3. IRON PHASE (META)STABILITY

3.1 Introduction

Bulk crystallization processes are widely used in the chemical industry to remove wanted and unwanted elements from leach solutions. In hydrometallurgical zinc circuits for example, elements such as iron, cobalt, cadmium, nickel, calcium, copper and lead are all removed in a series of complex precipitation (reaction crystallization), cementation (reduction crystallization) and crystallization processes (cooling crystallization). Even the electroplating process in these zinc-refining circuits can be regarded as a crystallization process, since it requires the same primary and secondary crystallization steps than those encountered in other crystallization processes.

The precipitate quality, expressed in terms of particle size and size distribution, impurity content and solids density, generally influences the economics of an operation as it directly impacts on the cost of down stream processing, loss of pay metals in residue streams and the production of a final product that meets client expectations. Gösele *et al.* [1990] indicated that if crystallization processes are not well controlled, gelatinous and voluminous products are formed which typically have a detrimental effect on down stream processes, such as liquid-solid separation processes, as illustrated in Figure 4.

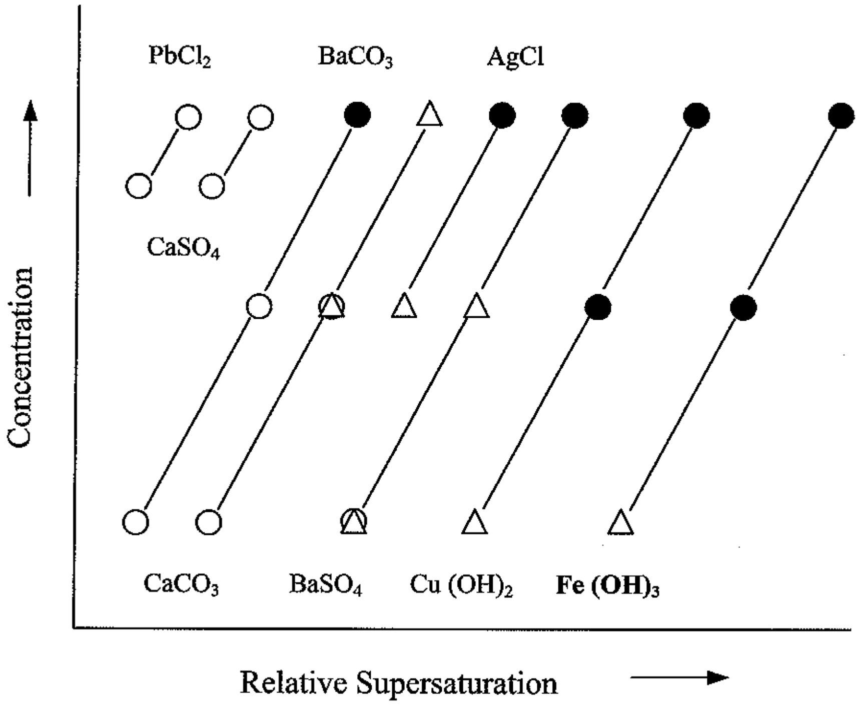

Figure 4. Simplified diagram of precipitation characteristics of various inorganic salts [After Gösele *et al.* 1990]. O = crystalline product, Δ = temporary gelatinous , ● = permanent gelatinous.

It follows from Figure 4 that control over the supersaturation and solute concentration is required to ensure the production of a product with adequate down stream processing potential. This is not a straightforward task, especially when poorly soluble phases, such as ferric iron hydroxides, are produced. Changes in the operating variables, which include temperature, pH and reduction-oxidation potential, supply the driving force, in the form of supersaturation, to crystallization processes and control the solute concentration. These changes not only influence the rate of the primary crystallization steps, i.e. nucleation and growth, but in some instances, such as for example reaction crystallization processes, it also influences the type of mineralogical phase that is produced and its stability. This is specifically the case when iron is precipitated from hot, dilute solutions where dilution is required to lower the solute iron concentration to improve cristallinity of the final product. By varying the pH and temperature, a series of products in the form of different mineralogical phases with different morphologies, particle sizes, size distributions and densities are produced. The different iron phases that could be produced in a sulphate-containing environment as a function of pH and temperature, as suggested by Babcan [1971], are shown in Figure 5.

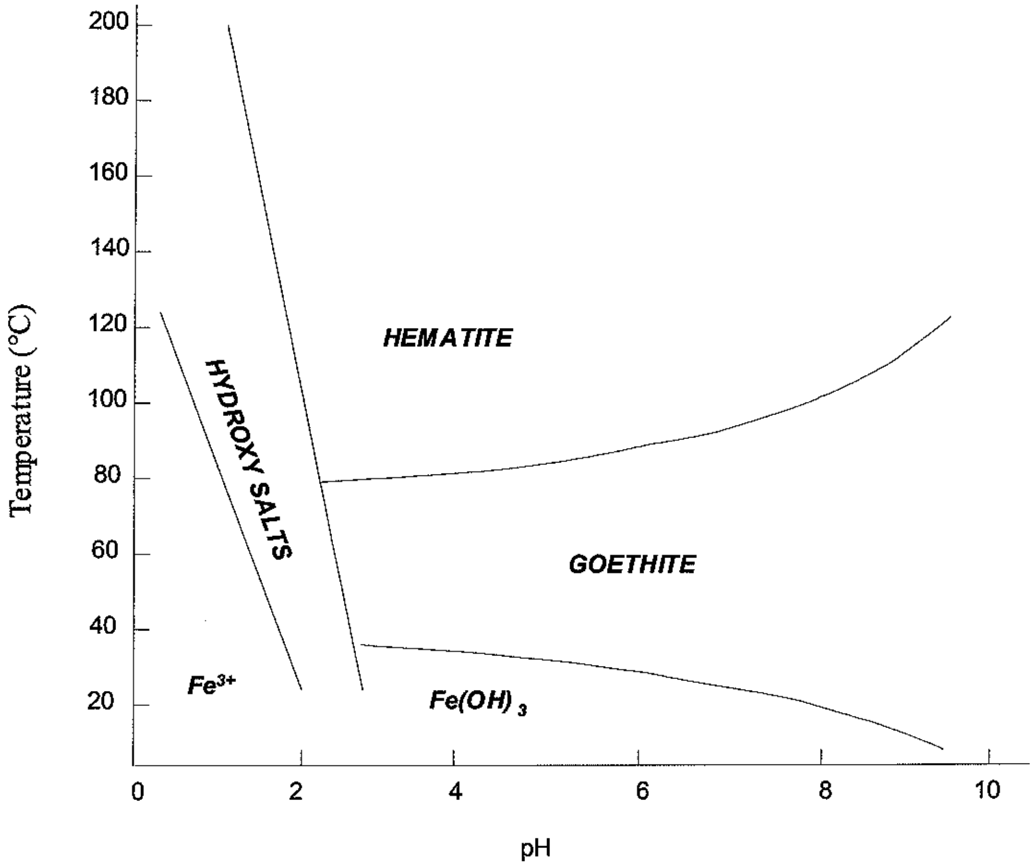

Figure 5. Stability diagram showing the conditions for the precipitation of different iron phases from 0.5 M ferric sulphate solutions [Babcan, 1971]. Hydroxy salts = basic iron sulphates.

The iron phases shown in Figure 5 are all equilibrium phases and therefore do not include metastable or intermediate phases. The equilibrium phases, however, are not always present in industrial iron residues or residues that contain significant amounts of iron. In some environments, it was shown that phases such as ferrihydrite [Jambor and Dutrizac, 1998; Loan *et al.*, 2001] and schwertmannite [Claassen *et al.*, 2002], which are metastable towards goethite, are produced, as discussed earlier.

As was mentioned earlier, temperature and pH not only define the stability of iron phases, as illustrated in Figure 5, but also impact on the kinetics of the precipitation process, due to their influence on supersaturation. The level of supersaturation, and specifically the critical supersaturation, is described by the so-called metastability curve or metastability limit. The metastable zone, which is the region between the solubility curve and the metastability limit, exists due to the activation energy required to form new particles and defines the supersaturation that might be present when no new nuclei are formed. Within this zone, particle growth in the form of molecular growth is favoured. This results in fewer, bigger and denser particles of a uniform size, whereas above the metastability limit, nucleation and agglomeration growth are the dominant processes [Dirksen and Ring, 1991; Kind, 2002]. This also influences the final product quality since agglomerated particles tend to have much larger surface areas.

Therefore, in order to optimize product quality, specifically in reaction crystallization processes, not only the type of species formed and its stability need to be considered, but also the role that supersaturation plays due to its effect on the primary crystallization processes. In the case of iron precipitates, variables such as pH and temperature determine both the supersaturation and the stability of the species precipitated.

Experimental work was done to establish the influence of temperature and pH on the stability of ferrihydrite and schwertmannite, the range of the metastable zone in a seeded environment, product quality parameters and the relative supersaturation.

