Heavy metal precipitation by sulphide and bicarbonate: evaluating methods to predict anaerobic digester overflow performance

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Abstract

Overflow from an anaerobic, sulphate reducing, reactor was used to precipitate copper, iron and zinc from aqueous solutions. Two predictive methods, one generated empirically using data from synthetic solutions and one based on thermodynamic speciation software were evaluated. Both methods could accurately predict zinc precipitation. The inability of the software packages to account for amorphous and colloidal precipitates led to inaccurate models for copper and iron. The empirical models could account for this, but not the presence of organic acids. These factors could be incorporated into future models to enhance their accuracy.

1 Introduction

South Africa is a developing country that is both water scarce and water stressed. The sustainability of SA’s water resources is threatened, both in terms of quantity and quality. If the current patterns of water usage are maintained, SA will fully utilise all its natural water sources by 2027 (Odendaal, 1997). Already there are a number of regions in the country that rely on expensive transfer schemes, as demand for water has far exceeded available resources.

The quality of South Africa's water resources is declining, primarily as a result of increasing salinity, but also as a result of metal pollution and eutrophication (Neytzell-De Wilde, 1992). One of the major sources of both salinity and heavy metal contamination is acid mine drainage (AMD), originating from operating and abandoned mines as well as rock piles and tailings. It is generated by the bacterially catalysed oxidation of sulphide minerals, most commonly pyrite (FeS_2), in the presence of water and oxygen. Initially the soluble iron occurs in the ferrous (Fe^{2+}) form, but upon further exposure to oxygen rapidly oxidises to the ferric (Fe^{3+}) form, which can chemically oxidise additional pyrite. Ultimately the ferric iron undergoes hydrolysis and leads to precipitation of ferric hydroxide. The entire process can be summarised as follows:

$$FeS_2 + {}^{15}/_4O_2 + {}^{7}/_2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

This shows that each mole of pyrite oxidised ultimately produces four moles of proton acidity, making this one of the most prolific acid generating reactions in nature (Appelo and Postma, 1993). The acid can be responsible for further leaching of acid labile minerals resulting in a "classical" AMD discharge, having a low pH, high sulphate and iron load and potentially dangerous levels of other metals such as aluminium (Al), arsenic (As), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn).

The longevity of a polluting discharge depends on the rate of depletion of vestigial acidity as well as the scope for generation of juvenile acidity. Vestigial acidity refers to the release of contaminants during groundwater rebound and represents the relatively short, highly polluting, "first flush" phase. In contrast, juvenile acidity arises primarily from pyrite oxidation as a result of seasonal water table fluctuations (Younger, 1997; 1998). AMD originating from waste rock piles, slag heaps and slimes dams fall into this latter category. In these cases the polluting discharge is likely to persist until all the exposed sulphide minerals have been oxidised, which may take centuries.

The chemical precipitation of heavy metals, primarily by lime addition, has historically been the preferred method for the treatment of acid mine drainage (Dean *et al.*, 1972). While this method is effective and relatively cost effective, when compared to complex physico-chemical strategies, it does have disadvantages in terms of the characteristics of the resulting sludge and the fact that minimum solubilities of the specific metal hydroxides occur at different pH values. The use of sulphide has become an increasingly popular option (Bhattacharyya *et al.*, 1981; Feng *et al.*, 2000). Sulphide precipitation occurs effectively over a broad pH range and precipitation of certain metals can be achieved at low pH values.

The cost associated with regular chemical dosing over a prolonged period has resulted in a shift in research focus towards active and passive biological treatment systems. Many of these systems, such as artificial wetlands and sulphate reducing bacteria based systems still rely heavily on precipitation as the primary mechanism for removing metals from solution. While the reactive species may be of biological origin, the precipitation process is essentially the same as that which occurs in chemical based systems. The biological systems contain three weak acid-base systems, which are responsible for determining the pH. They are the carbonate system, the sulphide system and the water dissociation system. Based on the pK values for the various equilibrium reactions (Stumm and Morgan, 1996), the biological sulphate reducing system, where the pH rarely exceeds 8, will be dominated by the HCO_3^-, HS^- and $H_2S(aq)$ species. The ratio of alkalinity to aqueous sulphide generated depends on the carbon source and composition of the microbial consortium (Gibson, 1990).

