5. AGGLOMERATION

5.1 Introduction

Precipitation processes are characterized by high supersaturation levels and fast nucleation rates. If it is assumed that the range and distribution of supersaturation in a crystallizer is controlled reasonably well, dense nuclei with a relatively low surface area can be formed. However, even good quality nuclei formed in a well-controlled environment are usually less than one micron in diameter. Unless these nuclei are allowed to grow, downstream processing of precipitates, such as liquid-solid separation and storage, could be difficult and costly. Low solute concentrations typically required for the formation of relatively insoluble phases during precipitation processes, however, do not support the desired molecular growth rates required to make these processes viable. Particle growth in precipitation systems rather takes place through agglomeration, as indicated in Table 20.

Table 20. Different nucleation and growth mechanisms encountered in crystallization and precipitation processes [After Dirksen and Ring, 1991].

Initial Supersaturation	Colloid stability	Nucleation	Atomistic growth	Morphology
1-2	High	None	None	____
	Low	Heterogeneous	Slow, predominantly screw dislocation	Discrete well-formed crystals, no agglomeration
2-5	High	Heterogeneous	Slow, predominantly surface nucleation	Discrete well-formed crystals, no agglomeration
	Low	Heterogeneous	Dendritic	Poorly formed or dendritic crystals, no agglomeration
10-50	High	Heterogeneous	Dendritic	Poorly formed or dendritic crystals, no agglomeration
	Low	Homogeneous	Diffusion-limited	Colloid stability dependent, agglomerated
>1000	High	Homogeneous	Diffusion-limited	Colloid stability dependent, agglomerated

In precipitation processes, agglomeration growth (the process where stable nuclei and clusters are cemented together by isomorphic material) occurs at a much faster rate than molecular growth. Nuclei could grow to particulates as big as 100μm in diameter within a reasonable time period (< 5 hours). Even though agglomeration growth makes down stream processing in most precipitation processes possible, it generally results in the formation of particles with a high relative surface area and high impurity values. Optimisation in terms of product quality improvement of the agglomeration growth process is therefore required. In order to improve precipitate product quality, a good understanding of the impact of the different parameters on agglomeration is required. When agglomeration growth is broken down in stages, the various factors that influence the process become clearer. The three main steps include the following:

- Particles collide as a result of their properties and the hydrodynamic environment. This step is governed by the probability of collisions and/or the collision frequency.
- Next, the particles need to stay together for a period of time to allow interparticle bridges to be formed; this is influenced by interparticle forces/interactions.
- A step of consolidation where nuclei, clusters and particulates are cemented together through molecular growth.

Considering these steps, it follows that the properties of the particles, interparticle forces, fluid dynamics and properties of the solution might influence the agglomeration process and therefore the quality of the final product. It was found [Dirksen and Ring, 1991] that interparticle forces were affected by the addition of adsorptives, with agglomeration favoured by the addition of hydrophobic adsorptives. In terms of the effect of solution variables, it was also shown that agglomeration was generally supported by high temperature, high diffusivity, small particles, high particle number density, low viscosity, high supersaturation and strong bonding forces. The impact of changes in the hydrodynamic environment proved to be more complex, as the above-mentioned factors could promote agglomeration up to a point, after which disruption prevents agglomeration.

In industrial environments, however, not all these parameters are easily controllable. Furthermore, the quality of the solution to be treated is influenced by concentrate composition and the efficiency of upstream processes, which typically could vary considerably with time. A better understanding of the effect of easily controllable operating parameters such as pH, temperature, solute concentration, recycling of seed material and stirring rate on agglomeration would be useful. In addition, since it is not expected that all these parameters have an equally important role to play in the agglomeration process, their relative importance also need to be determined. This would enable the engineer and operator to focus on the specific variables that have the biggest influence on growth and final product quality.

In this study, the effect of the above-mentioned easily controllable operating parameters and their relative importance on the agglomeration of metastable iron phases such as ferrihydrite and schwertmannite were investigated. Since, most iron phases are relatively stable (poorly soluble), high relative supersaturation levels are encountered in iron precipitation processes, as indicated earlier. The high supersaturation levels in turn support agglomeration growth in these processes as indicated in Table 20. In a study of the Zincor iron removal process, Claassen [2002] identified the presence of agglomerates in the final precipitate as shown in Figure 33.

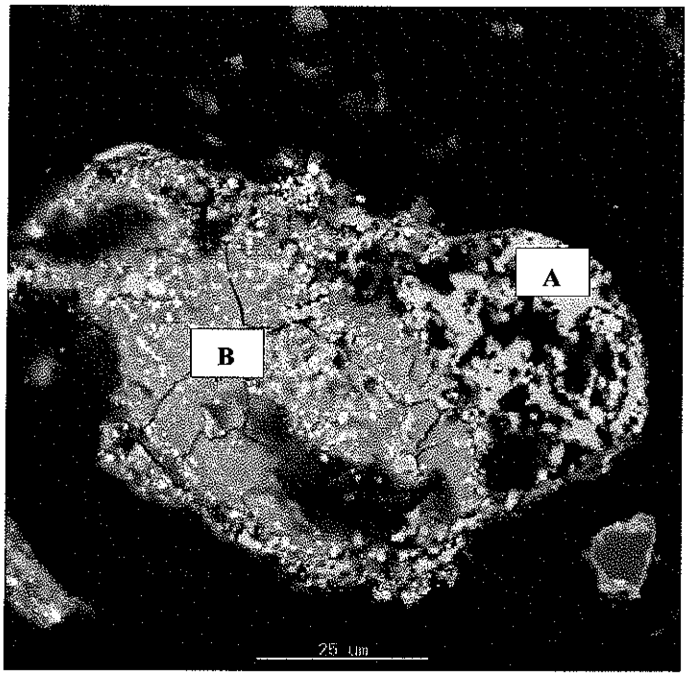

Figure 33. SEM image of agglomerated iron particles A (ferrihydrite) and B (schwertmannite) found in an industrial iron residue produced in the Zincor iron removal process. It also appears as though particle B consists of agglomerated primary particles and clusters of primary particles [Claassen, 2002].

