

Zinc sulfide as a solid phase additive for improving the processing characteristics of ferrihydrite residues

William R. Richmond,^{a,*} Mitch Loan,^b Mike Newman^c and

Gordon M. Parkinson^a

^a *Nanochemistry Research Institute and A.J. Parker CRC for Hydrometallurgy, Curtin University of Technology, GPO Box U 1987, Perth, 6845, Australia. Tel. +61 8 9266 3838, Fax. +61 8 9266 4699
E-mail : bill@power.curtin.edu.au*

^b *Materials Surface Science Institute (MSSI), University of Limerick, Limerick, Ireland*
^c *Zinifex Ltd., PO Box 315, 121 Woodstock St, Mayfield, NSW 2304, Australia*

Abstract

The effect of ZnS powders as additives for improving the physical and chemical properties of ferrihydrite residues has been studied in both kinetic and batch experiments. Four ZnS samples were compared: two industrial ZnS concentrates, high purity ZnS pieces, and a sample of synthetic ZnS nanoparticles. The industrial ZnS concentrates were found to be the most effective for promoting the transformation of ferrihydrite to hematite, and this effect was found to be due to their lower surface charge at pH 3, which promotes formation of mixed ZnS/ferrihydrite aggregates. For the high purity ZnS samples, aggregation was not favoured, and only goethite formation was promoted. The effect of particle size of the ZnS additive was also studied, and it was found that samples of smaller average particle size were more effective in promoting phase transformation. Measurement of filtration times and moisture content of ferrihydrite residues precipitated in the presence of ZnS showed only minor improvement in physical handling and indicated that better control of surface properties of the additive would be needed to optimise its effect on phase transformation.

1. Introduction

Iron is one of the most abundant elements on earth, so dissolved iron tends to arise as a process impurity in most hydrometallurgical operations. In many cases, the iron concentration is sufficiently high as to require its removal from process streams, and this usually involves precipitation of the iron as an oxide, by raising the pH of the process liquor. Solid-liquid separation and washing are facilitated by the precipitation of a dense residue, but the production of filterable residues has long been problematic in many processes. In the hydrometallurgy of zinc, examples of this iron removal step are seen in the “goethite” process,(Davey et al., 1976) the “paragoethite” process (McCristal et al., 1998) and the related “Zincor” process.(Claassen et al., 2002) As some of the names suggest, an aim in the development of these processes was to precipitate goethite in a crystalline, filterable form. It is now recognised however, that most hydrometallurgical iron residues contain ferrihydrite (Loan et al., 2002a; Loan et al., 2002b; Jambor et al., 1998), a poorly-crystalline iron oxyhydroxide and that, even if this phase is a minor component of the residue, its presence can have significant adverse effects on filterability.

The problems associated with ferrihydrite go beyond its poor filterability. Due to its small primary crystallite size (average diameter is typically 5-10 nm) and high surface area, ferrihydrite can readily adsorb a wide range of dissolved species, and if the element being refined is one of the species adsorbed during the iron removal process, then purification efficiency is reduced.(Zinck et al., 1998) The adsorption of toxins such as arsenic, selenium and lead can also present problems, due to the associated risk of their release from tailings into the environment.

Ferrihydrite is regarded as metastable, with transformation to more crystalline phases (goethite and hematite) having a variable rate, which can be controlled to some extent by temperature and pH. High temperatures and/or low pH are required for formation of hematite, while mixtures of goethite and hematite result from transformations at more moderate temperatures and pH ~3 or higher. The transformation is slow however, in relation to the temperature and pH conditions normally considered feasible in hydrometallurgical processes.

Oxidative dissolution of sphalerite with Fe(III) ion, and the associated reduction of Fe(III) to Fe(II), has been described in several studies and is a commercial method of leaching ZnS concentrates. We have recently published results showing that the addition of sphalerite (ZnS) particles to suspensions of ferrihydrite promotes the formation of goethite and hematite as a result of surface-mediated reduction of Fe(III) species to Fe(II) with associated dissolution of ZnS. (Loan et al., 2005) These findings suggest that ZnS could be used as an additive in iron precipitation to improve the crystallinity, and hence modify the physical properties of the oxyhydroxide residues.

The work described in this paper is an initial investigation of the effects of ZnS on some basic process handling characteristics of a ferrihydrite residue. Industrial zinc concentrates are used as solid phase additives to promote phase transformation of ferrihydrite and their effects on the residue are compared with the effects of pure ZnS. The influence of particle size and surface interactions are also investigated.

2. Experimental

2.1 Materials

Two ZnS concentrates were supplied by Zinifex Ltd. One originated from the Lennard Shelf mine in Western Australia, and the other from the Atacocha mine in Peru. Both concentrates had been ground to a similar particle size distribution. Details of the composition of the industrial ZnS concentrates used in this study are given in Table 1. Zinc sulfide pieces (Aldrich, ZnS 99.9 %) were used as a high purity source of ZnS for the purpose of comparison with the industrial samples. Samples of nanoparticulate ZnS were also used, and these were prepared by the reaction of zinc acetate with S²⁻ anions generated through the thermal decomposition of thioacetamide.(Vacassy et al., 1998) Transmission electron microscopy(TEM) and powder X-Ray Diffraction (XRD) analysis of this material confirmed that the particle diameter was approximately 30 nm. Aldrich ZnS pieces were also used for particle size tests. The pieces were ground with a mortar and pestle, then sized by wet sieving in ethanol and dried in an oven at 80 °C.

Table 1. Particle size data and major impurities in industrial ZnS concentrates used in this study.

ZnS Concentrate	Major Impurities (wt %)					Particle size data (µm)		
	Pb	Fe	Mn	SiO ₂	Ca	d ₁₀	d ₅₀	d ₉₀
Atacocha	1.55	5.40	0.50	2.20	0.95	0.759	5.94	24.93
Lennard Shelf	1.40	1.20	0.03	0.11	2.10	1.168	8.19	19.80

2.3 Batch experiments

The ZnS powder was added to 80 ml of iron(III) sulfate solution (0.25 mol L⁻¹ Fe³⁺) in a 100ml screw-top plastic bottle. 8.0ml of 6 mol L⁻¹ NaOH was added, the bottle

was sealed and the reagents mixed by vigorous shaking of the container. The pH was checked and if necessary adjusted to 3.0 (± 0.2) before placing the bottle into a laboratory bottle roller where it was maintained at 85 °C for 5 hours with gentle agitation. Filtration times were measured for 10 ml aliquots of the final suspension by filtration on a Gelman 0.22 μm cellulose membrane with a diameter of 36 mm, under a vacuum of -65 kPa. Filtration time represents the time taken from appearance of the first drop of filtrate collected until the filter cake was free of surface moisture. Moisture content of the filter cakes was determined by weight-loss on drying. The bulk samples were collected by centrifugation, and freeze-dried.

