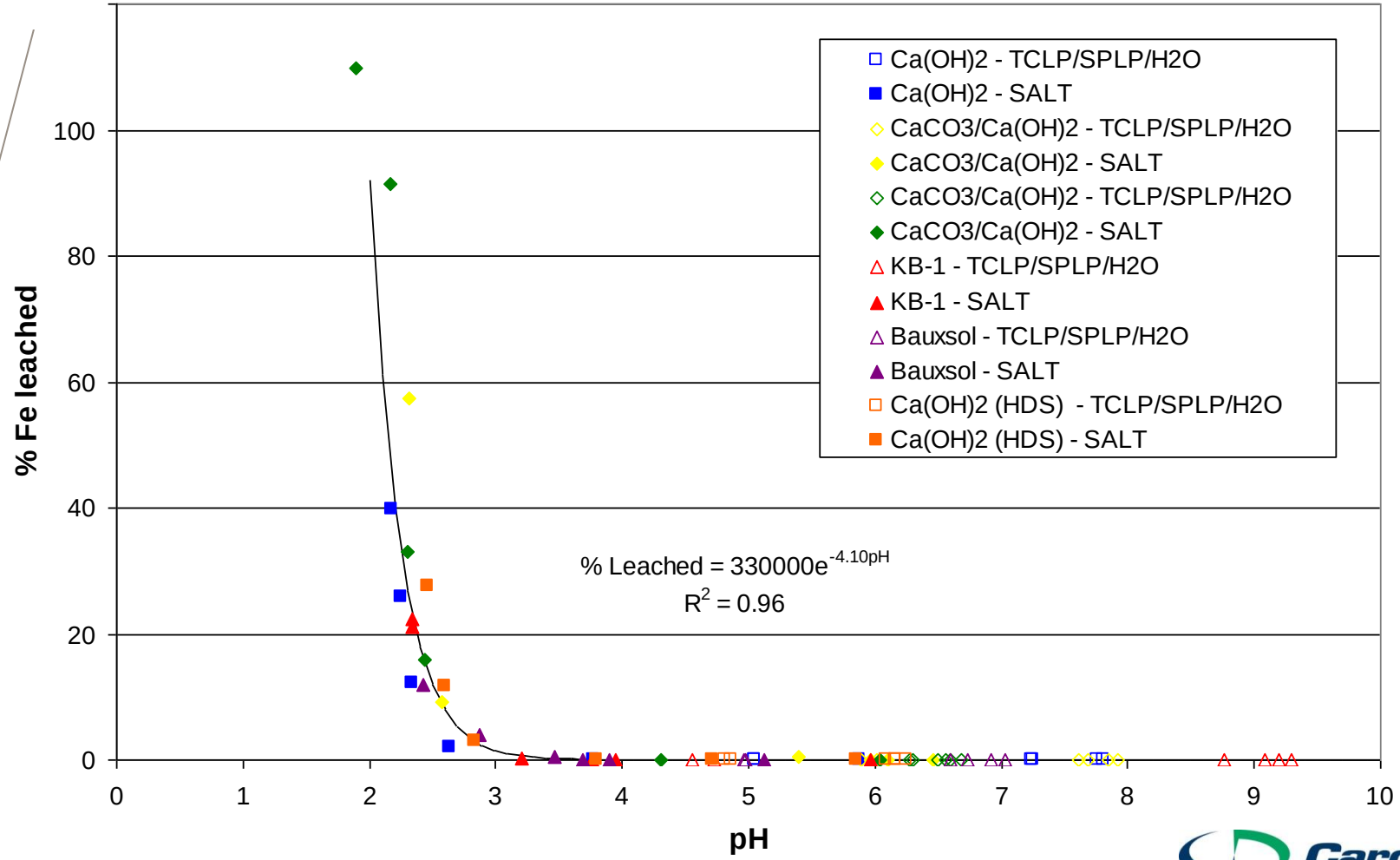
SALT tests the strength of chemical bonding

Designed to simulate disposal at a mine

Several extractions performed, each with a different amount of H_2SO_4

Most acidic solution pH<2.5

% leached – Iron



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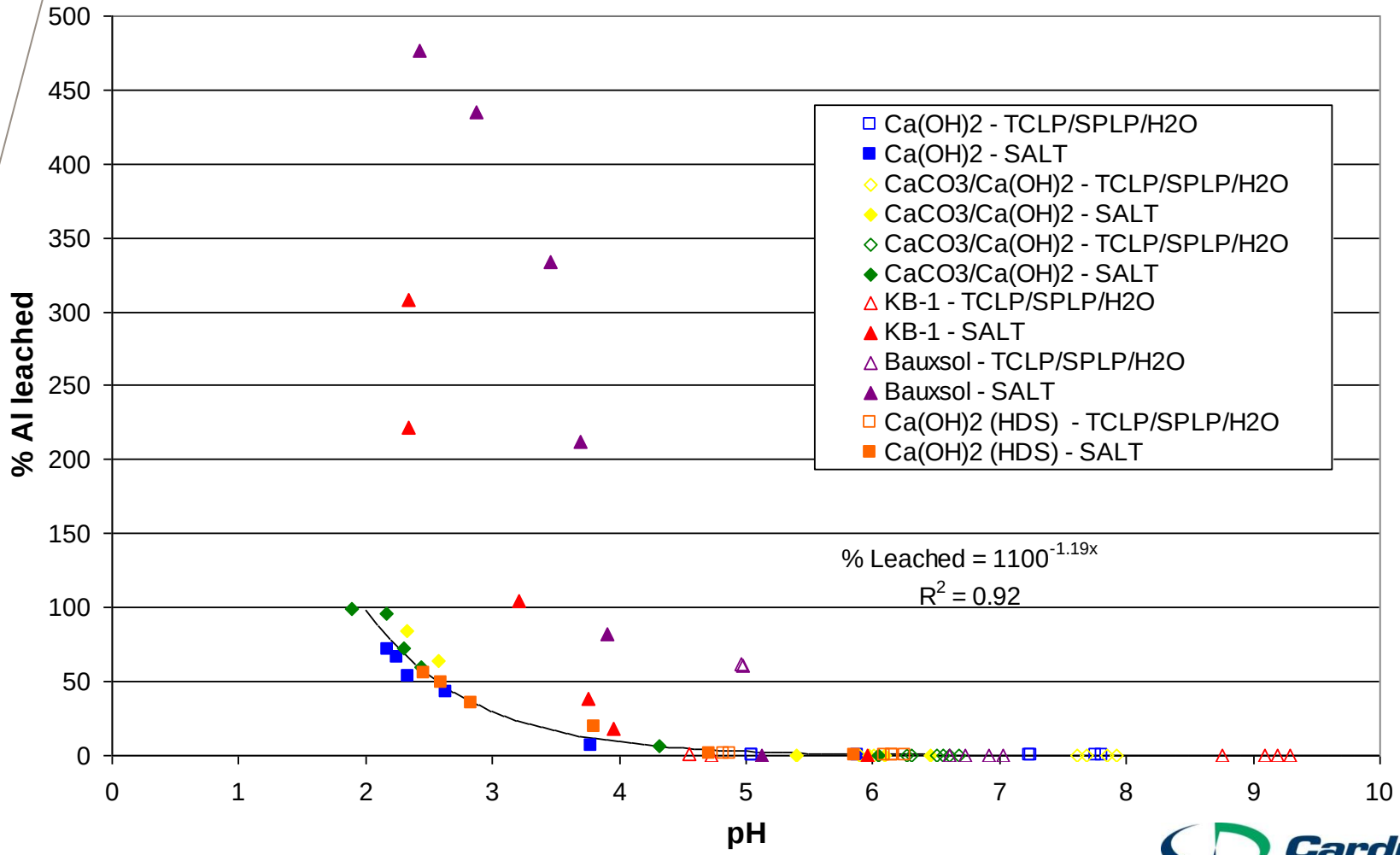
% leached – Aluminium