The agglomerated particles, shown in Figure 33, also supports the point previously raised, that even though agglomeration growth gives precipitates that could be effectively handled in down stream processes, an increase in the relative surface area of the particles usually result in increased losses of valuable metals, such as zinc. An attempt was therefore made in this study to find means to reduce the zinc losses associated with metastable iron phases present in many iron residues in the zinc industry.

5.2 Materials and methods

In an earlier investigation into the factors that influence the filterability of metastable iron phases, Claassen *et al.* [2003(a)] showed that pH, temperature and seed addition had a positive impact on the growth rate as well as the final particle size. For reasons highlighted in previous paragraphs, it was decided to also determine the relative importance of these and other operating parameters on agglomeration. The relative importance of the variables was studied using an algorithm, the so-called Hadamard matrix [Seyssiecq *et al*, 1998], combined with product quality parameters, such as the specific filter resistance and the degree of agglomeration, as characterized by the change in particle population density. Lastly, the specific influence of seed material on product quality parameters, such as the filterability, final particle size and precipitate purity, was studied in more detail.

5.2.1 Experimental setup and procedures

A continuous reactor with four baffles and a riser box was used in all experiments. The dimensions of the reactor are shown in Figure 6.

A hot iron solution made up with distilled water, $Fe_2(SO_4)_3$ and 5 g/L H_2SO_4 was continuously fed to the reactor in order to maintain a constant supersaturation level at a given set of conditions, details of which are shown in Table 21. The iron was precipitated with ZnO powder slurried to a consistency of 2.5% (mass/mass) using distilled water. The chemicals used were of CP grade. Both the reactant streams were fed at a rate of approximately 33 ± 4mL/min to the reactor. The outlet points of both streams were positioned just underneath the agitator blades on opposite sides of the reactor. Each experiment was terminated after one hour. At the end of each experiment, 250 mL slurry was extracted from the reactor. The slurry was filtered in a Buchner funnel with a surface area of 50 cm^2. 5 mL of a 0.1% non-ionic flocculant was added to aid filtration. The filtered solids were dried at 120°C for one hour to determine the moisture content and analysed to obtain the zinc content, as water soluble and acid soluble zinc, and the total sulphates present.

Samples of 10 mL each were also taken from the reactor at the beginning and end of each experiment to determine particle size and size distribution using the Malvern Mastersizer particle analyzer.

The experimental setup and procedures followed to determine the influence of pH and temperature on the degree of agglomeration were discussed elsewhere [Claassen *et al.*, 2003(a)].

5.2.2 Relative importance of the operating variables

A Hadamard matrix was used to determine the relative importance of each operating parameter on the agglomeration process. A Hadamard matrix is a n × n matrix with all the elements presented as +1 or –1. The first row and column can be arranged in such a manner that their elements are all +1. The matrix only exists if $n = 2$ or if n is divisible by 4. Furthermore, all parameters used in the matrix need to be independent from each other. The properties and uses of a Hadamard matrix are discussed in detail by Raghavarao [1971].

For the purpose of this study, the use and benefits of using a Hadamard matrix could be explained as follows. If the regression model is expressed as:

$$E(y) = \mathbf{X}b \qquad \text{....12}$$

where the elements of y are values determined in the experiments, such as specific filter resistance, iron removal efficiency and the degree of agglomeration in this case, and the columns of **X** are the values of the chosen operating parameters, then:

$$b = (\mathbf{X'X})^{-1}\,\mathbf{X'}y \qquad \text{....13}$$

The number of experiments could now be limited if only two points, a minimum and maximum value for example, for each parameter (covariate) is used; covariates are referred to as parameters and b is called the vector of parameters. These covariates are then included in the regression model as +1 and –1, the maximum and minimum values respectively. This causes the size of the regression coefficient to be half of the total possible influence of a covariate on y. Therefore, the +1 and –1 choice of covariates give a 2^n - factorial model, with observations only made at specific points, e.g. for 6 parameters, 8 observations or experiments are required instead of $2^6 = 64$ observations or experiments. Therefore, the number of experiments could be limited to a minimum without much influence on the statistical accuracy of the data, if a Hadamard matrix is used to determine the relative influence of parameters. In this study the relative influence of six parameters on agglomeration was determined. The parameters and their values are summarised in Table 21. Most of the boundaries chosen for the different parameters are typical of the Zincor iron removal process and other industrial environments where iron is precipitated in the form of ferrihydrite and schwertmannite.

Table 21. Parameters and their values used to determine their relative influence on the agglomeration of metastable iron phases.

Parameter	Minimum value	Maximum value
pH	2.6	3.2
Temperature	45°C	65°C
Stirring rate	400 rpm	600 rpm
Hot iron solution iron concentration, C_{Fe}	5 g/L	15 g/L
Mass of seed	10 g/L	100 g/L
Hot iron solution Zn concentration, C_{Zn}	0 g/L	80 g/L

For six parameters/covariates, the Hadamard matrix in the +1, –1 notation is presented in Table 22.

Table 22. Hadamard matrix of the parameters evaluated.

Experiment	pH	Temperature	Stirring rate	C_{Fe}	Seed mass	C_{Zn}
1	–	–	–	+	+	+
2	+	–	–	–	–	+
3	–	+	+	–	+	–
4	+	+	+	+	–	–
5	–	–	–	+	–	–
6	+	–	–	–	+	–
7	–	+	+	–	–	+
8	+	+	+	+	+	+

In Table 22 the (+) symbol corresponded to maximum values listed for each parameter in Table 21 and the (−) symbol was associated with the lower limit as mentioned earlier. The results, e.g. the specific filter resistance values K to R, obtained from the eight experiments were then used to solve equation 14 for each parameter as follows:

$$b_{pH} = (-K + L - M + N - O + P - Q + R)/8 \qquad \ldots.14$$

The values obtained for the different parameters were then compared with each other and ranked, i.e. the parameters are viewed as objects that are weighted. The value with the highest weight then indicated which parameter had the biggest influence on the agglomeration process for the specific product quality parameter, such as the filter resistance, iron removal efficiency or degree of agglomeration, evaluated.