2.2 Kinetic experiments

Iron(III) sulfate solutions (300 ml, $0.25 \text{ mol L}^{-1} \text{ Fe}^{3+}$) were placed in a batch reactor and warmed to 85°C with agitation *via* an overhead stirrer. The ZnS powder (1.5 g) was added and the solution neutralized to pH 3.0 (± 0.2) by addition of a small volume (~ 10 ml) of 8 mol L^{-1} NaOH solution. The resulting iron oxide suspension was then kept at 85°C, with stirring, for a period of 5 hours, while the pH was maintained with drop-wise additions of dilute H_2SO_4 or NaOH solutions when required. The reaction mixtures were sampled at intervals and the iron oxide precipitate collected by filtration on a Gelman 0.22 μm cellulose membrane. The filter cakes were immediately cooled in a freezer and then freeze-dried.

Analyses

Zinc concentrations in reaction solutions were determined by flame AAS analysis

using a Varian SpectraAA-10 instrument with a spectraAA-100/200 PC upgrade.

Zeta potentials were measured on a Malvern Zetasizer Nano ZS, with pH control achieved by suspending the particles in sodium phosphate or sodium citrate buffer solutions.

Transmission Electron Micrographs (TEM) were recorded on a JEOL 2011 TEM operating at 200 kV. The samples were dispersed in de-ionized water with the aid of ultra-sonication, then cast and dried onto a conventional holey carbon-coated copper grid. Powder X-ray diffraction patterns were recorded on a Siemens D500 Powder Diffractometer using Cu-K α radiation (30 mA, 40 kV). Samples were step scanned from 3° to 70° 2 θ , at 0.02° increments, using a counting time of 5 s per increment.

3. Results and Discussion

3.1 Effect of additive particle size

A recent study proposed that the ability of ZnS to promote the transformation of ferrihydrite to goethite and hematite arises *via* adsorption of the ferrihydrite nanoparticles onto the ZnS surface, allowing the oxidative dissolution of ZnS to couple with reduction of iron(III) in ferrihydrite (Loan et al., 2005). If this is the case, then it is reasonable to expect that differences in the surface area of the solid ZnS additive would have an influence on its effectiveness in promoting phase transformation.

Figure 1 shows the XRD patterns measured for reaction products obtained in batch experiments containing 5 g/ L ZnS of different average particle diameter. A control sample prepared in the absence of the ZnS additive is also shown. Peaks due to low crystallinity goethite are observed in all patterns, along with peaks due to the ZnS

additive, and the background electrolyte (Na_2SO_4), which was not completely washed from the residues. A qualitative comparison of the relative intensities of the goethite peaks in these patterns shows that the $<60\ \mu\text{m}$ sample seems to have promoted goethite formation to a greater extent than the $>125\ \mu\text{m}$ sample which, in fact, differs little from the control sample.

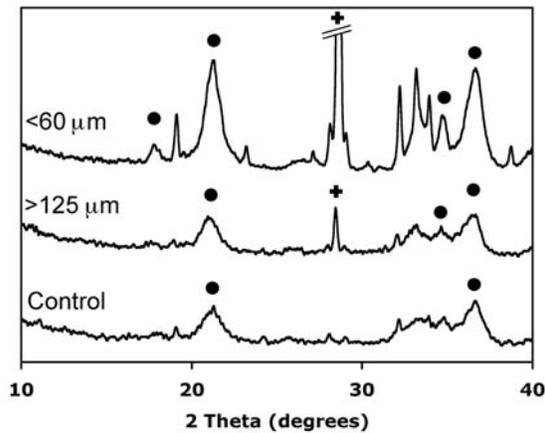


Figure 1. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25\ \text{mol L}^{-1}\ \text{Fe}^{3+}$ solution in the presence of $5\ \text{g/L}$ Aldrich ZnS of different particle sizes and aged at $85\ ^\circ\text{C}$ and $\text{pH}\ 3$ for 300 minutes. These are compared with the pattern obtained for a control sample containing no ZnS additive. Particle sizes are shown on the right, and peaks due to iron oxide phases and zinc sulfide are marked as follows: λ = goethite, $:$ = ZnS. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

The effect of decreasing particle size of the ZnS additive is also demonstrated in the levels of dissolved zinc measured in the reaction solution (Table 2). As one would expect, the Zn²⁺ concentrations increase with decreasing particle size as finer particles are more easily dissolved.

It is important to note that no hematite was formed in these experiments. Indeed, in all cases where “pure” ZnS additives were used, only goethite formation was promoted, while industrial ZnS concentrates promoted formation of both goethite and hematite, as described in a previous study.(Loan et al., 2005) Possible reasons for this are discussed further below.

Table 2. Dissolved Zn²⁺ in batch experiments using Aldrich ZnS of different size distributions.

Particle Size range (μm)	Dissolved [Zn ²⁺] (mol L ⁻¹)	% ZnS dissolved
>125	7.03×10^{-4}	1.21
90-125	2.98×10^{-3}	5.17
60-90	4.11×10^{-3}	7.12
<60	5.98×10^{-3}	10.36

3.2 Comparison of different ZnS additives

A comparison of the XRD patterns obtained for iron oxyhydroxide samples collected at various times after ZnS addition can be used to provide a general description of the order in which the different phases are formed in the reaction mixtures. In all experiments, the initial phase to precipitate was 2-line ferrihydrite, which is subsequently transformed to other phases, most commonly goethite and/or hematite. The XRD patterns of selected samples collected in an experiment in which Atacocha ZnS was used

as the solid-phase additive are shown in Figure 2. The sample collected 40 minutes after neutralization was the first to show peaks indicative of hematite, while goethite formation was not evident before about 60 minutes.