3.2 Experimental

The experimental work performed comprised three parts. The first part of the study focused on the determination of the metastable zone and the relative supersaturation levels, followed by an investigation into the benefits of stagewise precipitation. Lastly, information was gathered on the influence of specifically temperature and pH on some product quality parameters.

3.2.1 Determination of the metastable zone and supersaturation levels

The experimental arrangement consisted of a sealed, flat-bottomed stirred tank reactor with a diameter (D) of 120mm and working volume of 2L, equipped with four outer baffles. It was stirred with a three-blade marine-type impeller with diameter $d \simeq D/2$ rotating at 1000 rpm. The temperature was controlled within 1°C of the setpoint using a heating mantle and controller.

Experiments were conducted at temperatures of 50, 70 and 90°C and at pH values ranging from 1.5 to 3.5. For each experiment, a solution containing 5 g/L sulphuric acid and about 11.5 g/L Fe as $Fe_2(SO_4)_3$ was prepared. The pH was raised manually at a rate of approximately 0.5 units every 20 minutes on the forward cycle using $Ca(OH)_2$ powder (pH range 1.5 to 2.5) and ZnO powder (pH range 2.5 to 3.5). On the reverse cycle (pH 3.5 to pH 1.5), 98% sulphuric acid was added drop wise to lower the pH at the same rate mentioned above. Each experiment was repeated at least three times. Samples were taken at regular pH intervals, except over the critical pH range, where the critical supersaturation level was exceeded, where samples were taken more frequently. Approximately 10 mL solution was extracted during the sampling process. Each sample was immediately filtered and the extracted solution was analysed for ferric iron concentration and pH. Distilled water and chemicals of CP grade were used in all experiments.

3.2.2 Stagewise precipitation

The experimental setup used comprised three crystallizers in series, each with an active volume of 3.96L and an inside diameter of 16cm. Each reactor was equipped with four outer baffles fixed to the wall of the vessel, a riser box and overflow launder, as shown in Figure 6.

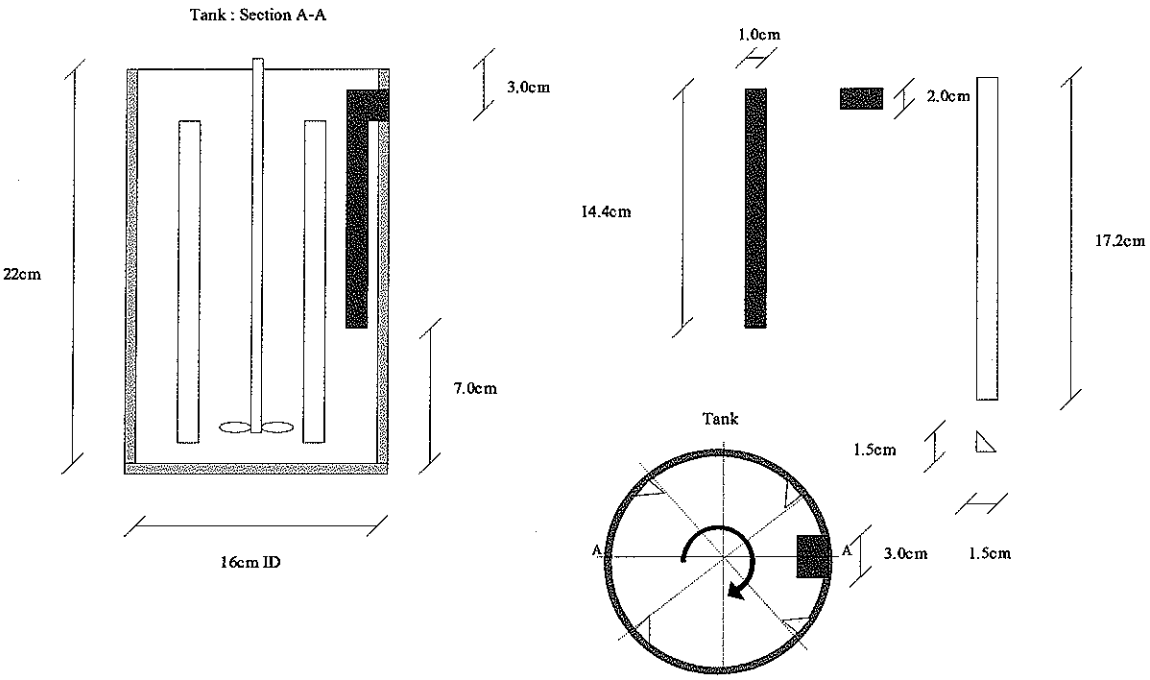

Figure 6. Dimensions of the crystallizer used to determine the influence of stagewise precipitation on product quality.

Three-blade marine type impellers, with diameters d $\simeq$ D/2.5, were used at a stirring rate of 600 rpm to keep the solids in suspension. Table 3 gives a summary of the experimental conditions used to determine the influence of stagewise precipitation on product quality parameters.

Table 3. Experimental conditions used to determine the influence of stagewise precipitation on product quality.

	Parameter		Flow	
Experiment	Temperature (°C)	pH profile	Iron solution (mL/min)	Calcine slurry (mL/min)
Base case	65	3.20	26.9	41.1
		3.31	***	***
		3.39	***	***
1	65	3.20	26.9	41.1
		2.80	1.33	***
		2.94	***	***
2	65	2.50	29.0	36.1
		3.00	***	2.5
		3.09	***	***
3	65	2.50	26.9	45.0
		2.74	***	***
		3.01	***	0.8

The hot iron solution contained 5 g/L free acid and 15 g/L iron, added as $Fe_2(SO_4)_3$. Roasted zinc calcine, in the form of a 7.5% calcine slurry prepared with distilled water, was used as neutralising agent. The calcine used had a d_{50} value of about 38µm and ZnO content of approximately 70%. In all experiments the calcine slurry and hot iron solution were pumped continuously to the first of three reactors in series to control the pH at the predetermined setpoints. The two streams were placed on opposite sides of the reactor with the outlet points positioned just below the agitator blades. Hot iron solution and ZnO slurry were also pumped on separate lines to reactors 2 (Experiments 1 and 2) and 3 (Experiment 3), respectively, to adjust the pH values as indicated in Table 3.

Samples of 250 mL each were taken from reactor 3 at the end of each experiment, which lasted for about three hours, and immediately filtered. The solution samples were analysed for pH and ferric iron concentration. The filter cakes were weighed and dried to determine the moisture content and analysed for zinc and iron. The dry solids density of each sample was also determined. Wet filter cake samples were taken and mixed with distilled water to determine particle size and size distribution using a Malvern particle size analyser.

3.2.3 Determination of the influence of temperature and pH on product quality

In order to determine the influence of pH and temperature on product quality parameters such as cake moisture content, particle solids density, particle impurity content (zinc and sulphate) and particle size, the sealed glass precipitator with an active volume of 2L, mentioned earlier, was used in a continuous mode. Hot iron solution containing 5 g/L free acid and 10 g/L iron, added as $Fe_2(SO_4)_3$, as well as a 2.5% ZnO slurry were continuously pumped to the reactor using peristaltic pumps. All the reagents used were of CP grade.

The outlet points of the reactant streams were placed just below the agitator blades on opposite sides of the vessel. The level in the reactor was controlled with another peristaltic pump. The flow rate of ZnO slurry varied with a change in the pH setpoint as summarised in Table 4.

Table 4. Average hot iron solution (HIS) and ZnO slurry flow rates used to precipitate iron at different pH setpoints.

pH	HIS flow rate (mL/min)	ZnO slurry flow rate (mL/min)
1.8	21.1	< 1
2.2	21.1	10
2.6	21.1	14
3.0	21.1	16
3.4	21.1	17

Experiments were performed at temperatures of 50, 60, 70 and 80°C. Each experiment ran for three hours and was repeated at least three times. At the end of each experiment, two 250 mL samples were taken. The first sample was filtered and dried at 120°C for one hour to determine the cake moisture content. The other sample was filtered and the cake washed with 1 L of hot water. The filtrate extracted prior to the hot water wash, was analysed for ferric iron and pH. The washed filter cake was again dried at 120°C for one hour, analysed for zinc and sulphate and the dry solids density determined.

Wet filter cake samples of about 5 mL each were also taken and mixed with distilled water at ambient temperature to determine the product mean particle size and size distribution using a Malvern particle size analyser.

XRD analyses were also performed on the dried, washed filter cake. Cu-Kα radiation at a wavelength of approximately 0.154 nm was used.

