

The formation of high density sludge from mine-water with low iron concentrations

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Abstract

The high-density sludge (HDS) process is recognised as the preferred method of treating mine water containing high metal concentrations. The method is based on the addition of hydroxides to raise the pH and precipitate the metals as a sludge that settles to a much higher density than achieved by conventional alkali neutralisation processes. This is achieved in a two stage neutralisation process using recirculated sludge to act as a seed for further metals precipitation. HDS is formed by mixing either:

- the alkali and recirculated sludge prior to adding the mine water, or;
- the recirculated sludge and the mine water prior to adding the alkali.

The choice between the two methods is project specific and can only be determined by pilot trials.

A typical HDS plant will produce a sludge that settles to between 35 and 50% solids and can be mechanically dewatered to between 50 and 70% solids. In comparison the sludge produced by a conventional plant will settle to between 2 and 5% and can be mechanically dewatered to between 25 and 40% solids. The HDS process is therefore particularly advantageous where large amounts of sludge are generated or where sludge disposal costs are significant.

Most HDS plants are treating waters dominated by iron chemistry and use slaked lime as a reagent. Current wisdom is that high density sludge cannot be formed from mine water dominated by non iron species nor using other alkali reagents.

A series of pilot plant trials have been jointly undertaken by Unipure Europe Ltd and Cardiff University to establish the mechanisms controlling the formation of HDS from a variety of synthetic mine waters using sodium hydroxide as an alkali source. These trials have demonstrated that HDS can be formed from mine waters containing low iron concentrations and by the use of sodium hydroxide as the neutralising reagent.

Introduction

The use of alkali neutralisation to remove dissolved metals from industrial effluent, mine water and groundwater is a well established technique. The process is based on the solubility relationships shown in Figure 1 (Coulton et al, 2003b) and relies on the addition of an alkali to raise the pH and make the metals insoluble. However the resultant hydroxide sludge tends to be voluminous and typically only settle to between 2 and 4% (w/w) dry solids (Bosman, 1974; Kostenbader, 1970). The use of conventional alkali neutralisation to remove large metal loads can therefore result in the generation of a large volume of sludge. Typically such sludges can be mechanically dewatered to around 30 % (w/w) dry solids, resulting in a sludge that contains 2 tonnes of trapped water for every tonne of dry solids.

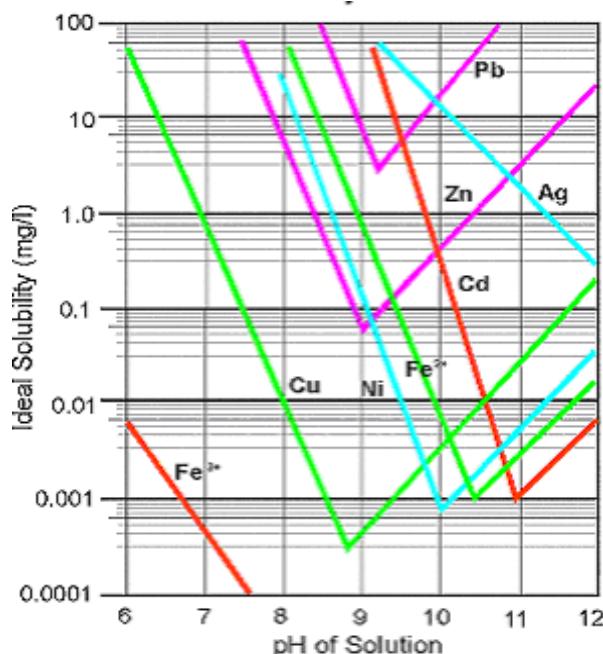


Figure 1 Theoretical Metal Solubility Graphs

The high density sludge process was developed in the 1960's (Kostenbader et al, 1970) to counter this problem, by using recirculated sludge to encourage particle growth rather than the formation of new hydroxide par-

ticles. The process has been widely adopted by the mining industry where the relatively high metal concentrations and large flows make sludge volume minimisation imperative. Typical HDS plants include the UK Environment Agency's Wheal Jane Mine water project, which is designed to treat up to 350 litres/s of mine water with a combined metal concentration of 500mg/l. (Coulton et al, 2003a).