XRD patterns of products formed in the presence of the Lennard Shelf ZnS were generally very similar to those shown in Figure 1, but goethite peaks were evident at an earlier stage in the reaction (about 40 minutes) while hematite peaks did not appear until after 180 minutes, and even after 5 hours, the low intensity of the hematite peaks indicated that less hematite had formed than in the presence of the Atacocha ZnS.

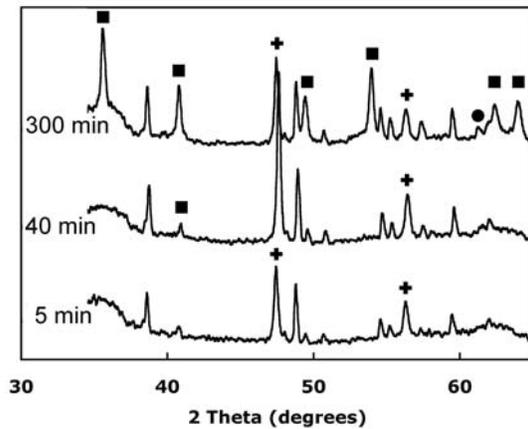


Figure 2. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25 \text{ mol L}^{-1} \text{ Fe}^{3+}$ solution in the presence of 5 g/L Atacocha ZnS and aged at $85 \text{ }^\circ\text{C}$ and $\text{pH } 3$. Reaction times are shown on the right, and peaks due to iron oxide phases and zinc sulfide are marked as follows: ν = hematite, λ = goethite, $+$ = ZnS. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

It has been shown that the solid-solution iron content of sphalerite has a pronounced effect on its dissolution rate, with a high iron content resulting in much faster leaching. (Dutrizac, 1992) Examination of the tabulated data for the industrial concentrates (Table 1) shows that the Atacocha concentrate has a higher iron content and

a finer particle size than the Lennard Shelf sample, and both of these characteristics would be expected to lead to higher reactivity compared with the Lennard Shelf concentrate.

While industrial ZnS concentrates were found to promote formation of both goethite and hematite, only goethite was observed in products formed in the presence of the higher-purity ZnS additives. Kinetic experiments using both Aldrich ZnS (<60 μm) and a nanoparticulate ZnS sample synthesized in-house showed only minor enhancement of goethite formation relative to control experiments carried out in the absence of any additive. This suggests that the surface area of the additive may be only a minor factor in determining its efficacy in promoting phase transformation, and that the presence of impurities, such as iron, in the ZnS additive may play a far more important role.

The ability of ZnS to promote transformation of ferrihydrite seems to be due to its role in reducing Fe^{3+} to Fe^{2+} , so we examined the role of Fe^{2+} more closely by neutralizing an Fe(II) sulfate solution to pH 3, in the absence of any additive, and then ageing the precipitate at 85 °C. Since the reactor was well agitated and the Fe(II) solution had been warmed to 85 °C over a period of about 30 minutes before neutralization, partial aerial oxidation led to the presence of some Fe^{3+} , and thus a small amount of ferrihydrite was precipitated as the initial product. This precipitate was then aged in the presence of a relatively high concentration of Fe(II) over a period of 5 hours. The results of this experiment are shown in Figure 3, where XRD patterns obtained for samples taken 5 minutes and 300 minutes after neutralization are presented. It can be seen that 2-line ferrihydrite is the initial phase formed, as in other kinetic experiments, but that the main

product of phase transformation after 300 minutes is hematite, although some minor peaks indicating the presence of goethite are also observed.

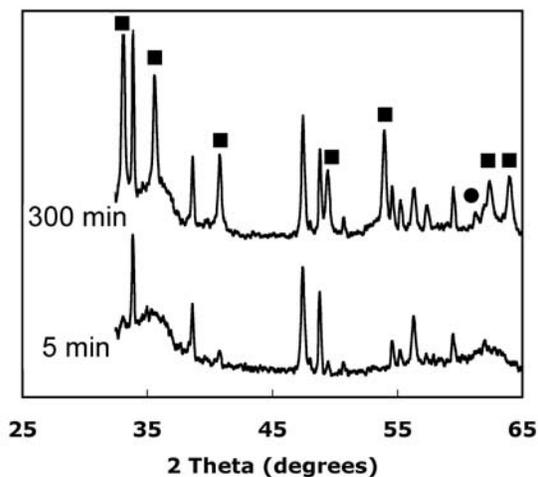


Figure 3. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25 \text{ mol L}^{-1} \text{ Fe}^{2+}$ solution and aged at $85 \text{ }^\circ\text{C}$ and $\text{pH } 3$. Reaction times are shown on the right, and peaks due to iron oxide phases are marked as follows : ν = hematite, λ = goethite. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

This experiment clearly shows that, under the temperature and pH conditions we have employed, the formation of hematite is promoted in the presence of Fe(II). Previous work has established that hematite and goethite form by different pathways: goethite by nucleation and growth in the bulk solution, and hematite by a combination of solution-mediated dehydration/rearrangement processes within ferrihydrite aggregates. (Cornell et al., 2003) Anything that increases the solubility of ferrihydrite can therefore promote the formation of both goethite and hematite. Thus, addition of a reductant, such as ZnS, provides a means to dissolve ferrihydrite by virtue of the higher solubility of Fe^{2+} relative

to Fe^{3+} , and dissolution of ferrihydrite makes more iron available in solution for precipitation of the more thermodynamically stable phases.

We have seen that reduction of Fe(III) to Fe(II) is the key to the role of ZnS in promotion of ferrihydrite transformation, but the question remains as to why the industrial ZnS concentrates are so much more effective than the pure ZnS samples. The answer to this question is provided by the zeta potential measurements presented in Figure 4. A comparison of the pH dependence of surface charge for each of the ZnS samples used in this study shows that the industrial concentrates have a much lower isoelectric point (I.E.P.) than the pure ZnS samples. This is likely to have significant consequences for the aggregation behaviour of the ZnS and ferrihydrite phases when the two are mixed at low pH. Since ferrihydrite is known to carry a positive surface charge at acidic pH, we would expect that electrostatic attraction should favour the aggregation of ferrihydrite with the industrial ZnS concentrates at pH 3. The higher purity ZnS samples carry little or no surface charge at this pH, so we would expect only weak association between particles of ferrihydrite and the ZnS surface.