In terms of the filterability of the precipitates, the specific filter resistance of the solids produced was again calculated using equation 9.

The degree of agglomeration for each experiment, as indicated by the relative reduction in the number of particles present, was calculated from the particle number density data obtained from the Malvern particle analyses (refer to Appendix 3). The number density was calculated at t_0 (N_0) and t_{1hr} (N_{1hr}). The degree of agglomeration was then calculated as follows:

$$\text{Degree of agglomeration} = [1 - (N_{1hr}/N_0)] \times 100 \qquad \ldots.15$$

5.2.3 Influence of seed mass and seed size

The influence of changes in the initial seed mass and mean seed size on agglomeration was investigated with all the other parameters fixed at pre-determined values. The experimental conditions used to study the influence of seed mass and size on the agglomeration degree, final particle size, specific filter resistance and solid purity are summarised in Tables 23 and 24, respectively. Enough seed material was prepared to perform the experiments in triplicate. The seed material was produced using the experimental setup shown in Figure 6 and the procedure described in section 3.2.3. The pH and temperature during the experiment were maintained at 3.0 and 60°C, respectively (refer to section 3 for chemical composition of the seed).The seed material was dried, milled and properly mixed. The mean particle size of the seed was 5.04 μm, as determined using the Malvern Mastersizer. The full particle size distribution of the seed is shown in Appendix 1.

Table 23. Experimental conditions used to evaluate changes in the initial seed mass on precipitate product quality.

No.	pH	Temperature (°C)	Stirring rate (rpm)	C_{Fe} (g/L)	Seed mass (g/L)	C_{Zn} (g/L)
1	3.2	65	600	10	10	0
2	3.2	65	600	10	25	0
3	3.2	65	600	10	50	0
4	3.2	65	600	10	100	0
5	3.2	65	600	10	150	0

Table 24. Experimental conditions used to evaluate changes in the initial seed size on precipitate product quality.

No.	pH	Temperature (°C)	Stirring rate (rpm)	C_{Fe} (g/L)	Seed size (μm)	C_{Zn} (g/L)
1	3.2	65	600	10	2.2	80
2	3.2	65	600	10	5.3	80
3	3.2	65	600	10	6.8	80
4	3.2	65	600	10	12.4	80

The seed particles used to evaluate the effect of the seed size were prepared by milling four parts of a batch of seed, separately for different times, to give the mean seed sizes indicated in Table 24. An initial seed concentration of 50g/L was used in each experiment.

5.3 Results and discussion

The results obtained from the experimental trials using the conditions listed in Table 21 together with their Hadamard arrangement are summarised in Table 25.

Table 25. Precipitate characteristics obtained for the operating variables indicated.

No.	pH	Temp. (°C)	Stirring rate (rpm)	C_{Fe} (g/L)	Seed mass (µm)	Zn conc. (g/L)	Filter resistance (Pa.s.m^{-2})	Fe removal efficiency (%)	Degree of agglomeration (%)
1	2.6	45	400	15	100	80	4.80×10^{11}	92.81	60.9
2	3.2	45	400	5	10	80	4.09×10^{11}	99.77	-69.9
3	2.6	65	400	5	100	0	5.04×10^{10}	98.71	62.1
4	3.2	65	400	15	10	0	5.34×10^{10}	99.98	-40.9
5	2.6	45	600	15	10	0	2.47×10^{11}	95.82	-137.4
6	3.2	45	600	5	100	0	6.46×10^{10}	99.87	37.6
7	2.6	65	600	5	10	80	1.20×10^{12}	93.32	-6.7
8	3.2	65	600	15	100	80	5.67×10^{10}	99.98	67.5

The vector (*b*) of each variable was calculated from the results shown in Table 25 according to equation 11 and ranked. The outcome of this exercise is presented in Table 26.

Table 26. Relative importance of the different operating parameters evaluated.

Parameter	Specific filter resistance		Fe removal efficiency		Degree of agglomeration	
	b-value	Order of importance	*b*-value	Order of importance	*b*-value	Order of importance
pH	-1.74×10^{11}	1	1.34	1	1.92	4
Temperature	1.97×10^{10}	4	-0.30	3	23.85	2
Stirring rate	7.16×10^{10}	5	-48.62	6	-6.41	5
Hot iron solution iron concentration	-1.11×10^{11}	3	0.33	2	-9.13	6
Mass of seed	-1.57×10^{11}	2	-1.34	4	60.38	1

Precipitation processes are generally only used in industrial processes if the liquid-solid separation step(s) can be performed economically. Furthermore, precipitation is utilised as a purification or concentration step and the efficiency of such an operation is of utmost importance. Specific attention is therefore given to the specific filter resistance and iron removal efficiency in the discussions that follows. Since the degree of agglomeration strongly influences the filterability of iron residues, the factors that impact on this process are also discussed. Emphasis is put on the relative influence of the operating parameters on the precipitation of metastable iron phases.

From Table 26 it is evident that pH, seed concentration, iron solution iron concentration and temperature have the biggest effect on filterability and iron removal efficiency. In terms of the degree of agglomeration the seed concentration, temperature and pH together with a significant change in solution viscosity (change in solution zinc concentration) need to be considered to optimise the agglomeration step. Overall, pH is the most important parameter, followed by the seed concentration, temperature and iron solution iron concentration. This outcome implies that:

- Every effort needs to be made to improve pH control in iron precipitation processes. The impact of pH on iron precipitate quality should also be seen in light of the relative small pH window of 2.6 to 3.2 that was evaluated, i.e. a small change in pH in this range could have a significant effect on agglomeration, iron removal efficiency, the filterability and purity of the precipitate.
- Seed addition is essential to ensure good quality iron precipitates. However, it is often not considered or neglected in industrial processes. In this study, special attention is given to the utilisation of seed to improve iron precipitate quality.
- Adequate dilution is required in iron precipitation processes to improve the efficiency of the step.
- Changes in the physico-chemical parameters were of greater importance than changes in the hydrodynamic environment for the range of each operating parameter explored.

