

REACTOR DESIGN FOR METAL PRECIPITATION IN MINE WATER TREATMENT

Report to the Water Research Commission

by

Alison Lewis, Jeeten Nathoo and Thebe Mokone

Crystallization and Precipitation Unit
Department of Chemical Engineering
University of Cape Town

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EXECUTIVE SUMMARY

BACKGROUND

While research to date in South Africa has led to a detailed understanding of the biological sulphate reduction process and the implementation of a potential process, key aspects require further understanding and optimisation for the successful implementation of this technology.

The biological treatment process is partly motivated through its ability to generate easily separable metal sulphide precipitates. However, metal sulphide precipitation is well known to be an extremely difficult process to manage and control. Because of their low solubility, metal sulphide salts inevitably form extremely small particles that are difficult to separate from solution. However, in much of the literature on sulphate reduction processes, the metal sulphide “removal” is cited, without taking into account that the very small size of the solids formed might preclude them from being actually removed from the solution. An example is given below: “The reactor removed more than 97.5% of the initial concentrations of Cu, Zn and Ni, while only >77.5% and >82% of As and Fe were removed, respectively” (Jong and Parry, 2003). It is this issue that is the main focus of this research work.

The main aim of the research was to:

- Understand the fundamental mechanisms in the metal salt precipitation component of the sulphate reducing bacteria process;
- Define the operating conditions to achieve effective metal precipitation in a fluidised bed reactor as an individual unit operation in the sulphate reducing bacteria process.

The secondary aims were to:

- Establish the nature of the relationship between the processing conditions and the reactor performance;
- Develop an understanding of how the processing conditions influence the product characteristics;
- Extend the new approach for supersaturation control to the sulphide/ bicarbonate system.

RESULTS AND CONCLUSIONS

In order to understand the metal salt precipitation mechanisms in the mixed sulphide/bicarbonate system that is characteristic of the sulphate reducing bacteria process, investigations were carried out into metal sulphide precipitation in both a seeded fluidised bed reactor and gaseous hydrogen sulphide bubble column.

- The presence of bicarbonate ions in solution during the process was found to have no effect on the **nature** of the metal precipitate produced and only **metal sulphide** precipitate was formed during the process.
- However, the presence of the bicarbonate ions in solution during the process had a significant effect in **enhancing the precipitation** of metal ions from solution, but this was at the expense of the particle characteristics, since the formation of **fine particles** in solution was found to be **higher** than previously reported.
- It was found that **aggregation** of metal precipitate onto the seeds due to fine-grain aggregation was partly responsible for removal of some metal precipitate from solution. **Settling** of large particles at the bottom of the reactor due to fine-fine aggregation was possibly the main factor responsible for the observed metal removal efficiency.
- Metal ion conversion during **mixed metal** sulphide precipitation is controlled by the pH-dependent solubility of the resulting metal sulphide salts.

- ▣ Removal efficiency of the process for **mixed metal sulphides** is reduced by the poor inter-particle interaction due to the negatively charged surfaces of the individual particles.
- ▣ Metal precipitation in the **bubble column** was found to be accompanied by a rapid drop in pH which caused the solution to become depleted of supersaturation. Thus, particle size enlargement through **aggregation** and/or flocculation **became inhibited**.
- ▣ It was found that the level of supersaturation was ten orders of magnitude lower in the bubble column reactor than in the fluidized bed reactor. However, this **significant decrease in supersaturation** had a **negligible effect** on the particle size of the resulting precipitate.

The implications of this are that, even though metal sulphides are highly insoluble, and thus theoretically able to remove metals and sulphides to very low levels, in practical terms, the particle characteristics are extremely difficult to control.

At this stage, it is clear that, even with the mass transfer limitation introduced by using a gaseous source of sulphide, the supersaturation generated is many orders of magnitude higher than that required for controlled particle characteristics and some other method of particle control is necessary.

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The Reference Group responsible for the project consisted of the following members:

Mr HM du Plessis	:	Water Research Commission (Chairman)
Prof AE Lewis	:	University of Cape Town (Project Leader)
Mr IW van der Merwe	:	Proxa (Pty) Ltd
Mr PJ du Toit Roux	:	Sasol Technology
Mr N Ristow	:	Phatamanzi Water Treatment (Pty) Ltd
Ms L Petrik	:	University of the Western Cape

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1 INTRODUCTION

1.1 Background

While research to date in South Africa has led to a detailed understanding of the biological sulphate reduction process and the implementation of a potential process, key aspects require further understanding and optimisation for the successful implementation of this technology.

The biological treatment process is partly motivated through its ability to generate easily separable metal sulphide precipitates. However, metal sulphide precipitation is well known to be an extremely difficult process to manage and control. Because of their low solubility, metal sulphide salts inevitably form extremely small particles that are difficult to separate from solution. However, in much of the literature on sulphate reduction processes, the metal sulphide “removal” is cited, without taking into account that the very small size of the solids formed might preclude them from being actually removed from the solution. An example is given below: “The reactor removed more than 97.5% of the initial concentrations of Cu, Zn and Ni, while only >77.5% and >82% of As and Fe were removed, respectively” (Jong and Parry, 2003). It is this issue that is the main focus of this research work.

Experimental studies have shown clearly that metal sulphide precipitation requires controlled physicochemical conditions and the control of high levels of supersaturation. Hence it is of prime importance to understand the fundamental mechanisms in force and thus to define the operating conditions to achieve effective metal precipitation. The two reactors of choice for this work are the fluidised bed reactor (using aqueous sulphide) chosen for its favourable solid/liquid separation characteristics, and the bubble column (using gaseous sulphide).

This project used as its focus the sulphate reduction process flowsheet in which the metals are precipitated upstream of the sulphate reduction reactor. The motivation for focusing on this process is the already considerable research effort that has been devoted to the development and understanding of the sulphate reduction and sludge hydrolysis aspects of the process. The motivation for separating out the metal precipitation aspects from the rest of the process is as follows:

- a. The desirability of producing a metal-rich biological sludge as part of a process design is becoming increasingly questionable as disposal regulations and costs become more stringent. In this context, it is preferable to produce a separate, concentrated metal salt precipitate.
- b. The conditions for optimum metal salt precipitation are highly unlikely to be the same as those for optimum sulphate reduction. If each process is to be optimised, it is preferable to separate out the unit operations and optimise each separately.
- c. In cases where the metals contained in the effluent stream have potential value, it would be useful to be able to separate them out from the biological sludge for potential recycle.
- d. In cases where the metals are highly toxic, it is also preferable to be able to concentrate the toxic component of the waste, and thus be able to dispose of it selectively.

2 OBJECTIVES

The primary aim of the research project was to:

- Understand the fundamental mechanisms in the metal precipitation component of the sulphate reducing bacteria process;
- Define the operating conditions to achieve effective metal precipitation in a fluidised bed reactor as an individual unit operation in the sulphate reducing bacteria process.