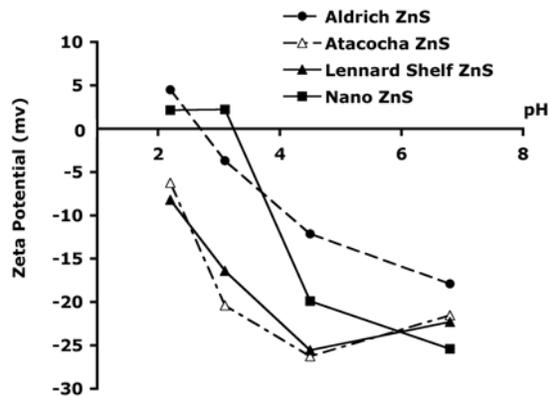


Figure 4. Plots of zeta potential vs. pH for the four ZnS samples used in this study.

The formation of mixed ferrihydrite/ZnS aggregates provides an explanation for formation of hematite in systems where industrial ZnS additives were used. When reduction takes place within ferrihydrite aggregates, the Fe(II) is formed at the site of hematite formation. When the ZnS and ferrihydrite particles are not closely associated however, as is the case with the high purity ZnS samples, Fe(II) must diffuse into the ferrihydrite aggregates in order to have any positive effect on dehydration or dissolution of ferrihydrite. Thus the promotion of goethite formation (in the bulk solution) is the only effect observed in these cases.

3.3 Physical characteristics of iron oxide residues

A series of batch experiments was carried out with the aim of investigating whether the physical handling properties of the iron oxide residues could be improved by addition of ZnS. The physical properties of interest here are the filtration time and the moisture content of the filtered solids. Figure 5 shows the effects of increasing additive concentration on the filtration rates of iron oxide residues produced in the presence of each of the four ZnS samples we tested. In each case there is an initial marked decrease in filtration time at an additive concentration of 5 g/L, but further addition of ZnS does not provide any further improvement in the filtration time.

XRD analysis of the residues showed that increasing the additive concentration to 20 g/L did appear to increase the relative amounts of goethite and/or hematite present in the residues, but all residues still displayed the broad reflections of 2-line ferrihydrite in their background. So we must conclude that under the condition of our experiments, even

20 g/L is an insufficient concentration of additive to provide complete transformation of ferrihydrite to more crystalline phases, even with the more effective industrial ZnS concentrates. It seems likely therefore, that the reduction in filtration time is not due to

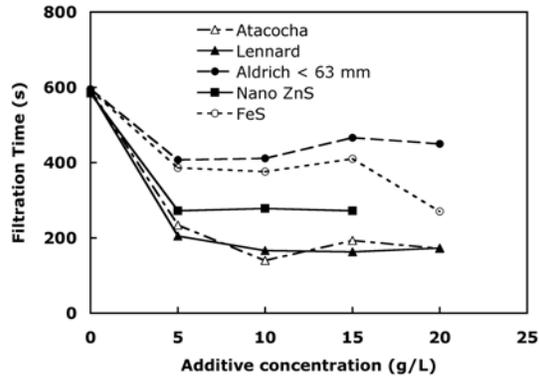


Figure 5. Plots of filtration time vs. additive concentration for each of four different ZnS samples.

the formation of goethite and hematite in the mixtures, but is rather a consequence of the aggregation processes described in the previous section. In other words, the electrostatic interaction between ferrihydrite and the ZnS additive results in the formation of mixed aggregates that can “mop up” some of the fine particle fraction of the residue and make it easier to filter.

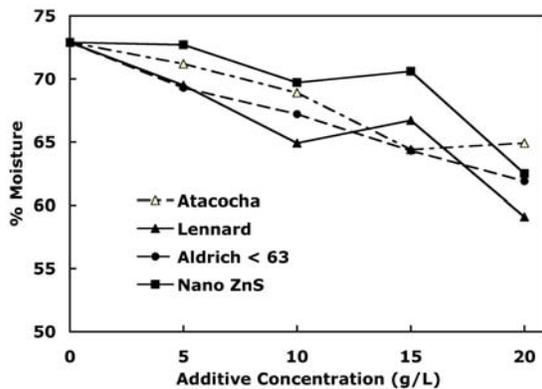


Figure 6. *Plots of moisture content vs. additive concentration for each of four ZnS samples*

Moisture contents of the residues obtained with different amounts of ZnS additive are presented in Figure 6. The graph shows that there is a modest decrease in moisture content as the amount of ZnS is increased, but the effect is very small, and can probably be attributed to the lower moisture content of the additive itself rather than to formation of hematite and goethite in the residues.

The results of the physical tests show that the use of ZnS has the potential to significantly improve the filterability of ferrihydrite residues, but the conditions for its application have not been optimised in these experiments. It is clear that the process handling characteristics are dominated by the ferrhydrite phase, so the benefits of forming more crystalline phases are unlikely to be seen in the filtration characteristics of the residue if only a portion of the ferrihydrite is transformed. Improving the process will require a more careful control of surface interactions between the additive and the ferrhydrite precipitate so that the ZnS particles are well dispersed within ferrihydrite aggregates. It should also be noted however, that continuous crystallisation can provide better control over product crystallinity and aggregation than batch processes, so the use of ZnS additives in a continuous process may well provide greater improvements in the physical handling characteristics of the precipitate.

4. Conclusion

The experiments described here have confirmed that the ability of ZnS to promote transformation of ferrihydrite to more crystalline goethite and hematite arises from its role as a reductant. Since Fe(II) is more soluble than Fe(III) under the conditions we have studied, reduction of Fe(III) species to Fe(II) makes more iron available for crystallization of goethite, which forms by nucleation and growth in the bulk solution. In order to promote transformation to hematite however, the ferrihydrite and ZnS additive particles must be closely associated in mixed aggregates, so that Fe(II) is supplied to the site of hematite formation.

Comparison of ZnS additives of different particle size and different composition has shown that both of these factors influence the efficacy of the additive in promoting phase transformations of ferrihydrite. Surface interaction between the ZnS additive and ferrihydrite is a key aspect of the mechanism by which phase transformation is promoted, and indeed, the effect was first suggested through the fortuitous observation that ferrihydrite seemed to coat the surface of sphalerite particles in paragoethite residues. Thus, as ferrihydrite nanoparticles adsorb onto the ZnS surface and allow the oxidative dissolution of ZnS to couple with reduction of iron(III) on the ferrihydrite surface, sphalerite samples of high surface area will generally tend to be more effective.