As most mine waters contain high concentration of iron and, lime is the cheapest source of reagent, current wisdom is that high density sludge can only be formed when high iron ratios are present (Kostenbader et al 1970, Bosman 1983, Vachon et al) and by using a calcium based alkali. Following requests from a number of clients for a low capital cost high density sludge plants, Unipure Europe in conjunction with Cardiff University undertook a series of batch tests and continuous pilot plant trials to establish whether high density sludge could be created from low iron effluents using sodium hydroxide rather than lime.

Batch Tests

Batch tests (Bosman, 1983) were initially undertaken on a synthetic mine water containing 150mg/l of iron to establish where the use of a calcium based alkali was necessary for the formation of HDS. The trials involved the repeated neutralisation of fresh mine water samples using NaOH, Ca(OH)₂ and Mg(OH)₂. The solids produced from each neutralisation test were allowed to settle and transferred to the next mine water sample to be neutralised. The settled solids volume at the end of each batch test was used an indicator for the formation of HDS. As the transformation from conventional low density sludge to HDS occurred the settled sludge volume decreased despite the increase in sludge mass that occurred with successive batches. Figure 2 indicates the results obtained for some 35 batch trials and reveals the formation of HDS from both sodium and calcium hydroxide. It is interesting to note from Figure 2 that:

- Initially the low density sludge produced by sodium hydroxide occupied nearly twice the volume of that produced by Ca(OH)₂ and 3 times that produced by Mg(OH)₂. This is in accordance with generally accepted experience that Mg(OH)₂ tends to produce the less voluminous sludge and NaOH the most.
- However after 20 cycles the sludge volume produced by the NaOH and Ca(OH)₂ occupied a smaller volume than the MgOH sludge.

- After 31 cycles the NaOH sludge occupied only 15% more volume than the Ca(OH)₂ sludge. This difference did increase to about 60% after 34 trials
- Even after 37 cycles the Mg(OH)₂ sludge had not formed HDS although the slight reduction in volume indicated limited transformation may have occurred.

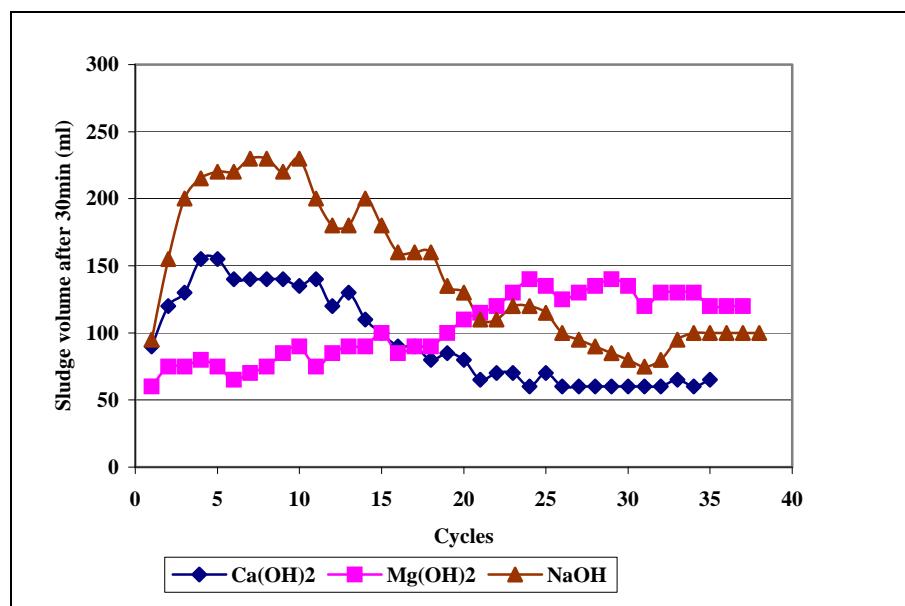


Figure 2 Settled sludge volumes using different reagents

It was concluded from the cyclic batch trials that:

- HDS could be formed from sodium hydroxide and the presence of calcium ions is not required.
- The use of magnesium hydroxide may not result in a lower HDS volume than that produced by lime or sodium hydroxide.