3.3 Results and discussion

3.3.1 Iron phase (meta)stability and the role of the supersaturation level in iron precipitate product quality

3.3.1.1 Determination of the metastable zone

In order to develop a (meta)stability diagram for iron precipitated from a ferric iron solution under industrial conditions and to calculate typical supersaturation levels present during this process, the metastability zone for iron precipitation had to be determined first. This was done using a method of cycling the pH between a lower and higher limit at different temperatures. The ferric iron concentration as a function of pH at a specific temperature was then plotted, as shown in Figures 7 to 9 (also see Appendix 1). The critical pH values for nucleation (A) and solubilisation (B) were then determined by extrapolation of the slope of the ferric concentration versus pH line to the initial ferric concentration.

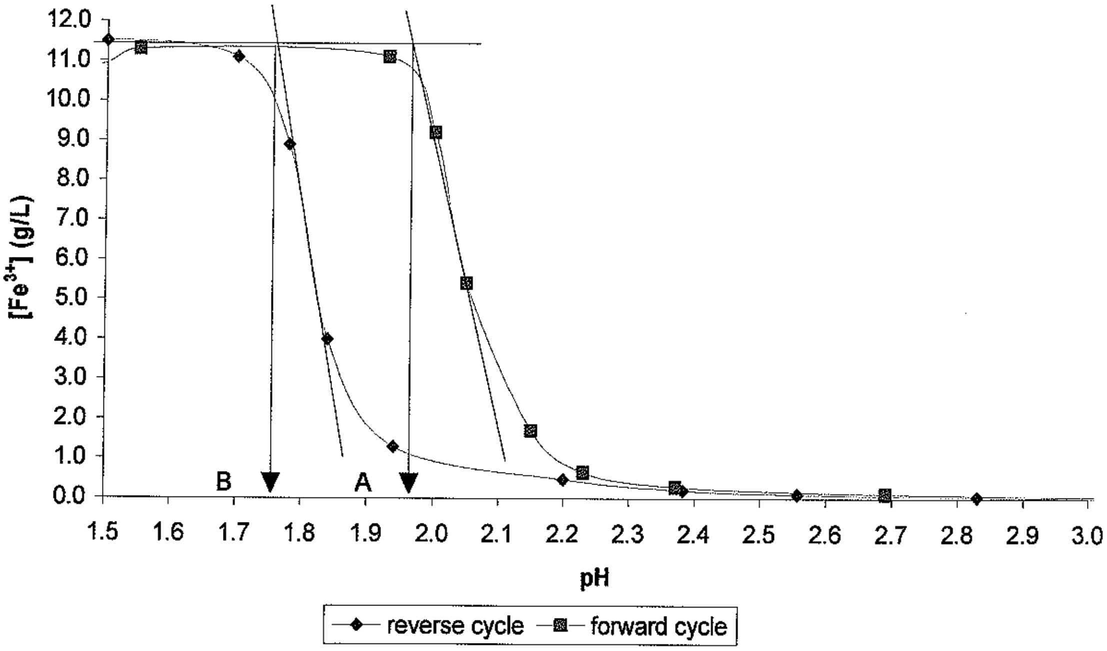

Figure 7. Average ferric iron concentration as a function of pH determined at 50°C. The pH was changed stepwise in increments of 0.5 pH units every 20 minutes. The pH was increased by adding $Ca(OH)_2$ and ZnO powder and decreased by adding 98% H_2SO_4. The total sulphate concentration varied between 0.2 and 0.25 moles/L.

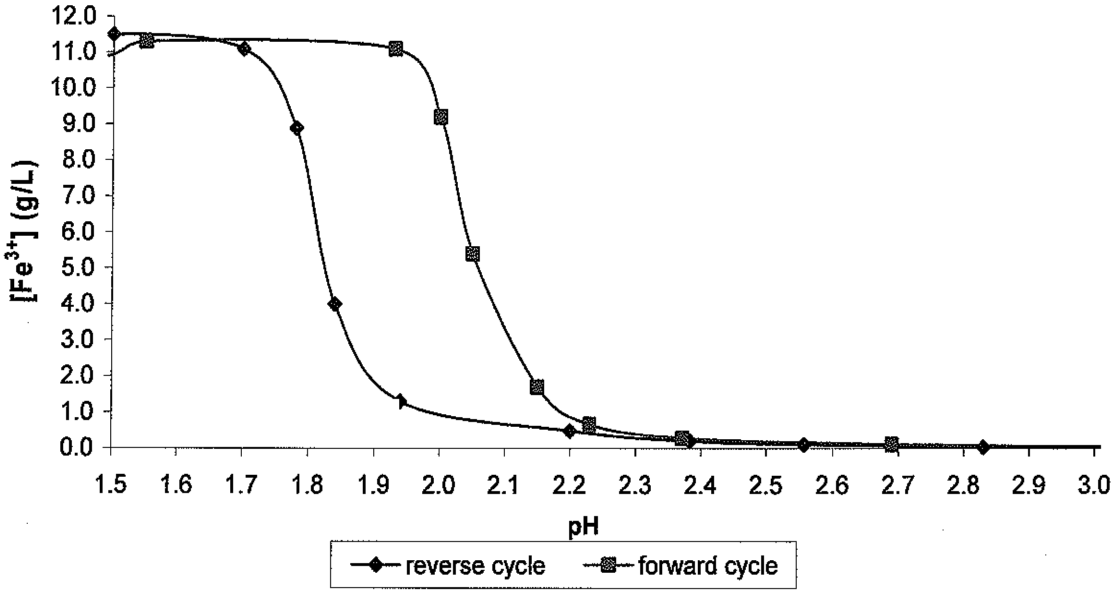

Figure 8. Average ferric iron concentration as a function of pH determined at 70°C. The pH was changed stepwise in increments of 0.5 pH units every 20 minutes. The pH was increased by adding $Ca(OH)_2$ and ZnO powder and decreased by adding 98% H_2SO_4.

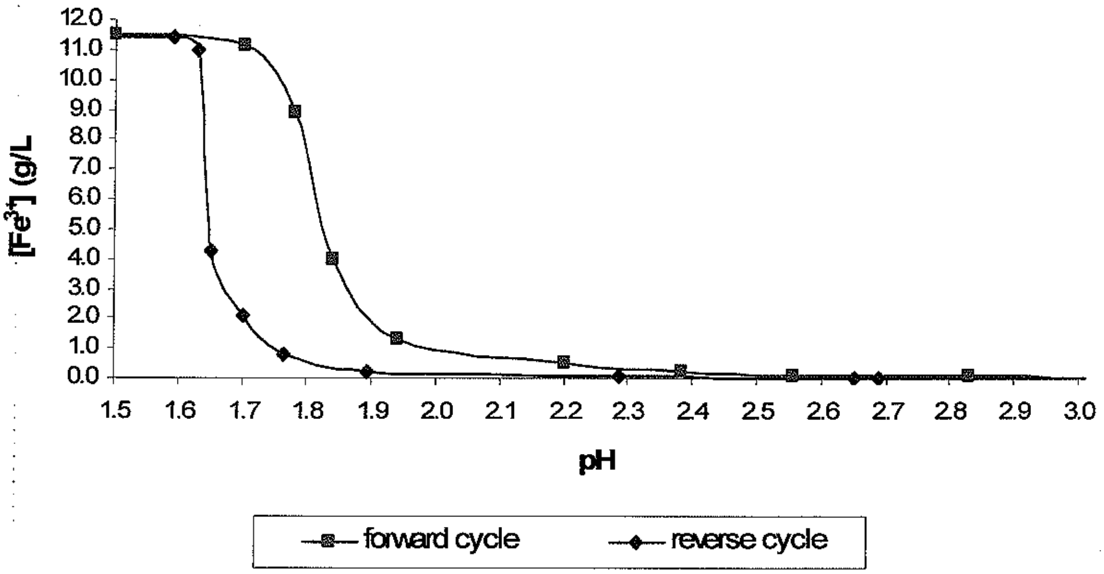

Figure 9. Average ferric iron concentration as a function of pH determined at 90°C. The pH was changed stepwise in increments of 0.5 pH units every 20 minutes. The pH was increased by adding $Ca(OH)_2$ and ZnO powder and decreased by adding 98% H_2SO_4.

From the data presented in Figures 7 to 9, the critical pH values of nucleation (e.g. point A, pH ≈ 1.97, Fig. 7) and solubilisation (point B, pH ≈ 1.76, Fig. 7) were determined. The critical pH values for nucleation and solubilisation, defining the boundaries of the metastable zone as a function of temperature, are shown in Figure 10.

