Fines Formation (and Prevention) in Seeded Precipitation Processes[†]

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Abstract

An overview of three studies on seeded precipitation in a fluidised bed reactor (FBR) is presented. The objective of using the FBR is to remove dissolved metals as precipitated metal salts onto a seed surface. For the nickel hydroxy-carbonate system ($S = \pm 10^5$), particle enlargement was found to occur by a combination of growth and aggregation. The concentration of fines correlated with the degree of supersaturation in the reactor, which suggests that fines formation was due to homogenous nucleation, attrition of rough growth precipitate, or a combination of the two. Reducing the local supersaturation by multiplying the feed points was found to be a successful fines control strategy.

For the mixed nickel/cobalt sulphide system, ($S = \pm 10^{11}$ for nickel and $\pm 10^{12}$ for cobalt), a significant quantity of fines was formed but these eventually aggregated onto the seeds. In contrast, for the copper sulphide system ($S = \pm 10^{34}$), the fines formed immediately but never aggregated onto the seed material and it was not possible to control the supersaturation levels to the extent that fines formation was avoided.

Keywords: Precipitation, Metal sulphide, Nucleation

1. Introduction

Although industrial applications of precipitation have a long history and precipitation has been studied scientifically since the 1930s, understanding of this operation is still very limited¹⁾. Industrially, precipitation reactions are generally carried out in very simple reactor systems. Probably over 90% of industrial precipitation processes are carried out in ordinary stirred tank reactors operated either batch-wise or continuously²⁾. Major problems, however, often occur in control of precipitation processes, specifically in understanding the effect of processing conditions on reactor performance and product characteristics such as precipitate morphology, purity and particle size distribution^{3, 4, 1)}. In addition, the design of industrial crystallisers is still experience-based⁵⁾, and geometric and time-dependent variations are not

taken into account. It is therefore hardly surprising that these strategies fail almost without exception⁶⁾. The problem is even more challenging in the field of industrial precipitation, where the default reactor design is a simple stirred tank, invariably quite inadequate for product control.

A significant amount of research has been conducted into the development of more efficient precipitation processes. The development of the seeded fluidised bed, or pellet reactor, offers a number of potential advantages over conventional precipitation options. The technology was initially employed for the softening of drinking water by calcium carbonate precipitation⁷⁾ and the removal of phosphates from waste water, producing calcium phosphate⁸⁾. More recently, fluidised bed reactors have been used for the removal of metals (nickel, copper and zinc) from solution^{9, 10, 11, 12)} as carbonates or as sulphides. Kaksonen and co-workers¹³⁾ used biologically generated sulphide and alkalinity as the reagents to precipitate zinc and iron from acidic waste water in a fluidised bed reactor, whilst Esposito and co-workers¹⁴⁾ used the same sulphide source but precipitated only zinc from acidic waste water.

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The seeded fluidised bed reactor can provide a suitable environment for a controlled precipitation process in a stable environment. The key feature is to promote heterogeneous nucleation of precipitate on the large surface area provided by the seed material by operating under controlled supersaturation conditions. Homogeneous nucleation, which produces very small particles (fines) that are difficult to remove from the process stream, is thus minimised. The fluid velocity in the reactor, typically between $10\text{--}35\text{cm.s}^{-1}$, prevents the cementing together of the seed particles¹²⁾ but should also be sufficiently low to avoid attrition of the precipitate layer. As the thickness of the precipitate layer covering the seed particles increases, those pellets are more difficult to fluidise, and become segregated in the lower portion of the bed. This allows the larger pellets to be removed and replaced with fresh seed material.

The overall aim of this work is to characterise the mechanisms occurring in order to relate the effect of processing conditions on reactor performance and product characteristics (precipitate morphology, purity and particle size distribution).

2. Materials and Methods

2.1 Reactor design

A laboratory-scale fluidised bed reactor (**Fig. 1**) consisting of a borosilicate glass column, 150 cm high with an internal diameter of 2.5 cm, sealed from the atmosphere, was used. The reactor was filled with beach sand (95-97% SiO_2) (250-500 μm) as a seed material, to a resting height of 20, 70 or 90 cm. Reagent feed ports and sampling ports were situated at various positions along the length of the column. The base of the column consisted of a conical glass fit-

ting, packed with glass beads of decreasing diameter (10^{-2} mm) that promoted uniform distribution of the upward flow and provided a support for the seeds.