The secondary aims were to:

- Establish the nature of the relationship between the processing conditions and the reactor performance
- Develop an understanding of how the processing conditions influence the product characteristics
- Extend the new approach for supersaturation control to the sulphide/ bicarbonate system

3 LITERATURE REVIEW

Several processes for the removal of metal ions from industrial wastewater are currently applied, which are based on the precipitation of metal salts. In recent years, the use of biologically produced alkalinity for wastewater remediation, prior to discharge into the environment, has become more prominent. The use of biological treatment techniques is based on the reduction of sulphate by sulphate reducing bacteria (SRB) to produce bicarbonate alkalinity and sulphide ions, both which can be employed to neutralise acidic effluents and effect the precipitation of metal ions from solution as metal sulphides (Kaksonen et al., 2006). Thus far, a significant amount of work has been expended on the development of such treatment processes (van Houten et al., 2000; Kaksonen et al., 2003; Moosa, 2000; Dvorak et al., 1992). However, an understanding of the nature and control of precipitates produced during these processes is still lacking.

Luther et al. (1996), Harmandas and Koutsoukos (1996), Rickard (1995), Mishra and Das (1992) and Bryson and Bijsterveld (1991) studied precipitation of metal ions from solution as metal sulphides. According to these authors, the physics of nucleation and crystal growth processes involved during metal sulphide precipitation process are very complex. These processes are complicated by the fast reaction kinetics and the formation of highly insoluble metal salts (van Hille et al., 2005; Rickard, 1995).

Due to the fast reaction kinetics and the highly insoluble nature of the resulting metal salt, precipitates with small particle sizes and difficult solid-liquid separation characteristics are often formed during metal sulphide precipitation process. Lewis and van Hille (2006), van Hille et al. (2005) and Veeken et al. (2003) showed that such precipitates require controlled physico-chemical conditions. Al-Tarazi (2004) also showed that the reactor type, mass transfer and metal concentration have a considerable influence on the morphology of the particles produced during metal sulphide precipitation. Hence, it is important to understand the fundamental mechanisms involved in the process and thus to define the operating conditions to achieve effective metal precipitation.

In this study, the precipitation behavior and particle evolution during metal sulphide precipitation in a fluidised bed reactor and a gaseous bubble column reactor was investigated using synthetic wastewater solution containing zinc ions. The fluidized bed reactor was employed since classification of the solids in the bed permits for removal of particles with pre-specified size (Nývlt, 1982). On the other hand, gas-liquid mass transfer limitation was employed to limit the rate of metal sulphide precipitation in the bubble column reactor by using gaseous H_2S as the precipitating reagent (Jones and Rigopoulos, 2001).

Metal precipitation experiments were first carried out in a seeded FBR using an aqueous mixture containing sulphide and bicarbonate ions (mixed sulphide/bicarbonate system). For this part of the study, the effect of bicarbonate ions on the nature of the resulting metal salt, conversion and the removal efficiency of the process was investigated. In addition, the manner in which the formed metal salt is removed from solution was explored. In the second part of the study, a gaseous H_2S (in the absence of bicarbonate ions) was used to precipitate metal ions from solution in a bubble column reactor. Subsequently, the particle size results obtained from both the fluidised bed reactor and the bubble column reactor, under different operational conditions, were evaluated to

determine if the change in the level of supersaturation when a gas-liquid mass transfer limitation was employed had any significant effect on the on the particle size of the resulting metal salt precipitate

4 EXPERIMENTAL

4.1 Materials and Methods

All the materials ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, NaHCO_3 and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) used were analytical grade, obtained from Merck and Sigma-Aldrich. Hydrogen sulphide gas used in the bubble column experiments was obtained from Air Liquide and consisted of a gaseous mixture of 10% H_2S and 90% N_2 . De-ionised water from Milli-Q system was used to prepare all the solutions. All the experiments performed in this study were carried out in duplicate.

4.2 Fluidised bed reactor

A continuous laboratory scale fluidised bed reactor consisting of a Perspex column with an internal diameter of 2.5cm and a total height of 160cm was used for this investigation. The reactor was filled to a resting height of 45cm with silica sand (250 – 500 μm) as a seed material. A spherical glass bead was used at the bottom of the reactor to support the seeds and allow for uniform distribution of the upward liquid flow. On either side of the column there were ten equally spaced inlet points directly opposite each other. At the top of the column, there were two outlets which were used for recirculation flow and overflow of the treated water. Table 1 shows the operational conditions used for the experiments. The inlet point for the metal solution was 10cm from the bottom of the reactor and the reagent feed points were placed 30cm apart starting 15cm from the bottom of the reactor.

Table 1: Experimental Conditions

Reactor	Fluidised Bed	Bubble Column
Experiment number	FBR01 and FBR02	
Inlet Zn concentration	150 ppm (2.293 mM)	150 ppm (2.293 mM)
Bed height at zero flow	45cm	
Inlet $\text{Zn}^{2+}/\text{S}^{2-}$ molar ratio	1:1	
Inlet $\text{S}^{2-}/\text{HCO}_3^-$ molar ratio	1:4	
Re-circulation flow rate	220ml/min	
Reagent flow rate	50ml/min	
Zn feed flow rate	50ml/min	
Superficial velocity	0.7470cm/s	
Number of reagent feed points	2FP	
Gas flow rate		300ml/min

Samples were collected from six sampling points placed 20cm apart and starting 30cm from the bottom of the column along the height of the column. Each sampling port was sealed with a rubber septum and liquid samples were withdrawn from the centre of the column using a hypodermic syringe and needle. Two portions of sample (20ml each) were collected from each sampling port during each time interval. The one portion was filtered through a 0.22 μm syringe filter and analysed to determine the dissolved zinc concentration. The other portion was treated by acid digestion before analysis to determine total zinc concentration. During each time interval, samples were also collected from the effluent stream to determine particle size distribution of the fine particles suspended in solution.

4.3 Bubble column

The bubble column reactor was a cylindrical glass column having a total length of 55cm and an internal diameter of 5cm. The column was operated under semi-batch conditions with a single batch of liquid and a continuous flow of gas. The gaseous blend was passed through the reactor by means of an airstone gas distributor fitted to the bottom of the column. The gas flow rate was controlled using a rotameter. Excess H_2S was passed into a NaOH trap before releasing the cleaned N_2 gas. All the experiments were conducted at room temperature and the operating conditions used in these experiments are shown in Table 1. Samples were collected from the reactor during and after the precipitation process to determine metal concentration, total dissolved sulphide and particle size distribution.

4.4 Analytical methods

The metal concentration was determined using a Varian SpectrAA 110, atomic absorption spectrometer in an air-acetylene flame. The sulphide concentration was measured by the methyl blue indicator test (standard analytical sulphide test measurement) using an Ultrospec 110pro to read the absorbance at 670 nm. Morphological and microstructural analyses of the precipitate and the seeds were performed by scanning electron microscopy (SEM). Energy-dispersive X-ray (EDX, employing an EDAX[®] analytical EDX system) and CHNOS thermo analysis were used for semi-quantitative elemental analysis of the formed precipitate. The crystalline phase of the precipitate was determined by XRD. The precipitate used in these experiments was obtained by removing the precipitate-rich liquor from the reactor at the end of each experiment followed by freeze-drying for 48 hrs. The particle size distribution of the suspended precipitate was measured using a Malvern Mastersizer (model: MS S LB). pH was measured using a Microprocessor pH Meter (pH 212) from Hanna Instruments. For the fluidised bed reactor experiments, the pH was measured for each sample while, for the bubble column, the pH was measured using two pH probes mounted to the top and the bottom of the reactor. The measured particle size distributions were analysed using moment transformation to make inferences to particle formation processes (Randolph and Larson, 1988; Bramley et al., 1996).