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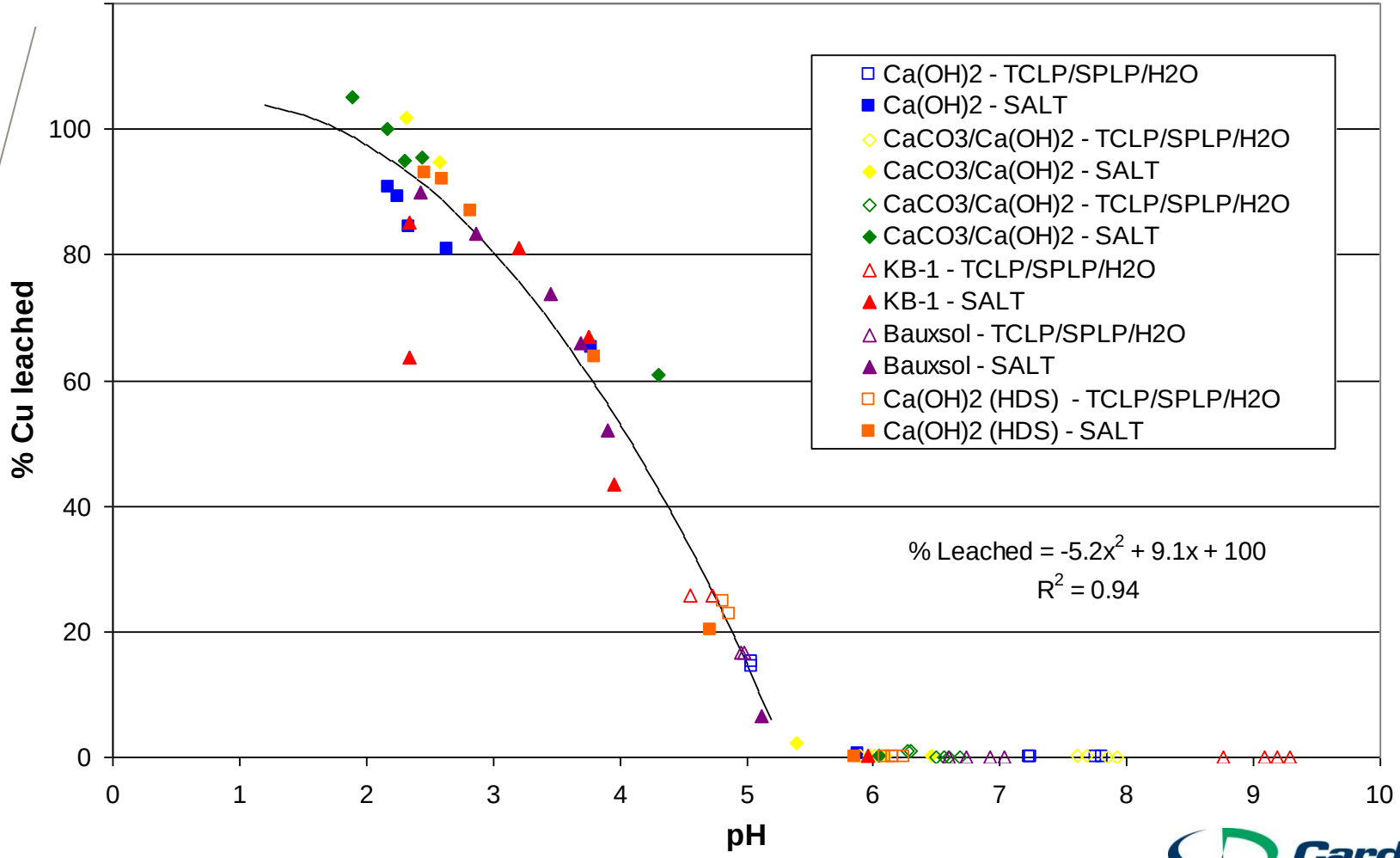
% leached – Copper



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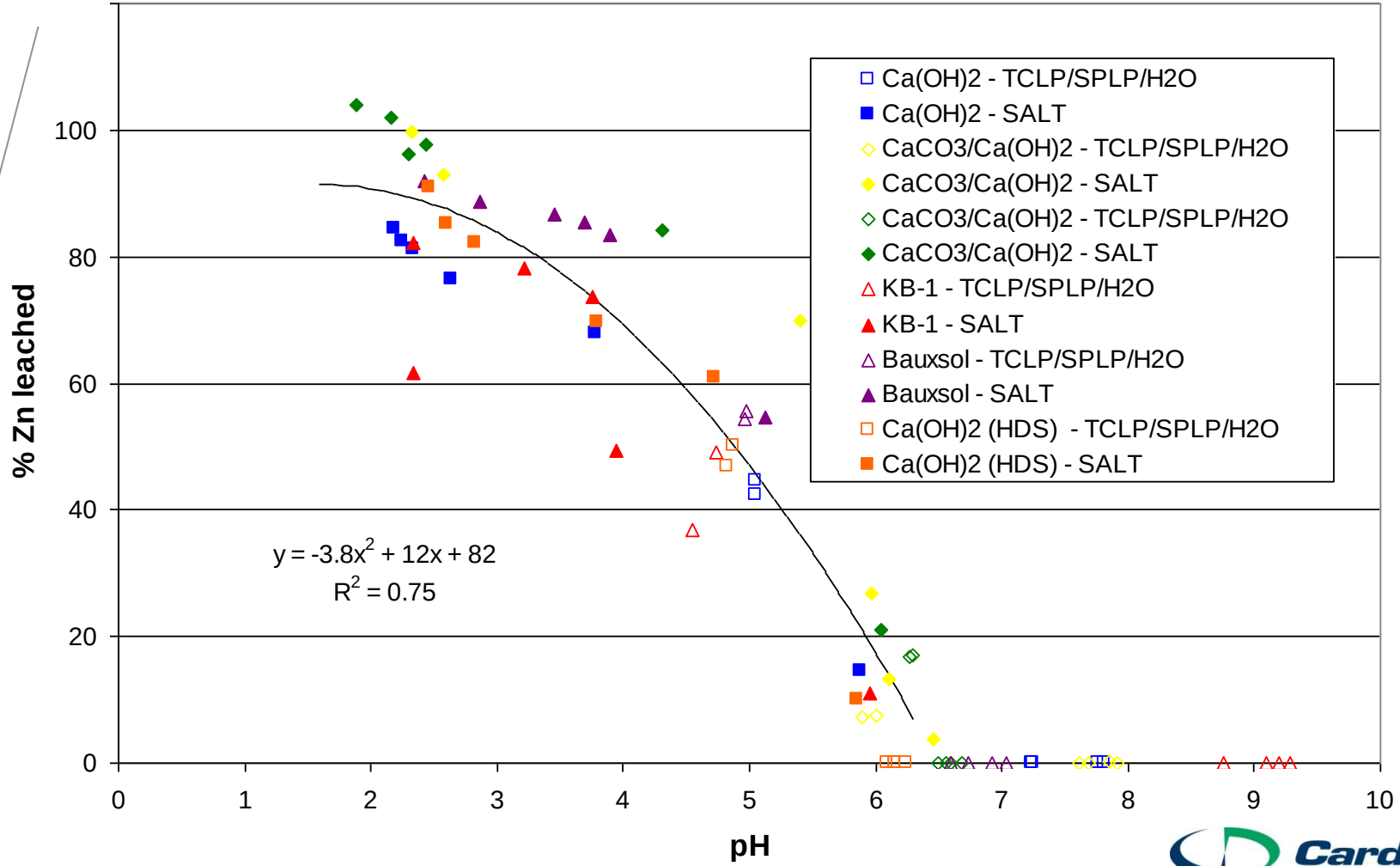
% leached – Zinc



