4. MIXING AND PRECIPITATION

4.1 Introduction

Precipitation of poorly soluble phases such as iron hydroxides is generally associated with fast reaction kinetics resulting in rapid nucleation. High nucleation rates in turn are known to have a detrimental effect on product quality. The product quality can therefore be greatly influenced by mixing efficiency if the process is mixing controlled. The importance of controlling the mixing environment during precipitation processes stems from a difference in the timescales of the various mixing environments (macro-, meso- and micro mixing environments) compared to the timescales of the precipitation processes present in a typical precipitator as summarised in Figure 23.

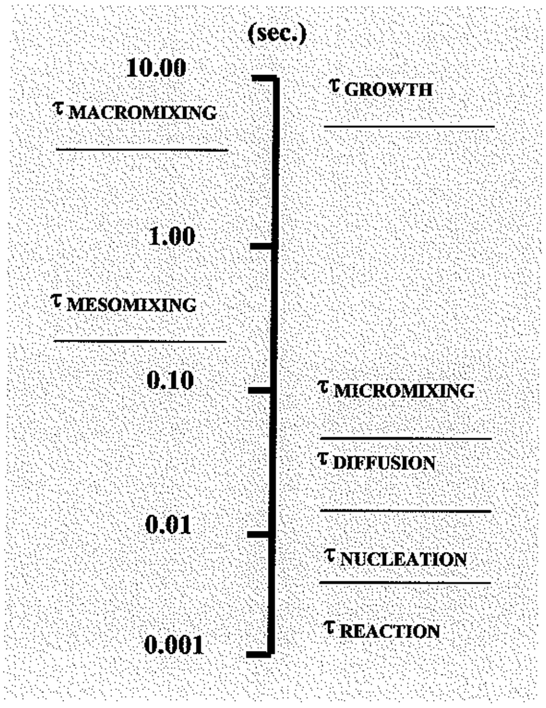

Figure 23. Illustration of the difference between mixing and precipitation (nucleation and growth) time scales [Adapted from Vicum *et al.*, 2004].

In Figure 23 macromixing refers to fluctuations in concentration on the scale of the reactor diameter and the characteristic time for this level of mixing is the reactor circulation time. Mesomixing refers to mixing at the scale of the reactant inlet tubes, with the tube diameter and the inlet flow rate that influence the mixing time. On the micro scale (vortex scale), micromixing describes the segregation state of a fluid element in terms of its volume and homogeneity. The timescale of micromixing is influenced by the amount of energy dissipated in a system and the properties of the fluid. Since the reaction and nucleation rates in precipitation processes could be orders of magnitude faster than the mixing times, as illustrated in Figure 23, inhomogeneities in species concentration throughout the reactor are expected to occur. This in turn influences the supersaturation, which determines the rates of nucleation and growth. The fact that all the processes shown in Figure 23 occur simultaneously in a precipitator, as well as the difficulties associated with scaling up laboratory scale experiments to plant scale processes, make the study of the mixing environment in precipitation processes and the prediction of the range and distribution of supersaturation relatively difficult.

Different mixing strategies have therefore been investigated in an effort to improve product quality in precipitation processes [Gösele and Kind, 1991; Franke and Mersmann, 1995; Van Leeuwen *et al.*, 1996 (a); Van Leeuwen *et al.*, 1996 (b); Baldyga and Orciuch, 2001]. These and other studies focussed on the influence of the type of process (batch, semi-batch or continuous), location of the feed points, type of mixing (mechanical, jet, etc.), micromixing effects (energy input), mesomixing effects (nozzle design) and macromixing effects (reactor design and type of impeller) on product quality in precipitation processes. Of particular interest is the work done by Gösele and Kind [1991] and later Van Leeuwen *et al.* [1996 (b)] on the so-called three-zone approach for precipitation processes. The three-zone model, illustrated in Figure 24, represents the three main mixing environments found in a mixed reactor, namely the macromixing (pumping action of the impeller/ recirculation time), mesomixing (mixing intensity at the reactant inlets) and micromixing (mixing intensity at the impeller tip/stirring rate) regions.

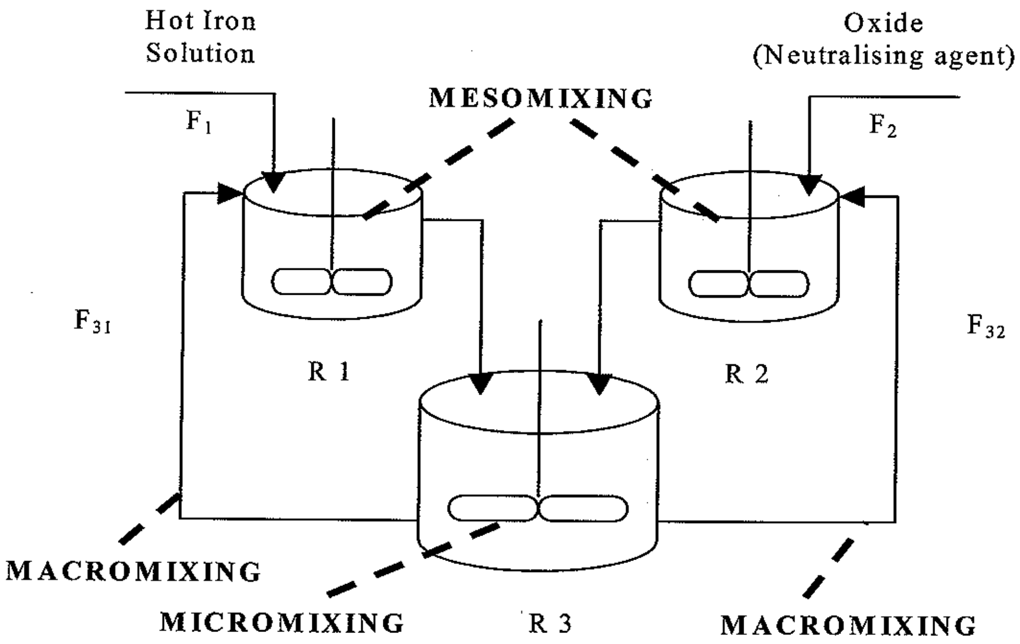

Figure 24. Three-zone model used to study the influence of mixing on iron precipitate product quality [Adapted from Gösele and Kind, 1991].