Several authors (Rose *et al.*, 1998; Chang *et al.*, 2000; Foucher *et al.*, 2001; Glombitza, 2001) have described AMD treatment systems based on biologically generated sulphide and alkalinity. Typically this work has focused more on the sulphate reduction and process development, rather than the chemistry of the precipitation. The result is that fairly broad assumptions have been made as to the nature of the precipitation process and the characteristics of the precipitate formed.

Chemical speciation modelling is a popular technique that can be used to predict the equilibrium condition existing in treated acid mine waters. As these models are based on thermodynamic rather than kinetic data, some of the species predicted to occur at equilibrium may not have been formed during the timescale of the treatment. This is particularly true in treatment systems where the volume to be treated necessitates a relatively short retention time. In addition, most thermodynamic databases are incomplete, particularly in terms of information on metal sulphide species.

This paper focuses on the performance of overflow from an anaerobic sulphate reducing reactor as a metal (Cu, Fe and Zn) precipitating agent and compares the results obtained to predictions based on thermodynamic modelling (MinteqA2 and OLI Systems Inc.) and experiments performed using synthetic chemical reagents.

2 Materials and methods

All experiments were performed using acid-washed borosilicate glassware. pH measurements were made using a Cyberscan 2500 pH meter, alkalinity determined by titration against 0.02N H_2SO_4 and aqueous sulphide determined using a Merck Spectroquant test kit. Metal analysis was performed using a GBC 909AA atomic absorbtion spectrophotometer, linked to a GBC integrator.

Metal stock solutions ($CuSO_4.5H_2O$, $FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$, all Merck) were made up to a concentration of 1.574mM. Sulphide (Na_2S) stock solutions (0.05M and 0.1M) and bicarbonate ($NaHCO_3$) stock solutions (0.1M and 0.5M) were made up using analytical grade reagents (Merck). Anaerobic digester overflow was obtained from a sulphate reducing reactor, seeded with a bacteria consortium isolated from the algal integrated ponding system at the Grahamstown sewage treatment works and maintained on a modified Postgate B growth medium. The digester overflow had a pH of 7.80, an aqueous sulphide concentration of 33mM and a bicarbonate concentration of 133.6mM. A portion of this overflow was centrifuged at 10 000rpm for 10 minutes to removed the bacterial cells and particulate organic matter. The centrifugation had no effect on the pH or sulphide concentration, but the bicarbonate concentration was reduced to 126.3mM.

Experiments with the synthetic solutions were performed, in duplicate, according to a statistical design (based on response surface methodology), with a minimum of six metal to sulphide molar ratios, ranging from 2:1 to 1:2, and bicarbonate to sulphide ratios of 1:1, 2:1, 4:1 and 6:1. In the case of iron and copper additional metal to sulphide ratios were examined, focussed on the region where the morphology of the precipitate changed from crystalline to amorphous. In all cases 100ml of the metal solution was added to 10ml of the bicarbonate and sulphide mix. The flasks were stoppered and placed on an orbital shaker for 120min. The pH was measured after 1, 30, 60 and 120min. At 60 and 120min a 10ml sample was removed for metal analysis. A portion of the sample was filtered through a 0.45µm nylon membrane filter, a portion centrifuged at 5 000rpm for 5min and a portion allowed to settle for 10min, with the metal concentration determined in the filtrate and supernatants respectively.

The response surface methodology technique of statistical analysis was used to determine the effect each individual variable (ie. the metal to sulphide ratio and bicarbonate to sulphide ratio) and their combined effect on the percentage of metal removed from solution (Meyers and Montgomery, 1995). The interaction between these variables was determined through the development of a mathematical model that describes the performance of each system. As the relationship between the variables is not necessarily linear, a second order polynomial model, with interaction was utilised. The following equation represents the model on which the response surface of each metal was based:

$$z = \beta_0 + \beta_1 \text{*B:S ratio} + \beta_2 \text{*M:S ratio} + \beta_3 \text{*B:S ratio}^2 + \beta_4 \text{*M:S ratio}^2 + \beta_5 \text{*B:S ratio*M:S ratio}$$

This model accounts for the individual effects of both ratios as well as the possible interaction between the B:S and M:S ratio. A t-test was performed to determine the significance of each variable in the equation. Further analysis showed that in the case of zinc and iron a third order model accounted for a significantly greater portion of the observed variability. This introduced four additional terms.