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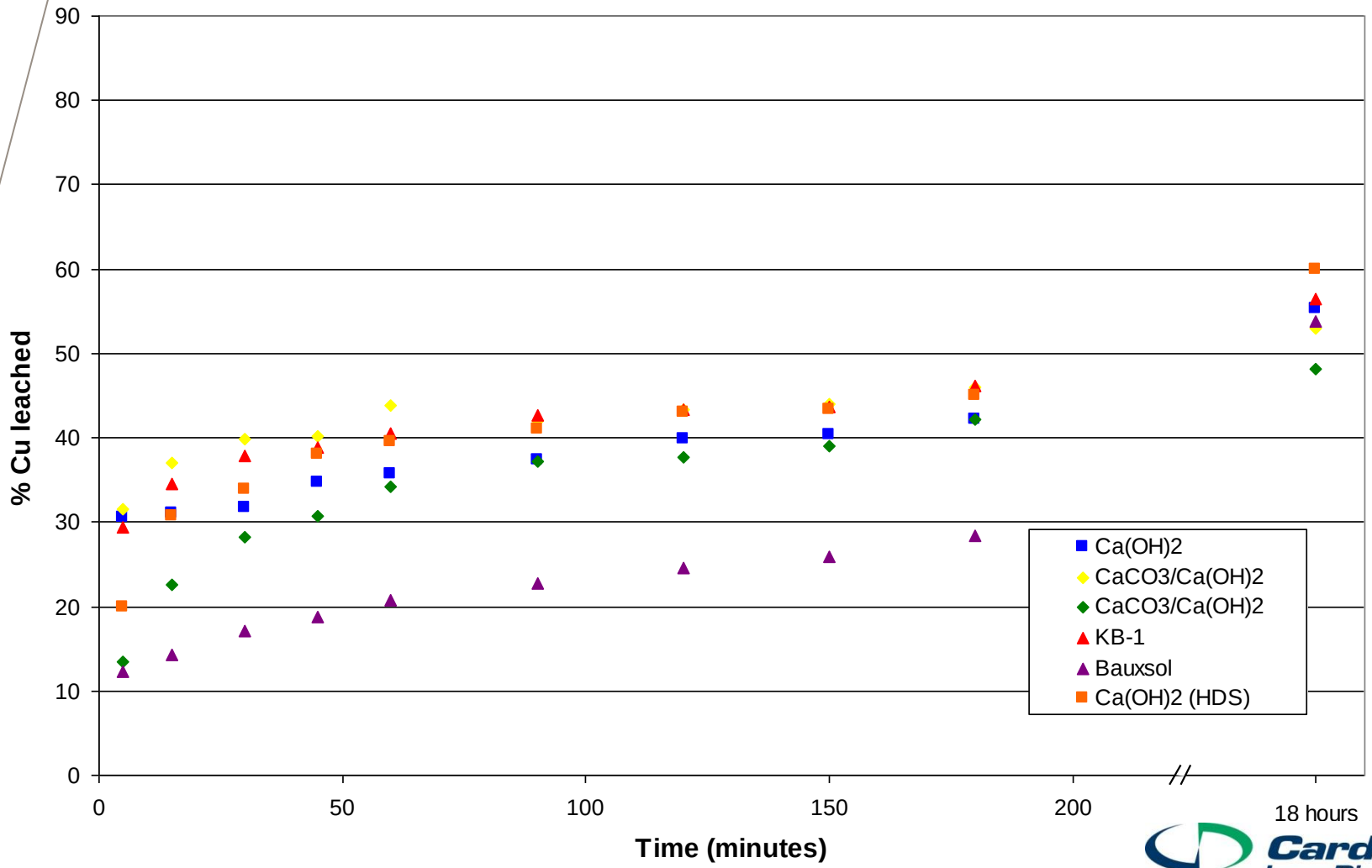
% Cu Leached versus Time



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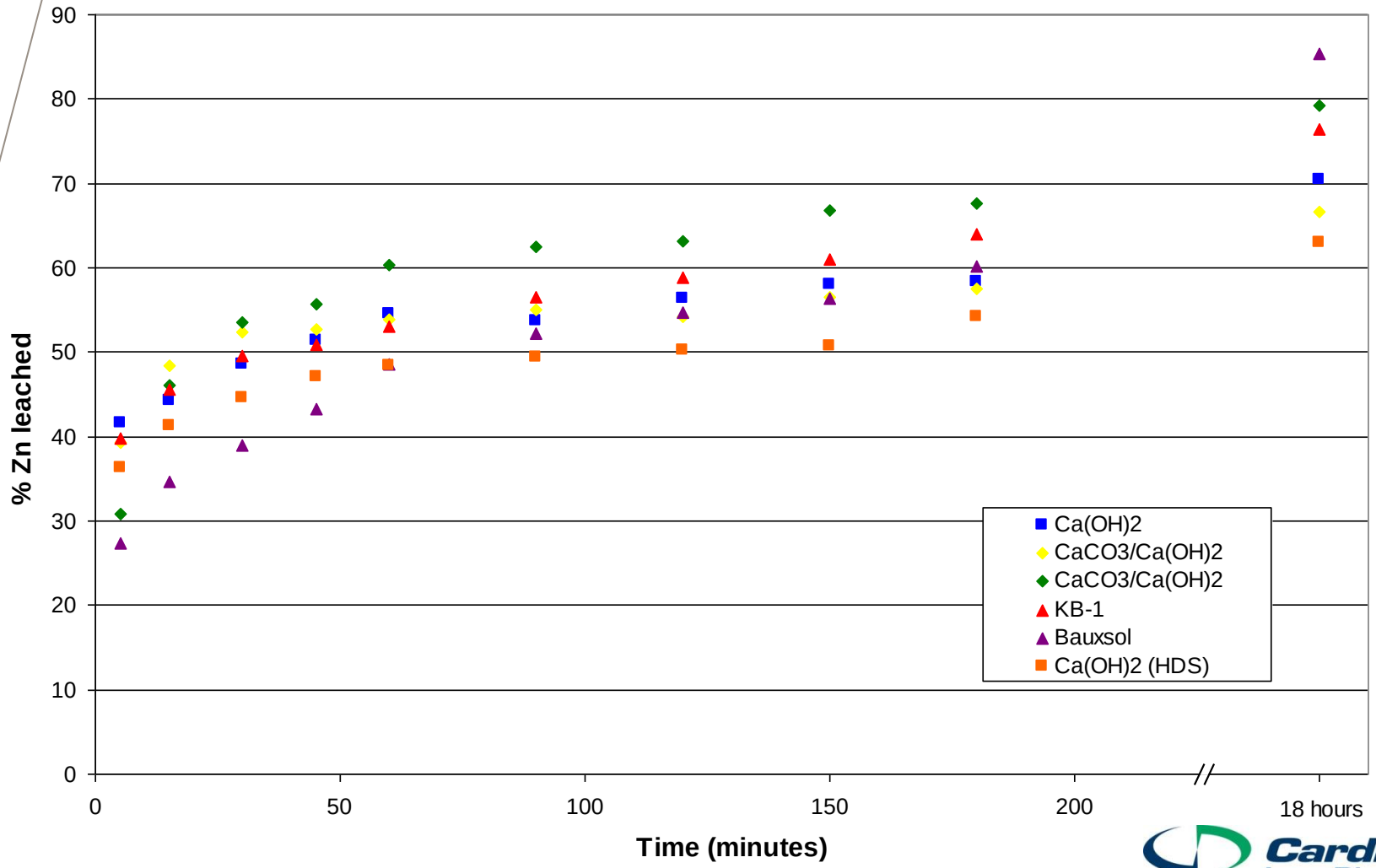
% Zn leached versus Time