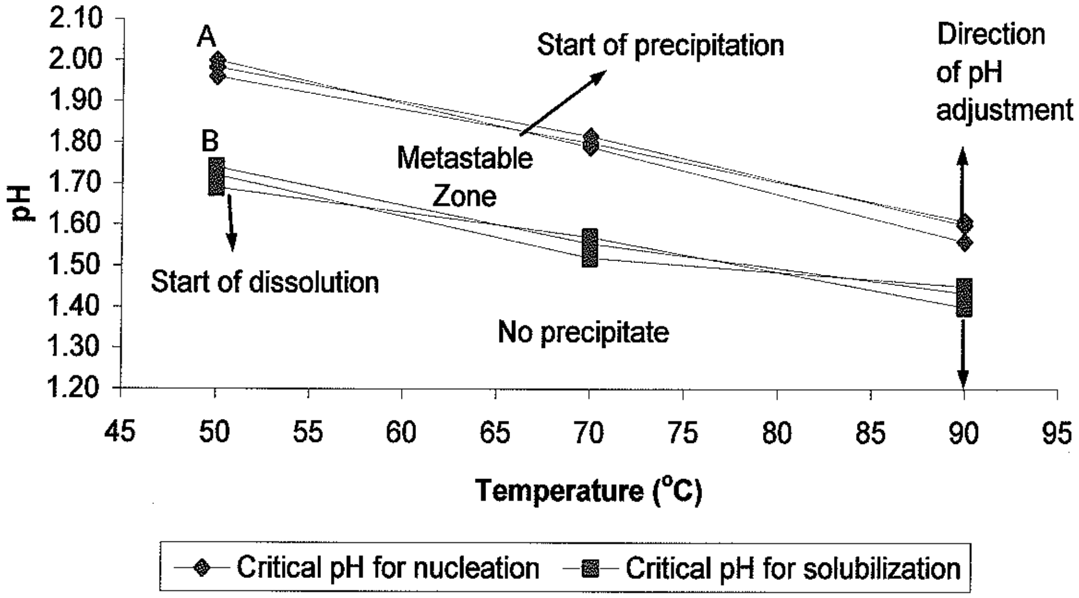

Figure 10. Illustration of the metastable zone determined for the precipitation of iron from a ferric iron solution containing approximately 11.5 g/L Fe as $Fe_2(SO_4)_3$ and 5 g/L H_2SO_4. The pH was varied using $Ca(OH)_2$ and ZnO powder, and 98% H_2SO_4 .

According to the definition of the metastable zone, the equilibrium solubility limit forms the lower boundary of the metastable region. However, the width of the metastable region may be reduced by an increase in temperature, the presence of isomorphic and anisomorphic material [Garside *et al.*, 1972 and Mullin and Ang, 1976] and a mixing intensity such as the 1000 rpm used. When the solubility limit determined in this study (Figure 10) is compared with the equilibrium solubility limit, the reduction in the width of the metastable zone is evident, as shown in Figure 11. STABCAL^{TM} software with the available NBS-database was used to calculate the equilibrium $[Fe^{3+}]$ solubility line X (refer to Appendix 2) and the data for line Y was taken from the literature [Cornell and Schwertmann, 1996]. Lines X and Y show the equilibrium solubility of goethite, which is the equilibrium phase for ferrihydrite and schwertmannite, as a function of pH. It is clear from Figure 11 that there is reasonable agreement between the two lines for pH values smaller than about 3.0. In this study iron concentrations reflected by line X was used for the calculation of the relative supersaturation, as will be shown later.

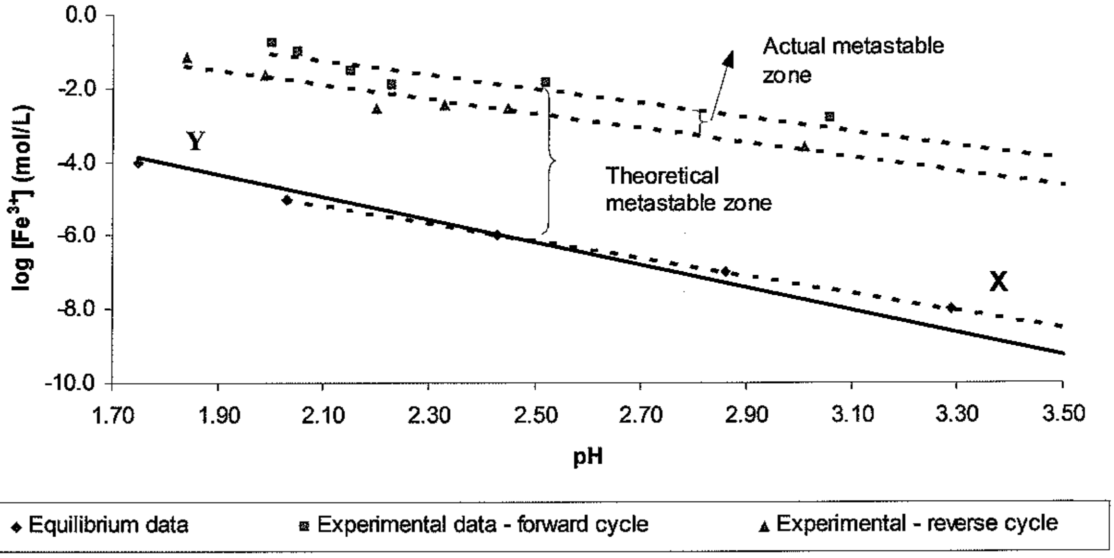

Figure 11. Ferric concentration as a function of pH for the precipitation of iron at 50°C from a ferric iron solution containing approximately 11.5 g/L Fe as $Fe_2(SO_4)_3$ and 5 g/L H_2SO_4. The pH was varied using $Ca(OH)_2$ and ZnO powders, and 98% H_2SO_4. The experimental reverse cycle line forms the new solubility limit.

It follows from Figure 11 that a high degree of supersaturation is required to initiate precipitation and that the relatively small metastable zone of between 0.2 and 0.3 pH units (from Figure 10), would require precise control to achieve good precipitate properties. Claassen *et al.* [2003(b)] have shown that iron removal processes are frequently operated at pH values above the metastability limit. This results in an increase in the supersaturation levels, which in turn leads to an increase in the nucleation rates with resultant finely divided, poorly crystalline particles, which tend to agglomerate [Dirksen and Ring, 1991] to give a final product with relatively high impurity levels. Furthermore, the choice to utilise the metastability limit to improve product quality is influenced by factors such as the co-precipitation of other phases, i.e. phases resulting from the presence of silica in some industrial hot iron solutions, the value of the product being removed, as recycling has a cost implication, the reduction in the concentration of oxygen or gaseous reagents at low pH values (goethite iron removal process) and the need to precipitate a specific iron phase, such as ferrihydrite, that is stable only at higher pH values.

Therefore, although the metastable zone might be useful in the chemical industry, i.e. in the production of pigments, the factors mentioned above need to be considered in metallurgical processes. It nonetheless, provides useful information that could be used to improve product quality in some iron removal processes. Firstly, it could act as a control reference point to lower supersaturation in an iron precipitation process, and/or it could be used to calculate typical supersaturation levels in a specific application, as illustrated in the following paragraphs. Secondly, it could be used to illustrate why stagewise precipitation [Demopoulos, 2003] could improve iron precipitate product quality. Generally, the solute concentration changes stepwise with a step change in temperature (cooling crystallization) or pH (reaction crystallization) within the metastable region. By using the same principle, even at conditions outside the metastable zone, it was shown that product quality could be improved as discussed later.

3.3.1.2 Determination of supersaturation and the (meta)stability diagram

The relative supersaturation present during a precipitation process typically determines the quality of the precipitate, with poorer quality precipitates being formed at high levels of supersaturation. The relative supersaturation (σ) present during the precipitation experiments were calculated using the minimum concentration required to initiate precipitation substituted in equation 4, and shown in Figure 12 as a function of pH and temperature.

$$\sigma = (c - c_{eq})/c_{eq} = \Delta c/c_{eq} \qquad .....4$$

Where: c = actual solute concentration (mol/L)

c_{eq} = equilibrium solute concentration (mol/L)