5 RESULTS

5.1 Fluidised bed reactor

5.1.1 Precipitate characterisation

Since a mixed sulphide/bicarbonate system was used to precipitate the metal ions from solution, the metal salts produced during the experiments were characterised with respect to their chemical composition to determine whether metal sulphide and/or metal carbonates were formed during the process.

The EDX results obtained for the fluidised bed reactor experiments are shown in Table 2. These results are compared in Table 2 with the results reported by Rhadhika et al. (2006) for high purity zinc sulphide and zinc sulphide precipitates produced using biologically produced hydrogen sulphide. The results were found to correspond well with those reported and showed that a zinc sulphide precipitate with a molecular formula of ZnS was the predominantly formed metal precipitate.

Table 2: EDAX analysis of different ZnS particles

Experiment	Sample	Constituent	Weight %	Atomic %
FBR01	SF01-A	O	0.78	2.50
		S	24.68	39.30
		Zn	74.53	58.20
	SF01-B	O	0.77	2.54
		S	20.29	33.51
		Zn	78.94	63.95
FBR02	SF02-A	O	1.31	3.94
		S	30.30	45.59
		Zn	68.39	50.47
	SF02-B	O	0.83	2.67
		S	22.94	37.00
		Zn	76.24	60.32
Rhadika et al. (2006)	High purity ZnS	S	30.60	47.40
		Zn	69.40	52.60
	SRB produced-ZnS	S	30.30	47.00
		Zn	69.70	53.00

To verify the absence of metal carbonates in the formed metal precipitate, the same samples used for EDX analysis were further analysed for C, H, N, O and S content using a CHNOS thermo analyser. The results obtained are shown in Table 3. A carbon content averaging between 0.25 and 1.61 wt% (i.e. negligible) was obtained for all the samples and no oxygen was detected in any of the analysed samples. Although these results are semi-quantitative, they give a reasonable indication that neither metal carbonates (MeCO_3) nor metal oxides (MeO) were formed during the precipitation process.

Table 3: CNHOS analysis results

Element	FBR01		FBR02	
	SF01-A	SF01-B	SF02-A	SF02-B
C	0.5 ± 0.00	0.26 ± 0.01	1.61 ± 0.08	0.25 ± 0.015
H	1.63 ± 0.09	2.05 ± 0.015	1.80 ± 0.075	1.33 ± 0.005
N	-	-	-	-
O	-	-	-	-
S	22.81 ± 0.095	22.55 ± 0.25	22.88 ± 0.05	23.40 ± 0.28

Based on this evidence, X-ray diffractograms of typical sulphides were recorded to determine the crystalline phase of the formed zinc sulphide. According to Roy et al. (2006), zinc sulphide exists in three different crystalline forms, i.e. sphalerite, cubic (zinkblende) and hexagonal (wurzite), all exhibiting different but closely related XRD patterns. Figure 1 shows the XRD spectrum obtained from sample SF02-A. Broad XRD peaks were obtained for all the samples analysed.

According to Jovanović et al. (2007), if the produced zinc sulphide has crystallite sizes in the nanometer range, the XRD peaks broaden. In such cases, it becomes difficult to identify the crystalline phase of the formed zinc sulphide. This is most likely the case for this precipitate. Nonetheless, a comparison between Figure 1 and Figure 2 shows that there is a correlation between the broad XRD peaks.

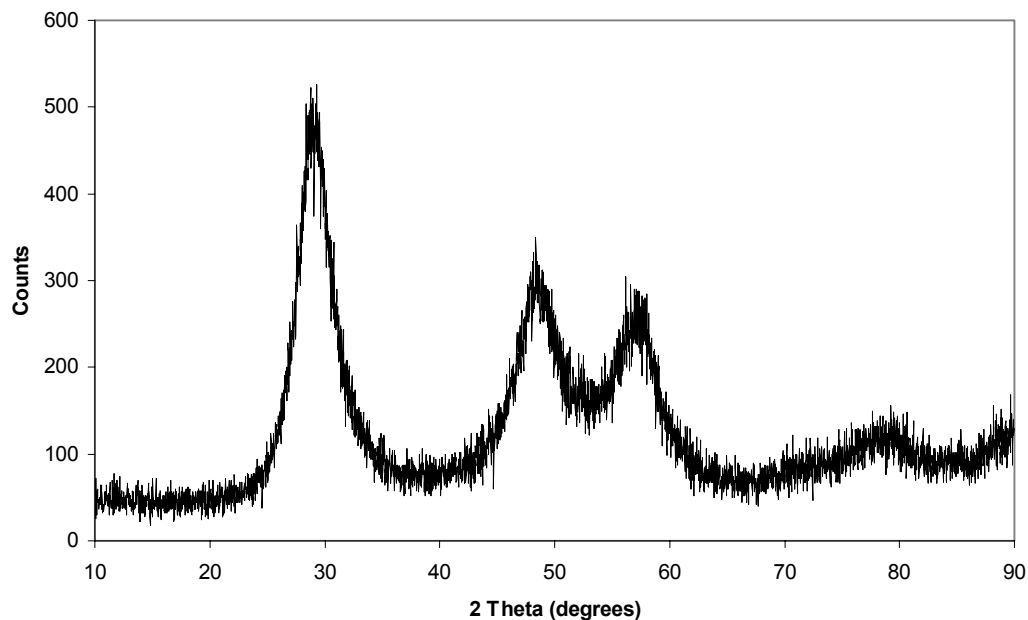


Figure 1: X-ray diffractogram of ZnS precipitate obtained from sample SF02-A.

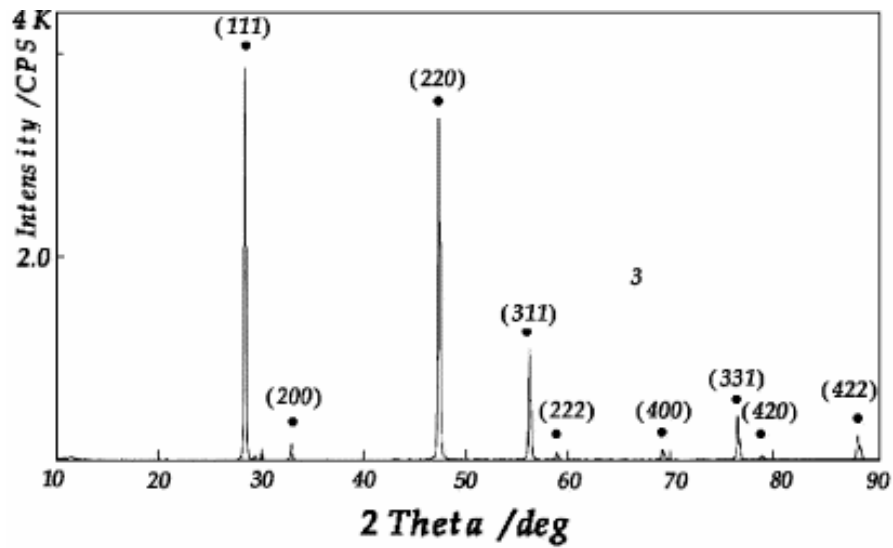


Figure 2: X-ray diffractogram of crystalline sphalerite (Xiao et al., 2003)

5.1.2 Effect of bicarbonate ions on conversion and removal efficiency

Figure 3 shows the results obtained for Zn^{2+} ion conversion, removal efficiency, fines concentration and pH as a function of reactor height. Removal efficiency during metal precipitation in a seeded fluidised bed reactor represents the quantity of metal removed from solution onto the seeds, whilst the conversion represents the total quantity of metal converted into metal precipitate (of any size). The difference between conversion and removal efficiency is the amount of precipitated metal salt which remains suspended in solution and is represented by the fines concentration in Figure 3.