The bicarbonate to sulphide ratio in the digester overflow was fixed, which precluded a matrix experimental design. A volume of digester overflow was calculated, such that the metal to sulphide ratio was the same as for the synthetic experiments. Deionised water was added to make the volume up to 10ml, after which the metal solutions were added and the experiments performed as previously described.

MinteqA2 and OLI were used to predict the metal precipitation and equilibrium pH at each of the points in the experimental matrix. These predictions were analysed using the same statistical approach to generate a third order model and response surface, which was compared to that generated using the experimental data.

3 Results and discussion

For the synthetic solutions the addition of iron and copper to the bicarbonate/sulphide mixture resulted in a very rapid reaction, leading to a colour change from the clear solution to an inky black and dark brown colour respectively. In both cases, where the molar ratio of metal to sulphide was 1:1 or lower it was not possible to remove the resulting complex by either filtration or centrifugation. The zinc experiments, however, showed a different trend. Addition of the metal solution did not result in an instant, dramatic reaction, rather a distinct white precipitate became visible within two minutes. This precipitate could be readily removed by filtration or centrifugation and settled within five minutes after being removed from the shaker. The three-dimensional surfaces generated from the statistical analysis of the synthetic solution data are shown in Figures 1-3. In all cases precipitate removal was achieved by filtration.

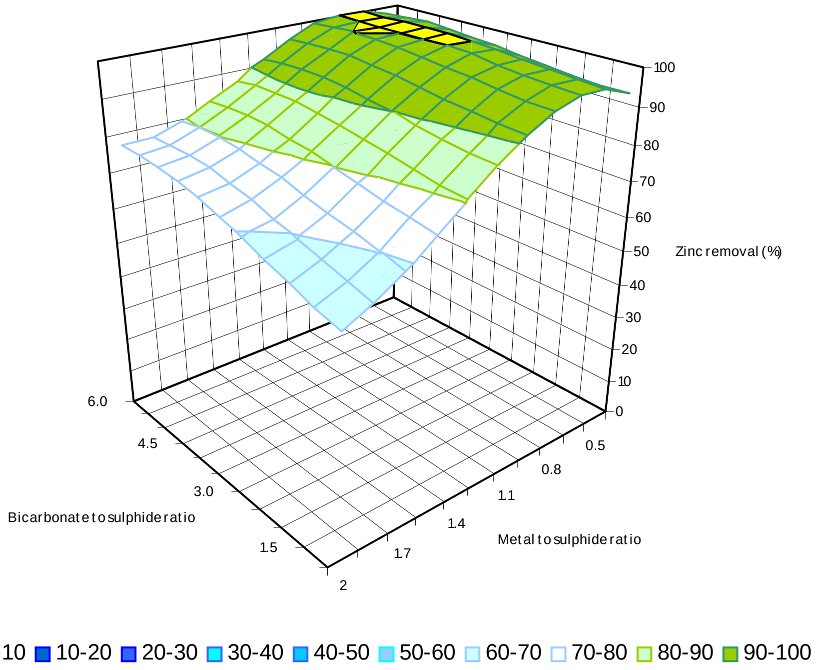

Fig. 1. Response surface, modelling zinc precipitation by a combination of sulphide and bicarbonate. Note: Y-axis (M:S ratio) scale reversed to allow better visualisation of the surface.

The model ($R^2 = 0.92$), with P values in parentheses, for the zinc surface is shown below:

$z = 57.21 - 1.66*B:S + 126.26*M:S + 1.24*B:S^2 - 115.21*M:S^2 - 1.03*B:S*M:S - 0.13*B:S^3 +$
(0.867) (0.011) (0.643) (0.006) (0.871) (0.602)
$26.03*M:S^3 - 0.20*B:S^2*M:S + 1.60*B:S*M:S^2$
(0.018) (0.728) (0.386)

The R^2 value indicates that model accounts for over 90% of the experimental variation, while the t-test show that the metal to sulphide ratio terms are the most significant variable. The P values of the interaction effects indicate that these factors are relatively insignificant. Visual analysis of the surface indicates that the bicarbonate to sulphide ratio is only important where there is an excess of zinc relative to sulphide. In this situation a portion of the zinc precipitates as $Zn(OH)_2$, with increased hydroxide precipitation as the bicarbonate concentration increases. At a metal to sulphide ratio of 1:1 and below, ZnS precipitation dominates and the effect of the increasing bicarbonate concentration is negligible, accounting for the high P values.