The fundamental reasons why these variables influence agglomeration, filterability of the precipitate and the iron removal efficiency are discussed in the following paragraphs.

5.3.1 Influence of the operating pH, temperature and solution iron concentration

The influence of pH and temperature on the degree of agglomeration is shown in Figures 34 and 35, respectively, indicating that agglomeration is optimum at a pH around 3.0 and increases significantly up to temperatures around 60°C. These results are in good agreement with earlier work [Claassen *et al.*, 2003(a)], which showed the same trends for the filterability of iron precipitates.

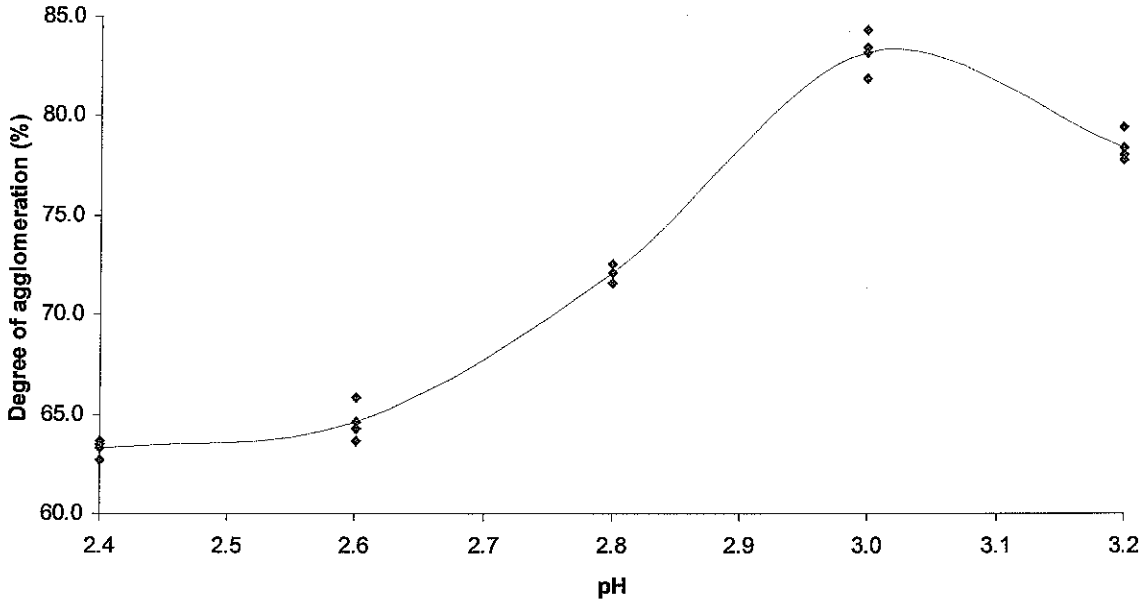

Figure 34. Influence of pH on the degree of agglomeration for the precipitation of metastable iron phases at 60°C and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

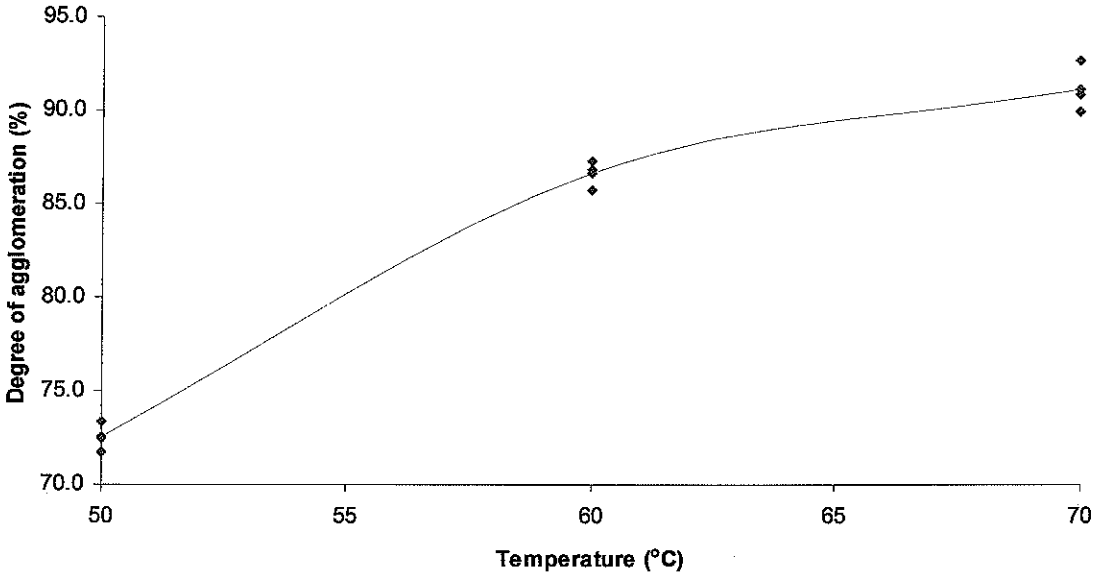

Figure 35. Influence of temperature on the degree of agglomeration for the precipitation of metastable iron phases at a pH of 3.0 and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

pH, temperature and iron solution iron concentration influence agglomeration in several ways. It is known that these variables influence the supersaturation level, which is the driving force for precipitation. Supersaturation in turn influences the final particle size, size distribution and morphology of the precipitates and therefore its filterability amongst other things. It is well known that small, low-density particles are formed at high supersaturation levels [Gösele *et al.*, 1990], which occur at low temperatures, high pH values and high initial solute concentrations. It was shown earlier that the relative supersaturation present during iron precipitation varies between about 1,000 and 30,000 at pH values between 1.85 and 3.5 and temperatures ranging from 50°C to 90°C, i.e. at a pH of about 1.85 and a temperature of 90°C, the relative supersaturation was estimated at 1,000, but at a pH of 3.5 and a temperature of 50°C, it increased to about 30,000. Therefore, an increase in pH causes supersaturation to increase as the solubility of iron decreases. The results summarised in Figure 4 indicate an increase in the degree of agglomeration up to a pH of about 3.0, whereafter it decreases. It is proposed that the solution iron concentration available only supports agglomeration up to a pH of about 3.0, whereafter the increase in the population density outweighs the agglomeration rate. On the other hand, an increase in temperature at a fixed pH results in a reduction in the solute concentration (refer to Figures 7 to 9), which is required to produce better quality iron precipitates as indicated in Figure 5.