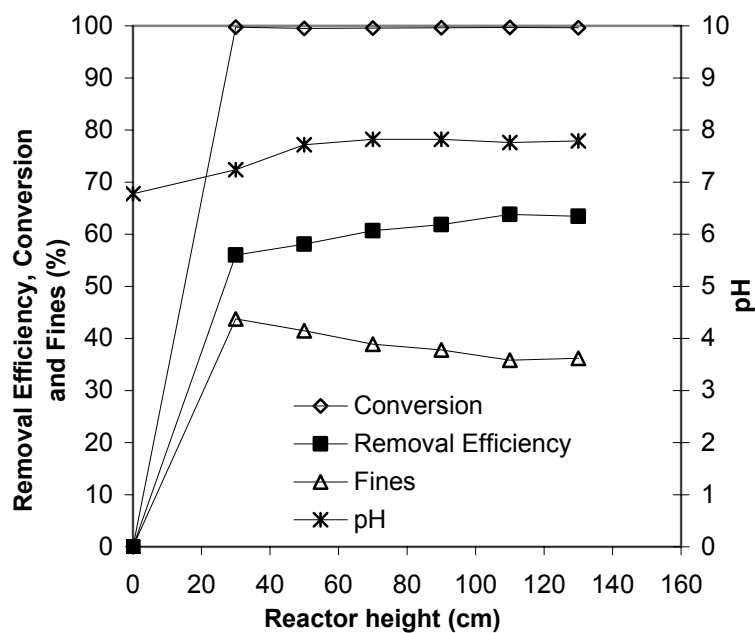


Figure 3: Change in conversion, removal, fines and pH with height of a fluidised bed reactor in a mixed sulphide/bicarbonate system

Contrary to the results reported by van Hille et al. (2005) and Lewis & van Hille (2006) for sulphide precipitation in the absence of bicarbonate ions, where the metal conversion was approximately 90%, a metal conversion of approximately 100% was obtained in this study. According to Karbanee (2007), precipitation of metal ions as metal sulphides from solution is dependent on the availability of HS^- ions in solution, which in turn is dependent on pH. Due to the buffering effect of the bicarbonate ions, the pH of the solution remains relatively unchanged between 7 and 8. Under these conditions, sulphide speciation equilibrium tends towards HS^- ions and therefore precipitation of metal ions as metal sulphides is enhanced. Thus, the increased conversion observed in this study could be attributed to the presence of bicarbonate ions in solution during the precipitation process. Esposito and co-workers (2006) also reported an increase in metal conversion when the concentration of bicarbonate ions in solution was increased in their study.

Although increased metal conversion was observed in this study, this was at the expense of the removal efficiency. The removal efficiency obtained in this study was $\pm 65\%$, as seen in Figure 3. In the studies carried out by van Hille et al. (2005) and Lewis & van Hille (2006), these authors found that the minimum removal efficiency of approximately 58% was obtainable for the highly sparingly soluble metal sulphide, such as copper sulphide, under the conditions of very high supersaturation. On the other hand, when metal sulphide precipitation was carried out under the conditions of lower supersaturation, removal efficiency of up to 70% was obtained for the highly sparingly soluble metal sulphides and up to 80% removal efficiency was obtained for the less sparingly soluble metal sulphides, such as nickel sulphide and cobalt sulphide.

It was concluded that supersaturation has a significant effect on the removal efficiency of the process during metal sulphide precipitation. In addition, these authors found that the metal conversion was linearly related to the level of supersaturation during the metal sulphide precipitation process, but that a change in the level of supersaturation during metal sulphide precipitation in a fluidised bed reactor had little effect on the quantity of fine particles produced. For all their investigations, the amount of fine particles produced remained relatively unchanged at $\pm 15\%$ under different supersaturation conditions.

In this study, however, the amount of fine particles produced was found to be significantly higher at $\pm 35\%$. The observed increase in the amount of fine particles produced was attributed to the enhanced precipitation of metal ions as metal sulphides. When precipitation of metal ions from solution was enhanced, the level of supersaturation generated was also increased and thus, the rate of primary homogeneous nucleation became significantly higher. As a result, the amount of fine particles formed in solution was increased.

5.1.3 Factors responsible for the observed metal removal efficiency

According to Seckler (1994), the metal removal efficiency of the process during metal precipitation in a seeded fluidised bed reactor is a function of the quantity of material precipitated onto the seeds due to fines-grain aggregation and/or settling due to fines-fines aggregation. Guillard et al. (2001) and Costodes & Lewis (2006) studied nickel carbonate precipitation in a fluidised bed reactor. These researchers found that growth of metal precipitate onto the seed was the main factor responsible for the removal of metal

precipitate from solution during metal carbonate precipitation. To determine the factors responsible for metal removal efficiency observed in this study, additional experiments were carried out to determine the extent of metal growth onto the seed. In addition, the change in the number of fine particles leaving the reactor in the effluent stream was monitored over time by measuring the particle size distribution of the suspended precipitate.

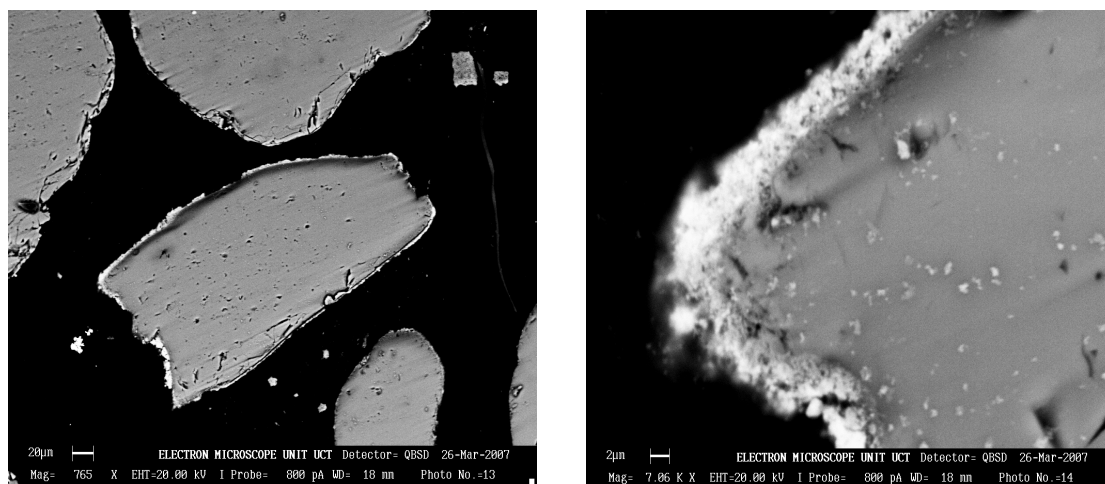


Figure 4: SEM micrograph of ZnS coated sand grain showing poor growth onto the seed surface (thickness of ZnS coated $\pm 2 \mu\text{m}$).