The response surface and third order model equation for the iron precipitation is shown below.

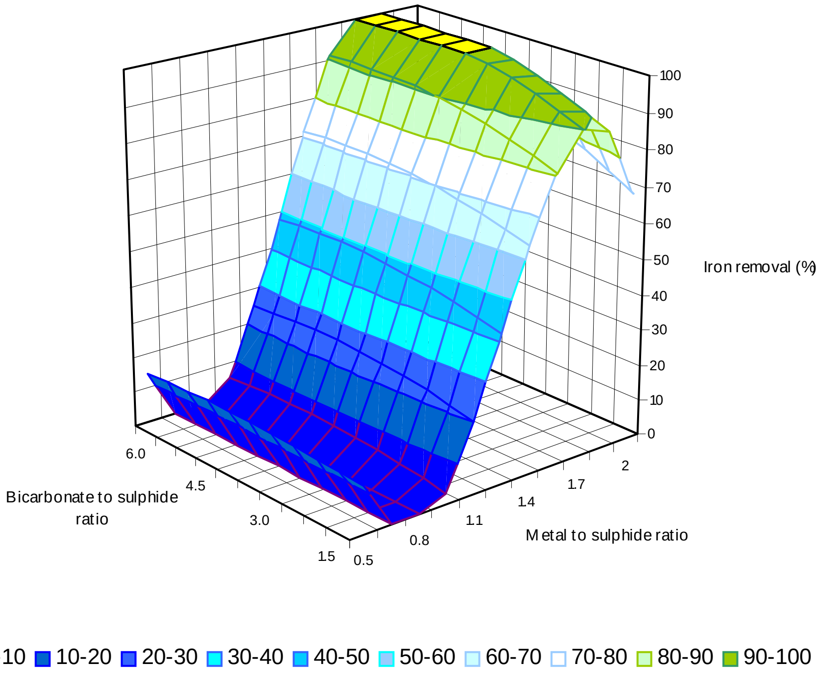

Fig. 2. Response surface, modelling iron precipitation by a combination of sulphide and bicarbonate

The model ($R^2 = 0.93$), with P values in parentheses, for the iron surface is shown below:

$$z = 237.5 - \underset{(0.998)}{0.03*B{:}S} - \underset{(<0.001)}{767.92*M{:}S} + \underset{(0.974)}{0.20*B{:}S^2} + \underset{(<0.001)}{730.30*M{:}S^2} + \underset{(0.926)}{1.32*B{:}S*M{:}S} - \underset{(0.974)}{0.02*B{:}S^3} - \underset{(<0.001)}{195.48*M{:}S^3} - \underset{(0.765)}{0.42*B{:}S^2*M{:}S} + \underset{(0.708)}{1.62*B{:}S*M{:}S^2}$$

The shape of the surface is significantly different to that of the zinc surface, with efficient precipitation only achieved where the iron to sulphide molar ratio is 1.5:1 or greater. Below this ratio the product of the reaction could not be removed by either filtration or centrifugation. The most likely explanation for this is the formation of an amorphous or colloidal precipitate, due to excessively high local supersaturation. The supersaturation ratio given by

$$SS = \frac{\alpha_{Fe^{2+}}\alpha_{S^{2-}}}{K_s{}^{0}{}_{,FeS}}$$

where $K_s{}^{0}{}_{,\ \mathrm{Fes}}$ is the thermodynamic solubility product for FeS. Harmandas and Koutsoukos (1996) investigated the formation of ferrous sulphides in aqueous solutions at an iron to sulphide ratio of 1:1. They found that at near neutral pH (7.1-7.4) the precipitate formed was mackinawite, while at pH 5.4-5.6 amorphous FeS was formed. However, the concentrations of iron and sulphide under the conditions where mackiniwite formed were between 1.0 and 5.0 x 10^{-5}M, while the concentrations used at the lower pH were at least an order of magnitude higher (5.0-7.0 x 10^{-4}), resulting in a significantly higher SS. This, rather than the pH could account for the formation of the amorphous precipitate. In addition, Harmandas and Koutsoukos (1996) found that the amorphous precipitates were very sensitive to oxidation by atmospheric oxygen. This is consistent with the current results and previous experimental work (van Hille, 2001).