Furthermore, it was proposed [Sakamoto *et al.*, 1976; Yamada, 1980; Veesler *et al.*, 1994; Ilievski and White, 1994; Johnston and Cresswell, 1996] that diffusion of growth species across a particle surface is faster at higher temperatures, providing a higher probability of cementation of particles. If supersaturation is controlled below the point where 2-line ferrihydrite is formed (pH below about 2.95 and temperature greater than about 75°C according to Figure 14), higher pH values and solute concentrations should also promote agglomeration as it supplies the material that cements particles together. Since all tests were conducted at constant supersaturation, agglomeration took place for the duration of each experiment. This is not the case for batch processes where a depletion of the solute concentration with time has a detrimental effect on agglomeration and the economics of downstream processes.

In terms of iron precipitation, an increase in pH causes supersaturation to increase as the solubility of iron decreases due to the formation of a variety of iron species. However, it appears from Figure 34 as though the increase in supersaturation only supports agglomeration up to a pH of about 3.0, where after the supersaturation is consumed by an increase in the nucleation rate. On the other hand, the effect of temperature on supersaturation is probably a result of the increased surface diffusion rates of iron molecules at higher temperatures, which support the formation of particle bridges required for agglomeration.

In terms of the three steps of the agglomeration process discussed earlier, it appeared therefore as if pH, temperature and the initial iron concentration impacted on phase 3, namely, the phase of consolidation.

5.3.2 Influence of mixing, seed addition and solution viscosity

Even though it was shown that, for the range of stirring rates evaluated, the mixing intensity did not have a significant impact on the variables used, the role of mixing in precipitation processes should not be underestimated, as it impacts on the range and distribution of the supersaturation [Franke and Mersmann, 1995; Van Leeuwen *et al.*, 1996 (a); Van Leeuwen *et al.*, 1996 (b); Baldyga and Orciuch, 2001]. It is known that the supersaturation influences the rate of nucleation, which determines the final particle size and size distribution as discussed in the previous paragraph. The relationship between the quality of the precipitate and mixing is not simple, and increased mixing may either increase or decrease the filterability of a precipitate as shown earlier.

Furthermore, changes in the hydrodynamic environment could impact on agglomeration and the specific filter resistance if the probability of particle collisions and the formation of interparticle bridges are influenced [Seyssiecq *et al*, 1998]. These steps are influenced by the amount of energy dissipated (stirring rate) in a precipitation system, since a change in the stirring rate not only changes the collision frequency of particulates, but could also result in particles either bouncing off each other, or keeping out of range of inter-particle forces due to a change in its kinetic energy. Increased collision rates generally cause disagglomeration. Low agglomeration rates are therefore expected at both low and high stirring rates, and will result in smaller particles and increased filter resistance. Other variables that influence agglomeration include the particle population density, expressed in terms of the initial seed mass, the initial seed size and the viscosity of the solution.

Figure 36 indicates that the degree of agglomeration is optimal at solids concentrations between about 15 g/L and 35 g/L (Zone B). Agglomeration is limited by the probability of particle collisions at values below about 15 g/L (Zone A) and dissagglomeration starts to dominate at levels above of about 35 g/L (Zone C).

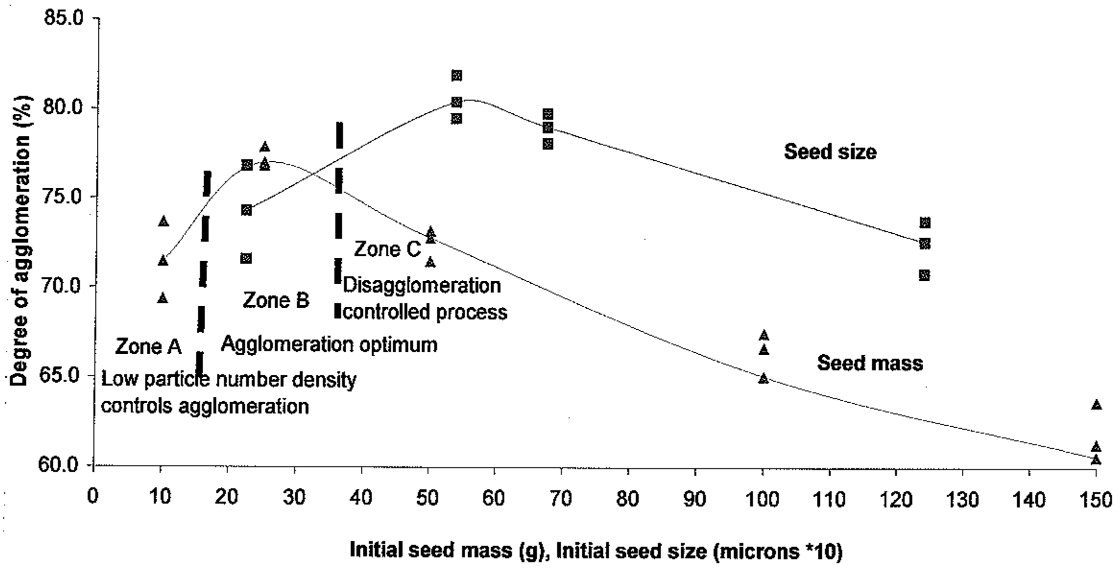

Figure 36. Influence of the initial seed size and seed mass on the degree of agglomeration for the precipitation of metastable iron phases at a pH of 3.2, 65°C and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

The change in the final mean particle size of the precipitate produced as a function of the initial seed mass followed the same trend than the degree of agglomeration, as indicated in Figure 37.