Figure 4 shows SEM micrographs for a cross-sectional view of a metal coated sand grain. The results show a very thin layer ($\pm 2\mu\text{m}$) of metal precipitate on the seed. It is clear that, compared with the coating layer with a thickness of $\pm 5\mu\text{m}$ reported by Guillard et al. (2001) and Costodes & Lewis (2006) for nickel carbonate precipitation, the coating efficiency during this process is not very effective.

When the particle size distribution of the particles leaving the reactor in the effluent stream was monitored over time, it was found that the number of particles leaving the reactor was initially high (before steady state was reached) but that the number decreased significantly after 90 minutes and remained relatively unchanged throughout the process (at steady state), as shown in Figure 6. This behaviour indicates that small particles were initially formed in solution and subsequently underwent secondary particle processes such as aggregation and ageing (Kind, 2002). According to Kind (2002), the behaviour of the initially formed primary particles during precipitation processes is governed by the interfacial forces between them. Judat and Kind (2004) proposed a growth mechanism for sparingly soluble substances, illustrated in Figure 5 that could apply to the metal sulphide precipitates produced in these processes. The residence time in the reactors is probably too short for the ripening to take place and so the mechanism is halted at the self assembled aggregation stage, resulting in final product particles that are composed of aggregates of the fine primary particles.

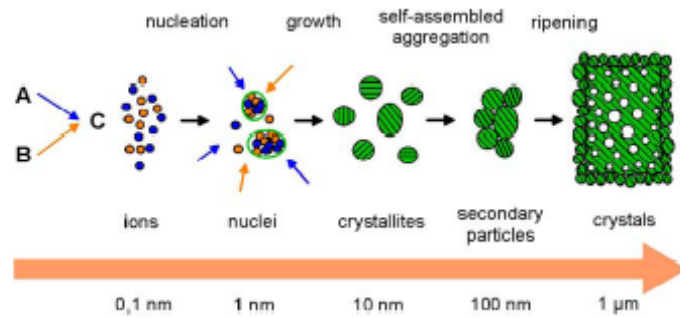


Figure 5: Schematic diagram of the proposed growth mechanism for sparingly soluble barium sulphate (Judat and Kind, 2004)

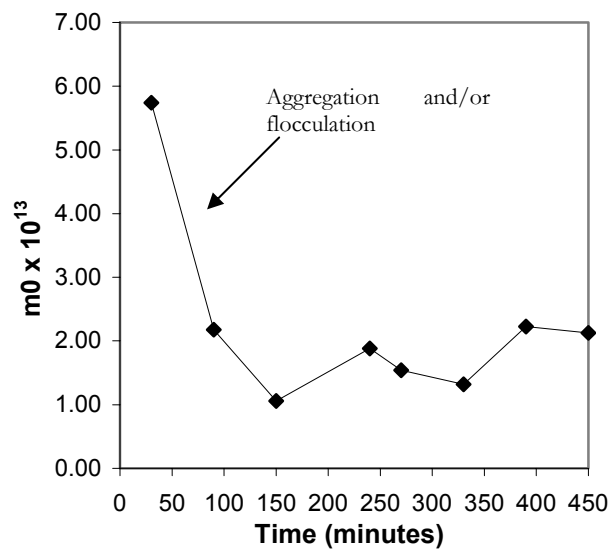


Figure 6: Number of fine particles leaving the reactor in the effluent stream over time

To determine if the secondary particle processes played a significant role during the process, the precipitate that settled at the bottom of the reactor and separated from solution was recovered at the end of each experiment and examined to determine its morphology. Figure 7 shows the SEM micrographs of the recovered precipitate, which clearly show the aggregation of small particles to form larger ones.

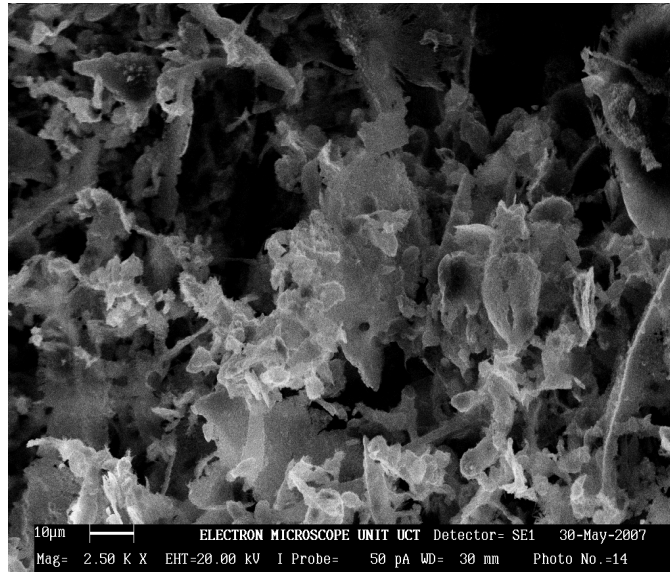


Figure 7: SEM micrograph showing the morphology of the ZnS precipitate recovered from the bottom of the reactor

Based on this evidence, it was concluded that growth of metal precipitate onto the seeds due to fine-grain aggregation was partly responsible for removal of some of the metal precipitate from solution and settling of large particles at the bottom of the reactor due to fine-fine aggregation was probably the main factor responsible for the observed metal removal efficiency.

5.1.4 Mixed metal precipitation

Figure 8 shows the conversion for a mixed metal precipitation process in a fluidised bed reactor. Metal ion conversions greater than 97% was obtained for Fe^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} from the early stages of the process. For Mn^{2+} and Mg^{2+} , on the other hand, very low conversions were obtained in the beginning of the process. Only after the pH rose to above 7.5, did the conversion for Mn^{2+} and Mg^{2+} ions started to increase and continue to increase until to $\pm 85\%$ and $\pm 35\%$ respectively, when the pH was around 8.9. The observed differences in the conversion for the different metal ions can be ascribed to the pH-dependent solubilities of the metal sulphide salts, as illustrated in Figure 9. The MgS salt is soluble over the entire range of pH, and Mg^{2+} is removed as $\text{Mg}(\text{OH})_2$.