A metal-rich sulphate solution, together with the re-circulation stream, was pumped into the reactor from the bottom of the column. The re-circulation stream helped to fluidise the bed. Air was excluded from the system, as air bubbles ascending through the column could result in the loss of seed material to the re-circulation or effluent streams. The column reactor was also sealed on the top to minimise losses to the atmosphere. The aqueous reagent (either sodium sulphide or sodium carbonate) was introduced via up to six inlet points on the side of the reactor. The inlet points were equally spaced, 10 cm apart, with the first point being 10 cm from the base of the reactor. The splitting of the reagent inflow reduced the local supersaturation around the inlet points. Up to eleven equally spaced sampling points on the side of the reactor were used to obtain data for column profiles. The first point was situated 15 cm from the base of the reactor with additional points at 10 cm intervals. Each sample port was sealed with a rubber septum and liquid samples were withdrawn from the centre of the column using a syringe and needle. A sample port 5 cm from the base of the column allowed the removal of coated seed particles for further analysis.

A pH probe (Hanna) was maintained at the level of the effluent port, above the maximum bed height, to monitor the effluent pH. All reagents ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and H_2SO_4) were analytical grade, obtained from Merck. Solutions were made up to required concentrations using distilled water. Liquid samples obtained from the sample ports, the recycle stream and the effluent stream were each filtered through a $0.22\text{-}\mu\text{m}$ ny-

Fig. 1 Schematic representation of the seeded fluidised bed reactor.

Table 1 Experimental conditions for the three case studies

<i>Variable</i>	<i>FBR Ni(OH)CO₃</i>	<i>FBR Ni & CoS</i>	<i>FBR CuS</i>
Supersaturation (S)	Lowest	Moderate	Highest
Supersaturation (S)	1.05×10^5	2.42×10^{11} (Ni) 1.99×10^{12} (Co)	5.6×10^{34}
[M ²⁺] : [Anion ²⁻] (mole:mole)	1 : 2	1 : 1	1 : 1
[Co ²⁺]total (ppm)	-	50	—
[Ni ²⁺]total (ppm)	100	120	—
[Cu ²⁺]total (ppm)	—	—	150
Inlet flow $Q_{\text{feed}} = Q_{\text{Reagent}}$ (ml/min)	60	50	50
Anion ²⁻ concentration (ppm)	204	93	75.7
Reagent feed points	1, 2 and 6	3	3
Recycle Ratio : (Recycle flow/ ($Q_{\text{feed}} + Q_{\text{Reagent}}$))	1.42; 1.67; 3.11	1	2.24
Retention time (sec)	97, 87, 55	212	131
Temperature (°C)	24 ± 2 °C	23 ± 2 °C	24 ± 2 °C
pH	8.4-9.7	7.12-7.56	6.03-6.97
Resting bed height (cm)	20	70	90

ion membrane filter and analysed to determine pH (Cyberscan 2500 pH meter), and metal in solution (Varian SpectrAA-30 atomic absorption spectrophotometer). Unfiltered samples were used to determine the total metal concentration. The efficiency of the column was defined in terms of the metal removal efficiency as well as the metal conversion defined by equations (1) and (2). Fines were identified by the difference between the total and dissolved metal concentrations. For the nickel-hydroxy-carbonate process, the PSD of the fines was measured using an electro-zone sensing technique (Coulter Counter Multisizer III) in the detection range from 0.4 to 12.0 μm .