As with the zinc surface, the metal to sulphide ratio controls the shape of the surface. The large values of the coefficients of these terms and the associated P values indicate the extent to which they dominate the model. An increase in bicarbonate concentration only has an effect where the metal to sulphide ratio is greater than 1.5:1. In that region some of the iron would precipitate as a hydroxide or carbonate.

The response surface and second order model equation for the copper precipitation is shown below.

The model (R^2 = 0.79), with P values in parentheses, for the copper surface is shown below:

z = 26.2 +15.09*B:S ratio – 99.34*M:S ratio –2.06*B:S ratio^2 + 62.74*M:S ratio^2
(0.076) (<0.005) (0.062) (<0.001)
– 2.11*B:S ratio*M:S ratio
(0.462)

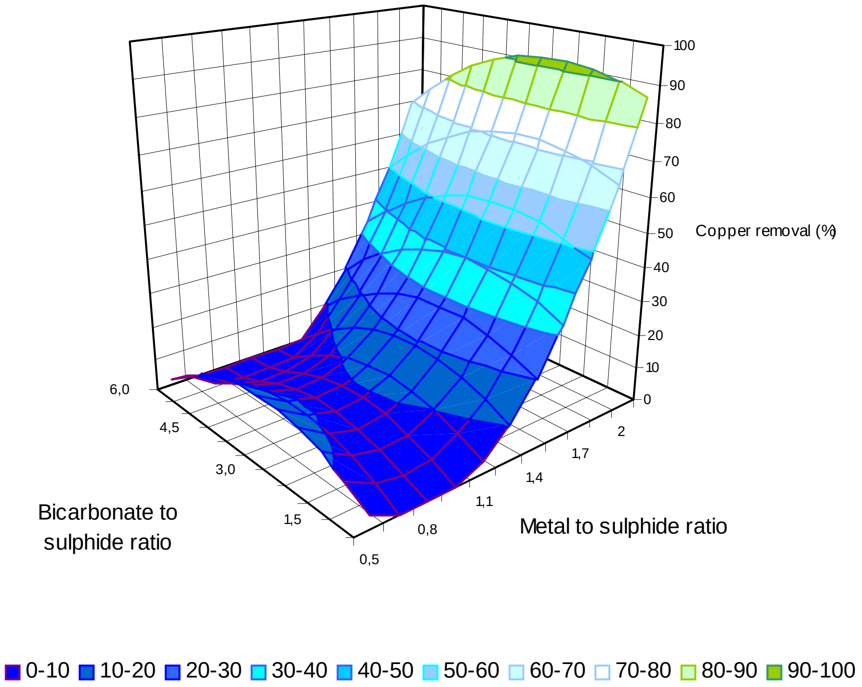

Fig. 3. Response surface, modelling copper precipitation by a combination of sulphide and bicarbonate

Copper presented the most complex situation and also highlighted a deficiency of the model. As with iron, an easily removable precipitate was only formed under a narrow set of conditions, where a significant stoichiometric excess of copper existed. In the case of copper a third order model did not significantly improve the predictive value of the model. Unlike the situation for iron, where the bicarbonate concentration had a negligible effect once sulphide dominated the system, the bicarbonate concentration had a significant effect on the product formed. This is highlighted in Table 1.

Table 1. Mean copper precipitation values (% removal) at various M:S and B:S ratios (n=2).

	M:S ratio							
B:S ratio	2:1	1.8:1	1.75:1	1.6:1	1.5:1	1:1	1:1.5	1:2
1:1	67.69	78.51	78.08	25.67	10.36	4.30	8.85	7.56
2:1	78.53	84.21	86.23	72.30	16.10	8.24	8.70	7.29
4:1	89.99	91.23	92.74	14.89	5.02	9.50	8.84	8.60
6:1	92.29	9.78	8.56	7.88	7.22	7.30	7.66	7.38

Table 1 shows that at a M:S ratio of 2:1 the results are consistent with those for zinc and iron, with increasing precipitation achieved as the bicarbonate concentration increases. The same trend occurs at the 1.8 and 1.75:1 ratios, except where the bicarbonate concentration is six times that of the sulphide, at which point the resulting product cannot readily be removed from solution. At a metal to sulphide ratio of 1.6:1 an easy to handle precipitate was only formed when the B:S ratio was in the region of 2:1. The consequence of this for the model is that at a B:S ratio of 6:1 the surface is less accurate, particularly at M:S ratios between 1.6 and 2:1. This would account for the lower R^2 value as well the increased significance of the B:S ratio factors.