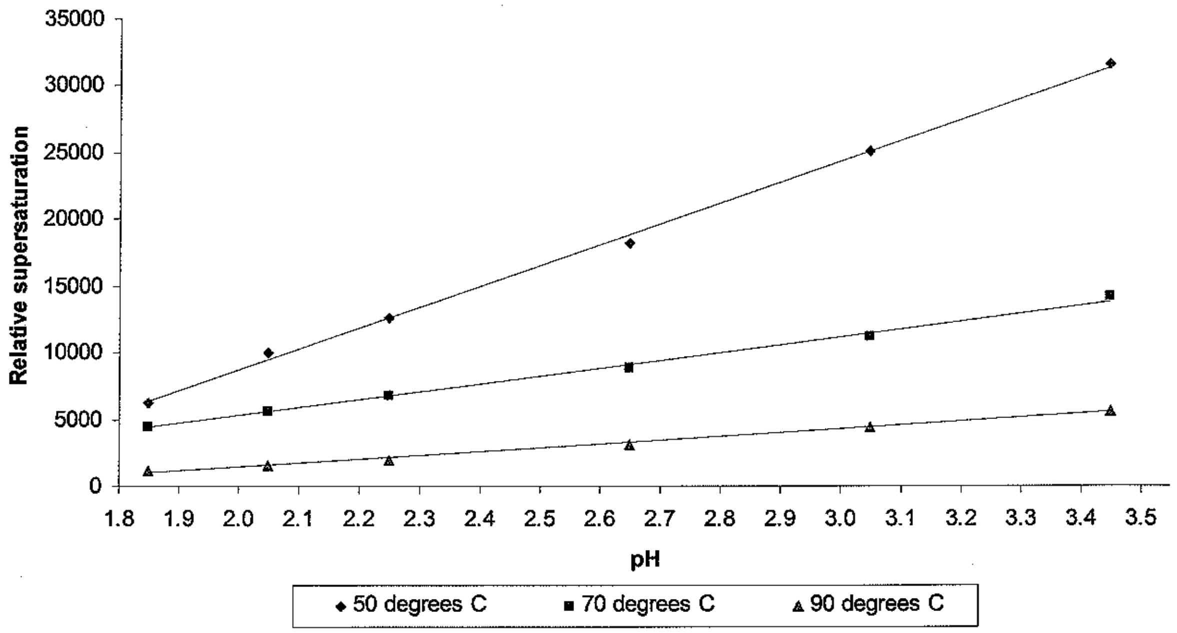

Figure 12. Relative supersaturation required as a function of pH at different temperatures for the hydrolysis of ferric iron from iron solutions containing approximately 11.5 g/L Fe added as $Fe_2(SO_4)_3$ using $Ca(OH)_2$- and ZnO powder to control the pH.

From Figure 12 it is clear that lower degrees of supersaturation are required for precipitation of iron at higher temperatures and lower pH values. Better quality precipitates could thus be expected for such conditions. This was indeed found to be the case in previous work [Claassen *et al.*, 2002] where open structured ferrihydrite was produced at a temperature of 65°C and a pH of 3.2, compared to more dense schwertmannite, obtained at 65°C and a pH of 2.7, as shown in Figure 13.

Figure 13. SEM backscattered image of an iron bearing particle, showing open structured ferrihydrite particles (Particles A) covered with a more dense structured schwertmannite layer (Portion B) [Claassen *et al.*, 2002].

The zones for metastable iron precipitates may be defined in terms of temperature and pH by considering the chemical analyses, in the case of the hydroxy salts, and XRD analyses, in the case of ferrihydrites, and are shown as Figure 14.

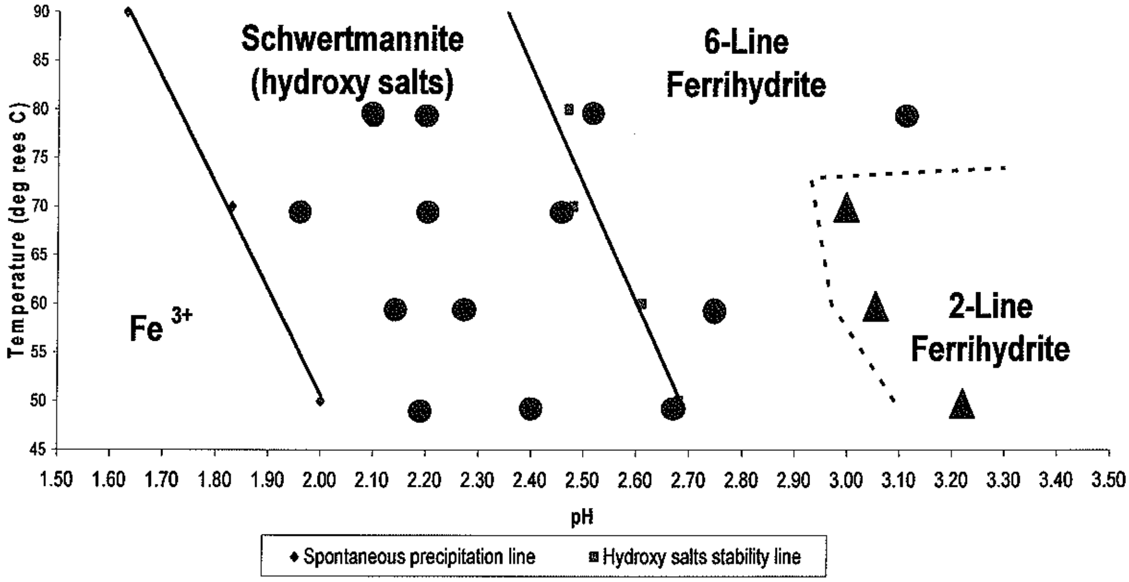

Figure 14. Metastability diagram for ferric iron hydrolysis from a 10 g/L Fe (added as $Fe_2(SO_4)_3$ solution) using ZnO powder to control the pH. ●= 6-line ferrihydrite and schwertmannite and ▲ = 2-line ferrihydrite obtained from XRD analyses. The total sulphate concentration varied between 0.2 and 0.25 moles/L during all experiments.

In Figure 14, the boundary between the hydroxy salts (schwertmannite) and ferrihydrite was obtained by washing the precipitates produced in the continuous reactor with hot water, and noting the conditions where the sulphate content started to rise, as indicated in Figure 15.

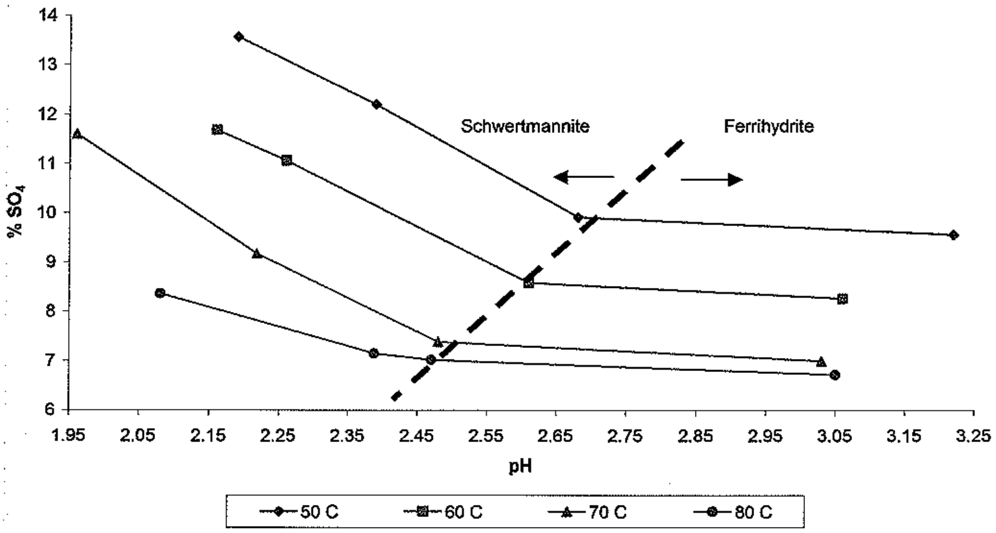

Figure 15. Influence of pH and temperature on the sulphate content of iron precipitated from a hot iron solution containing 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder to control the pH in a continouos reactor.

The different iron phases and their crystallinity were identified using XRD analyses. The data obtained for the 60°C isoterm are summarized in Table 5.

Table 5. X-ray diffraction results obtained from synthetic iron precipitate samples produced in a continuous reactor at 60°C.

pH	d-values (nm)		
	Schwertmannite	2-line ferrihydrite	6-line ferrihydrite
3.06		Uncertain	
		Uncertain	
		0.2561	
		Very weak	
		Very weak	
		0.1506	
		Very weak	
2.75			0.5033*
			0.3323*
			0.2554
			0.2219
			0.1927
			0.1702
			0.1510
			Very weak
2.16	0.4895		
	0.3423		
	0.2526		
	0.2214		
	0.1940		
	0.1648		
	0.1517		
	Very weak		

* Indicate presence of schwertmannite

The data obtained in Table 5 is in good agreement with work done by Bigham *et al.* [1990], Jambor and Dutrizac [1998] and Claassen *et al.* [2002].

The determination of the schwertmannite (meta)stability region at elevated temperatures is unique as it has previously only been identified in natural environments [Bigham *et al.*, 1990, 1994, 1996]. It also appears from Figure 15, as if there is a definite hydroxy salt/schwertmannite phase transition line, as indicated in Figure 14, which supports the notion of schwertmannite as a separate phase, rather than being ferrihydrite with adsorbed sulphate. In the temperature range 50°C to 90°C, this transition line is between 0.1 and 0.2 pH units above the line reported by Babcan [1971] who worked at 0.5 M $Fe_2(SO_4)_3$ (refer to Figure 5). It is known that the stability regions for iron oxide and oxy-hydroxide phases are extended to lower pH values due to the presence of high sulphate levels. This is a result of the formation of iron sulphate complexes and buffering of the pH. The latter is caused by the combination of free H^+ ions with bisulphate ions. The net effect is that oxide and oxy-hydroxide iron phases are stable at higher free acid concentrations.