From Figure 24 it is clear that the influence of the three mixing regimes on product quality can be studied in isolation by varying the recirculation flow rates (F_{31} and F_{32}), the total residence time (mixing time) and the mixing rates in R1, R2 and R3. The three-zone model, as well as different reactor designs and variations in the feed point locations, were used in this study to determine whether the quality of iron precipitates can be improved when the mixing regime is changed. The need to investigate the influence of changes in the mixing environment on iron precipitate quality arise from the fact that it has received relatively little attention compared to the other factors used to control supersaturation during iron precipitation. In the zinc industry, for example, the jarosite process was developed [Patents, 1964; 1965(a); 1965(b)] to produce a crystalline product with the addition of an alkali element at high temperatures and pH values below 2 (refer to Figure 3). These conditions force the supersaturation down as it increases ferric iron solubility. Furthermore, in the goethite iron removal process developed later [Patents, 1966; 1972], supersaturation is effectively controlled by the rate of ferrous iron oxidation using air, which is relatively slow at high temperatures and pH values of around 2.5. But, it is when ferric iron solution is neutralized at pH values greater than about 3.0, as is the case in the so-called para-goethite process [Loan *et al.*, 2002] and similar Zincor process [Claassen *et al.*, 2002] as well as many other industrial processes, that a more voluminous product containing higher impurity values is produced. If conditions are not well controlled in these processes, a product that is difficult to treat in down stream processes, such as gelatinous precipitates, can be produced, as illustrated earlier in Figure 4. Figure 4 also indicates that crystalline products can be produced from dilute solutions at low relative supersaturation levels. Improved control over the range and distribution of supersaturation during ferric iron precipitation is required in many industrial processes, as the morphology and high impurity content of the products typically produced in this manner, have a detrimental effect on the economics of the operations, as it increases the cost of down stream processes (solid-liquid separation processes and residue storage), and in some cases contributes to the loss of valuable metals [Claassen, 2002].

In this section the influence of changes in the macro, meso and micromixing environments on iron precipitate quality was studied by giving attention to mainly the following areas:

- The mean residence times were calculated from residence time distribution (RTD) data obtained for a CSTR and a draft tube baffled reactor [Fogler, 1999]. This was done to evaluate the impact of changes in the type of impeller, mixing rate, reactor design, feed point location and type of pre-mixer on the mixing efficiency, i.e. to evaluate the influence of changes in the macro and micromixing environments on the residence time of a species. Furthermore, since efficient mixing is required in precipitation systems, as alluded to in previous paragraphs, the use of the mean residence time to indicate optimal mixing conditions were evaluated.
- The three-zone model approach was used to isolate the effect of macro, meso and micromixing on iron precipitate quality.
- The influence of changes in the reactor geometry and feed point location on product quality was studied.

4.2 Experimental

4.2.1 Residence time distribution and the mean residence time

The mean residence times were calculated from the distribution of residence times for a CSTR and a draft tube baffled (DTB) reactor. The dimensions of these reactors are shown in Figures 6 and 25, respectively. 10 mL of a 20% NaCl solution was pulse injected into the inlet to the reactor at the start of each experiment. The change in the NaCl concentration in the outlet of the different reactors evaluated was then measured with a conductivity meter. Each experiment was terminated after 35 minutes. Experiments were conducted in triplicate. The variables and their ranges used to determine the RTD and mean residence times in a CSTR and DTB reactor are summarized in Table 7.

Table 7. Variables and their ranges used to determine the RTD and mean residence times in a CSTR and DTB reactor.

Experiment	Variable	Range		
1	Reactor type	CSTR	____	DTB reactor
2	Stirrer speed (rpm)	200	400	600
3	Type of agitator	Flat, 2-blade	Pitched, 3-blade	Pitched, 4-blade
4	Feed point position	Near the agitator	____	At the solution interface
5	Type of pre-mixer	Y-mixer	____	T-mixer

The pre-mixers used were pipe mixers with an inside diameter of 3mm. The outlets of these mixers were placed near the agitator blades in each experiment.

In all experiments, distilled water was fed at a constant rate of 440mL/min to the CSTR and 435mL/min to the DTB reactor. The water inlet point was placed near the agitator blades. The NaCl used was of CP grade.

For the calculation of the mean residence times, the concentration curve (C(t)) was first constructed from the conductivity measurement data. The accuracy of the data captured was checked by performing a mass balance at the end of each experiment. The residence time distribution function was then calculated using equation 5, followed by equation 6 for the calculation of the mean residence time t_m.

$$E(t) = C(t)/{}_0\int^{\infty} C(t)dt \qquad \text{....5}$$

$$t_m = {}_0\int^{\infty} t \times E(t)dt \qquad \text{....6}$$

The so-called five-point quadrature formula [Fogler, 1999] was used to calculate the areas underneath the concentration and distribution function curves.

4.2.2 Three-zone model approach to improve iron precipitate product quality

The experimental arrangement used in this part of the study is shown in Figure 22. All the reactors (R1-R3) were sealed and baffled vessels. The dimensions of reactor 3 (R3) were shown in Figure 6. In the case of R1 and R2, four 5mm wide baffles were used in each vessel to assist mixing. Reactors with volumes of 600mL, 1000mL, 1500mL and 2500mL were fabricated and used in positions R1 and R2 (refer to Table 8). To determine the influence of the macromixing environment on product quality, a parameter called the Exchange Rate Ratio (Er) was defined as follows (refer to Figure 22):

$$Er = F_{31}/[F_{31} + F_{32}] \qquad \text{....7}$$

In order to eliminate the effects of a change in the total residence time (total mixing time remained constant at about 1 hour) with changes in Er, the volumes of R1 and R2 were changed by means of using different reactor sizes. The levels in R1 and R2 were controlled at preset values with peristaltic pumps. Changes made to the volumes of these vessels also necessitated adjustments to the energy input (stirring rate) to these reactors to eliminate the effect of changes in the mesomixing environment. The Er was calculated with respect to low and high values of F_{32}. The experimental parameters used to determine the influence of changes in the Exchange Rate Ratio on iron precipitate product quality are summarised in Table 8.

Table 8. Experimental parameters used to determine the influence of solution exchange rates on iron precipitate product quality using the three-zone model approach.

Er	Reactor volume (mL)			Flow (mL/min)				Stirring rate (rpm)		
	R1	R2	R3	F_1	F_2	F_{31}	F_{32}	R1	R2	R3
0	0	0	4010	38.7	28.2	0.0	0.0	0	0	600
0	0	480	4010	38.7	28.2	0.0	7.1	0	210	600
0	0	820	4010	38.7	28.2	0.0	12.7	0	270	600
0	0	1150	4010	38.7	28.2	0.0	18.3	0	310	600
0.15	589	3335	4010	38.7	28.2	9.7	54.8	230	530	600
0.15	202	1140	4010	38.7	28.2	3.2	18.3	180	300	600
0.35	1070	1980	4010	38.7	28.2	17.4	32.3	310	410	600
0.35	610	1140	4010	38.7	28.2	9.9	18.3	240	320	600
0.45	1070	1310	4010	38.7	28.2	17.4	21.3	310	330	600
0.45	920	1140	4010	38.7	28.2	15.0	18.3	280	320	600
0.55	1070	880	4010	38.7	28.2	17.4	14.2	310	280	600
0.55	1370	1140	4010	38.7	28.2	22.4	18.3	330	320	600
1.00	640	0	4010	38.7	28.2	9.7	0.0	240	0	600
1.00	1100	0	4010	38.7	28.2	17.4	0.0	310	0	600
1.00	1450	0	4010	38.7	28.2	23.2	0.0	350	0	600
1.00	2380	0	4010	38.7	28.2	38.7	0.0	440	0	600

In these experiments CP grade ZnO powder was used as neutralising agent. Experiments were also conducted using roasted zinc calcine instead of the CP grade ZnO powder. The zinc content and some of the main impurity values of the calcine used, are shown in Table 9.