Supersaturation is again a key factor in understanding the precipitation behaviour, however the situation is more complex. The equation for calculating supersaturation ratio described previously yields similar results irrespective of the bicarbonate concentration, which does not adequately describe the observed results. It is proposed that the HS^- species, rather than total aqueous sulphide species, controls supersaturation and precipitation. Previous work (Hammack *et al.*, 1993; van Hille, 2001) has shown that copper can effectively be removed from solution, as a readily settling precipitate, using gaseous hydrogen sulphide. This process is rate limited by the mass transfer of sulphide from the gaseous to the liquid phase. Due to the rapid reaction kinetics the supersaturation ratio remains low and precludes the formation of an amorphous precipitate.

Thermodynamic modelling of the synthetic precipitation systems yielded similar results for all three metals. In all cases, at M:S ratios of 1:1 and below at least 99.9% of the metal was predicted to precipitate as the metal sulphide. At ratios above 1:1, all available sulphide reacted with metal to form a metal sulphide and some additional hydroxide precipitation occurred due to the presence of the bicarbonate. In addition, there was no significant difference between the models generated using

MinteqA2 and OLI Systems Inc. The response surface generated using the copper predictions is shown in Figure 4.

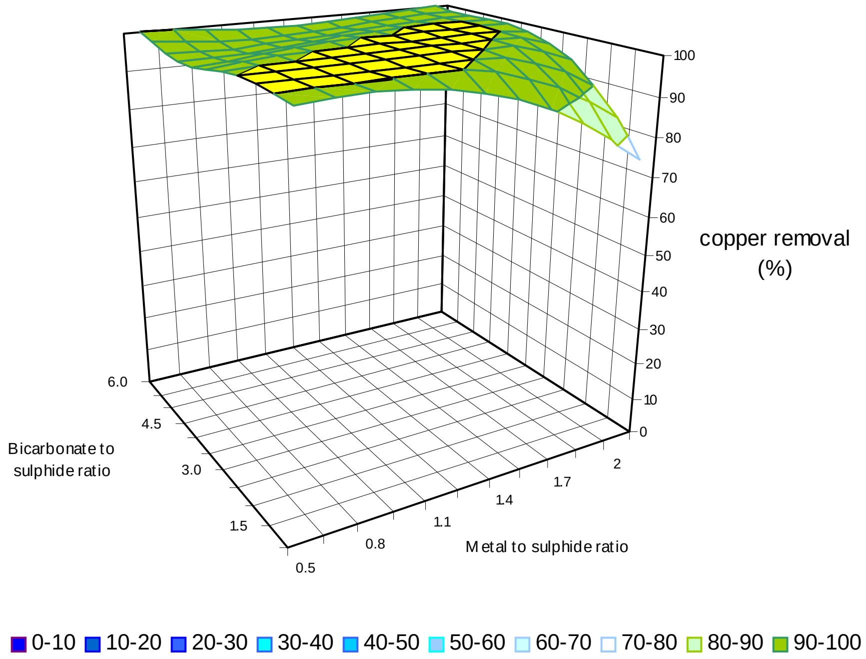

Fig. 4. Response surface obtained using data points generated using the aqueous species modelling software MinteqA2. The data points were obtained by modelling the 32 conditions tested experimentally

The surface in Figure 4 is significantly different from those obtained for the experimental copper and iron systems. The fact that the predictions are based only on thermodynamic data and represent an equilibrium situation means that amorphous or colloidal precipitates, which occur due to high supersaturation and may take several hours to days to mature into thermodynamically stable crystalline froms, cannot be accounted for. In addition, the thermodynamic databases tend to be incomplete or inaccurate. For instance, Shea and Helz (1988) presented stability constants for five copper sulphide and polysulphide complexes of importance in anoxic waters. Neither of the applications tested included data for these complexes. The two software packages were able to generate predictions for zinc that closely resembled the experimental surface.