It appears from Figure 15 rather as if both ferrihydrite and schwertmannite contain variable amounts of sulphate, which probably result from a change in morphology, with a change in pH and temperature, and the increased stability of ferrihydrite with an increase in pH and temperature, above the hydroxy salt stability line. If the data in Table 5 is considered, it appears as though schwertmannite is also present at pH values above the hydroxy salt stability line (6-line ferrihydrite region), as indicated by the presence of peaks at approximately 17 and 27 2θ, which are not well defined in the case of ferrihydrite, as shown in Figure 16.

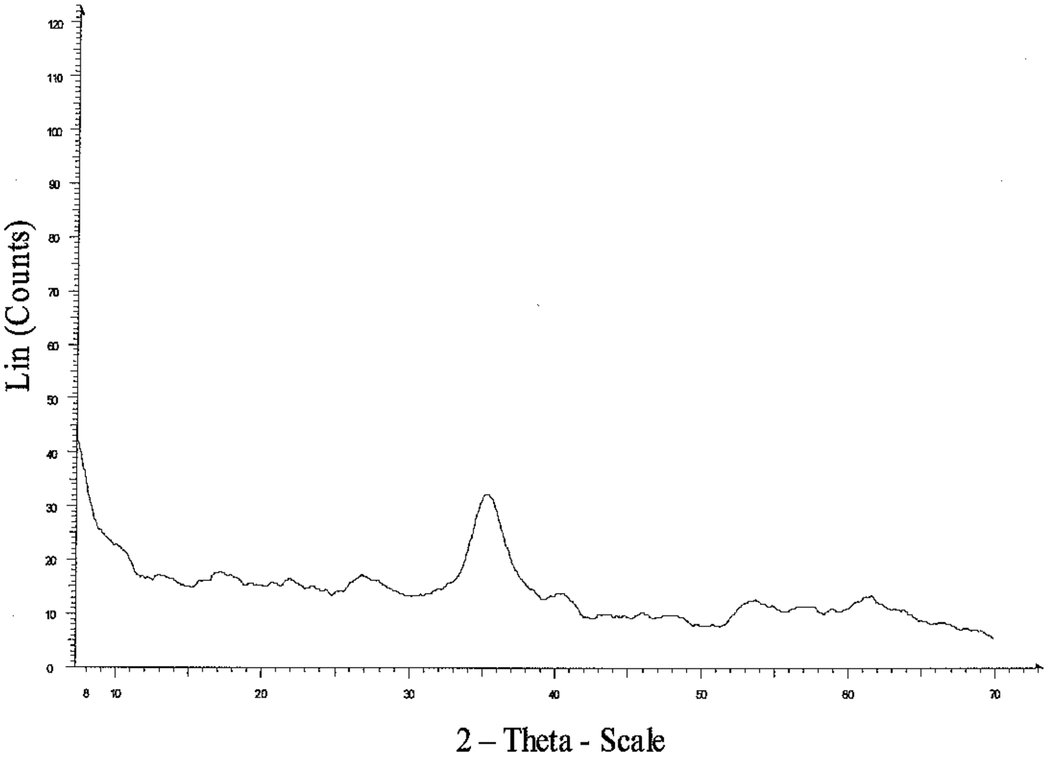

Figure 16. X-ray diffractogram of a poorly crystalline synthetic iron precipitate produce at 60°C and a pH of 2.75 in a continuous crystallizer.

The stability of iron hydroxy sulphates in the acidic pH region stems from the presence of species such as $FeSO_4^+$ in iron sulphate media, that is believed to play an important role in the formation of these phases [Ashurst and Hancock, 1977]. Species such as $Fe_2(OH)_2(SO_4)_2$ were also found in sulphate solutions, which is believed to be the precurcers of iron hydroxysulphate precipitates [Yakovlev *et al.*, 1977].

Finally, the influence of supersaturation on the cristallinity and product quality of iron phases produced at temperatures between 50 and 90°C and pH values between about 1.5 and 3.5, can be summarized by combining the data presented in Figures 12 and 14, as shown in Figure 17. Although the different precipitates may be formed over a range of supersaturations, it can be expected that the best quality precipitates would be formed at lower degrees of supersaturation.

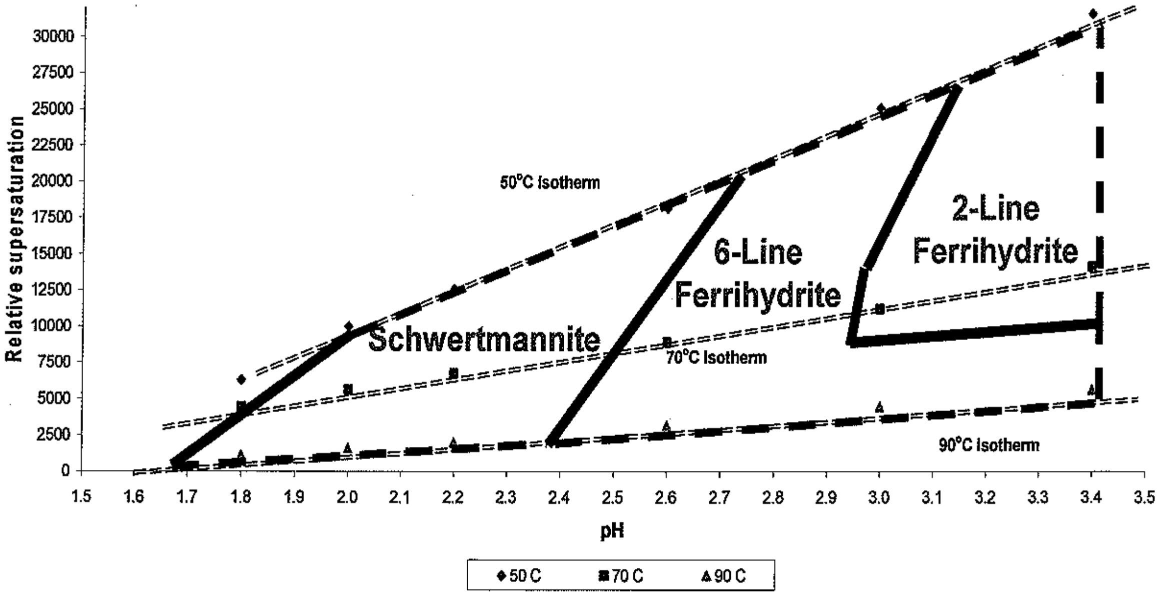

Figure 17. Phase stability of iron precipitates in terms of relative supersaturation and pH .

3.3.1.3 Stagewise precipitation

Stagewise precipitation is done by operating within the metastable zone to improve product quality. The applicability of this approach to a process operated above the metastable region was evaluated. Table 6 summarises the results obtained when iron was removed stagewise using three continuous crystallizers in series.

Table 6. Results obtained from stagewise iron removal experiments performed at 65°C.

Experiment	pH profile	Moisture (%)	Water soluble Zn* (%)	Weak acid soluble Zn** (%)
Base case	3.20 3.31 3.39	57	2.86	5.41
1	3.20 2.80 2.94	54	1.57	3.83
% Improvement		**5.3**	**45.1**	**29.2**
2	2.50 3.00 3.09	43	1.18	3.65
% Improvement		**24.6**	**58.7**	**32.5**
3	2.50 2.74 3.01	46	1.22	4.02
% Improvement		**19.3**	**57.3**	**25.7**

* Filter cake washed with hot water only to remove water soluble zinc

** Filter cake washed with a pH = 1.5 solution to remove entrapped zinc

In the base case experiments, hot iron solution was contacted with calcine slurry at a pH of 3.2 in the first of three reactors in series, where after the pH increased without further additions to about 3.4 in the last reactor. According to Figures 14 and 17, 2-line ferrihydrite was probably produced at a relatively high relative supersaturation level of about 17000 in this process. Particles with a high surface area were probably formed, which would explain the relatively high moisture and impurity content in terms of water soluble and weak acid soluble zinc values of the precipitate summarized in Table 6.

In Experiment 1, a leach/acidification step was performed at pH 2.80 in the second reactor. This mode of operation is utilised in the Zincor roast-leach-electrowinning zinc refinery [Claassen et al., 2003(b)] to remove iron from zinc-rich process solutions. During the acid wash step, some 2-line ferrihydrite particles were probably dissolved and reprecipitated as 6-line ferrihydrite and schwertmannite (refer to Figure 14 and Table 5) at relative supersaturation levels around 15000. This leaching step resulted in a reduction in the relative particle surface area as well as the zinc content of the solids formed, as shown in Table 6.