Table 9. Chemical composition of the calcine used to precipitate iron using the three-zone model approach.

Zn (%)	Fe (%)	Pb (%)	SiO_2 (%)	Cu (%)	Mn (%)
55.70	5.18	3.00	2.86	1.00	0.92

The calcine used had a d_{50} of about 18µm. It was added as a 15% (mass/mass) slurry prepared with distilled water. 10 g/L initial seed with a d_{50} of about 6µm was also used. The experimental parameters used to determine the influence of changes in the macromixing environment on iron precipitate quality for the case where industrial zinc calcine is used as neutralising agent, is summarized in Table 10.

Table 10. Experimental parameters used to determine the influence of solution exchange rates on iron precipitate product quality using the three-zone model approach and industrial zinc calcine as neutralising agent.

Experiment	Reactor volume (mL)			Flow (mL/min)				Stirring rate (rpm)		
	R1	R2	R3	F_1	F_2	F_{31}	F_{32}	R1	R2	R3
Base case			4010	30.1	38.9					600
HIS recirculation	600		4010	30.1	38.9	13.6		240		600
Calcine slurry recirculation		1150	4010	30.1	38.9		38.9		320	600
HIS and calcine slurry recirculation	600	1150	4010	30.1	38.9	13.6	38.9	240	320	600

The effect of mixing time on iron precipitate product quality was investigated by changing the recirculation flow rates at an Er of 0.5. The mixing time was defined as follows:

$$M_t = Volume_{TOTAL} / [F_{31} + F_{32}] \qquad \text{....8}$$

Where: $Volume_{TOTAL} = Vol_{R1} + Vol_{R2} + Vol_{R3}$

The experimental parameters used to determine the influence of changes in the mixing time (macromixing) on iron precipitate product quality are summarised in Table 11.

Table 11. Experimental parameters used to determine the influence of mixing time on iron precipitate product quality using the three-zone model approach.

Mt (min)	Reactor volume (mL)			Flow (mL/min)				Stirring rate (rpm)		
	R1	R2	R3	F_1	F_2	F_{31}	F_{32}	R1	R2	R3
0	350	350	750	7.3	5.3	0	0	200	200	260
3	350	350	750	7.3	5.3	242	242	200	200	260
6	350	350	750	7.3	5.3	121	121	200	200	260
15	350	350	750	7.3	5.3	48	48	200	200	260
30	350	350	750	7.3	5.3	24	24	200	200	260
60	350	350	750	7.3	5.3	12	12	200	200	260

To determine the influence of micromixing on iron precipitate product quality, the agitator speed in reactor 3 (R3) was varied at a fixed Er and Mt. The experimental parameters used to determine the influence of changes in the energy dissipation in R3 on iron precipitate product quality are summarised in Table 12.

Table 12. Experimental parameters used to determine the influence of micromixing on iron precipitate product quality using the three-zone model approach.

Er	Mt (min)	Reactor volume (mL)			Flow (mL/min)				Stirring rate (rpm)		
		R1	R2	R3	F_1	F_2	F_{31}	F_{32}	R1	R2	R3
0.35	6	600	1100	4010	38.7	28.2	9.9	18.3	240	310	200
0.35	6	600	1100	4010	38.7	28.2	9.9	18.3	240	310	400
0.35	6	600	1100	4010	38.7	28.2	9.9	18.3	240	310	600
0.35	6	600	1100	4010	38.7	28.2	9.9	18.3	240	310	800

4.2.3 Influence of reactor design and feed point location on iron precipitate quality

4.2.3.1 Reactor design

The crystallizers used to precipitate iron included an open baffled reactor, shown in Figure 6, a draft tube reactor with dimensions shown in Figure 25, a fluidised bed reactor shown in Figure 26 and a pipe mixer with inside diameter of 5mm in the form of a Y-piece combined (upstream of) with the baffled reactor, shown in Figure 6.

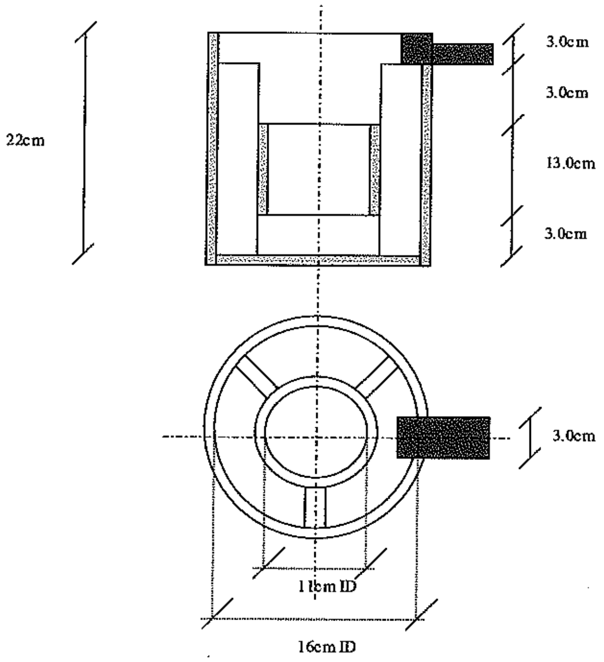

Figure 25. Dimensions of the draft tube reactor used to precipitate iron from a hot iron solution.

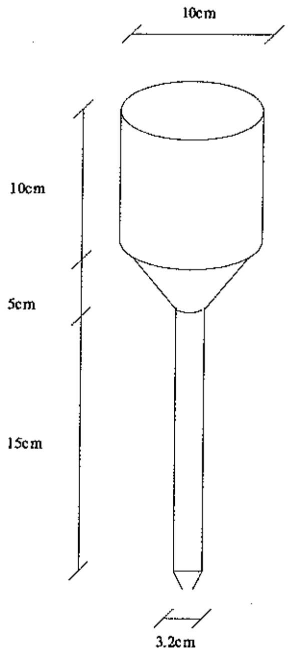

Figure 26. Dimensions of the fluidised bed reactor used to precipitate iron from a hot iron solution.

The experimental parameters used to investigate the influence of reactor design on iron precipitate product quality are summarised in Table 13.

Table 13. Experimental parameters used to determine the influence of reactor design on iron precipitate quality.

Reactor	Active reactor volume (mL)	Flow (mL/min)		Stirring rate (rpm)
		Iron solution	Oxide slurry	
Open baffled	4010	38.2	27.8	400
Draft tube	3970	38.2	27.8	390
Fluidised bed (air agitation)	1300	9.6	7.0	≈3500 mL/min
Pipe - open baffled reactor combination	4020	38.2	27.8	400

In these experiments, the hot iron solution and ZnO slurry feed points were placed on opposite sides of the reactors with the outlets positioned beneath the agitator blades.