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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

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Part 2: Magnetic Sludge Process

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Background & Objectives

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

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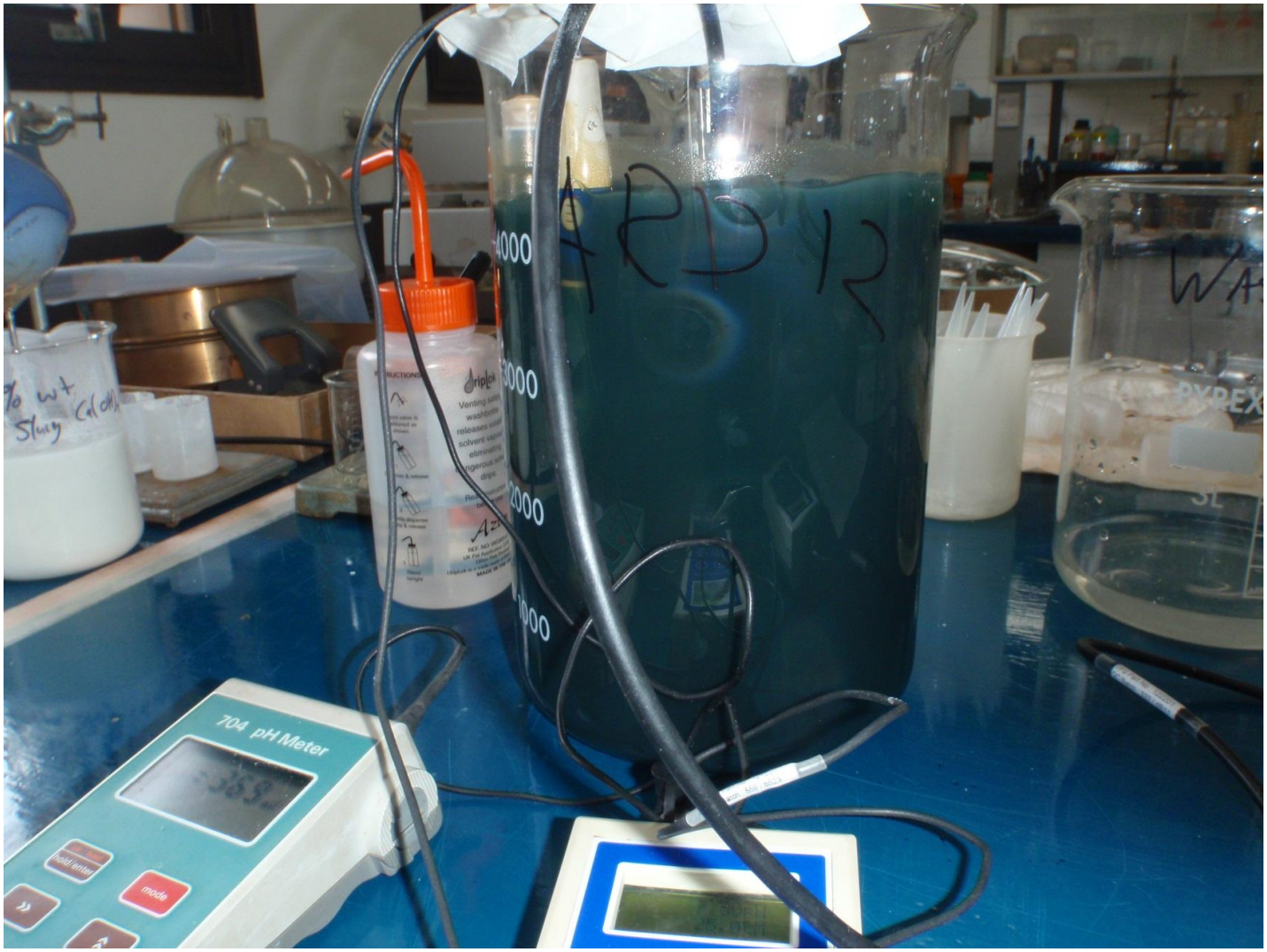
Laboratory Batch Reactor