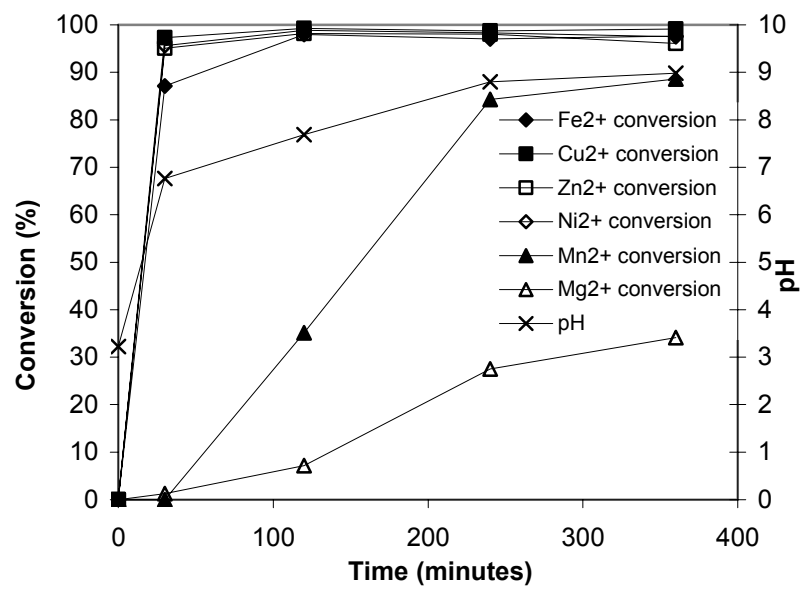


Figure 8: Change in conversion and pH during mixed metal sulphide precipitation in a fluidised bed reactor

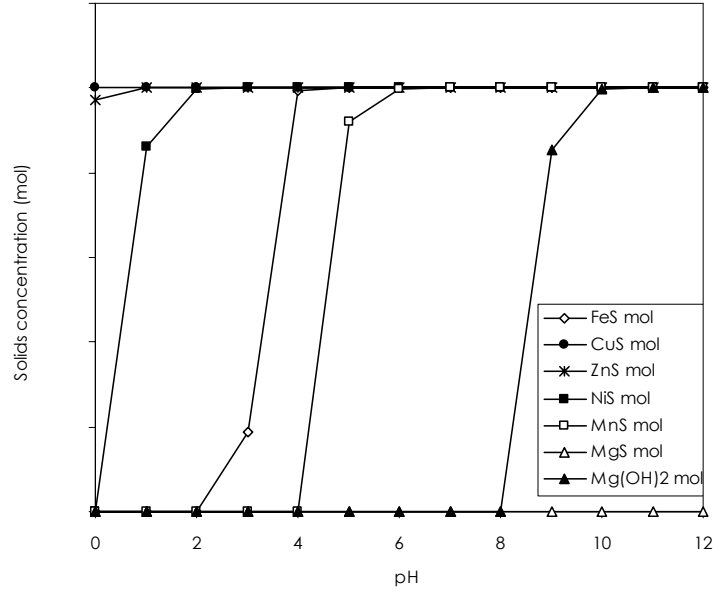


Figure 9: Effect of pH on metal sulphide formation

Although high conversion was obtained for most of the metal ions, the removal efficiency for all the metal ions was very low, as shown in Figure 10. The removal efficiency for Fe^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} ions, which showed conversions higher than 97% from the early stages of the process, was lower than 10% throughout the process. For Mn^{2+} and Mg^{2+} the removal efficiency was also low but slightly higher than that obtained for the other metals.

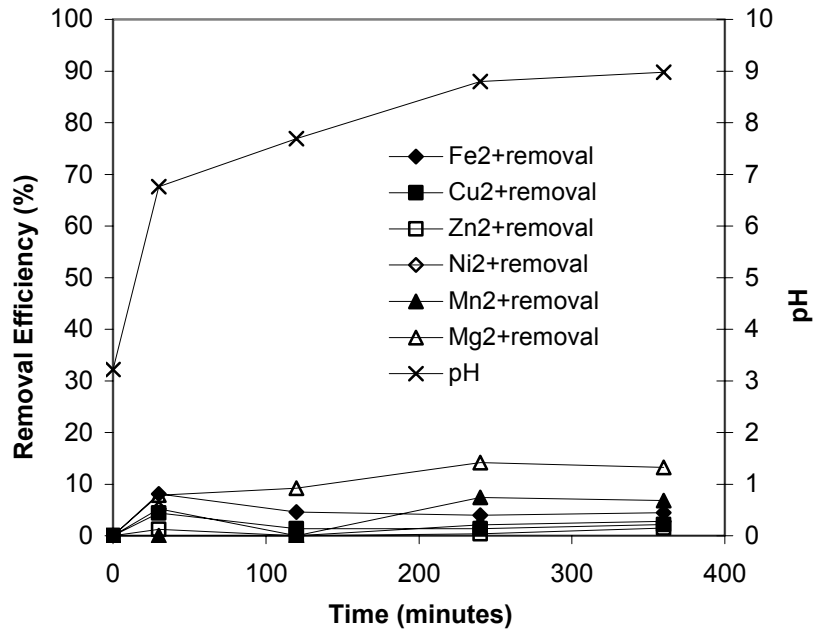


Figure 10: Change in removal and pH during mixed metal sulphide precipitation in a fluidised bed reactor.

Contrary to the single metal precipitation results, which showed a decrease in the number of suspended fine particles due to fine particle size enlargement over time, the particle size of the suspended fine particles for mixed metal precipitation was found to decrease

over time, as shown in Figure 11, where N-25cm, N-55cm, N-85cm, N110cm are the number distributions of particles 25, 55, 85 and 110cm from the base of the reactor respectively.