4.2.3.2 Role of feed point location

In this part of the study the open baffled (see Figure 6) and draft tube (see Figure 25) reactors were used. The details of the experiments conducted are summarised in Table 14.

Table 14. Experimental parameters used to determine the influence of feed point location on iron precipitate quality.

Reactor	Feed point location	Total reactor volume (mL)	Flows (mL/min)		Stirring rate (rpm)
			Iron solution	Oxide slurry	
Open baffled reactor	Distant, at surface	4010	38.2	27.8	400
Open baffled reactor	Distant, beneath stirrer	4010	38.2	27.8	400
Open baffled reactor	Side by side, at surface	4010	38.2	27.8	400
Open baffled reactor	Side by side, beneath stirrer	4010	38.2	27.8	400
Draft tube reactor	Distant, at surface	3970	38.2	27.8	390
Draft tube reactor	Distant, beneath stirrer	3970	38.2	27.8	390

Note: 'Distant' means diametrically opposed

In all the experiments three-blade marine type impellers were used as mixers. The pH and temperature in reactor 3 (R3) were controlled at 3.2 ± 0.1 and 60°C ± 1°C, respectively. Each of the experiments referred to in Tables 8, 11 and 12 was terminated after two hours whereas the rest of the experiments were stopped after one hour. At the end of each experiment, 250 mL slurry was extracted from reactor 3 (R3). The slurry was filtered in a Buchner funnel with a surface area of 50 cm^2. 10 mL of a 0.1% non-ionic flocculant was added to aid filtration. The filterability of the precipitates was then determined using equation 9.

$$\alpha\eta = (2\,t\,\Delta p\,A)/VH \qquad \ldots 9$$

Where:
$\alpha\eta$ = specific filter resistance of the filter cake [$Pa.\,s.m^{-2}$]
t = filtration time [s]
Δp = differential pressure [Pa]
A = filtration area [m^2]
V = filtrate volume [m^3]
H = filter cake thickness [m]

The filtered solids were dried to determine the moisture content and analysed to obtain the dry solids density, zinc content (water soluble and acid soluble zinc), iron content and the total sulphates present.

The hot iron solutions used were made up with distilled water and contained 5 g/L H_2SO_4 and 10 g/L Fe added as $Fe_2(SO_4)_3$. ZnO powder slurried to a concentration of 5% (mass/mass) with distilled water was used as neutralising agent. Chemicals used were of CP grade.

4.3 Results and discussion

The performance of crystallization processes is dependent on the ability to predict and control the range and distribution of supersaturation. Whereas this is relatively easy to do, for example, in cooling and evaporative crystallisation processes, the same cannot be said for precipitation processes (e.g. for reaction and reductive crystallization). The introduction of reagents with their own chemical and physical properties, especially if solid phase reagent(s) are used, the formation of another poorly soluble solid phase with its own characteristics and the interaction between these phases and their environments contribute, amongst other things, towards the difficulties typically experienced to control and model supersaturation.

In order to improve control over supersaturation in iron precipitation processes, an attempt was made in this study to first of all determine how sensitive iron precipitate product quality is to changes in the mixing environment, and secondly to determine means of improving product quality through focusing on the macro-, meso- and micromixing regimes. Lastly, the influence of changes in the macro and micromixing environments on the mean residence time for two reactor types was also determined, since mixing efficiency is often expressed in terms of the mean residence time.

4.3.1 Three-zone model approach to improve iron precipitate product quality

4.3.1.1 Role of macromixing

As far as the influence of the Exchange Rate Ratio (Er) on precipitate quality is concerned, the influence of ferric iron solution recirculation (Er = 1), oxide recirculation (Er = 0) and a combination of the two (0 > Er < 1) on the specific filter resistance and purity of the precipitate were specifically studied at a fixed mixing time (Mt). Figure 27 shows the effect of neutralizing agent and iron solution recirculation on specific filter resistance. The flow ratios used in these experiments were calculated as follows:

$$\text{Iron solution recirculation flow ratio} = F_{31} / F_1 \qquad \text{....10}$$

$$\text{Oxide recirculation flow ratio} = F_{32} / F_2 \qquad \text{....11}$$

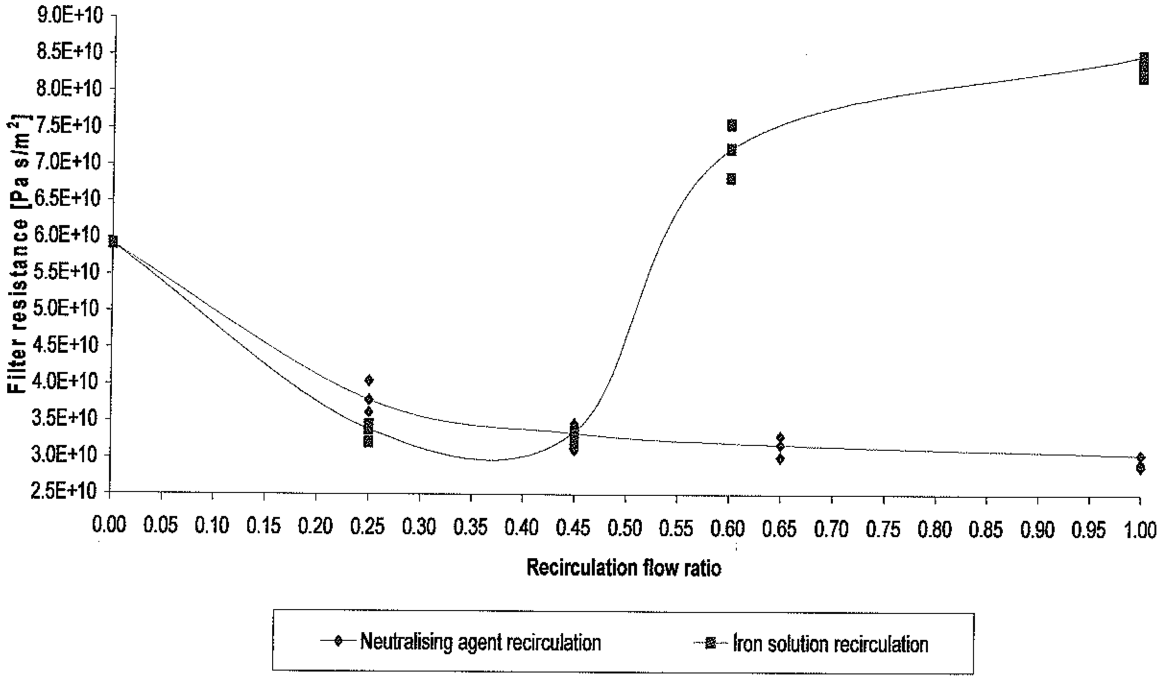

Figure 27. Effect of iron solution and oxide slurry recirculation on specific filter resistance for iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

When the two recirculation flows were combined to give Er values between zero and one, a similar graph than for iron solution recirculation was obtained as illustrated in Figure 28.