Treated Synthetic ARD



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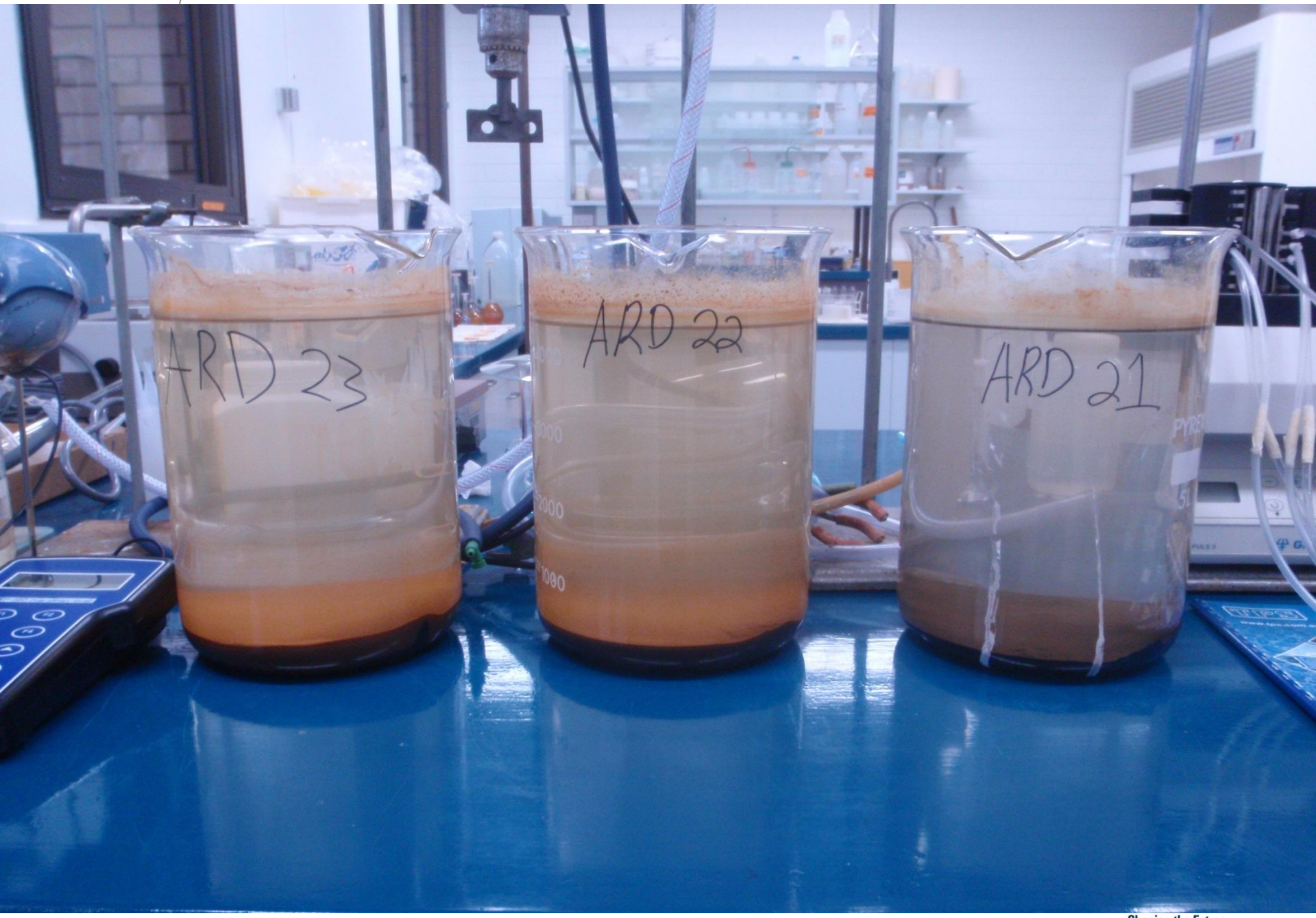
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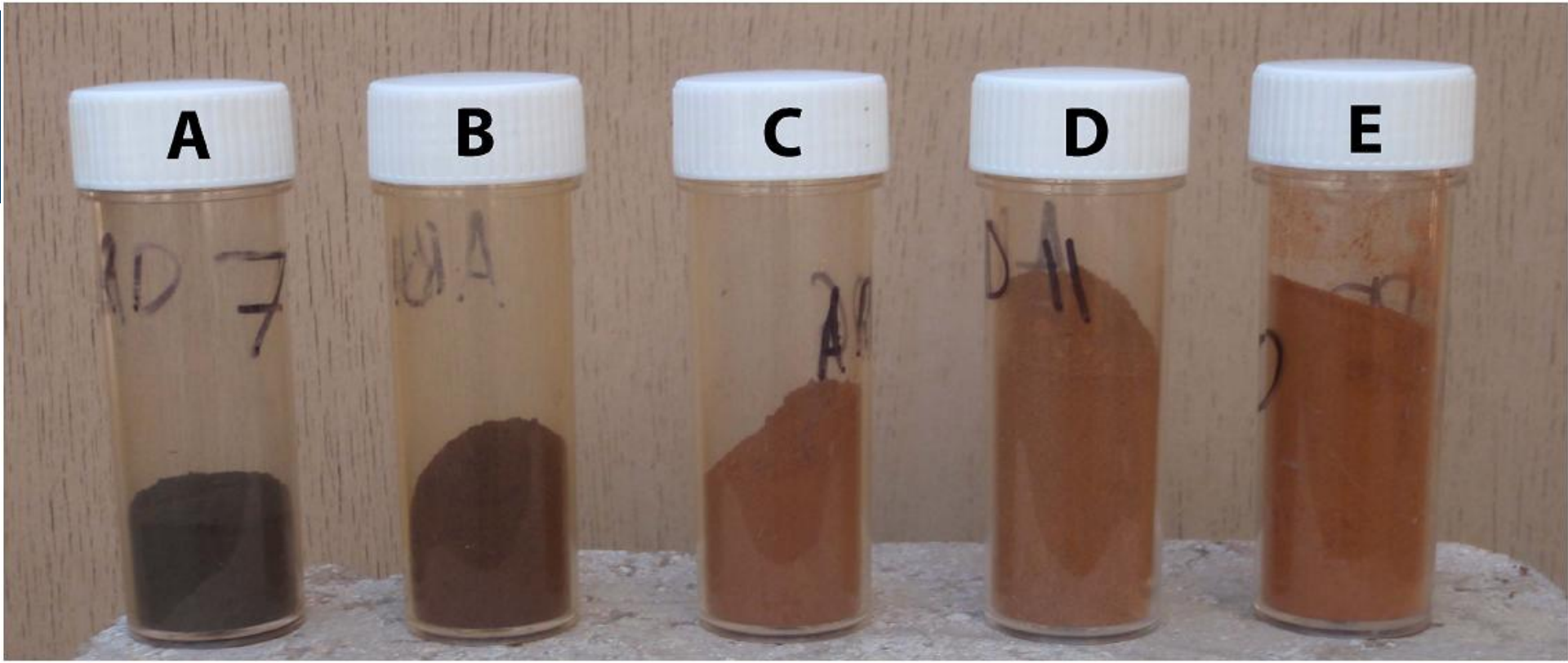
ARD 21



A,B – strongly magnetic maghemite/magnetite sludges;

C-E - non-magnetic poorly crystalline sludges

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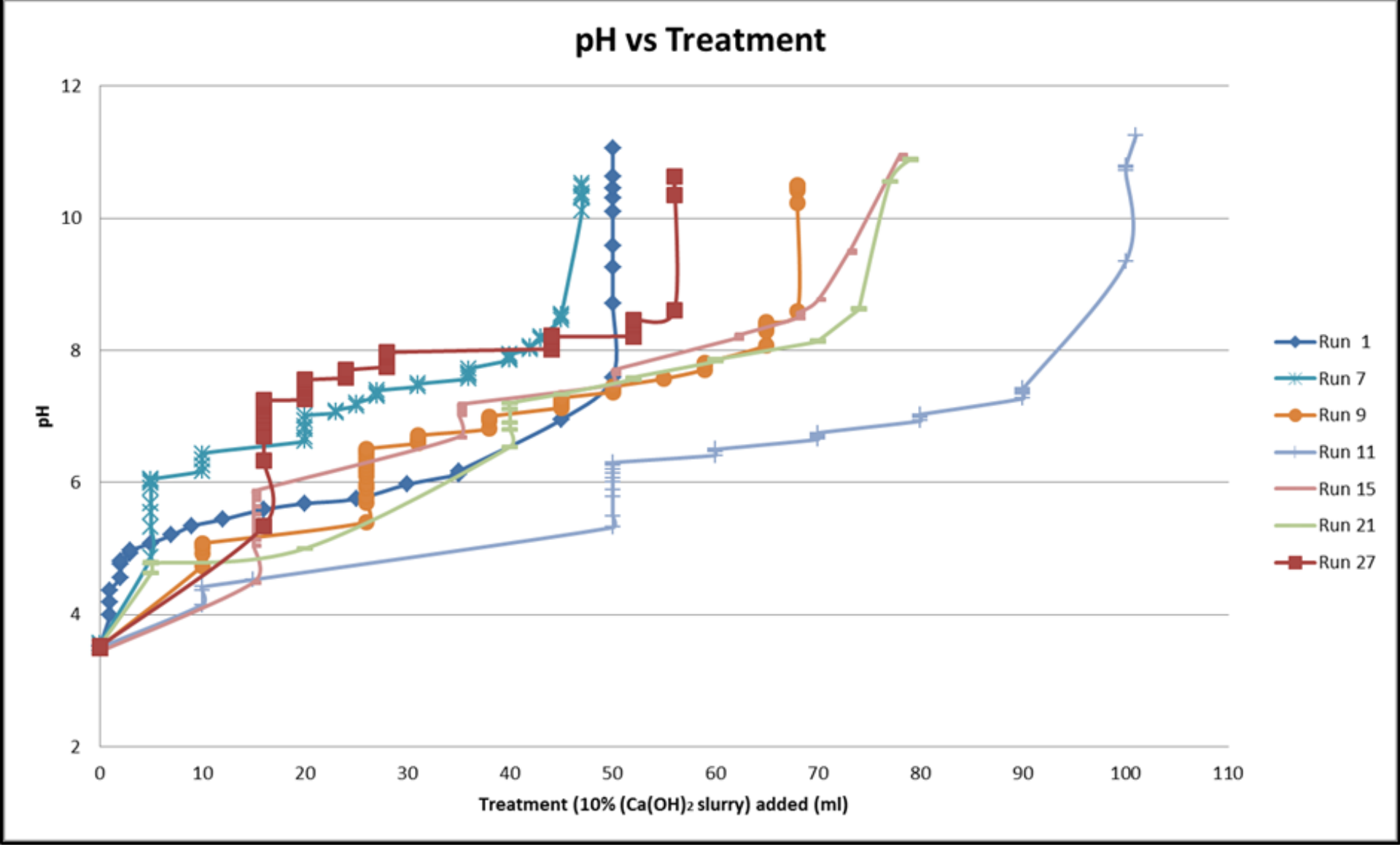