The role of impurities in the ZnS additives is somewhat more complex, although the results of our experiments clearly showed that “pure” ZnS samples did not promote phase transformation of ferrihydrite to the same extent as the industrial samples, which contained a few wt% of other metals, most notably iron. It seems that the presence of solid-solution iron in the ZnS structure makes the additive more reactive and thus enhances its ability to reduce Fe(III) to Fe(II). Another important consequence of the

presence of impurities in the ZnS structure is the effect on surface charge of the suspended particles, and the results described here suggest that this is an important factor in regard to the relative amounts of goethite and hematite formed in the phase transformation.

The pure ZnS samples used in this study were found to have iso-electric points close to pH 3, which was the pH to which iron solutions were neutralized, so there was little electrostatic attraction to drive hetero-aggregation between ferrihydrite and the additive. These additives only promoted goethite formation. The industrial ZnS samples had their iso-electric points at much lower pH, presumably due to the presence of impurities such as Fe, and were able to promote formation of both goethite and hematite. We believe this difference arises because hematite formation is promoted primarily by the reduction of Fe(II) to Fe(III) at sites *within* ferrihydrite aggregates, while goethite is formed by nucleation in the bulk solution.

Physical tests of the ferrihydrite residues produced in the presence of ZnS additives showed minor improvements in both filterability and moisture content, and again these effects were most evident with the industrial additives. Our results suggest that additives that are more effective in promoting phase transformation of ferrihydrite, particularly those that promote hematite formation, also produce the largest improvements in filterability of the residues. It is not clear however, whether the improved filterability is a direct consequence of the ferrihydrite transformation, or simply due to the additive acting as a filtering aid. It is unlikely that the minor improvements in the physical properties of the residues could justify commercial application of ZnS as an additive at the levels we have employed here, but there is certainly scope for further development. In particular, it is important to recognise that, in the ideal case, the majority

of the ZnS should dissolve in the process, so that the zinc content of the residue remains low. Detailed examination of ZnS dissolution and the zinc content of the residues was beyond the scope of this work, but it remains an important objective for future studies. The work described here has outlined the importance of particles size and surface charge of the ZnS additive, and future work should be aimed at optimisation of these properties in order to achieve the best possible balance between the amount of additive used, and the degree of phase transformation achieved.

Acknowledgements

This research has been supported under the Australian Government's Cooperative Research Centre (CRC) Program, through the AJ Parker CRC for Hydrometallurgy. M. Loan thanks the Australian Research Council and Zinifex Ltd. for support in the form of an Australian Postgraduate Award (Industry).

References

1. Davey, P.T. and T.R. Scott, 1976. Removal of iron from leach liquors by the "goethite" process. *Hydrometallurgy* 2, 25-33.
2. McCristal, T.G. and J. Manning, Conversion of the Pasminco Hobart smelter to paragoethite., in *Zinc and Lead Processing*, P. Hancock, Ed. 1998, The Metallurgical Society of CIM: Montreal. pp. 439-453.
3. Claassen, J.O., E.H.O. Meyer, J. Rennie, and R.F. Sandenbergh, 2002. Iron precipitation from zinc-rich solutions: defining the Zincor Process. *Hydrometallurgy* 67, (1-3), 87-108.
4. Loan, M., G.M. Parkinson, O.G.M. Newman, and J.B. Farrow, 2002a. Iron oxy-hydroxide crystallization in a hydrometallurgical residue. *Journal of Crystal Growth* 235, 482-488.
5. Loan, M., T.G. St Pierre, G.M. Parkinson, O.G.M. Newman, and J.B. Farrow, 2002b. Identifying nanoscale ferrihydrite in hydrometallurgical residues. *JOM - Journal of the Minerals Metals and Materials Society* 54, (12), 40-43.

6. Jambor, J.L. and J.E. Dutrizac, 1998. Occurrence and Constitution of Natural and Synthetic Ferrihydrite, a Widespread Iron Oxyhydroxide. *Chemical Reviews* 98, 2549-2585.
7. Zinck and J.E. Dutrizac, 1998. The Behaviour of Zinc, Cadmium, Thallium, Tin and Selenium during Ferrihydrite Precipitation from Sulphate Media. *CIM Bulletin* 91, (1019), 94-100.
8. Loan, M., G.M. Parkinson, and W.R. Richmond, 2005. The effect of zinc sulfide on phase transformations of ferrihydrite. *American Mineralogist*. 90, 258-261.
9. Vacassy, R., et al., 1998. Synthesis of controlled spherical zinc sulfide particles by precipitation from homogeneous solutions. *Journal of the American Ceramic Society* 81, (10), 2699-2705.
10. Dutrizac, J.E., 1992. The leaching of sulfide minerals in chloride media. *Hydrometallurgy* 29, 1-45.
11. Cornell, R.M. and U. Schwertmann, 2003. *The Iron Oxides*. 2nd Edn. ed. Weinheim: VCH.

Tables

Table 1. Particle size data and major impurities in industrial ZnS concentrates used in this study.

ZnS Concentrate	Major Impurities (wt %)					Particle size data (μm)		
	Pb	Fe	Mn	SiO ₂	Ca	d ₁₀	d ₅₀	d ₉₀
Atacocha	1.55	5.40	0.50	2.20	0.95	0.759	5.94	24.93
Lennard Shelf	1.40	1.20	0.03	0.11	2.10	1.168	8.19	19.80

Table 2. Dissolved Zn²⁺ in batch experiments using Aldrich ZnS of different size distributions.