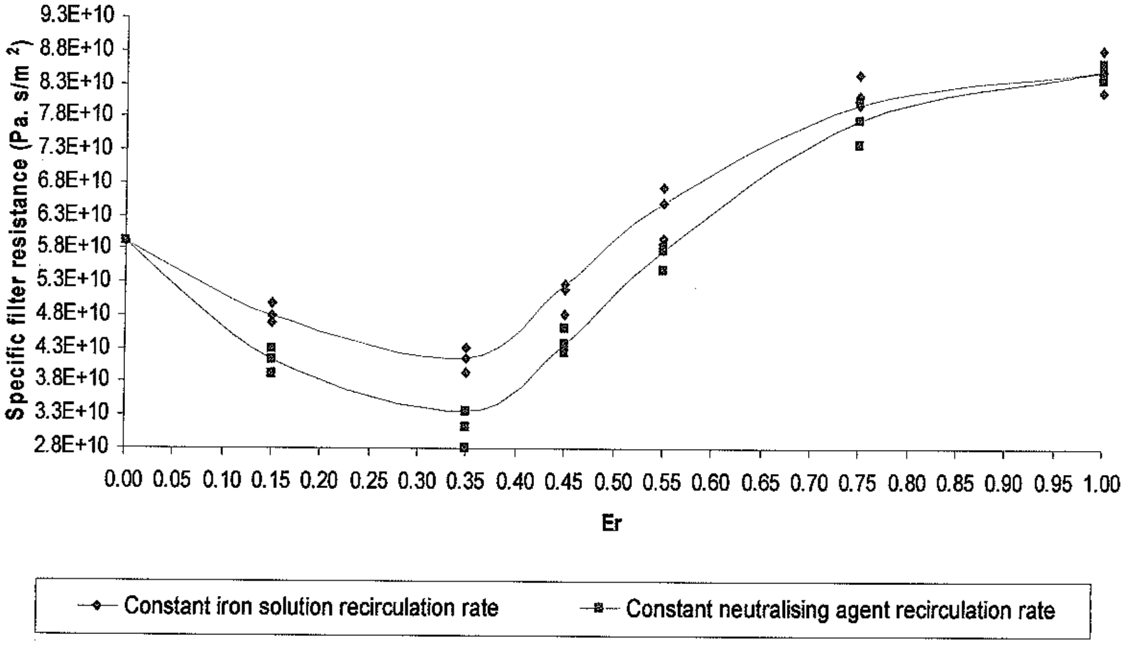

Figure 28. Effect of iron solution and oxide slurry recirculation on specific filter resistance for iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

Figures 27 and 28 indicate that iron precipitate product quality is relatively sensitive towards mass transfer in the inlet regions (inlet regions represented by reactors R1 and R2) as precipitate filterability improved by about 50%. An optimum was achieved at Er values around 0.35. The graphs also indicate that the filterability of the precipitate is more sensitive towards changes in the iron solution recirculation flow rates (cation mass transfer). The reduction in the filter resistance of the material obtained through these experiments was also accompanied by improvements in the purity of the precipitate as shown in Figures 29 and 30.

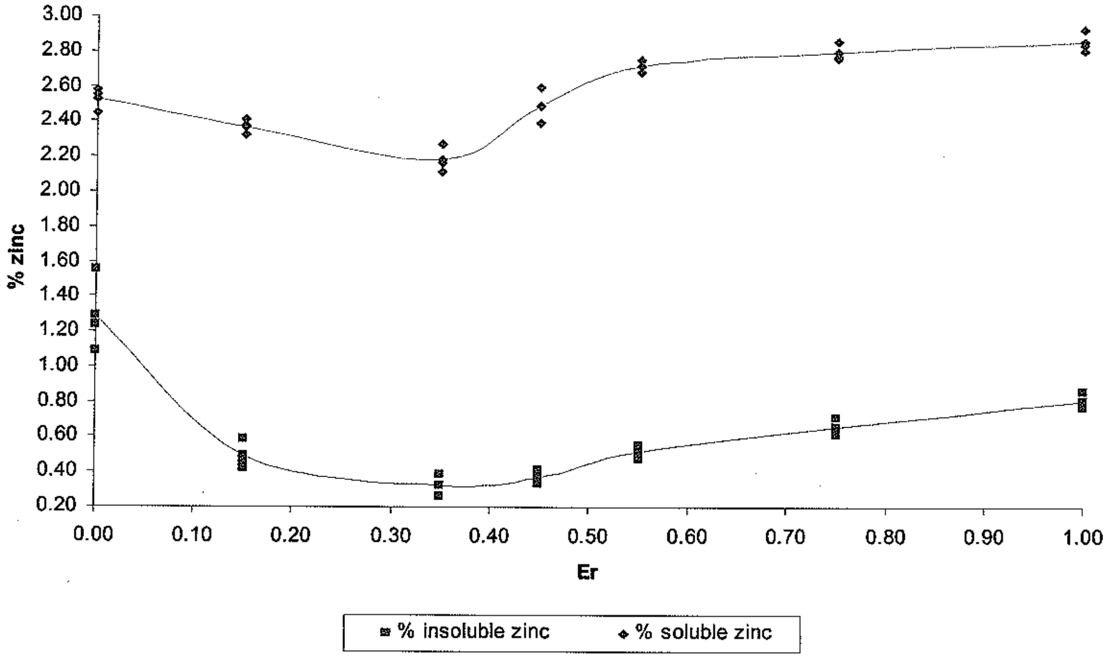

Figure 29. Effect of solution recirculation on the zinc content of iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

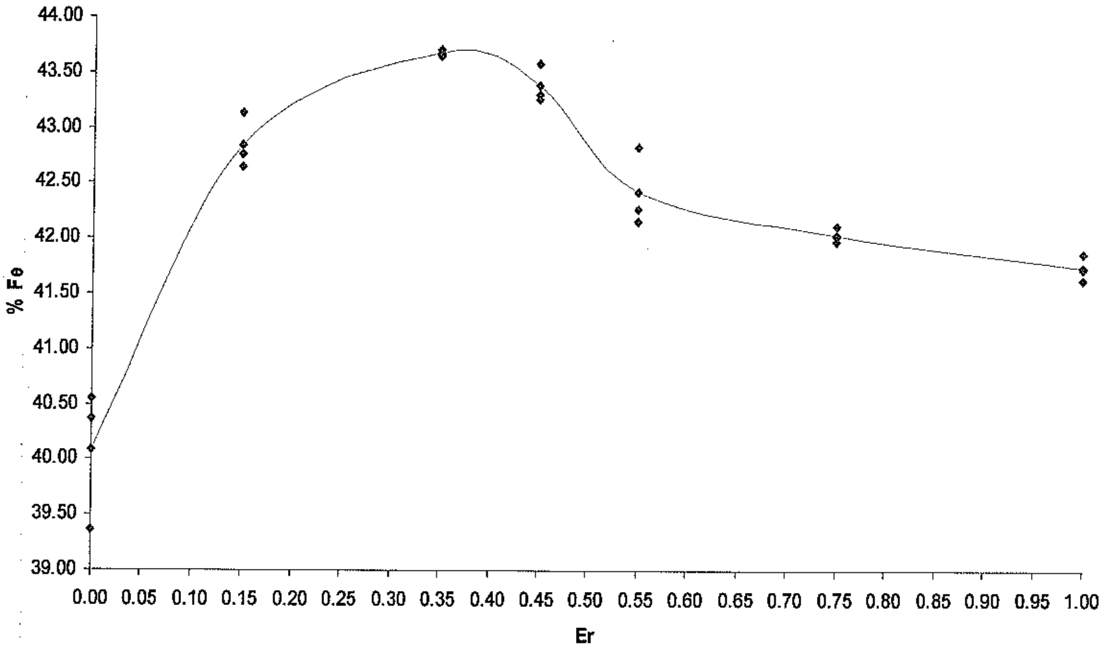

Figure 30. Effect of solution recirculation on the iron content of iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