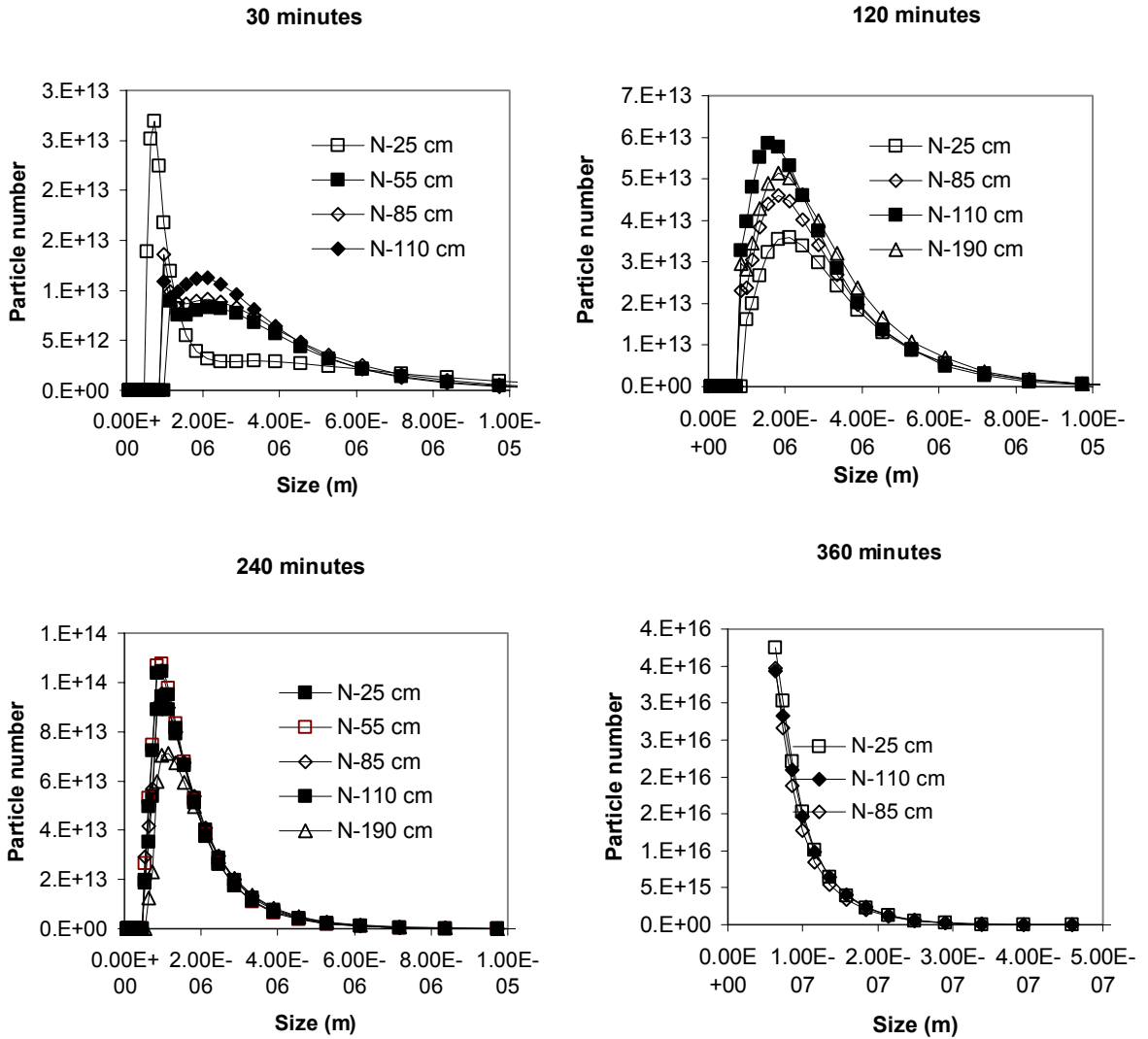


Figure 11: Number distributions of the suspended fine particles over time at each sampling point along the height of the reactor.

Thus, it was hypothesized that the interfacial forces necessary for fine-fine aggregation during mixed metal precipitation were suppressed due to the mixed nature of the precipitate produced during the process. To test this hypothesis, the surface properties of the metal precipitate produced during the single metal precipitation process and the mixed metal precipitation process were investigated using zeta potential measurements. Figure 12 shows the results obtained.

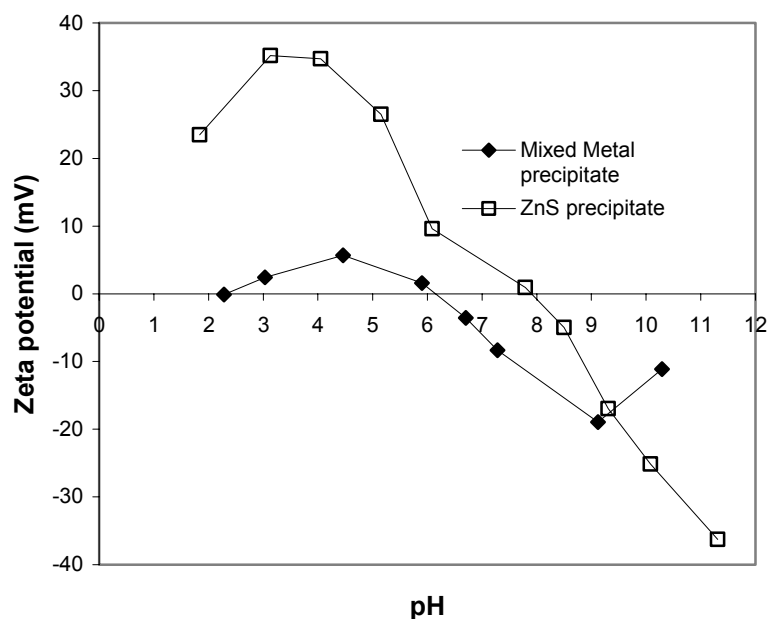


Figure 12: Effect of pH on the zeta potential of the metal precipitate produced from a single metal precipitation process and a mixed metal precipitation process.

For a single metal precipitation process the operating pH was stable at about 7.5 (see Figure 3) and the results in Figure 12 show that the surface charge on the particles at this pH is slightly positive. For the mixed metal precipitation process, when the pH results in Figure 10 and the zeta potential results in Figure 12 are related, the operating pH of the process is found to be higher than the iso-electric point (pH_{iep}) of the metal salt. Therefore the surface of the particles produced during the process is highly charged. According to Laskowski (2007), when the surface of the particles is highly charged the particle become hydrophilic and dispersed. As a result, the low removal efficiency and decreasing particle size observed during mixed metal precipitation can be attributed to the highly charged nature of the resulting particles and segregation as the pH of the process increases over time.

5.2 Bubble column

During the application of SRB in the treatment of metal containing wastewater, hydrogen sulphide may also be used for precipitation of metals by stripping the gas from the biogenic solution and streaming through the metal solution to precipitate metals (Vogel, 1996; Hao, 2000). Thus, the use gaseous H_2S as the precipitating reagent in a bubble column (without HCO_3^- ions) was investigated, to exploit the use of gas-liquid mass transfer limitation to control supersaturation. Figure 13 shows the results obtained for zinc sulphide precipitation.

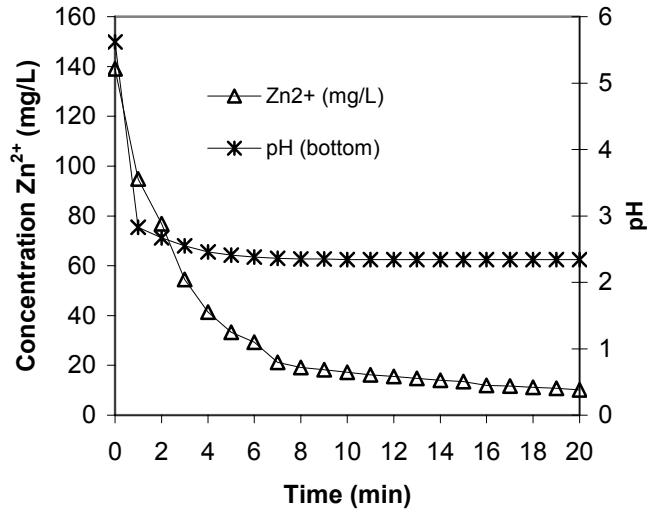


Figure 13: Change in metal ion concentration and pH as a function of time.

Precipitation of metal ions from solution was found to be accompanied by a rapid drop in pH. According to Al-Tarazi (2004), precipitation of metal ions from solution using gaseous H_2S is described by the following reactions:



Due to a release of protons when the equilibrium tends towards the right in Equation (3), the pH of the solution decreases. As the pH of the solution drops, the sulphide speciation equilibrium is reversed and favours aqueous H_2S . When this happens, the availability of the reactive HS^- ions in solution decreases and the reaction between metal ions and HS^- ions is suppressed.

The effect of the observed drop in pH on the change in number of particles is observed in Figure 14.