The zinc and copper precipitation achieved using the digester overflow as well as the pH after 120min is graphically depicted in Figures 5 and 6. The iron data followed a similar trend to that of copper and is not shown. In each case results are compared to those obtained using the synthetic solutions at bicarbonate to sulphide ratios of 4:1. The zinc data (Figure 5) shows no significant difference between the metal removals achieved using the biological or synthetic stream. There is little difference in the pH between the synthetic and biological systems at M:S ratios of 2:1 to 1:1, which is expected as all the available sulphide has reacted with zinc. The slightly lower pH observed in the biological systems is due to the presence dissolved organic acids, such as lactate and acetate, which originate from the growth medium. At M:S ratios below 1:1 an excess of aqueous sulphide is present, which accounts for the significant increase in the pH of the synthetic system. The presence of the organic acids buffers the biological systems, although this has a negligible effect on the zinc precipitation.

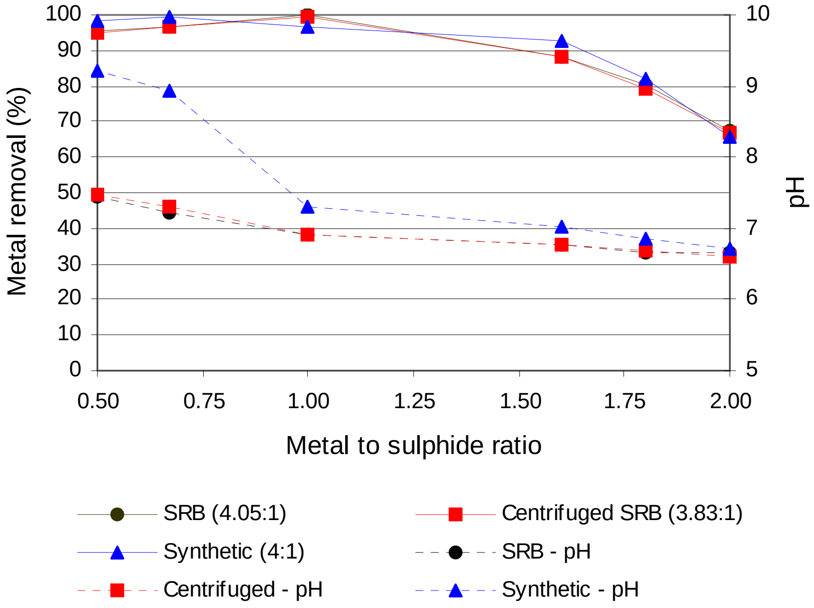

Fig. 5. A comparison of zinc precipitation and pH achieved by mixing of the metal solution with a synthetic sulphide/bicarbonate mixture and anaerobic digester overflow (T = 120min). The bicarbonate to sulphide ratios are shown in parentheses

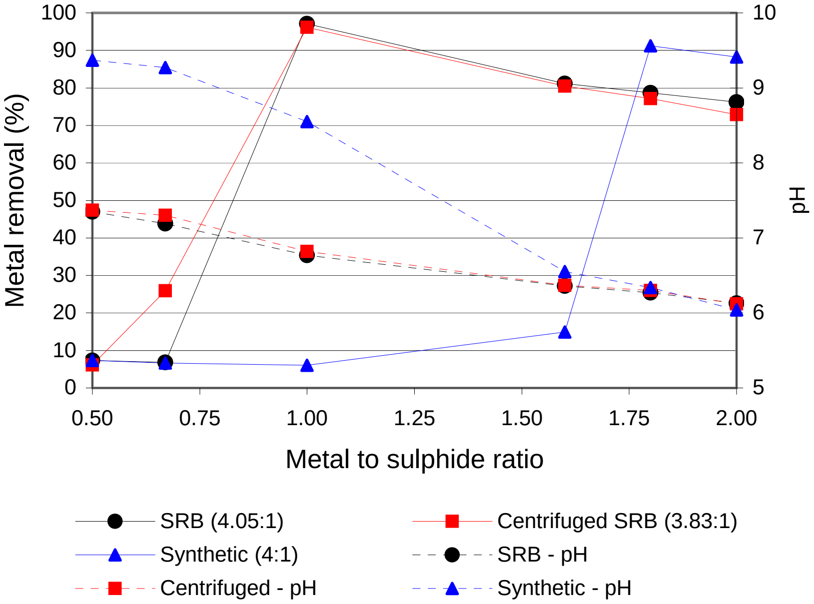

Fig. 6. A comparison of copper precipitation and pH achieved by mixing of the metal solution with a synthetic sulphide/bicarbonate mixture and anaerobic digester overflow (T = 120min). The bicarbonate to sulphide ratios are shown in parentheses