Figure 29 shows an almost 75% average reduction in the acid soluble zinc concentration (represents entrained $ZnSO_4$ solution and unleached ZnO) and a 14% average reduction in the water soluble zinc content (represents relative surface area of the particulates formed) of the iron precipitated at an Er of about 0.35. The iron content of the precipitate was also raised by almost 9%, as illustrated in Figure 30.

Although the data obtained clearly reflects the importance of effective mixing of the reagent streams with the bulk of the solution in reactor 3, the exact mechanisms involved are not fully understood. From Figure 27 it appears as though recirculation of bulk solution through reactor 2 (R2) resulted in a more dilute environment, which probably led to a reduction in supersaturation in the area around the oxide inlet point in R3. In the case of iron solution recirculation, it is proposed that the positive effect of initial dilution, up to Er values around 0.35, was probably overshadowed by an increase in supersaturation at higher Er levels, due to an increase in the iron concentration in reactor 1, caused by the redissolution of recycled solids in this vessel, which operated at pH values between about 1.45 and 1.80.

For the case where industrial zinc calcine was used as neutralising agent, the reduction in the insoluble zinc loss values was less than indicated in previous paragraphs for CP grade ZnO powder, as shown in Table 15.

Table 15. The effect of applying the three-zone model approach on iron precipitate quality when industrial zinc calcine was used as neutralising agent.

Experiment	Weak acid soluble Zn (%)	Average specific filter resistance (Pa s/m^2)
Base case (no recirculation)	6.85	4.55×10^{10}
HIS recirculation	5.92	3.91×10^{10}
% Improvement	**13.6**	**14.1**
Calcine recirculation	5.08	3.24×10^{10}
% Improvement	**25.8**	**28.8**
HIS and calcine recirculation	5.39	3.54×10^{10}
% Improvement	**21.3**	**22.2**

The lower than expected improvements in the zinc content of the iron precipitates produced using calcine with a d_{50}-value of 18μm, as neutralising agent, could probably be attributed to its lower reactivity, as defined by its mean particle size, compared to the ZnO powder, which had a d_{50}-value of 2μm. A reduction in the mean particle size of the calcine is expected to yield better results. The introduction of more fines, in the form of refractory materials, when calcine is used, could also have contributed to slightly lower filtration rates shown in Table 15 compared to the results shown in Figure 27. Furthermore, the reasons for the lower than expected improvement in the zinc content and filterability of the iron precipitate, in the case where only HIS was circulated ($F_{31}/F_1 \approx 0.45$), is not clear. It is possible that silica gel formation in R1 might have contributed to the slightly lower filterability of the precipitate [Claassen, 2002]. Calcine also contains refractory zinc, in the form of zinc ferrite and zinc silicates (excluding willemite) that cannot be leached at the conditions prevailing in R1. Nonetheless, the improvements of nearly 26% and 29% in the weak acid soluble zinc value and filterability of the precipitate, respectively, when only the neutralising agent is circulated, is noteworthy as it would significantly reduce water and weak acid soluble zinc losses associated with iron precipitates.

Regarding the influence of the mixing time on precipitate quality, it was found that an increase in mixing time resulted in an improvement in the filterability of the solids formed as shown in Figure 31. The high filter resistance at short mixing times probably resulted from increased nucleation rates that promoted colloid formation, as suggested by Nielsen [1964].

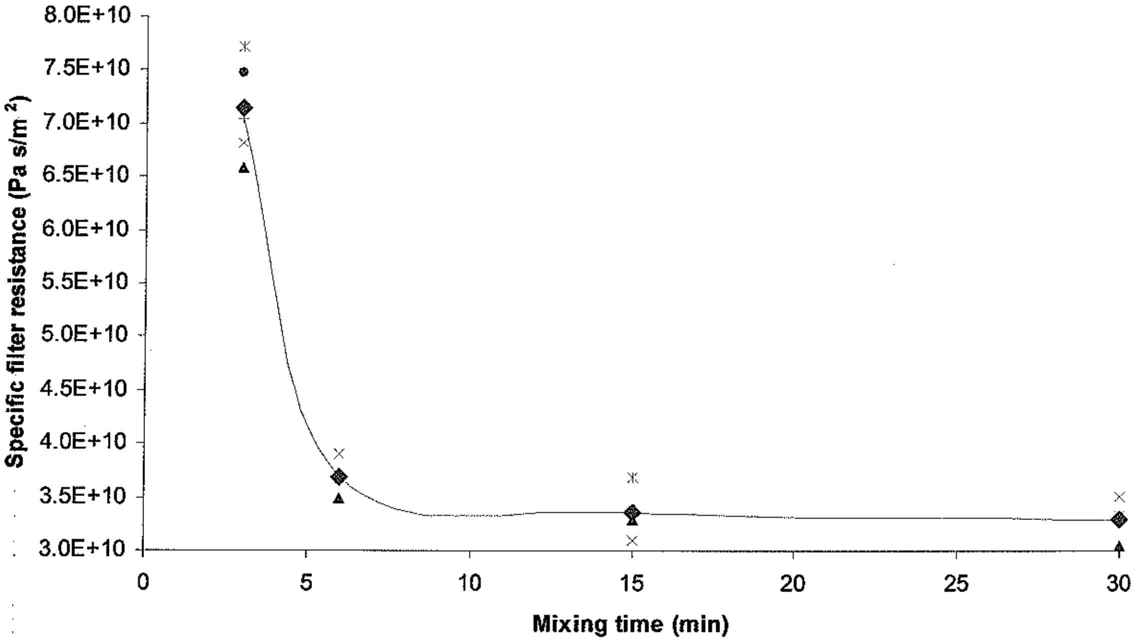

Figure 31. Effect of mixing time on the specific filter resistance of iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

4.3.1.2 Role of mesomixing

Changes in the mesomixing environment (stirring rates in reactors 1 and 2) had very little effect on the final iron precipitate product quality, as supersaturation in R1 and R2 was not altered during the process. The specific filter resistance of solids produced when the mixing rates in R1 and R2 was changed independently from 200rpm to 600rpm, changed by less than 10%.

