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PRODUCT QUALITY PARAMETERS IN THE REACTION CRYSTALLIZATION OF METASTABLE IRON PHASES FROM ZINC-RICH SOLUTIONS

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by

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ABSTRACT

Iron is often present in leach liquors produced in chemical and hydrometallurgical processes. It is known that voluminous iron precipitates with high impurity values are formed if the conditions during its formation are not controlled well. These products are also often difficult to treat in downstream processes. This study therefore focused on the determination of product quality parameters for the production of good quality iron precipitates from zinc-rich solutions. Special attention was given to the quality of metastable phases such as ferrihydrite and schwertmannite formed at elevated temperatures and in the pH range 1.5 to 3.5 in a continuous crystallizer. These phases are produced over a range of supersaturation levels with the best quality products formed at lower supersaturation. It was shown that most industrial processes are operated well above the metastability limit at relatively high supersaturation. However, stagewise precipitation of iron, even above the metastability limit, yielded better quality products.

It was also shown that localized supersaturation levels could be controlled through changes in the micro and macromixing environments. The three-zone model approach was used to improve the quality of ferrihydrite and schwertmannite precipitates. Changes in the reactor design and the position of reagent feed points also impacted on the quality of the precipitates. Control over the localized supersaturation not only ensures the production of good quality nuclei, but also impacts on particle growth, which is required to make downstream processing of precipitates possible.

In precipitation processes, growth mainly takes place through agglomeration as the rate of molecular growth is generally low. The final quality of iron precipitates is greatly influenced by the quality of the agglomerates formed during iron precipitation. A Hadamard matrix was used to indicate the relative importance of the most relevant operating parameters for the formation of good quality iron precipitates.

Keywords iron, precipitation, reaction crystallization, product quality, metastability, supersaturation, ferrihydrite, schwertmannite, mixing, agglomeration

EXECUTIVE SUMMARY

Crystalline products are generally produced according to specifications that meet market requirements. The factors that influence the quality of these products have been studied extensively to allow industry to adhere to product specifications. However, the same cannot be said for precipitation systems. The lack of knowledge in this area probably stems from the fact that precipitation processes often produce low value products, are generally more complex and are difficult to control if compared with crystallization systems. This is specifically the case when a poorly crystalline phase, such as an iron hydroxide, is produced from ferric ion solution as big changes in supersaturation often occur. These changes in supersaturation typically result in the formation of a voluminous product with a high relative surface area that is difficult to treat in solid-liquid separation and storage steps. In zinc-rich solutions, a poor quality iron precipitate could result in high zinc losses, which include water soluble zinc that is difficult to remove through washing of the precipitate, adsorbed zinc, unleached ZnO and entrained $ZnSO_4$ solution. The production of a poor quality precipitate also very often increases the cost of the operation, i.e. more thickening, filtration and product drying or storage capacity are required.

In order to address the relatively high zinc losses associated with iron precipitates formed through the hydrolysis of ferric ions in zinc-rich solutions as well as the costs associated with the iron removal operation, the following steps were followed to improve iron precipitate quality:

- Identification of the iron phases present in a sulphate medium in the pH range 1.5 to 3.5 and the mechanisms involved in its formation. Initial work started in 2000 with the study of the Zincor iron removal process and its residues whereas this follow-up study mainly focused on the relative stability of the phases present.
- Determination of the influence of operating variables on the quality of these phases through its influence on supersaturation, which in turn affects the rate of the primary precipitation processes (nucleation and growth).
- Determination of the rate-limiting step and the factors that influence this step.

- Determination of the parameters that influence agglomeration of primary iron precipitates.

These steps covered the chemical, i.e. the specific phases formed and mechanisms involved, as well as the physical, i.e. the formation and growth of the solid phase, aspects of the precipitation of iron from ferric sulphate solution.

This approach was applied in a study of metastable iron phases, which include ferrihydrite and schwertmannite. Specific attention was given to the influence of operating parameters such as pH, temperature, seed addition and the mixing environment through its influence on supersaturation, on product quality parameters, which include the filterability of the precipitate, purity, particle size and density. The relative importance of the above-mentioned operating parameters in the agglomeration process was also addressed.

The hydrolysis of ferric iron, at temperatures ranging from 50 to 90°C, and pH values between 1.5 and 3.5, resulted in the formation of metastable iron phases with different morphologies and qualities. The changes in the morphology and product quality of ferrihydrite and schwertmannite were linked to changes in the relative supersaturation. These phases were precipitated over relative supersaturation levels ranging from about 1000 to 30,000. Ferrihydrite and schwertmannite precipitates formed at relative supersaturation levels below approximately 5000, contained lower impurity levels and were easier to filter.

The (meta)stability regions of these phases were also determined as a function of temperature and pH. A clear transition line between the stability regions of ferrihydrite and schwertmannite was determined following the change in their sulphate contents with a change in pH. This finding dispels the notion that schwertmannite is nothing else but ferrihydrite with high sulphate values. The solubility curve, on the other hand, was determined using a technique where the pH was cycled between predetermined values at different temperatures, noting the points where a sudden increase and decrease in the ferric iron concentration occurred. The solubility curve occurred at much higher pH values than the equilibrium solubility line, giving rise to a much narrower metastable zone of 0.2 to 0.3 pH units. Operating within the metastable zone is therefore expected to be a difficult task. Nevertheless, it was shown that stagewise precipitation of iron, with controlled supersaturation above the metastable zone, increased the precipitate quality as defined by its purity.

Furthermore, since the nature of the iron precipitate formed is dependent on the degree of supersaturation, and as mixing may determine local supersaturation levels, the influence of the mixing environment on the quality of iron precipitates was investigated. In such processes the mixing rate is generally a few orders of magnitude slower than the rates of the chemical reaction and nucleation. Any change in the rate-limiting step is therefore expected to influence supersaturation, which in turn impacts on the nucleation and growth rates, which affect the final product quality. An effort should therefore be made to reduce supersaturation. In this study iron precipitate quality was improved by improving the mixing environment.

It is shown that the final product quality of iron precipitates formed through ferric iron hydrolysis is significantly improved by changes in the micro and macromixing environments. Results indicated that 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 using the three-zone model approach. The study also showed that product quality is more sensitive to cation (iron in solution) mass transfer than the mass transfer of the neutralizing agent in the region of the inlet points. 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.

Since 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 was also studied. The best results were achieved using a CSTR. The draft-tube-baffled (DTB) reactor, however, is expected to produce precipitates with superior quality when optimized. 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, as found in a DTB reactor, feed points could be placed far away from the impeller.

When the macromixing environment is however less homogeneous such as in a CSTR, better results were obtained with the feed points placed closer to the impeller.

Lowering the supersaturation, through changes in the operating parameters and mixing environment, effectively reduce the nucleation rate to give more dense precipitates. However, even good quality nuclei formed in a well-controlled mixing 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 encountered in 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 and was therefore studied in detail. The relative importance of some operating parameters was expressed in terms of the filterability of the solids formed, the change in the particle population density and iron removal efficiency, using the so-called Hadamard matrix. The effect of seed addition on the purity of agglomerates was also evaluated. It was found that specific attention should be given to pH control, seed addition, iron solution iron concentration and temperature control. Optimum agglomeration was found to occur at a pH of 3.0, 60°C, 15 to 35 g/L initial seed concentrations and initial seed sizes between 5 and 6μm. An initial seed concentration of 50g/L improved the filterability of the iron precipitate by about 80%.

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