Pilot Plant Trials

Separate pilot plant trials were undertaken using a synthetic solution comprising tap water containing 150 to 200mg/l of dissolved aluminium, zinc and manganese.

The plant layout is shown schematically in Figure 3 and consisted of;

- an influent water storage tank and feed pump,

- feed mixing chamber, stage I reaction tank,
- stage II reaction tank,
- flocculation chamber and a clarifier.
- Ancillary equipment comprises sodium hydroxide and flocculant make-up, storage and dosing systems and air supply.

The plant was designed to treat a flow of 10l/hr and have 30 minutes retention in both the Stage I and Stage II reactors.

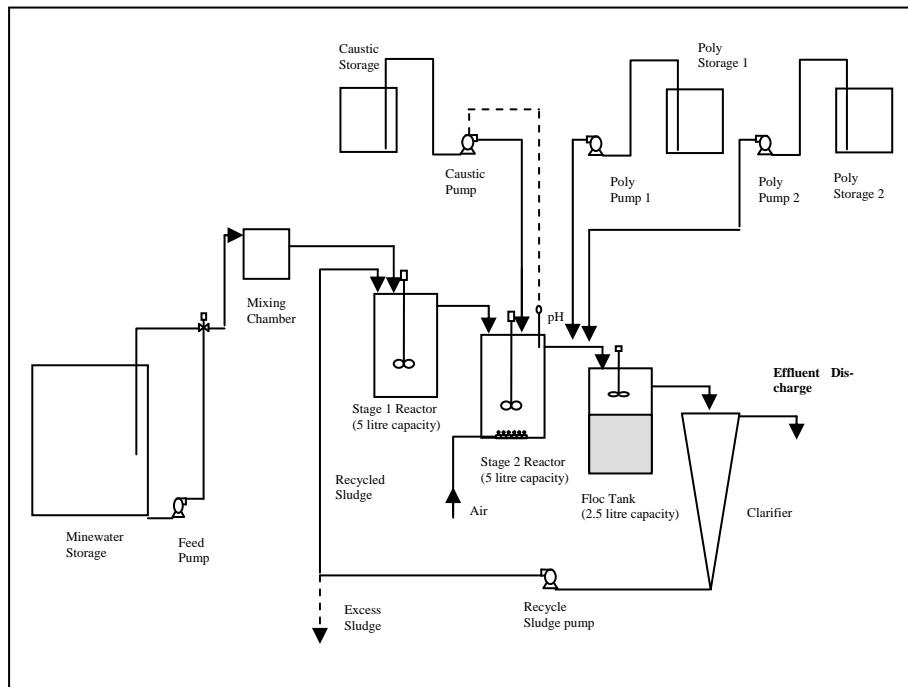


Figure 3 Schematic Diagram of the Pilot Plant.

The performance of the pilot plant was assessed by monitoring; water quality, reagent consumption, and sludge settlement characteristics (settling velocity and settled sludge density). Samples of both conventional and high density sludge were subjected to centrifuge dewatering trials and scanning electron microscope analysis.

Water Quality

A comparison of the influent and effluent water quality achieved during the trials is summarised in Table 1. This indicates 99%ile metal removal

and a treated effluent quality consistent with the standards typically imposed in the UK for discharge to either sewer or watercourse.

Table 1 Average Influent and Effluent Quality (dissolved)

	Al	Zn	Mn
Influent (mg/l)	151	177	217
Effluent (mg/l)	1.0	0.17	2.9

It is envisaged that lower residual metal concentrations could have been achieved by operating at a pH consistent with the minimum solubility shown in Figure 1.