In most experiments, neutralisation was largely complete at an endpoint of pH ~8

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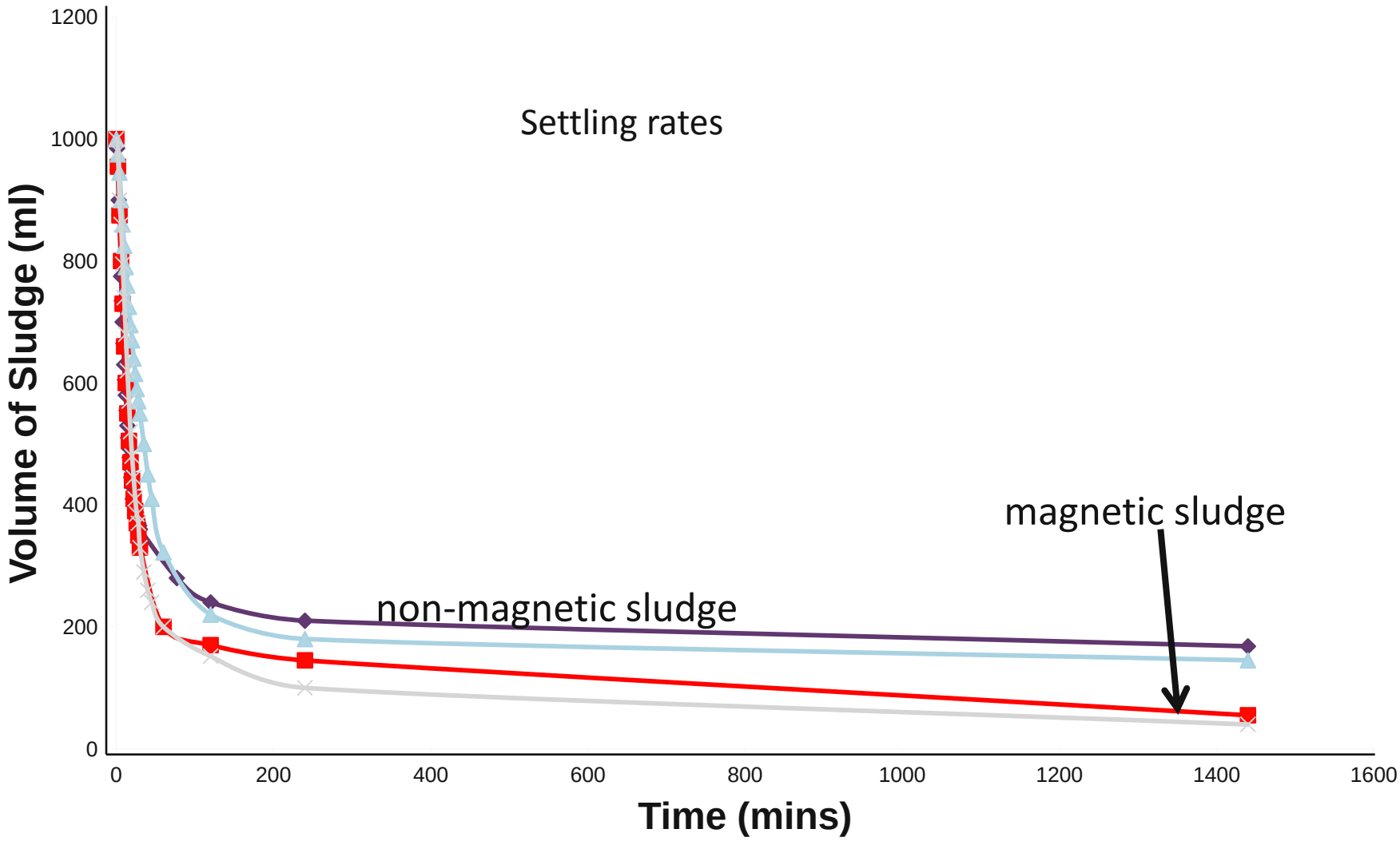

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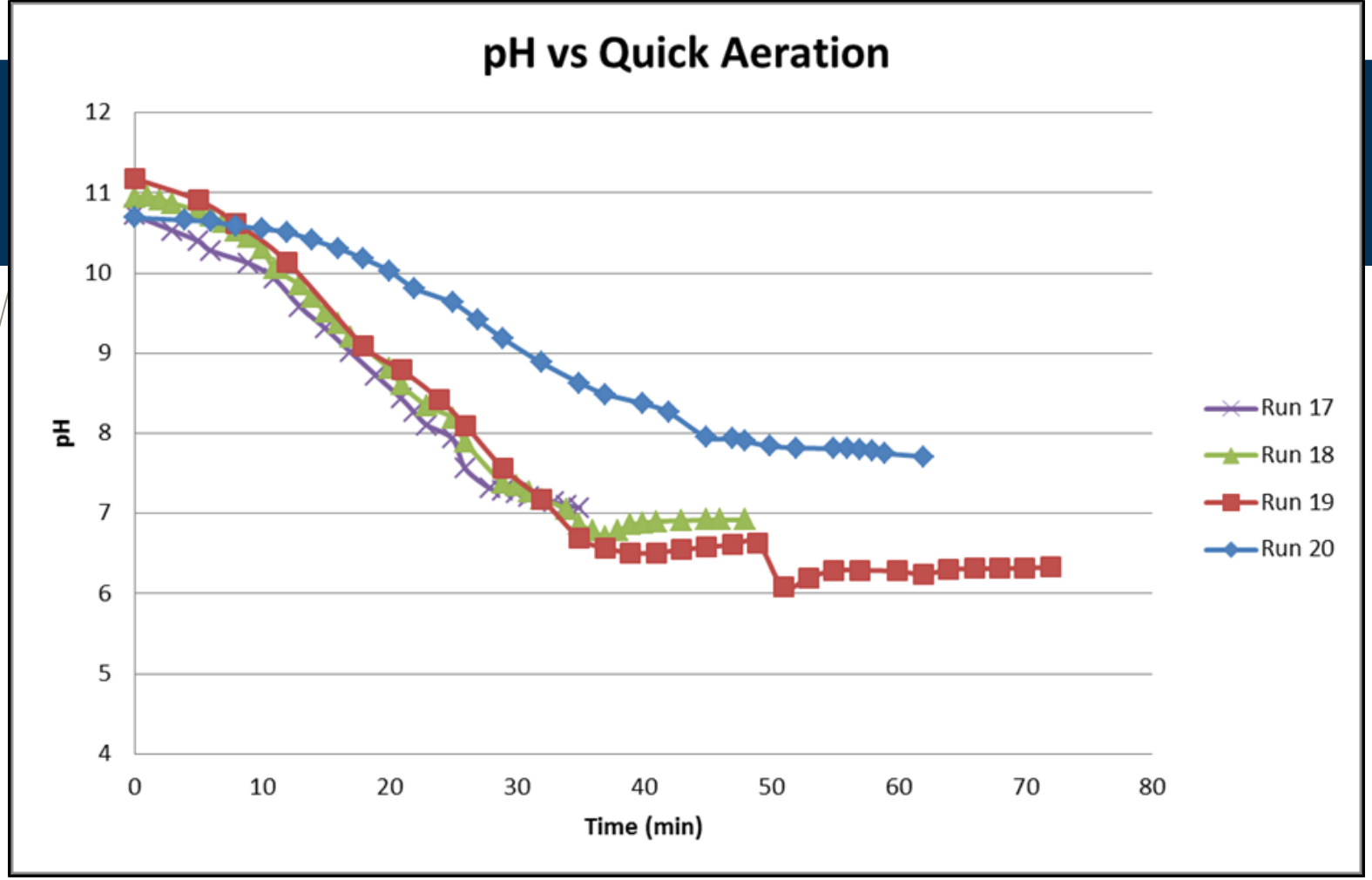