The trends for copper removal and pH (Figure 6) are significantly different from those for zinc (Figure 5), despite the fact that the concentrations of metal, bicarbonate, sulphide and organic acids are identical. This provides further evidence of the differences in the precipitation mechanisms. The differences in the pH and percentage metal removal at the M:S ratio of 2:1 is explained by the fact that copper precipitates in an alkaline medium at a lower pH than zinc. As a result a greater portion of the alkalinity is used for metal precipitation and the pH is lower. The presence of the organic acids reduces the available alkalinity, explaining why the copper precipitation is lower in the biological systems. This effect is negligible in the case of zinc because there is not enough alkalinity, even in the synthetic system, to raise the pH high enough to effect significant $Zn(OH)_2$ precipitation.

At a M:S ratio of 1.6:1 a significant decrease in copper removal is seen in the synthetic system. This can be attributed to the formation of an amorphous copper sulphide precipitate as a result of high supersaturation.

This is consistent with results obtained by Pattrick *et al.* (1997). In the biological systems, the organic acids buffer the pH at a lower value, effectively maintaining a lower HS^- species concentration. It is proposed that this species plays a key role in determining the supersaturation.

At an M:S ratio of 1:1 the copper removal in the synthetic system remains poor, but the pH increases significantly to 8.55. If all the sulphide reacted with copper to form the amorphous precipitate, the bicarbonate would buffer the system between pH 8.2 and 8.3. This, along with the fact that some copper is still precipitated suggests the formation of some polysulphide complexes, such as $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$. Shea and Helz (1988) have confirmed the presence of these complexes in anoxic waters. In this case some copper remains free to precipitate as $Cu(OH)_2$.

In the presence of excess sulphide the organic acids are no longer able to buffer the pH as effectively, resulting in an increase in the HS^- species concentration. This leads to the formation of amorphous CuS and a resulting decrease in copper removal. This is consistent with the trend observed in figure 6. Further experimental work is underway to quantitatively confirm the presence of the various copper-sulphide precipitates and complexes.

4 Conclusions

This investigation has shown that the precipitation of zinc for aqueous solution by a mixture containing sulphide and bicarbonate is dominated by the crystalline ZnS species. Increasing concentrations of bicarbonate ions, the presence of soluble organic acids and particulate organics had no effect on the formation of the ZnS product. The iron and copper systems are increasingly complex and are characterised by the formation of amorphous metal sulphide precipitates and possibly, soluble metal polysulphide complexes. It is proposed that this phenomenon is related to the concentration of specific sulphide species, rather than total sulphide concentration, particularly in the case of copper. The use of anaerobic digester overflow resulted in effective copper and iron precipitation over a wider range of metal to sulphide ratios than with synthetic solutions. This is attributed to the buffering effect of the soluble organic acids, which in turn affects the soluble sulphide speciation. The presence of particulate material in the digester overflow did not significantly effect the efficiency of metal precipitation for any of the metal systems investigated.

Both the empirical model, based on the synthetic system experiments, and the models generated by the software packages accurately predicted zinc precipitation by the anaerobic digester overflow under the experimental conditions. The inability of the software packages to account for the formation of relatively stable amorphous or colloidal precipitates, the absence of accurate thermodynamic data on some species and the fact that the predictions are only able to represent the system at thermodynamic equilibrium, precluded the generation of a model which accurately predicted copper or iron precipitation under the experimental conditions. This was true for both the synthetic and biological systems. While the empirical models were able to account for the formation of amorphous precipitates they could not account for the effects of the organic acids in the digester overflow. Further research needs to be conducted to determine if this factor can be incorporated into the model. Furthermore, the response of the individual metals in a mixed solution needs to be investigated.

Acknowledgements

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