4.3.1.3 Role of micromixing

Increased micromixing, as indicated by increased stirring in reactor R3, increased the specific filter resistance, as shown in Figure 32. This is probably due to the short micromixing times at the stirrer outlet giving rise to supersaturation peaks causing increased nucleation rates [Franke and Mersmann, 1995]. Higher energy inputs in precipitation systems are also known to break up precipitates due to their relatively low strength.

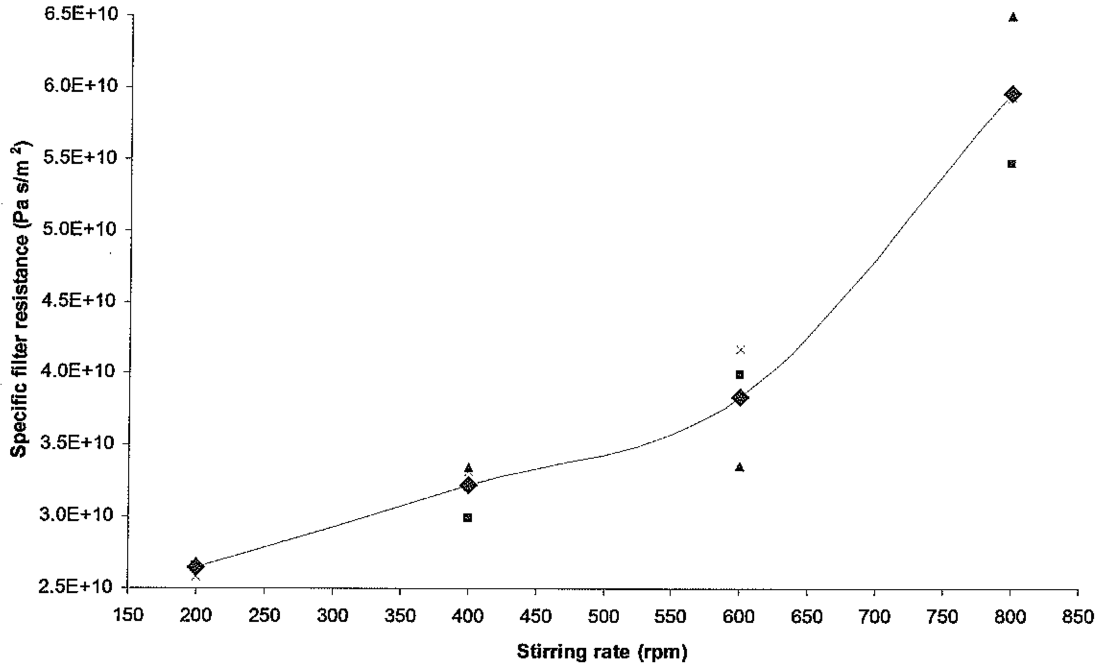

Figure 32. Effect of stirring rate, i.e. micromixing, on specific filter resistance of iron precipitated from an iron solution containing 5 g/L H_2SO_4 and 10 g/L Fe, added as $Fe_2(SO_4)_3$, using a 5% ZnO slurry as neutralising agent.

4.3.2 Influence of reactor design and feed point location on iron precipitate quality

In the case of precipitation processes, the chemical reaction and nucleation take place mainly in the contact zones around the reactant inlet points leading to high local supersaturation. The extent and distribution of supersaturation is influenced by the time it takes to disperse the reactants and blend it over the entire volume of the reactor. This in turn is influenced by, amongst other things, the design of the precipitator and the position of the feed points.

Furthermore, from the above paragraphs it appears as though product quality (specific filter resistance in this case) is more sensitive towards changes in the macro- than the micromixing environment, in the range between 200 and 600rpm, where the influence if macromixing was studied. If this is the case, the influence of reactor type and feed point position on product quality should be considered [Franke and Mersmann, 1995].

4.3.2.1 Role of reactor design

The reactors evaluated included a CSTR, a DTB reactor, a fluidised bed reactor and a pipe reactor. The stirring rate (refer to Table 13) for the mechanically stirred vessels was the same and selected to keep precipitated solids in suspension throughout each experiment. The average specific filter resistance of the solids produced in each of these reactors is summarised in Table 16.

Table 16. Average specific filter resistance of iron precipitates produced in different continuous reactors.

No.	Reactor type	Average specific filter resistance (Pa s/m^2)
1	Baffled reactor (CSTR)	3.66×10^{10}
2	Draft tube baffled reactor (DTB reactor)	6.34×10^{10}
3	Fluidised bed reactor	8.99×10^{10}
4	Pipe reactor – baffled reactor combination	1.01×10^{11}

Note: For 1, 2 and 4, reactant inlets beneath impeller. For reactor 3, inlets placed at opposite sides of the reactor at the bottom of the cylindrical section.

From Table 16 it appears as though improved mixing (macromixing) obtained with the DTB reactor (improved circulation flow around the draft tube) and the pipe reactor resulted in higher specific filter resistance values. This was probably due to shorter micromixing times achieved (faster macromixing rates give shorter micromixing times). The compartmentalisation (reduced mixing volumes) of the draft tube reactor and the small mixing volume (less dilution) of the pipe reactor, contributed towards higher nucleation rates and poor filterability. In both these reactors a well-mixed macrofluid was observed. This implies that the reactors were operated in the region of micromixing control. Franke and Mersmann [1995] showed that a macromixing-controlled environment is entered at lower mean specific power input values (lower stirring rates) for a DTB reactor, giving improved product quality (increased particle size). However, the product quality was shown to be sensitive towards feed point location when the mixing environment is macromixing controlled (lower stirring rates). At lower stirring rates solids might start building up in the reactor. If solids build up in a DTB reactor could be controlled and the optimum feed point location is found, a precipitate with superior qualities could probably be produced. On the other hand, a pipe reactor (T-piece or Y-piece) or specially designed mixing nozzles, should probably only be used in cases where solids are precipitated from very dilute solutions or where the solubility of the solid phase formed is in the g/L range.

The air mixed fluidised bed reactor also gave high filter resistance values, probably due to the presence of a poorly mixed macrofluid, resulting in an inhomogeneous mixing environment with high supersaturation levels and nucleation rates. Adequate dispersal of air in the fluidised bed proved to be essential to improve the filterability of the precipitate produced in this type of reactor. The main benefit of air mixing or jet mixing is that it eliminates the contact between particles and the blades to minimise particle breakage. This type of reactor should therefore be useful when the shear strength of precipitates is lower.

As far as the CSTR (open baffled reactor) is concerned, it appears as though adequate micro- and macromixing times were achieved. This allowed fairly good dilution of the reagents in the bulk, which lowered the supersaturation and nucleation rates. The reactor was therefore probably operated within the transition zone between the macro- and micromixing controlled environments. This type of reactor is the most commonly used reactor in the chemicals and metallurgical industries. It, however, leaves little scope to improve precipitate product quality compared to the DTB and fluidised bed reactors, i.e. limited particle breakage and well-mixed macrofluid conditions could be obtained simultaneously in these reactors, when optimized.

The influence of reactor type on other product quality parameters studied followed the same trend as the specific filter resistance data shown in Table 16. Table 17 indicates the impact that the type of reactor had on iron precipitate purity, mean particle size and dry solids density.