Drop in pH during aeration due to release of sulphate and acidity during conversion of green rust (ferrous hydroxide-sulphate) to ferric oxide/hydroxide

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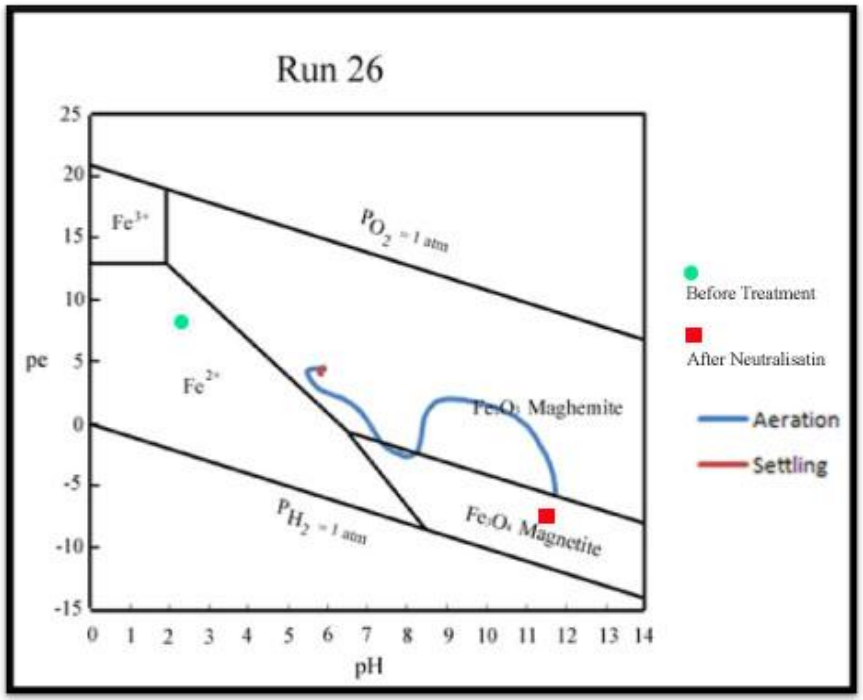
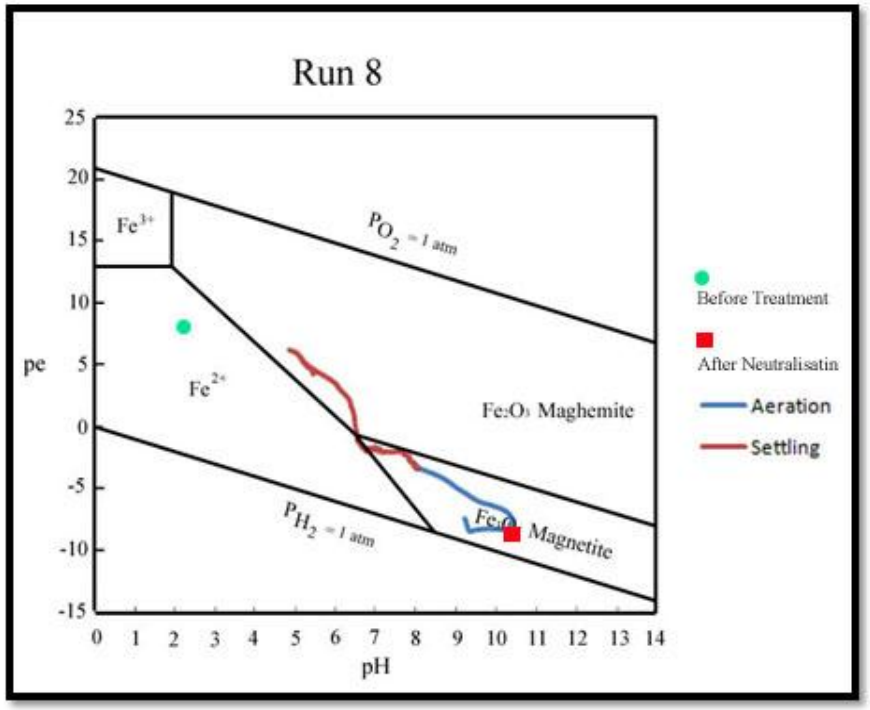
Run	Fe^{2+} mg/L	Cu	Zn	Al	N_2 sparg min/L	Aerat. time	Aerate rate	pH neut.	Fin pH	Sludge characteristics		
										Fe crystallinty	Magnetism	Minerals present
1	1800	0	0	0	5	24 hrs	Mod	11.0	6.6	Moderate	No	Lepidocrocite
2	1800	0	0	0	5	24 hrs	**Low**	11.6	6.9	High	Very strong	Maghemite/ magnetite
3	1800	0	0	0	5	24 hrs	**Low**	11.1	5.7	High	Very strong	Maghemite/ magnetite
4	1200	0	0	0	5	None		**7.27**	4.9	Low	No	Lepidocrocite
5	1200	0	0	0	5	24 hrs	Low	**7.64**	3.1	Moderate	No	Lepidocrocite
6	1200	0	0	0	5	None		10.7	8.3	Low	Slight	Lepidocrocite
7	1200	0	0	0	5	24 hrs	Low	10.3	5.1	High	Very strong	Maghemite/ magnetite
8	1200	0	0	0	**No**	24 hrs	Low	10.6	4.7	Low	No	Lepidocrocite
9	1200	**100**	**100**	0	5	24 hrs	**Low**	10.5	4.7	High	Very strong	Maghemite/ magnetite
10	1200	0	0	0	**No**	24 hrs	**Low**	11.2	4.4	Moderate	Strong	Lepidocrocite/ maghemite

Run	Fe^{2+} mg/L	Cu	Zn	Al	N_2 sparg min/L	Aeratn time	Aeratn rate	neut pH	Fin pH	Sludge characteristics		
										Fe crystallinity	Magnetism	Minerals present
11	1200	100	100	**100**	5	24 hrs	Low	11.2	7.1	Mod	No	Lepidocrocite
12	1200	0	0	**100**	5	24 hrs	Low	11.1	4.9	Mod	No	Lepidocrocite
13	1200	0	0	**100**	5	24 hrs	Low	11.0	5.4	Mod	No	Lepidocrocite
14	1200	100	100	**100**	5	24 hrs	Low	11.3	6.9	Low	Trace	Lepidocrocite
15	1200	100	100	0	5	60 m	**High**	10.9	5.5	Very low	Trace	Lepidocrocite
16	1200	100	100	0	5	45 m	**High**	10.8	5.1	Very low	No	Lepidocrocite
17	1200	100	100	0	5	35 m	**High**	10.7	4.5	Very low	Slight	Lepidocrocite
18	1200	100	100	0	5	50 m	**High**	10.8	4.3	Very low	No	Lepidocrocite
19	1200	100	100	0	5	70 m	**High**	10.8	5.5	Very low	No	Lepidocrocite
20	1200	100	100	0	5	80 m	**High**	10.6	7.4	Very low	No	Amorphous
	1200	**Seeded**		0	5	24hr	Low			Very High	Very Strong	Maghemite/ magnetite
	1200	**Seeded**		**100**	5	24hr	Low			High	Strong	Maghemite/ magnetite