Metal removal efficiency:

$$\eta (\%) = \frac{M_{\text{in}} - M_{\text{out, total}}}{M_{\text{in}}} \times 100 \quad (1)$$

M_{in} = metal concentration in the feed (ppm)

$M_{\text{out, total}}$ = metal concentration in the outlet (including fines) (ppm)

Metal conversion:

$$\eta (\%) = \frac{M_{\text{in}} - M_{\text{out, dissolved}}}{M_{\text{in}}} \times 100 \quad (2)$$

M_{in} = metal concentration in the feed (ppm)

$M_{\text{out, total}}$ = outlet filtered metal concentration (excluding fines) (ppm)

The experimental conditions for the case studies

are given in **Table 1**. All experiments were carried out a number of times under the same conditions to ensure reproducibility of the results. The supersaturations were calculated using OLI Analyser (OLI Systems Inc (2003)). In the OLI Analyser software, all of the solution equilibria are taken into account and the Ionic Activity Product is used to calculate the supersaturation. The Ksp values used to calculate the supersaturations were 6.4×10^{-18} for Ni(OH)₂ (no data was available in OLI for the hydroxy-carbonate species), $1 \times 10^{-19.4}$ for NiS and $1 \times 10^{-21.3}$ for CoS.

3. Case Study 1: Nickel hydroxy-carbonate precipitation

For the system with one reagent feed point (at 15 cm from the base), high levels of conversion and efficiency were measured, with both reaching 99% at the top of the column. See **Fig. 2**. The initial decrease in soluble nickel concentration and the presence of fines in the lower portions of the bed indicated the occurrence of homogeneous nucleation. The fines concentration as well as the pH decreased up the length of the bed, suggesting that the fines were aggregating onto the seeds. The pH decrease would account for the consumption of supersaturation caused by the process of aggregation.

The effect of increasing the number of feed points on the conversion, efficiency and fines concentration was also investigated, with two configurations being tested:

(a) 2FP with 2 reagent feed points (at $H= 10$ cm

Fig. 2 Change in conversion, efficiency, fines concentration and pH with reactor height.

and 40 cm)

(b) 6FP with 6 reagent feed points (at $H=10$ cm, 20 cm, 40 cm, 50 cm, 80 cm and 90 cm).

The results in **Fig. 3** show that, for the 2FP case, the crystallisation efficiency varied between 60 and 90% with the fines formation ranging from 2 to 80mg/L. For the 6FP case, the crystallisation efficiency varied between 80 and 99% and the production of fines between 3 and 17mg/L. **Fig. 4** illustrates the change in relative supersaturation with bed height for the 2FP and 6FP configurations. It is clear that the global supersaturation is higher for the 2FP than for the 6FP case but, moreover, the stability of the supersaturation for the 2FP case is less.

For the 2FP configuration, the fines concentration up the bed was highly erratic and poorly controlled. Also, the two peaks observed in the fines formation correlate almost exactly with the reagent feed points. This could be accounted for by the high local supersaturation at the reagent feed points, which causes

Fig. 4 Change in supersaturation with reactor height for 2FP and 6FP.

homogenous nucleation and results in the generation of fines. However, it is also possible that fines could be formed due to attrition in the bed.

Two plausible mechanisms can be proposed to account for fines formation and consumption. For the first mechanism, the reaction takes place in the immediate region near the feed point and nearly all the supersaturation is consumed to produce tiny crystals by primary nucleation. The remaining supersaturation is used for new growth onto the seeds and for aggregation of the fines onto the seeds.

The second mechanism is based on attrition or secondary nucleation mechanisms due to the turbulence in the bed and particle-particle or particle-wall collisions. Under conditions of high supersaturation, such as the 2FP configuration, the surface of the precipitate on the seeds became rough and thus additionally prone to attrition.

Fig. 3 Change in conversion, efficiency and fines concentration with reactor height for 2FP (left) and 6FP (right).

Fig. 5 Particle size distribution of fines in the fluidised bed reactor at various residence times.

Fig. 5 shows the effect of time on the PSD for the FP case, expressed as number density versus particle diameter. It was observed that, as the time increased i.e. from the bottom to the top of the column, the PSD broadened while its peak value shifted towards larger particle sizes with a slight increase in the particle number.

The observed shift of the peak size from 3.75 to 6.25 μm (between 13 and 28 s) is primarily due to the growth of tiny crystals to larger ones during their stay in the bed. However, in the same figure, after 46 s, the number of particles as well as their size decreased. The median diameter decreased from 6.25 to 4.75 μm . These decreases suggest that the larger fines are removed from the solution due to aggregation onto the surface of the seed.