Table 17. Influence of the type of reactor used for iron precipitation on the quality of the final product.

Reactor type	Average sulphate content (%)	Average dry solids density (g/cm^3)	Average mean particle size (μm)
Baffled reactor (CSTR)	9.13	2.91	14.10
Draft tube baffled reactor (DTB reactor)	9.64	2.55	13.58
Fluidised bed reactor	10.04	2.21	9.63
Pipe reactor – baffled reactor combination	14.01	2.03	6.09

From the data presented in Tables 16 and 17, it is clear that the type of reactor used to precipitate iron needs to be considered when the final product quality is of importance. It could also be argued that any change to the mixing environment (impeller dimensions and shape, geometry of the reactor and reactor type) needs to be carefully studied to ensure that it doesn't have a detrimental effect on product quality.

Other factors to consider include the concentration of the element to be removed, the specific energy input (influenced by the shape and size of the mixer), the properties of the precipitate (size and shear strength) and the feed point location. The latter is discussed in more detail in the following paragraphs.

4.3.2.2 Role of feed point location

The influence of feed point location on product quality in CSTR and DTB reactors are summarized in Table 18.

Table 18. Influence of feed point location on iron precipitate quality.

Reactor	Feed point location	Specific filter resistance (Pa s/m^2)	Sulphate content (%)	Dry solids density (g/cm^3)	Mean particle size (µm)
Open baffled reactor	Distant, at surface	4.72×10^{10}	9.81	2.89	13.46
Open baffled reactor	Distant, beneath stirrer	3.66×10^{10}	9.13	2.91	14.10
Open baffled reactor	Side by side, at surface	6.20×10^{10}	10.54	2.22	12.15
Open baffled reactor	Side by side, beneath stirrer	5.25×10^{10}	10.04	2.35	12.79
Draft tube reactor	Distant, at surface	6.84×10^{10}	9.70	2.51	13.16
Draft tube reactor	Distant, beneath stirrer	6.34×10^{10}	9.64	2.55	13.58

Note: 'At surface' means just above the solution interface; 'distant' means on the opposite side of the reactor

The data in Table 18 indicates that improved product quality is achieved when the feed points are placed on opposite sides of the reactor and near the agitator blades. Product quality in the DTB reactor is less sensitive towards feed point location because the micromixing process controls the precipitation process with a bigger difference expected at lower energy inputs. The CSTR is more sensitive towards feed point location indicating that the process is macromixing controlled as discussed earlier. More dilution is achieved when the inlet points are placed far away from each other and near the impeller. Mixing would probably have been better with the inlets placed below the solution surface compared to just above the solution interface, where dilution takes longer to occur.

4.3.3 Residence time distribution and mean residence time

In paragraphs 4.3.1 and 4.3.2 it was shown that iron precipitate quality is sensitive towards changes mainly in the macro and micromixing environments, as the precipitation process is mixing controlled. Optimal mixing conditions for every application therefore needs to be found, i.e. for new and existing equipment where precipitation is mixing controlled. One way of doing this is through the determination of the distribution of residence times for different reactors, mixing rates, impeller types and feed point location. The mean residence times obtained for these scenarios are summarized in Table 19.

Table 19. Average mean residence times calculated for different mixing regimes using residence time distribution data.

Experiment	Variable	Mean residence time (seconds)	
		CSTR	DTB reactor
1	Reactor type	471	463
2	Stirrer speed (rpm)		
	200	458	453
	400	465	459
	600	471	463
3	Type of agitator		
	Flat 2-blade	453	449
	Pitched 3-blade	456	450
	Pitched 4-blade	461	452
4	Feed point position		
	At the solution interface	465	459
	At the agitator blades	461	452
5	Type of pre-mixer		
	Y-mixer	458	445
	T-mixer	456	444

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From Table 19 it is evident that, for the range of the different variables chosen, the changes in the macro and micromixing environments had little effect on the mean residence times. This confirms that:

- Mixing efficiency expressed in terms of the mean residence time cannot be used as an indicator of the influence of changes in the macro and micromixing environments on product quality.
- The use of the mean residence time is probably limited to specifying total residence time/reactor volume required to allow particle growth in a precipitation system, since the chemical reaction and nucleation requires very little time to take place.
- The localized supersaturation, as determined by chemical and physical variables, has the biggest impact on product quality.
- It is better to use parameters, such as the filterability and purity of the precipitate, to evaluate the influence of changes in the mixing environment on product quality, as illustrated in previous paragraphs.

4.4 Conclusions

The study showed that iron precipitate product quality is sensitive to changes in the mixing environment. Of specific importance are changes in the micro- and macromixing environments. The three-zone model approach was used to separate the effects of macro- and micromixing on precipitate quality. It was shown that product quality was more sensitive to changes in the macromixing regime. Data obtained suggested that optimum product quality, expressed in terms of the specific filter resistance and solids purity, could be achieved at Er values around 0.35. The specific filter resistance of the solids was improved by about 50%, and the zinc content of the iron precipitates was reduced by about 75% and 14% for acid- and water soluble zinc, respectively. The results also showed that product quality is more sensitive to cation (iron in solution) mass transfer than to the mass transfer of the neutralizing agent in the region of the inlet points. In the case where zinc calcine was used as a neutralising agent, improvements of about 26% and 29% for weak acid soluble zinc losses and the filterability, respectively, were achieved. The smaller improvements were probably a result of the presence of refractory zinc in the calcine, silica gel formation and the introduction of more fines into the system.

As far as the influence of mixing time was concerned, it appears as though mixing times smaller than about 5 minutes should be avoided as it induced high supersaturation levels and fast nucleation rates.

Furthermore, when product quality is more sensitive to changes in the macro- than the micromixing environment, the influence of reactor type and feed point position on product quality should also be considered. It was shown that the best results were achieved using a CSTR. The DTB reactor, however, is expected to produce precipitates with superior quality when optimised. The study also indicated that feed points should be placed as far as possible from each other and in a position that gives adequate micro- and macro mixed fluids. The controlling mixing environment (micro- or macromixing controlled) generally indicates where feed points should be located. In a well-mixed macrofluid (DTB reactor), feed points could be placed far away from the impeller. When the macromixing environment is, however, less homogeneous (CSTR), better results were obtained with the feed points placed closer to the impeller.

The changes in the micro and macromixing environments, as discussed in this section, had little impact on the mean residence times calculated from residence time distribution data, obtained for the CSTR and DTB reactor. It is therefore recommended that parameters such as the filterability and purity of precipitates are rather used to indicate the influence of changes in the mixing environment on precipitate product quality. Due to the sensitivity of product quality towards the mixing environment, a proper understanding of the precipitation system is required before changes are made to the mixing system, reactor geometry and feed point locations.

Whereas the aim of this chapter was to ensure the production of good quality nuclei by controlling supersaturation through changes in the mixing environment, the following section focuses on growing these nuclei into particles with a relatively low surface area and good liquid-solid separation properties.