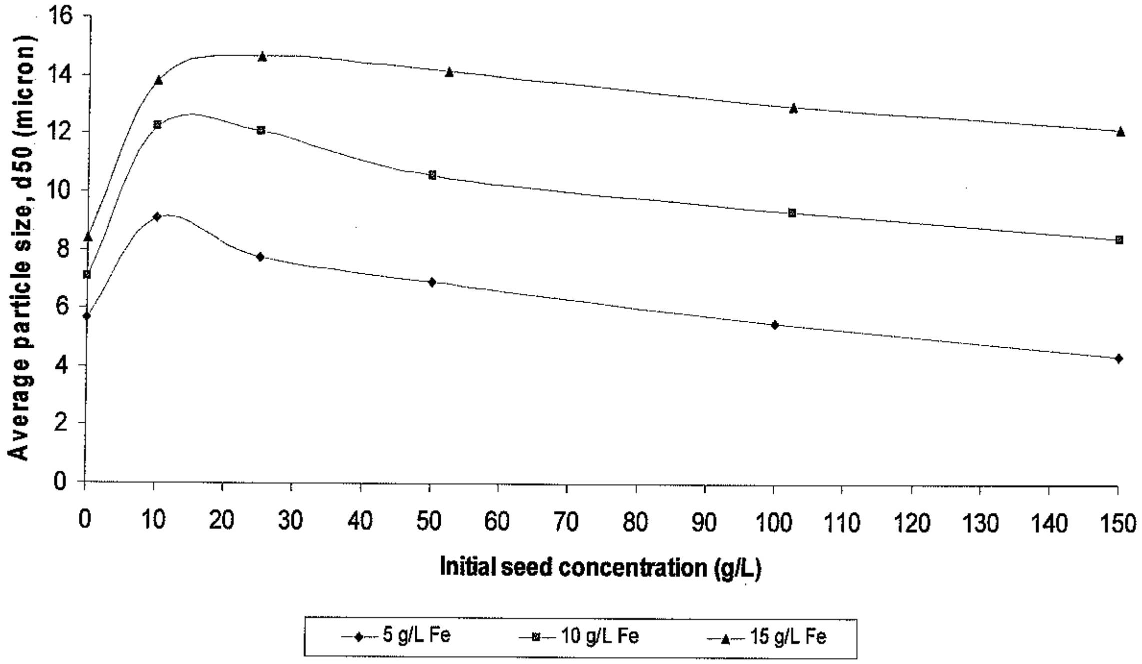

Figure 37. Influence of the initial seed mass on the final mean particle size for the precipitation of metastable iron phases at a pH of 3.2, 65°C and stirring rate of 600 rpm from an iron solution containing 5, 10 and 15 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

Figure 37 shows that particle growth was stimulated by an increase in the initial seed concentration up to levels of 10 - 30 g/L seed, depending on the initial hot iron solution iron concentration. It also shows that the initial iron concentration had a significant impact on the final particle size of the precipitate as alluded to earlier. The increase in the final particle size probably indicates that iron precipitated on the surface of the seed material, and so reduces the particle number density by stimulating growth through agglomeration. Therefore, an increase in the initial iron concentration could result in the formation of bigger particles, as it supplies the cement that is required to form the interparticle bridges, as was mentioned earlier. Higher initial iron concentrations also support the addition of more seed material, which could improve the purity of the iron precipitates formed, by reducing the zinc and sulphate contents, as shown later.

The influence of the initial seed size on the degree of agglomeration is also shown in Figure 36. It is clear from the experimental data that agglomeration is optimal at initial seed sizes around 6.0µm. This size more or less corresponds to the point where the process changes from orthokinetic to perikinetic agglomeration under the conditions used. Orthokinetic agglomeration takes place between particles at least an order of magnitude smaller than the smallest eddies in a well-mixed environment [Saffman and Turner, 1956]. At these eddy sizes, also called the Kolmogoroff or turbulence microscale, the particles move within the eddies and the movement of the particles are strongly influenced by the viscosity of the solution. No exchange of particles between eddies take place, which inhibits agglomeration growth. On the other hand, when larger particles contained in large eddies are mixed, the eddies exchange particles which then agglomerate. For the experimental setup and conditions used in this study, the Kolmogoroff microscale was calculated to give an eddy size of about 58µm, which indicates that particles between 5.5µm and 6.0µm are no longer contained in micro-eddies as discussed earlier. The Kolmogoroff microscale (λ_0) was determined with the following equation [Seyssiecq *et al*, 1998]:

$$\lambda_0 = [\nu^3/\varepsilon]^{0.25} \qquad \ldots.16$$

where the kinematic viscosity (ν) of the fluid was calculated as 4.23×10^{-7} m^2/s (from $\rho_{solution}$ = 1.326 g/cm^3 and viscosity = 5.512 $\times 10^{-4}$ N.s/m^2 measured separately) and the energy dissipation (ε) was calculated as 0.007 W/kg (energy dissipated = 0.038 kg.m^2/s and the slurry mass = 5.30 kg) with 80 g/L Zn in solution. The data in Figure 36 therefore indicates that agglomeration was influenced by viscosity effects up to a particle size of about 6µm, after which it was limited by a reduction in the number density of particulates as a result of agglomeration growth. For a solution containing 0 g/L Zn (used in the Hadamard matrix as minimum value), the value of λ_0 calculated was about 40µm (from $\rho_{solution}$ = 1.042 g/cm^3, viscosity = 3.800 $\times 10^{-4}$ N.s/m^2, energy dissipated = 0.038 kg.m^2/s and the slurry mass = 4.17kg measured separately). The critical particle size where agglomeration changes from an orthokinetic to a perikinetic process is therefore estimated at 4µm. Since the experiments included in the Hadamard matrix were performed with seed with an initial mean size of about 5.0μm, it probably initially followed an orthokinetic mechanism when the solutions contained 80 g/L zinc and a perikinetic mechanism for solutions with no zinc. This relative big change in zinc concentration is not expected to occur in industrial processes, but it illustrates the important role that solution viscosity could play in agglomeration processes. Furthermore, agglomeration in precipitation processes should be controlled to ensure that a change from an orthokinetic to a perikinetic dominated process takes place to support growth.