Affect of Aeration Rate



Rapid aeration



Slow aeration

Slow oxidation (aeration) allows crystal structures to reform to maghemite

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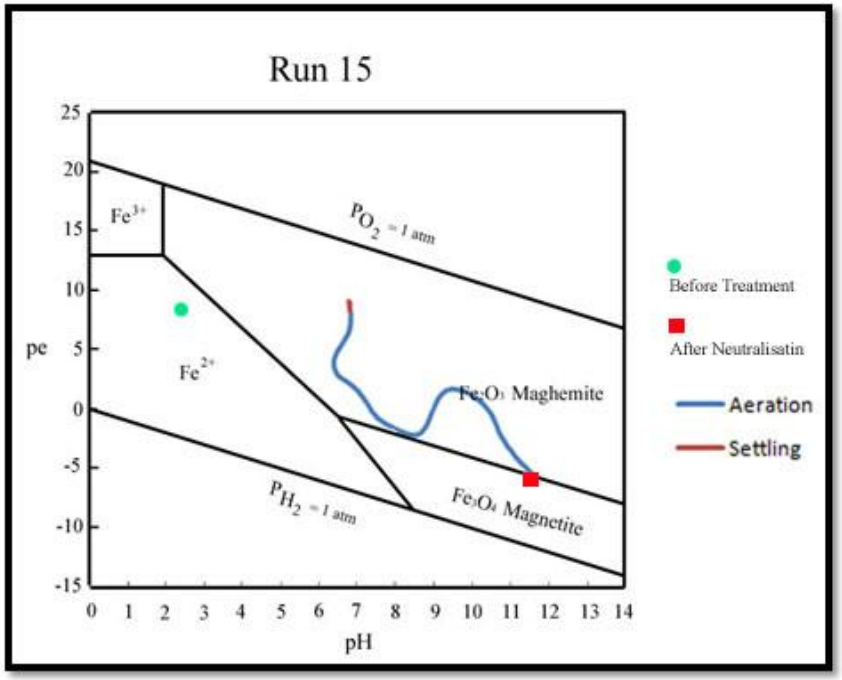
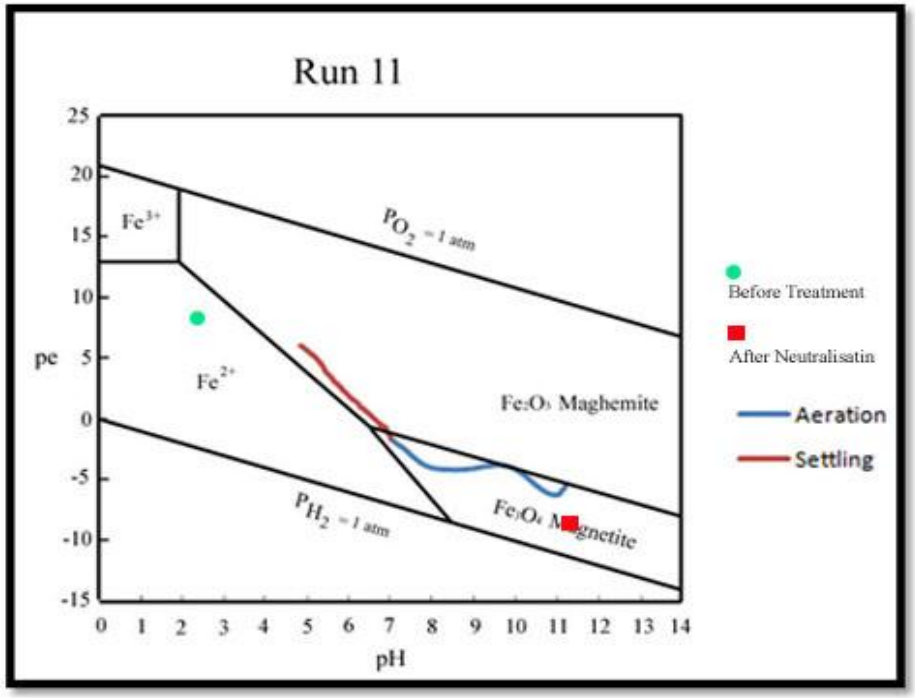
Affect of Aluminium and Seeding



With Aluminium



With Aluminium & Seeding

Seeding assists magnetite/maghemite formation

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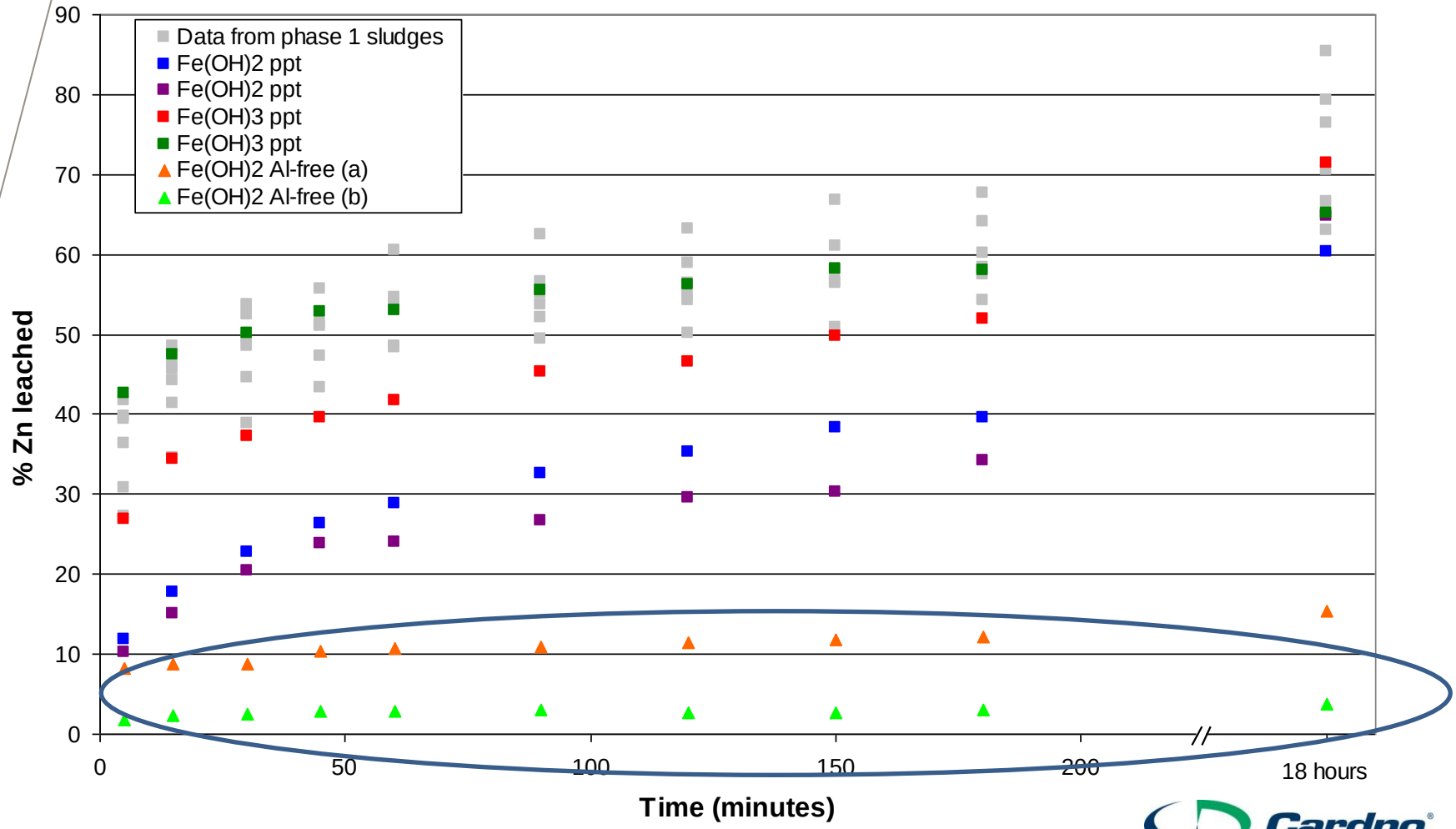
Leachability of Crystalline Sludges



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Results Summary

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)

- 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)

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Results Summary

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

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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 slugdes

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

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