Reagent Consumption

The average reagent consumption achieved during the trials is shown in Table 2, in terms of the calculated efficiency (theoretical consumption/Actual). Table 2 shows that reagent consumption was within 6.5% of theoretical indicating that the process operated very efficiently on sodium hydroxide.

Table 2 Average Sodium Hydroxide Consumption

Al	Zn	Mn
95%	100%	93.5%

In comparison most HDS mine water plant operating on lime achieve an efficiency of between 60% to 70%. The lower efficiency is due to a combination of:

- The consumption of lime in the formation of calcium carbonate (due to presence of CO₂ in the mine water) (Herman et al, 1983).
- Coating of the surface of the partially dissolved lime particles with metal hydroxides which prevent the particles from fully dissolving.

The better reagent efficiency partly offsets the additional cost of sodium hydroxide. In waters containing elevated sulphate and gypsum concentrations the use of sodium hydroxide reduces the sludge mass precipitated by minimising gypsum precipitation. The use of a sodium hydroxide based HDS process may therefore be financially attractive for industrial applications or small mine water schemes where:

- the additional cost of installing a powder lime handling facility can not be justified, or;
- sludge minimisation is important.

Sludge Characteristics

The formation of HDS is characterised by a high sludge settlement velocity, low settled sludge volumes and the relatively high settled solid concentrations. Unlike conventionally precipitated metal hydroxides, the settlement velocity remains high over a wide range of initial solids contents. This enables HDS plants to operate with reactor solids contents in excess of 5% (which is typically the settled solids content achieved by most conventional precipitation plants).

The variation of initial settling velocity and settled sludge density with the initial solids concentrations were therefore been used as the primary indicators of the formation of HDS in the pilot trials. These parameters were compared to the results from the commissioning of the Wheal Jane plant to provide a direct comparison with a calcium based HDS plant treating mine water containing 200mg/l iron and 100mg/l zinc.

Settlement Velocity

The variation of peak settlement velocity with initial solids concentration for the pilot trials are shown in Figures 4 to 6, together with the peak settling velocity/initial solids concentration data for the commissioning of the Wheal Jane Plant. As the initial settlement velocity is used to establish the area required to prevent the carry over of solids from the clarifier, a high value is beneficial in minimising the clarification area.

Figures 4 to 6 indicate:

- The settlement velocity of the zinc trials varied between 6 and 13 m/hr (with initial solids concentration up to 7% w/v).
- The maximum settlement velocity of the aluminium trials was 10 m/hr (with initial solids concentration up to 5% w/v).
- Once HDS was formed during the aluminium trials a settlement velocity of between 2 and 3 m/hr was achieved.
- The settlement velocity of the manganese trials varied between 8 and 13 m/hr (with initial solids concentration up to 3% w/v).
- Manganese and Zinc readily produced HDS.

- Manganese and Zinc settlement velocities were comparable to those achieved during the commissioning of the Wheal Jane MWTP