Seed addition was found not only to promote agglomeration, but it also improved the precipitate purity. Figures 38 and 39 show how the zinc and sulphate content of the iron precipitates changed with a change in the initial seed concentration.

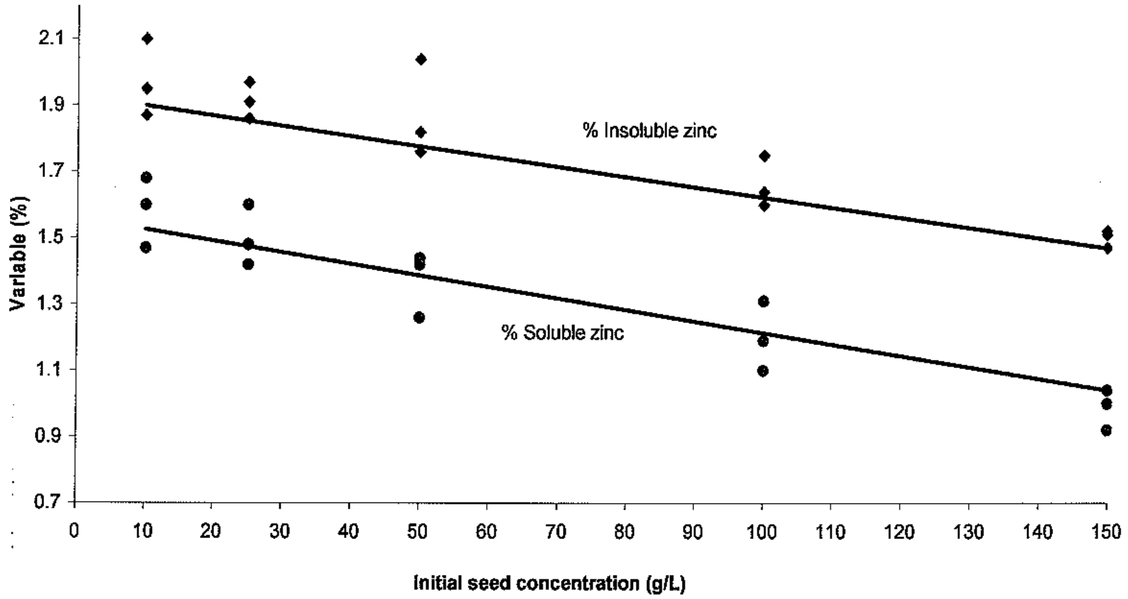

Figure 38. Influence of the initial seed concentration on precipitate zinc content for metastable iron phases formed at a pH of 3.2, 65°C and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

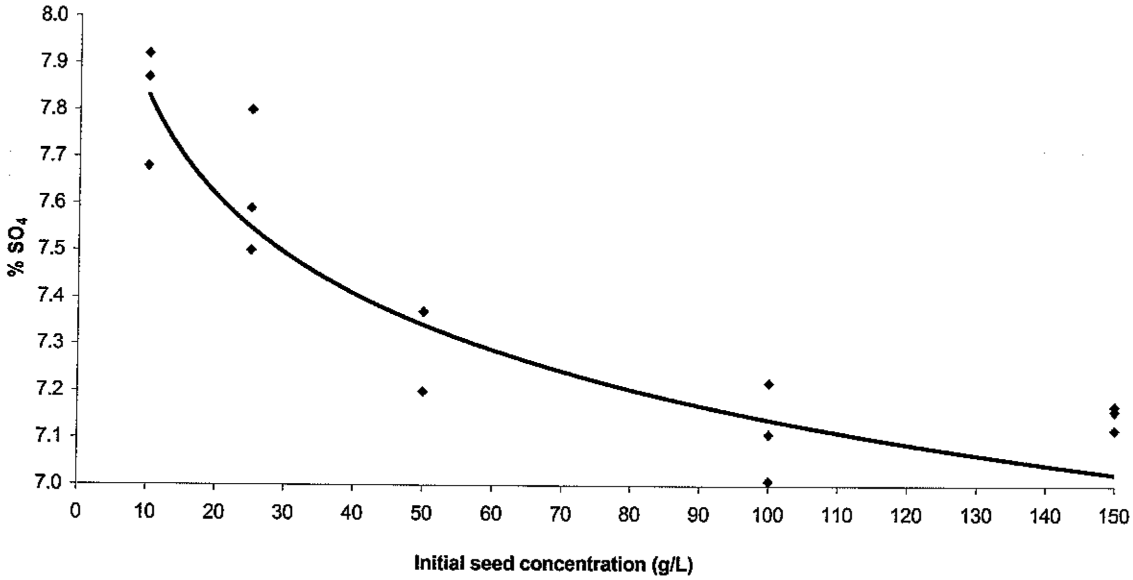

Figure 39. Influence of the initial seed concentration on precipitate sulphate content for metastable iron phases formed at a pH of 3.2, 65°C and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

In Figure 38, insoluble- and soluble zinc refer to acid- and water soluble zinc, respectively. The acid soluble zinc portion reflects the amount of unleached ZnO and encapsulated $ZnSO_4$ solution present in the precipitate, whereas the water soluble zinc present is an indication of the adsorbed solution and thus of the relative surface area of the agglomerates. As expected, less iron was precipitated on the surface of ZnO particles and more on the surfaces of seed particles as the seed concentration increased. In the presence of seed particles, the formation of new nuclei is expected to be limited, and it can be expected that the relative surface area of the final product will be lower with commensurate lower soluble zinc losses. This reduction in the relative surface area probably also contributed towards lowering the sulphate content, in the form of adsorbed sulphate complexes, on the precipitates, as shown in Figure 39.