From **Fig. 6**, it can be clearly seen that particles on the surface of the seed aggregated on the surface, but also grew into each other. The potential for generation of fines due to attrition of the rough layer aggregated onto the seed is also apparent, especially

in the 2FP case. It can also be noticed that the coated layer on the seed surface is deeper with 6FP than with 2FP.

Conclusions:

Fines concentration could be correlated to the degree of supersaturation, and excess fines were produced because of the poor distribution of the supersaturation in the lower portion of the bed. However, aggregation of fines onto the seed material occurred up the length of the bed. At the higher supersaturation measured in the 2FP case, the surface of the precipitate on the seed crystals became rough and prone to attrition, thus releasing attrited particles as fines into solution.

The 6FP configuration demonstrated that splitting the feed could effectively reduce the local supersaturation and thus improve the removal efficiency of the nickel by preventing homogenous nucleation. In addition, the smoother growth surface on the seed particles was less susceptible to attrition. More details of these two case studies can be found in (9) and (15).

4. Case Study 2: Mixed nickel cobalt sulphide precipitation

For the mixed nickel-cobalt sulphide precipitation (carried out using three reagent feed points), a similar phenomenon of fines formation in the lower portion of the bed followed by slow aggregation of the fines onto the seeds in the upper regions of the bed was observed. Only the nickel results are shown in **Fig. 7**, the cobalt results being very similar. The aggregation process was accompanied by an increase in pH, which could be due to either an excess of sulphide in the system or to the transition-metal-mediated oxidation of the bisulphide ion in solution¹⁶⁾, which releases hydroxide ions. More details of this case

Fig. 6 SEM micrographs of silica grain showing the surface texture for 2FP (left) and 6FP (right).

Fig. 7 Conversion, efficiency, fines concentration and pH for nickel in a mixed nickel-cobalt sulphide precipitation.

study can be found in (17).

5. Case Study 3: Copper sulphide precipitation

In contrast, for the copper sulphide case study illustrated in **Fig. 8**, fines were formed immediately but never aggregated onto the seed material. This contrasting behaviour compared with both the other case studies is most likely due to the extremely insoluble nature of copper sulphide and the resulting extremely high local supersaturation levels (10^{34}), which would be responsible for homogeneous nucleation and formation of fines. Because of the extremely insoluble nature of copper sulphide compared with the other two systems, the supersaturation is entirely consumed in the homogeneous nucleation process, with none remaining to achieve the fines aggregation

Fig. 8 Copper concentration in the reactor as a function of position in the bed.

observed in the other cases. More details of this case study can be found in Reference 18).

6. Conclusions

For the nickel-hydroxy-carbonate system, the relatively lower global supersaturation resulted in high metal removal efficiencies. Fines were formed at the reagent injection point, but aggregated onto the seeds up the length of the bed. Splitting the reagent feed points allowed the local supersaturation to be better controlled, and fines formation due to both homogeneous nucleation and attrition was minimised.

For the nickel/cobalt sulphide system, despite the much higher global supersaturation, it was still possible to control fines formation by multiplying the reagent feed points. This resulted in fines formation and aggregation onto the seed material with time.

For the copper sulphide system, the extremely low solubility resulted in such high global supersaturation that it was not possible to control the fines. Once they had formed at the feed points, they did not aggregate in the reactor.

The overall conclusion from this work is that control of fines via supersaturation control is possible, to some extent, via strategies such as multiplying the number of reagent feed points. However, for systems with extremely low solubilities and high global supersaturations, this control parameter cannot be used to prevent fines formation in seeded precipitation processes such as these.

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Author's short biography

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Alison Lewis graduated with a BSc (Chem. Eng), MSc (Chem Eng) and PhD, all from the University of Cape Town. She is also a registered Professional Engineer. After two years working in industry, she joined the Chemical Engineering Department at UCT. In collaboration with colleagues at the Technical University of Delft, she established a specialisation in crystallisation and precipitation processes in the Chemical Engineering Department in 2000. The Crystallisation and Precipitation Unit is an accredited university research unit and its focus is primarily around precipitation systems related to the mineral processing industry. Graduates from the Research Unit include: 1 PhD, 13 MSc and 47 Honours graduates. The publications include 36 international journal papers and books, 33 refereed international conference papers and 25 technical reports to industry.