Particle Size range (μm)	Dissolved [Zn ²⁺] (mol L ⁻¹)	% ZnS dissolved
>125	7.03×10^{-4}	1.21
90-125	2.98×10^{-3}	5.17
60-90	4.11×10^{-3}	7.12
<60	5.98×10^{-3}	10.36

Figure 1

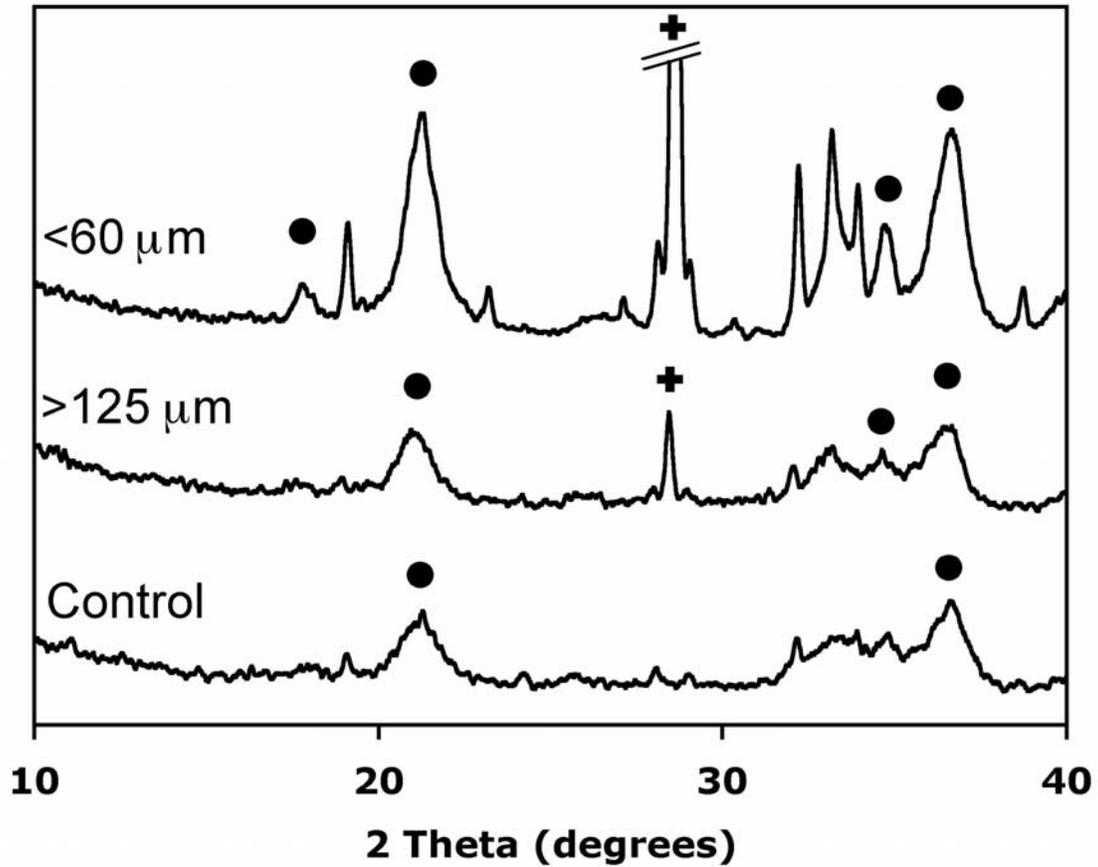


Figure 1. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25 \text{ mol L}^{-1} \text{ Fe}^{3+}$ solution in the presence of 5 g/L Aldrich ZnS of different particle sizes and aged at $85 \text{ }^\circ\text{C}$ and pH 3 for 300 minutes. These are compared with the pattern obtained for a control sample containing no ZnS additive. Particle sizes are shown on the right, and peaks due to iron oxide phases and zinc sulfide are marked as follows: λ = goethite, : = ZnS. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

Figure 2

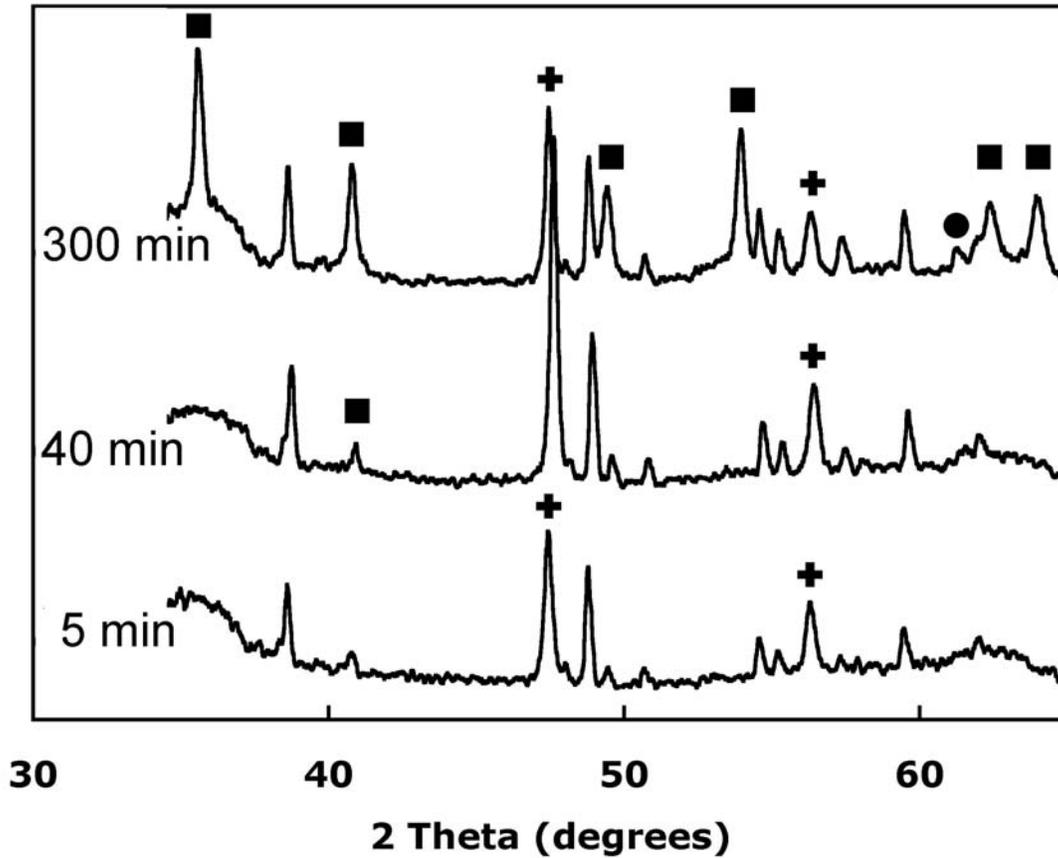


Figure 2. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25 \text{ mol L}^{-1} \text{ Fe}^{3+}$ solution in the presence of 5 g/L Atacocha ZnS and aged at 85 °C and pH 3. Reaction times are shown on the right, and peaks due to iron oxide phases and zinc sulfide are marked as follows : ν = hematite, λ = goethite, $+$ = ZnS. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