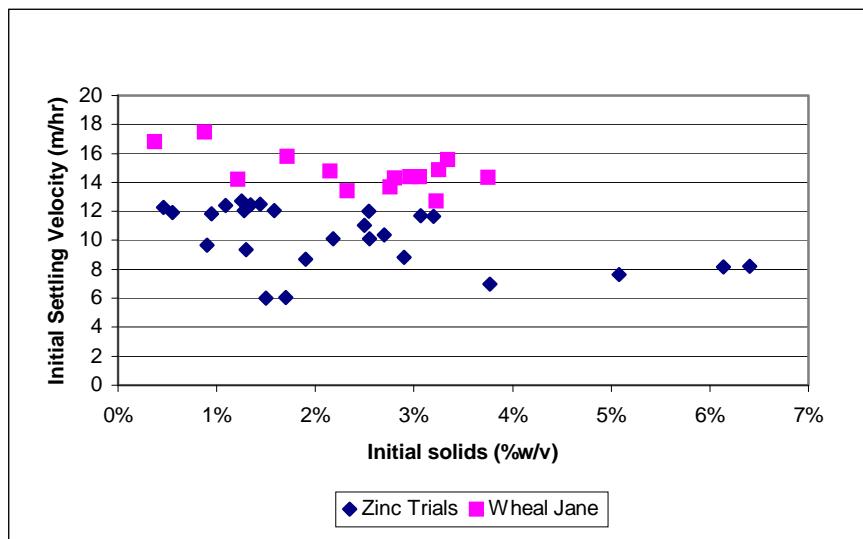


Figure 4 Initial Settling Velocity –Solids concentration Relationship for Zinc

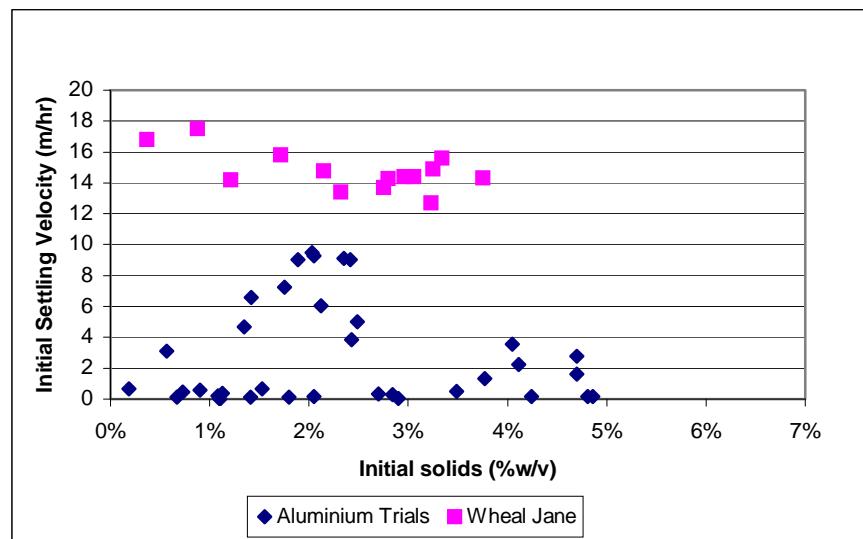


Figure 5 Initial Settling Velocity–Solids Concentration Relationship for Aluminium

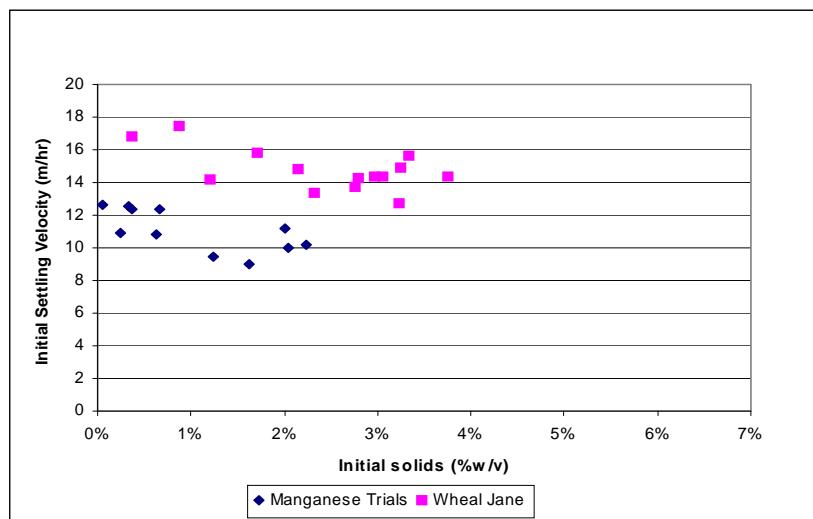


Figure 6 Initial Settling Velocity-Solids Concentration Relationship for Manganese

Settled Sludge Solids Content

The variation of settled solids concentration with initial solids concentration is shown in Figures 7 to 9, together with the Wheal Jane commissioning data. As the settled solids concentration determines the sizing of the solids handling equipment, maximising this parameter is an important part of designing an HDS plant. Figures 7 to 9 indicate:

- The maximum settled solids concentration of the zinc trials was circa 28% w/v.
- The maximum settled solids concentration of the aluminium trials was circa 18% w/v.
- The maximum settled solids concentration of the manganese trials was circa 23% w/v.
- Comparison of the manganese and zinc trials with Wheal Jane reveals that both the manganese and zinc sludges settled to higher solids concentrations.
- The aluminium trials produced a sludge that settled to approximately 70% of the solids concentration produced by the iron rich Wheal Jane Sludge.