Experiments 2 and 3 were used to investigate the influence of stagewise precipitation on some product quality parameters, i.e. the pH was incrementally increased to remove iron to the desired levels. In Experiment 2, the pH in the first reactor was controlled at 2.5, followed by an increase in pH, through the addition of calcine slurry into the second reactor to raise the pH to 3.0, where after it increased to about 3.1 in the last vessel. In the first reactor schwertmannite, which has a more dense structure than ferrihydrite, was probably produced at relative supersaturation of about 12000. The lower nucleation rates, at lower supersaturation, and improved leaching of the ZnO neutralising agent probably resulted in a significant reduction in the impurity levels of the final product, as is evident from the data presented in Table 6. The remaining supersaturation was then used in the second reactor to probably agglomerate the particles. In Experiment 3, the pH in the first reactor was again controlled at 2.5, and then left to increase to about 2.75 in the second reactor. Calcine was added to the third reactor to increase the pH to 3.00 to ensure adequate iron removal, which could explain the slight increase in the zinc values of the final product. These results indicate that the stagewise precipitation of iron, even above the metastability limit, could significantly improve product quality.

3.3.2 *Influence of temperature and pH on final product quality*

3.3.2.1 Solids moisture content

The moisture content of a precipitated product can be used to indicate its downstream processing potential in terms of its drying requirements and ease of handling, as it gives an indication of the relative surface area of the precipitates. Figure 18 shows how the iron precipitate moisture content is influenced by pH and temperature.

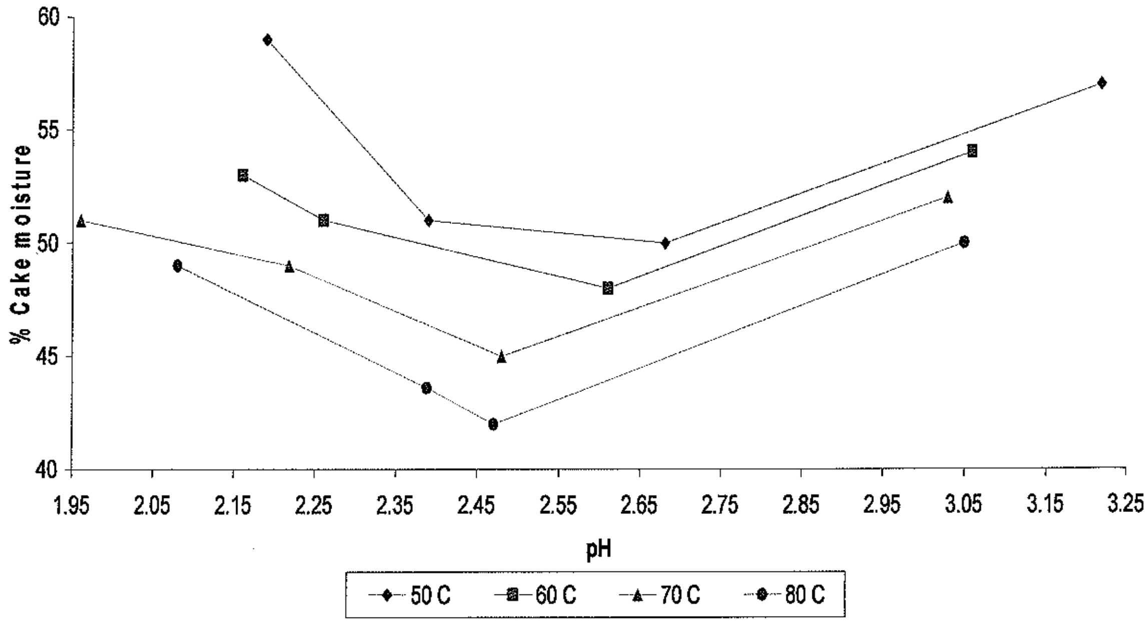

Figure 18. Filter cake moisture content for iron precipitates produced in a continous crystallizer from a hot iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder as neutralising agent as a function of pH and temperature.

The precipitate moisture content is significantly influenced by pH and temperature as indicated in Figure 18. Cake moisture decreases with an increase in temperature and reaches a minimum at pH values between 2.45 (80°C) and about 2.68 (50°C). The effect of temperature on precipitate moisture content is probably the result of the formation of more dense particles at higher temperatures as indicated by the results shown in Figure 19.

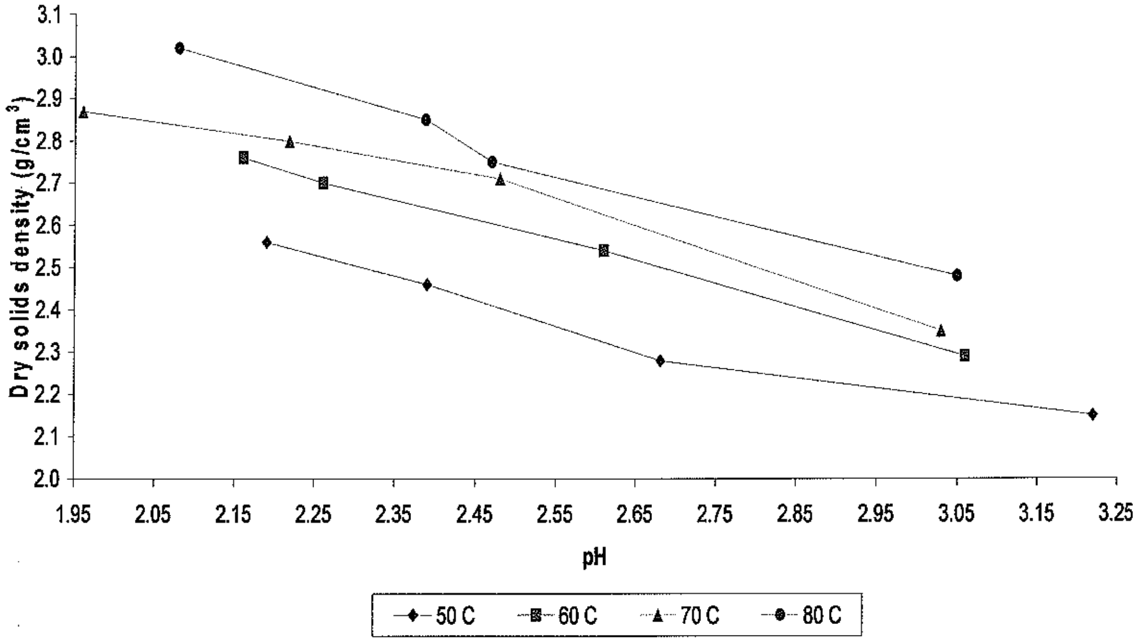

Figure 19. Influence of pH and temperature on precipitate solids density for iron precipitates produced in a continous crystallizer from a hot iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder as neutralising agent.

It is known that better quality precipitates are formed at higher temperatures as a result of the lower supersaturation levels required, as indicated in Figure 17. The increase in moisture content at lower and higher pH values is probably a result of a reduction in the mean particle size (increase in relative surface area) at lower pH and the formation of more voluminous particles at higher pH values. The high supersaturation levels generated at high pH values also supports fast nucleation rates and an increase in population density and surface area. Both the mean precipitate particle size and population density increase with increasing pH, as shown in Figures 20 and 21. The increase in size of the particles is most probably caused by agglomeration.

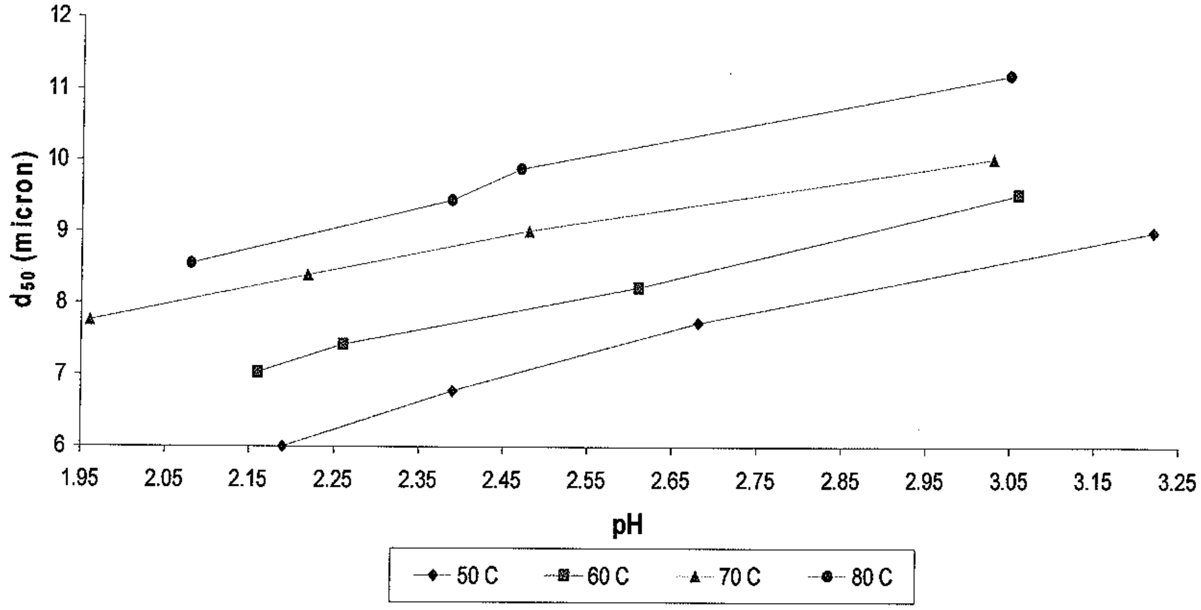

Figure 20. Influence of pH and temperature on precipitate mean particle size for iron precipitates produced in a continous crystallizer from a hot iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder as neutralising agent.