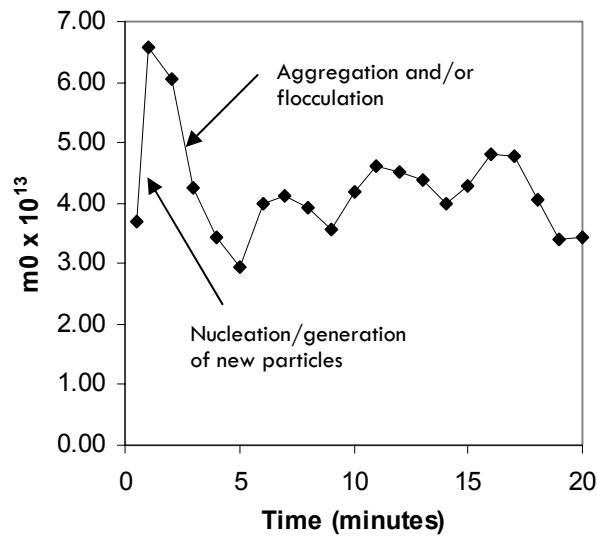


Figure 14: Change in number of particles formed inside the bubble column with time

As the availability of reactive HS^- ions decreases, the amount of supersaturation necessary for birth and growth of particles also decreases. As the pH continues to decrease, the solution becomes depleted of the initially produced supersaturation and aggregation and/or flocculation become inhibited due to lack of the supersaturation required to provide the growth medium for the inter-particle crystalline bridges.

5.3 Effect of operating conditions on particle size

To determine if the use of a gas-liquid mass transfer limitation had any significant effect on the particle size of the resulting metal salt precipitate, the particle size results obtained from both the fluidised bed reactor and the bubble column reactor, under different operational conditions, were evaluated and compared. For both the fluidised bed reactor and the bubble column reactor, the number based mean particle size of the formed precipitate was found to be very small, as shown in Figure 15. The number based mean particle size ranges from $\pm 3\mu\text{m}$ in the fluidized bed reactor to $\pm 2\mu\text{m}$ in the bubble column reactor, as shown in Figure 15. According to Söhnel and Garside (1992), such small particle size is generally associated with dominant primary homogeneous nucleation due to high levels of supersaturation during precipitation processes.

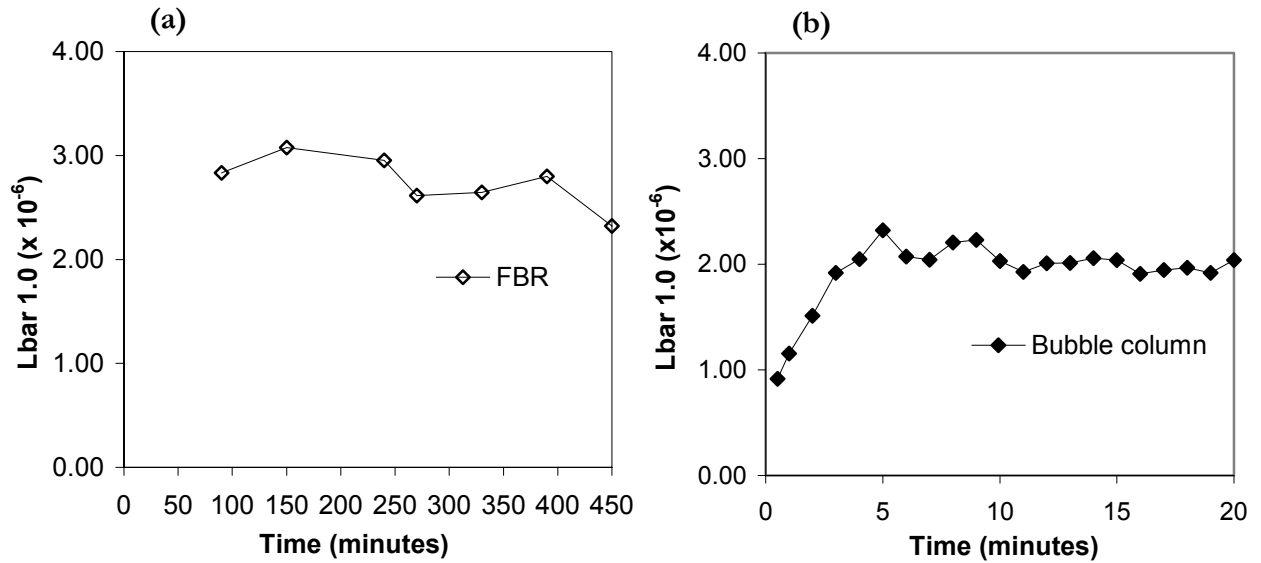


Figure 15: Change in number based mean size as a function of time for (a) fluidised bed reactor at steady state and (b) bubble column.

In this case, when a gas-liquid mass transfer limitation was employed in the bubble column reactor a ten orders of magnitude decrease in the level of supersaturation was observed, i.e. ten orders of magnitude decrease from the level of supersaturation obtained in the FBR. However, there was no significant effect on the particle size of the produced precipitate since the final particle size of the metal salt precipitate produced from both reactors was within the same range, as seen in Figure 15. According to Mersmann (2001), the nucleation mechanism, which is dependent on the supersaturation, may be seen as a direct function of the solubility of the system. At high solubilities (i.e. above 10^{-1} kg/m³), secondary or heterogeneous nucleation dominates. At solubilities below this value the nucleation mechanism changes to homogenous.

Costodes and Lewis (2005), using nickel carbonate, which has a solubility product of $K_{sp} = 10^{-11}$, and Seckler et al. (1996), using calcium phosphate, which has a solubility product of $K_{sp} = 10^{-27}$, studied metal precipitation in a seeded fluidised bed reactor. These authors proposed the use of multiple reagent inlet points along the height of the reactor to control the high levels of local supersaturation created during the process. Based on the evidence that a decrease of ten orders of magnitude in supersaturation from the fluidised bed reactor to the bubble column had no significant effect on the particle size of the formed precipitate, in this study, it is expected that no significant benefit would arise from using multiple reagent inlet points during metal sulphide precipitation process.

6 CONCLUSIONS

- The presence of bicarbonate ions in solution during the process was found to have no effect on the **nature** of the metal precipitate produced and only **metal sulphide** precipitate was formed during the process.
- However, the presence of the bicarbonate ions in solution during the process had a significant effect in **enhancing the precipitation** of metal from solution, but this was at the expense of the particle characteristics, since the formation of **fine particles** in solution was found to be **higher** than previously reported.
- It was found that **aggregation** of metal precipitate onto the seeds due to fine-grain aggregation was partly responsible for removal of some the metal precipitate from solution. **Settling** of large particles at the bottom of the reactor due to fine-fine aggregation was possibly the main factor responsible for the observed metal removal efficiency.
- Metal ion conversion during **mixed metal** sulphide precipitation is controlled by the pH-dependent solubility of the resulting metal sulphide salts.
- Removal efficiency of the process for **mixed metal sulphides** is reduced by the poor inter-particle interaction due to the negatively charged surfaces of the individual particles.
- Metal precipitation in the **bubble column** was found to be accompanied by a rapid drop in pH which caused the solution to become depleted of supersaturation. Thus, particle size enlargement through **aggregation** and/or flocculation **became inhibited**.
- It was found that the level of supersaturation was ten orders of magnitude lower in the bubble column reactor than in the fluidized bed reactor. However, this **significant decrease in supersaturation** had a **negligible effect** on the particle size of resulting precipitate.

The implications of this are that, even though metal sulphides are highly insoluble, and thus theoretically able to remove metals and sulphides to very low levels, in practical terms, the particle characteristics are extremely difficult to control.

At this stage, it is clear that, even with the mass transfer limitation introduced by using a gaseous source of sulphide, the supersaturation generated is many orders of magnitude higher than that required for controlled particle characteristics and some other method of particle control is necessary.

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