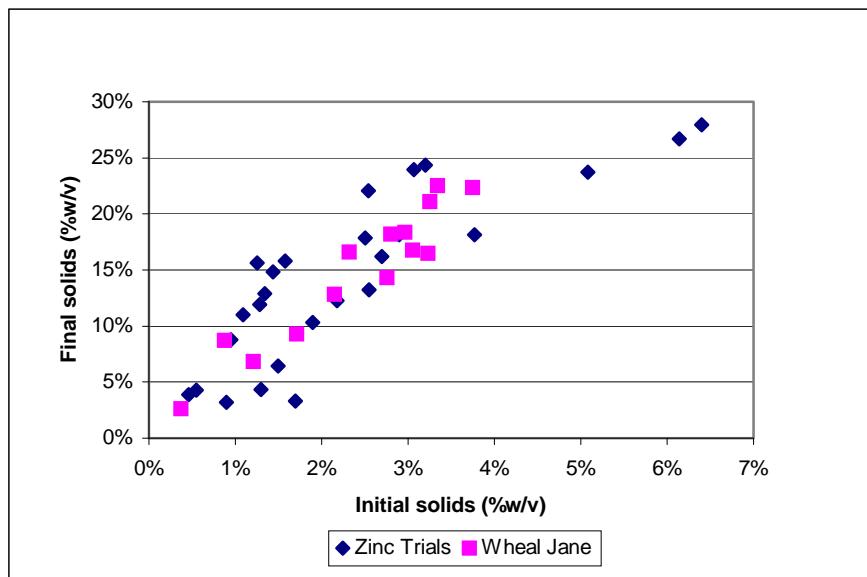


Figure 7 Final -Initial Solids Concentration relationship for Zinc

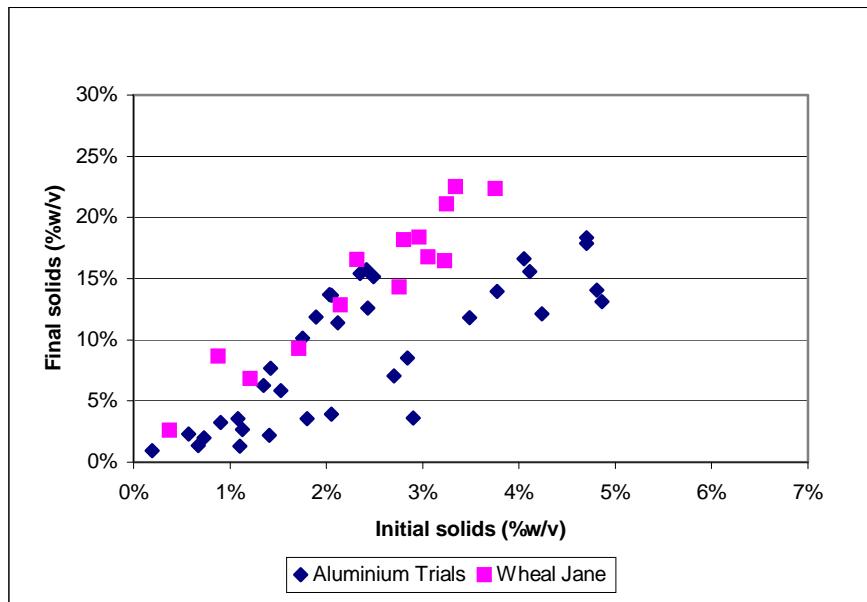


Figure 8 Final-Initial Solid Concentration Relationship for Aluminium

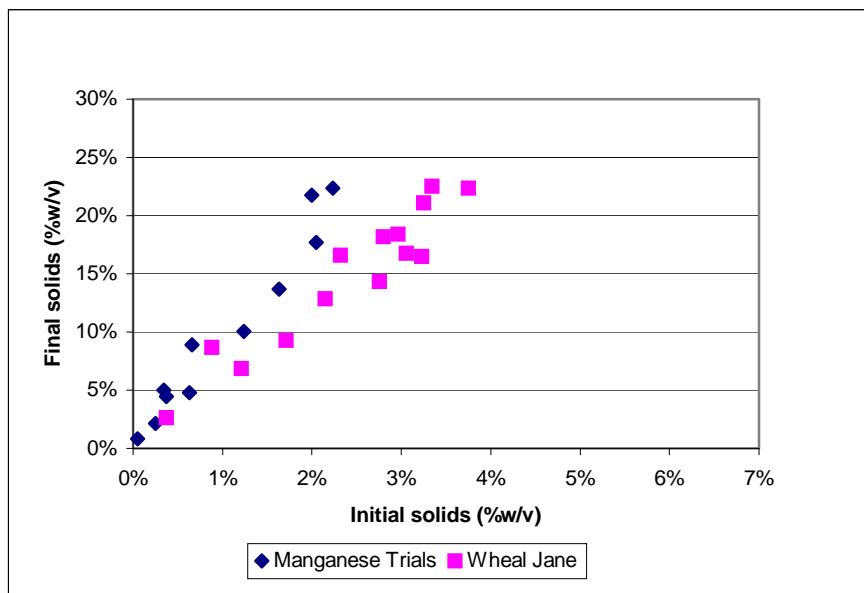


Figure 9 Final- Initial Solids Concentration Relationship for Manganese

Importantly the continuous pilot trials revealed that HDS sludge can be produced from metals other than iron and showed that HDS can be produced from aluminium, albeit to a low settled density.

Centrifuge Trials

Where minimisation of the sludge volume is a significant factor (due to limited storage volume or high disposal costs) mechanical dewatering can be used. To provide an indication of the volume reduction that can be achieved by mechanically dewatering samples of conventional and HDS sludge were dewatered in a laboratory centrifuge operating at 2000g. The results from these tests are summarised in Table 3 and indicate that HDS formation resulted in a significant reduction in both the Aluminium and manganese sludge volumes. The volume of zinc sludge was however only reduced by 16%.

Table 3 Solids Concentration achieved by 2000g Centrifuge

	Al	Zn	Mn
Conventional sludge (% w/v)	8.8	24.2	20.3
HDS sludge (% w/v)	26.5	28.8	36.0
Volume reduction	66%	16%	44%

Conclusions

The cyclic batch trials have demonstrated that HDS can form from a iron rich minewater using both NaOH and Ca(OH)₂. The trials showed that Mg(OH)₂ did not result in the formation of HDS after 40 cycles.

The continuous pilot trials have successfully demonstrated HDS formation using sodium hydroxide as an alkali source with bivalent (Zn²⁺ and Mn²⁺) and trivalent (Al³⁺) metals. The measured initial settling velocity for the NaOH sludge was lower than that achieved during the commissioning of the lime based Wheal Jane Mine water Treatment Plant. The variation of settled solids content with initial solids content has been found to be similar to that produced by a conventional lime based HDS plant.

Overall the trials have demonstrated that NaOH can be used as an alternative reagent for the formation of HDS. Whilst it has been demonstrated that lime is not required for the formation of HDS it is unlikely that NaOH will replace lime on most active mine water treatment plants. It is however a viable alternative for small or temporary installations where the cost of a powdered lime handling system can not be financially justified. The process will be of most benefit in the industrial sector where spiralling landfill prices make the minimisation of sludge mass imperative from both a financial and IPPC prospective.

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