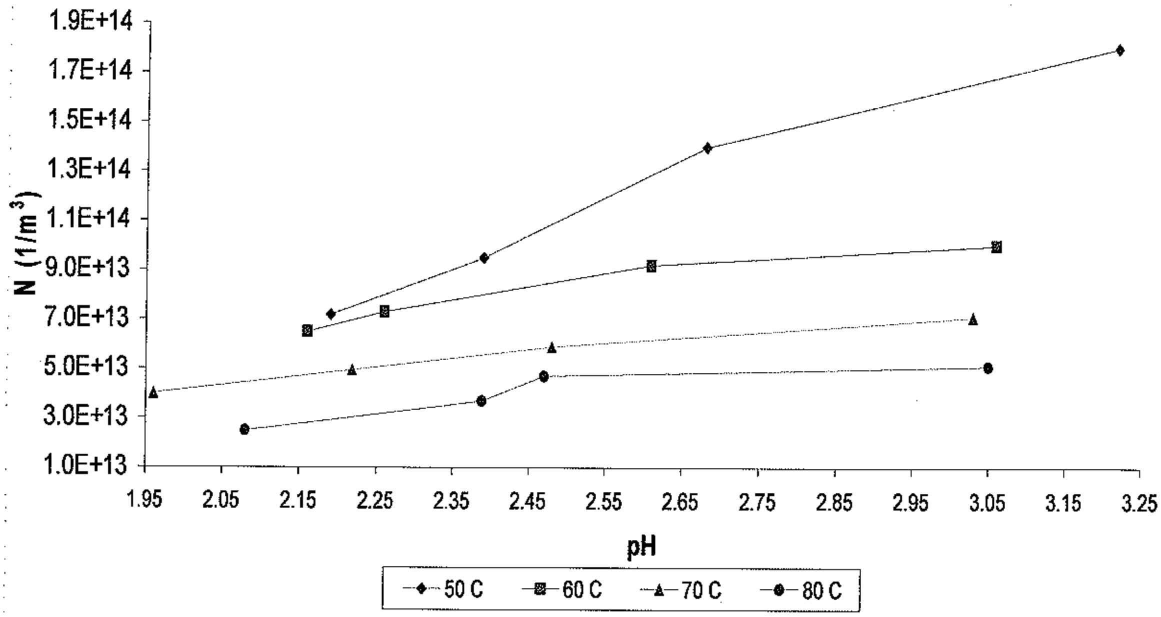

Figure 21. Influence of pH and temperature on precipitate population density obtained from Malvern particle anlyses for iron precipitates produced in a continous crystallizer from a hot iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder as neutralising agent.

3.3.2.2 Solids zinc content

Reaction crystallization requires a reagent to generate the necessary chemical driving force for solids formation from leach solutions. In the zinc industry, ferric iron is often removed through hydrolysis by contacting hot iron solution with zinc calcine containing approximately 70% ZnO, as summarized by Claassen *et al.* [2003(b)]. The use of a zinc containing neutralizing agent typically results in high zinc losses and often the production of iron residues with high sulphate loadings. Figure 20 shows the influence of pH and temperature on the zinc content of ferric iron precipitated through hydrolysis using ZnO as the neutralizing agent. The zinc content of iron precipitates increased significantly with an increase in pH and temperature as shown in Figure 22. This is probably a result of a combination of high supersaturation (at higher pH values) and faster diffusion of iron species to the growth points [Sakamoto, *et al.*, 1976 and Yamada, 1980], which could entrain unleached ZnO or zinc sulphate solution. The reduction in the reactivity of ZnO with an increase in pH, probably exacerbated the problem.

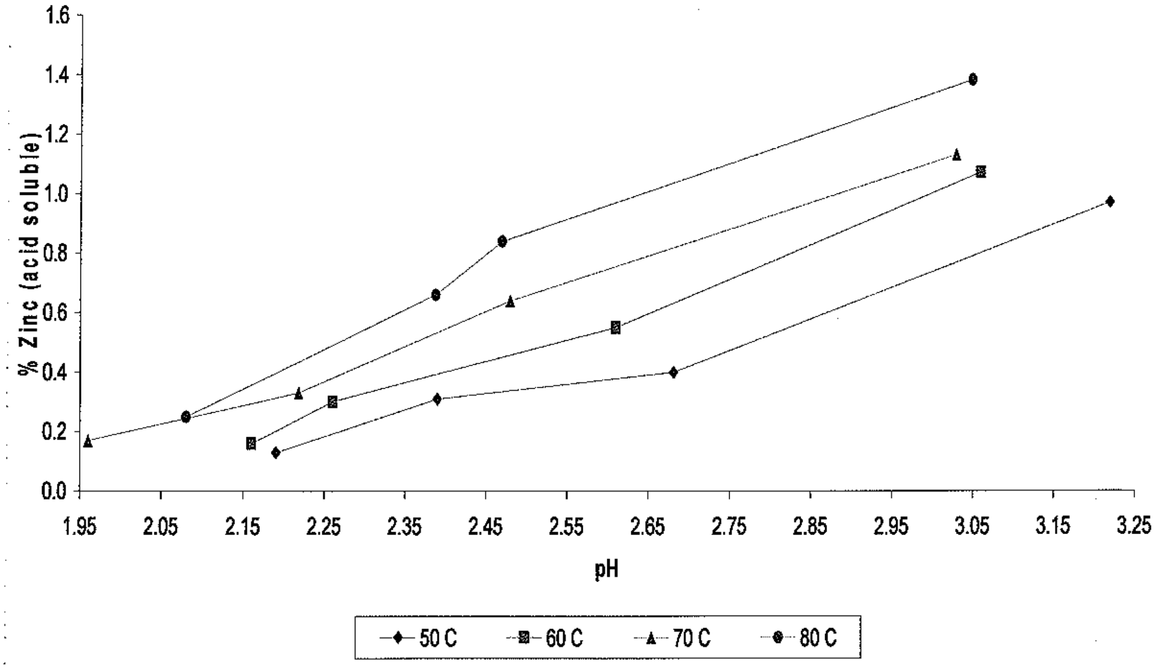

Figure 22. Influence of pH and temperature on the zinc content of iron precipitates produced in a continous crystallizer from a hot iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe (as $Fe_2(SO_4)_3$) using ZnO powder as neutralising agent.

3.4 Conclusions

Control over the factors that influence product quality in crystallization processes is of utmost importance as it affects the economics and ease of handling in down stream processes. It was shown that the type of phase produced and the supersaturation influenced final product quality. Hydrolysis of ferric iron in the temperature range 50°C to 90°C and at pH values between about 1.5 and 3.5, as typically used in many industrial processes, result in the formation of poorly crystalline, metastable iron phases such as ferrihydrite (2-line and 6-line) and schwertmannite. In this study, the stability regions of these phases were determined as a function of easily controllable parameters such as pH and temperature. Typical relative supersaturation levels required for the precipitation of ferrihydrite and schwertmannite were also calculated from data defining the metastable zone for ferric iron hydrolysis. It was shown that ferrihydrite and schwertmannite are formed over a range of supersaturation levels. Since supersaturation determines the rate of the primary crystallization processes, i.e. nucleation and growth, the morphology and product quality of these phases varied with changes in the parameters that influence supersaturation. It also appears as though hydroxy salts, which include schwertmannite, are generally of a better quality as indicated by a higher solids density and lower zinc content than oxy hydroxides, which include ferrihydrite, that were formed at higher relative supersaturation.

The study showed that even though poorly crystalline iron phases, such as schwertmannite and ferrihydrite, were produced, the quality of these phases could be improved by controlling the supersaturation. This could be done through careful selection of control parameters such as pH and temperature and using a stagewise precipitation process.

In addition to the role that pH and temperature play in determining supersaturation, the influence of changes to the mixing environment on supersaturation was studied. In the next chapter, special attention is given to the influence of changes in the macro and micromixing environments, reactor design and feed point location on precipitate product quality.