Figure 3

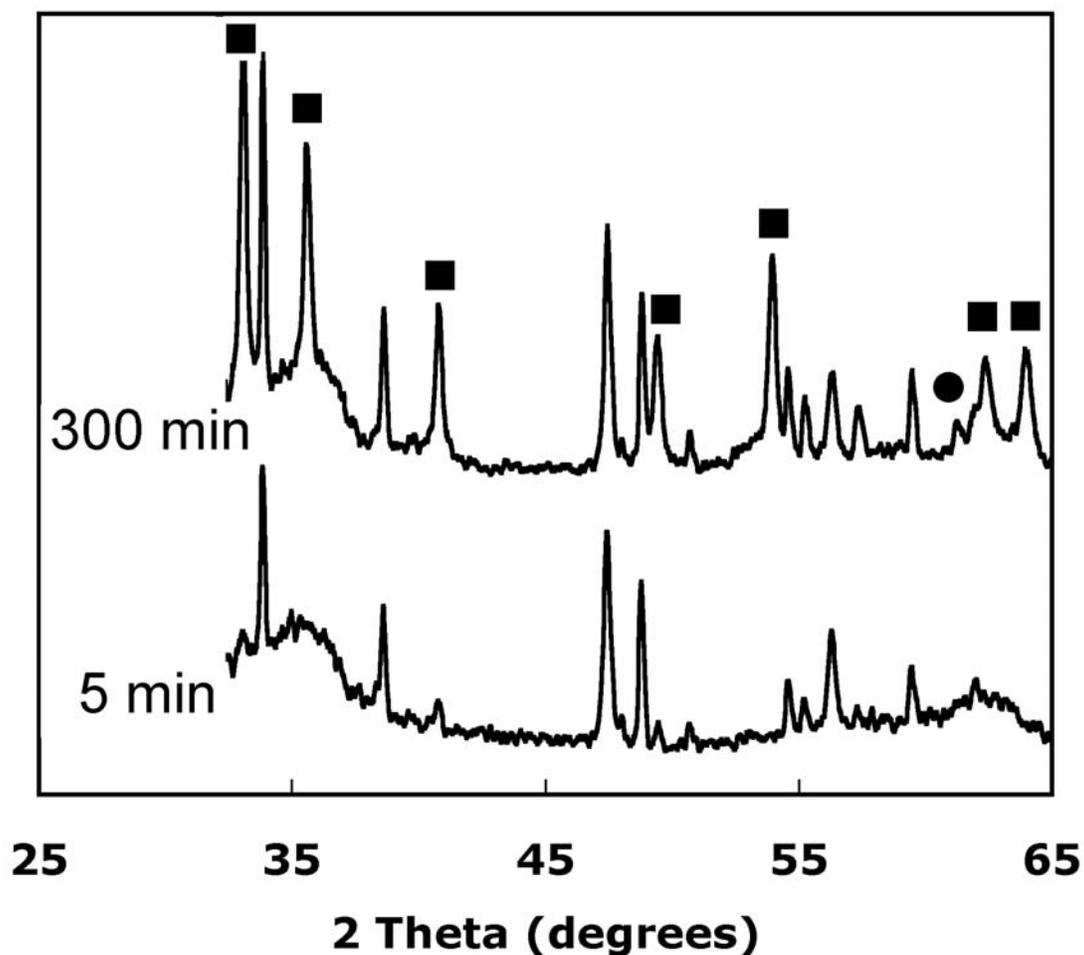


Figure 3. Powder XRD patterns of iron oxyhydroxide samples precipitated from a $0.25 \text{ mol L}^{-1} \text{ Fe}^{2+}$ solution and aged at $85 \text{ }^\circ\text{C}$ and $\text{pH } 3$. Reaction times are shown on the right, and peaks due to iron oxide phases are marked as follows : ν = hematite, λ = goethite. Sharp peaks not marked with a symbol are due to residual background electrolyte (Na_2SO_4).

Figure 4

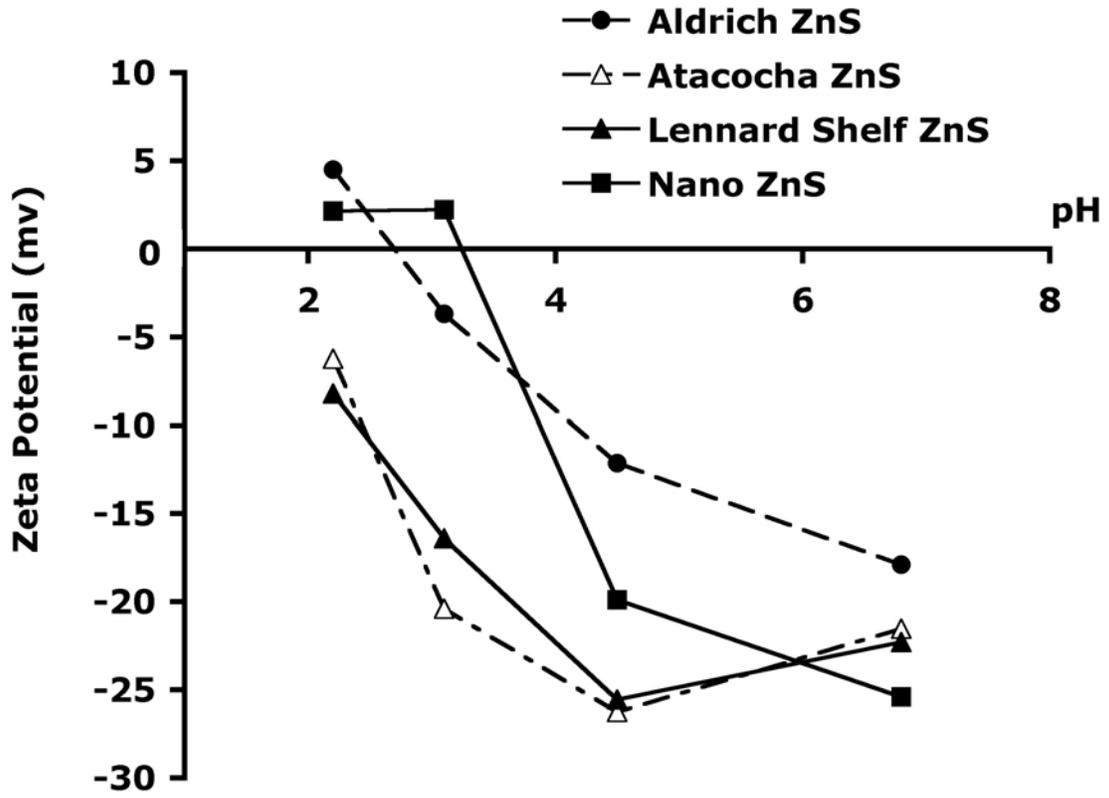


Figure 4. Plots of zeta potential vs. pH for the four ZnS samples used in this study.