In industrial zinc circuits, where an iron residue is often produced, the filterability (washability) of the precipitate determines the loss of zinc as water-soluble zinc and is of utmost importance. Figure 40 indicates how the addition of a relative small amount of seed material (up to about 50 g/L) could improve the filterability of iron precipitates by about 80%. The increased filterability is probably a result of a reduction in the particle population density and the formation of bigger particles, as indicated in Figure 37.

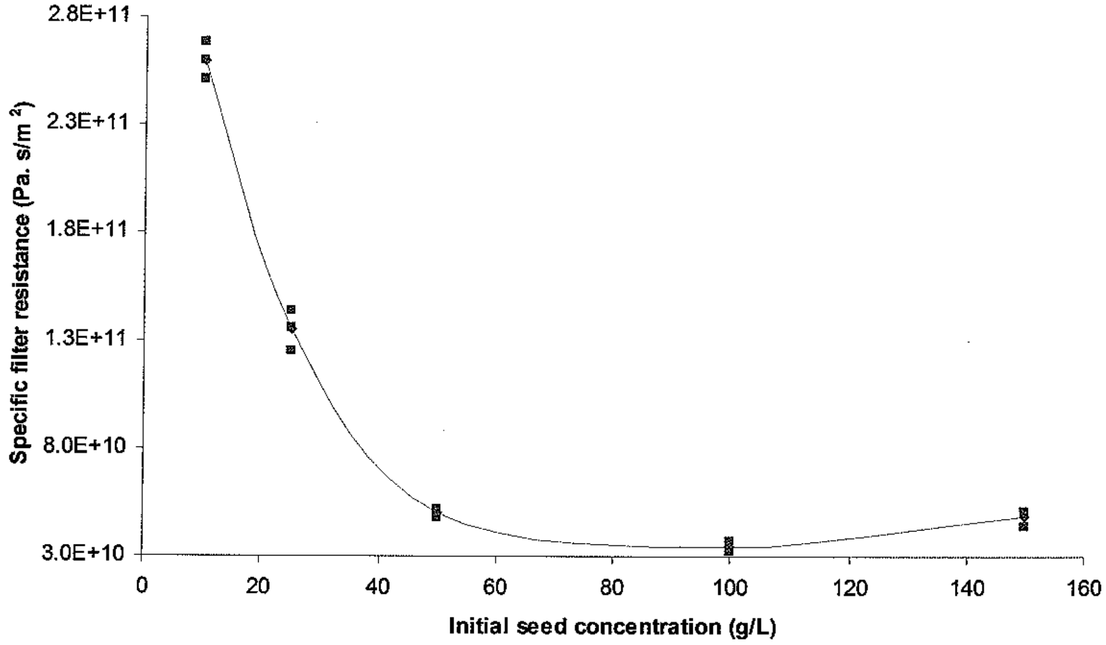

Figure 40. Influence of the initial seed concentration on the specific filter resistance of metastable iron phases formed at a pH of 3.2, 65°C and stirring rate of 600 rpm from an iron solution containing 10 g/L Fe, added as $Fe_2(SO_4)_3$, and 5 g/L H_2SO_4. A 2.5% ZnO slurry was used as neutralizing agent.

5.4 Conclusions

In crystallization processes, the nucleation- and growth steps determine the final product quality, i.e. the final particle size, particle size distribution and purity. These qualities in turn influence the down stream processing potential of the material. In order to improve the quality of metastable iron phases, such as ferrihydrite and schwertmannite, very often encountered in industrial environments, the factors that influence the growth process were considered. Since agglomeration is the dominant growth process in iron precipitation, specific attention was given to the operating parameters that influence the three stages of the agglomeration process. An algorithm, the so-called Hadamard matrix, was used to indicate the relative importance of these operating variables with respect to the degree of agglomeration, iron removal efficiency and the filterability of the product. This could assist the process engineer to focus on the more important parameters.

In terms of the relative importance of the operating variables, the study has shown that seed addition, temperature, pH and solution zinc content, which effects viscosity, had the biggest influence on the degree of agglomeration. It was shown that initial seed concentrations between 15 g/L and 35 g/L gave the optimum degree of agglomeration, probably due to the higher collision frequency achieved. The final product particle size was found to follow the same trend as the degree of agglomeration when the initial seed concentration was changed. Initial seed concentrations of up to 50 g/L were used to improve the specific filter resistance by about 80%. Seed additions also resulted in an improvement in the precipitate purity by reducing the zinc and sulphate contents of the final product.

Furthermore, temperature and pH influenced the consolidation of agglomerates through its influence on the supersaturation. It was shown elsewhere [Claassen *et al.*, 2003] that agglomeration growth is optimal at pH values around 3 and temperatures above 60°C. The influence of the solution zinc content or solution viscosity on the agglomeration process, stems from the effect that it has on the collision frequency of particles an order of magnitude smaller than the Kolmogoroff microscale. Optimum agglomeration was achieved with seed particles in the size range 5μm to 6μm.

The relative importance of operating variables with regards to the filterability of the precipitate and the iron removal efficiency, as iron is mostly removed as an impurity from hydrometallurgical circuits, was also determined. It was shown that pH, temperature, the hot iron solution iron concentration and seed addition had the biggest impact. The hot iron solution iron concentration influenced the final particle size as it impacted on the consolidation stage of the agglomeration process. The results have shown that higher hot iron solution iron concentrations supported agglomeration growth at higher seed concentration to give a coarser final product.

The study also indicated that, according to the outcome of the Hadamard matrix for the range of each operating parameter explored, the physico-chemical parameters were of greater importance than changes in the hydrodynamic environment. However, the mixing intensity could adversely affect the precipitation process through its influence on the first two stages of the agglomeration process, namely the probability of collisions and time allowed for particles to stay together, and the range and distribution of supersaturation and should therefore always be considered when an attempt is made to improve precipitate quality.