Figure 5

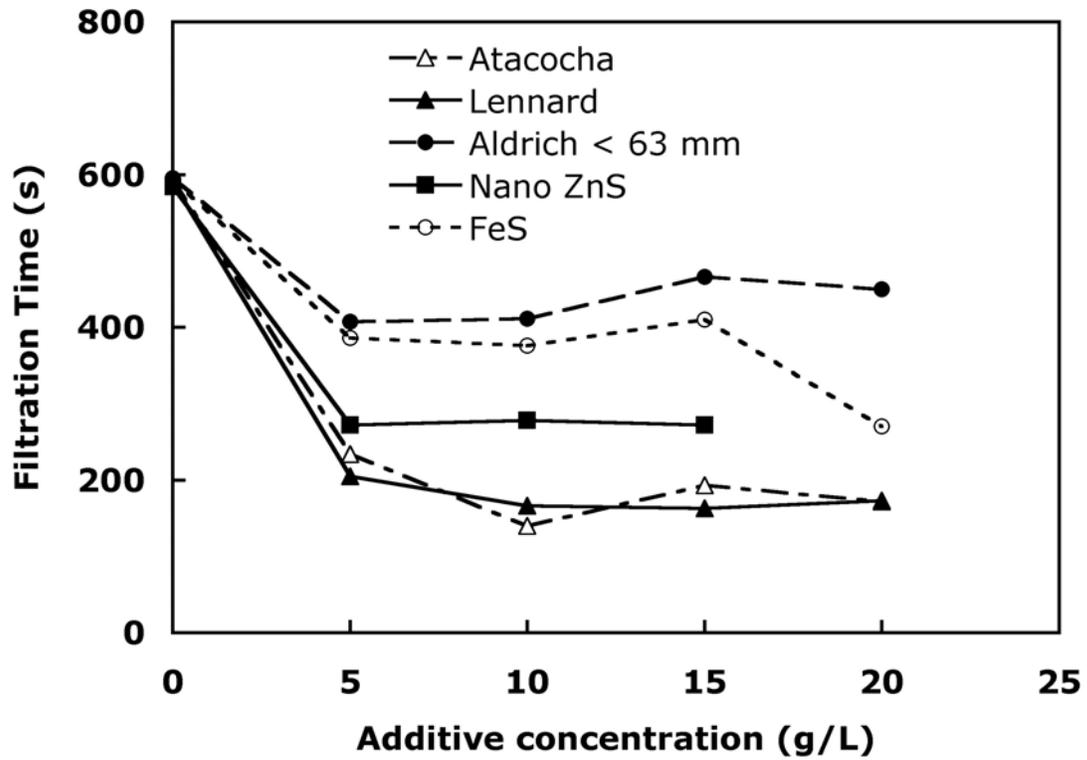


Figure 5. Plots of filtration time vs. additive concentration for each of four different ZnS samples.

Figure 6

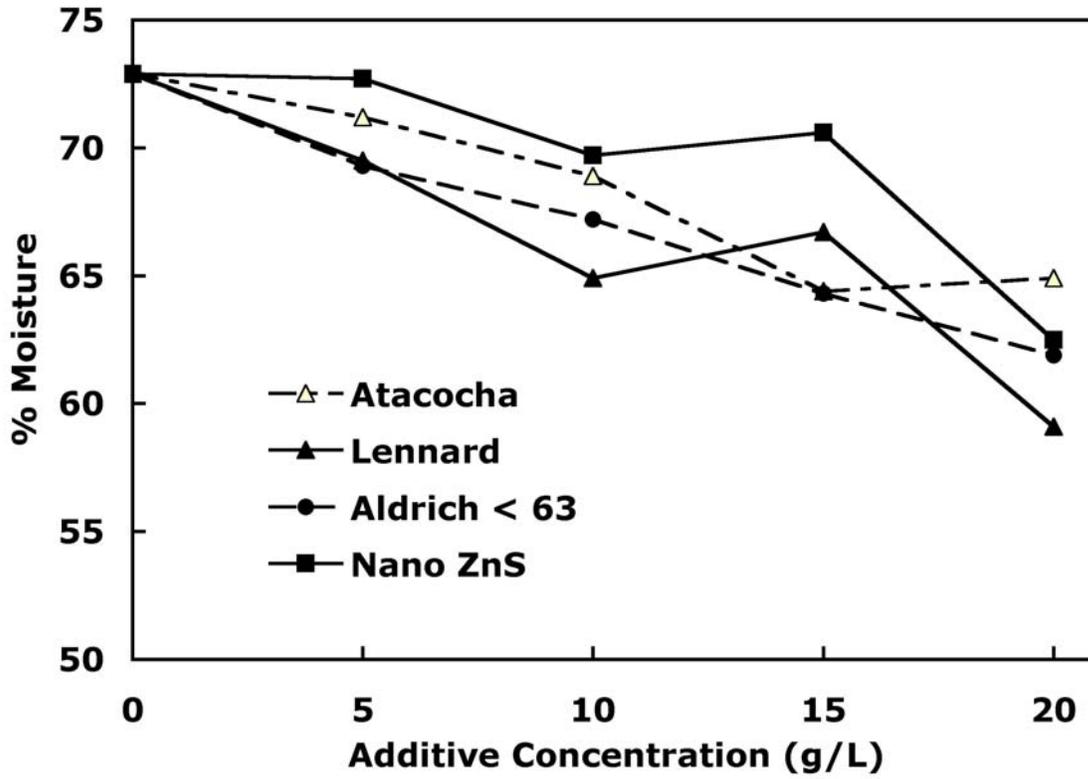


Figure 6. Plots of moisture content vs. additive concentration for each of four ZnS samples