6. SUMMARY

The quality of precipitated products produced in hydrometallurgical refining circuits, is of utmost importance as it greatly influences plant efficiency and the cost of the operation. However, product quality in precipitation systems hasn't received the same amount of attention as the quality of crystalline products. This probably stems from the fact that precipitation processes and their products are more complex than crystallization systems. This is specifically true for the precipitation of poorly crystalline iron phases from hot ferric sulphate media in the pH range 1.5 to 3.5.

In order to address the general lack of knowledge with regards to the production of good quality iron precipitates under the conditions listed here, an industrial iron removal process, the Zincor Process and its residues were studied. This was followed by a more detailed study into the role that supersaturation, the driving force for precipitation, plays during the formation of poorly crystalline phases as well as the factors that influence the nucleation and growth processes. The aim of this detailed study was, firstly, to determine typical supersaturation levels present during the precipitation of iron and its influence on the morphology of the final product, secondly, to determine the impact of changes in the mixing environment on product quality as it influences supersaturation and the rate of nucleation (precipitation systems are mostly mixing controlled) and, thirdly, to define the conditions required for optimal growth of the precipitated nuclei and primary particles as growth through agglomeration is required to improve the downstream handling properties of the iron precipitate.

The findings from the study of the Zincor iron removal process formed the basis of this document and are therefore briefly discussed. Results obtained from the detailed study into the factors that influence iron precipitate product quality, indicated that the type of phase(s) produced and its stability, the supersaturation present during its formation, changes in the mixing environment and particle growth, specifically agglomeration growth, had a significant impact on the quality of these precipitates. The results were therefore summarized in three chapters, namely, metastability in iron precipitation, mixing and precipitation and agglomeration.

The following paragraphs give a summary of the most important findings of the work performed on means to improve the product quality of poorly crystalline iron phases.

6.1 Metastability in iron precipitation

The understanding and control of the hydrolysis of ferric iron at elevated temperatures and a pH range between about 1.5 and 3.5 plays a critical role in the production of the desired quality iron precipitate. Firstly, it is known that the critical nuclei of phases such as ferrihydrite and schwertmannite are more stable than that of goethite. Ferrihydrite and schwertmannite are therefore mostly formed under the above-mentioned conditions and are metastable towards goethite, the most stable iron phase. The (meta)stability of schwertmannite, however, is not well-defined in industrial environments. Furthermore, the existence of schwertmannite as a mineral entity is questionable, i.e. it could be argued that it is ferrihydrite with a higher sulphate content as the crystal structure of this phase has not been determined yet. In this study the relative stability of schwertmannite and ferrihydrite as well as the typical supersaturation levels prevailing during their formation, was determined. It was shown that:

- A definite phase transition line was identified between the (meta)stability regions of ferrihydrite and schwertmannite for a series of pH and temperature values studied. It therefore appears as though schwertmannite does exist as a phase in its own right and that it could play an important role in industrial iron removal processes.
- Both schwertmannite and ferrihydrite contains variable amounts of sulphate. In fact, schwertmannite produced at a relatively low supersaturation, contains lower sulphate values than ferrihydrite produced at high relative supersaturation. This is discussed in more detail in the following paragraphs.
- Ferrihydrite is the more stable phase at pH values above about 2.70 at 50°C and its stability increases with an increase in temperature at a fixed pH. At pH values above about 3.0 and temperatures below approximately 70°C, two-line ferrihydrite was found to be the dominant phase. A small amount of schwertmannite was found to be present in this region.

Furthermore, it is also known that poor quality precipitates, i.e. fine, voluminous precipitates with high relative surface area and impurity values, are formed when the critical supersaturation is exceeded. The critical supersaturation level is indicated by the so-called metastability limit. This is the point where a sudden decrease in the iron concentration occurs. In this study, the metastability limit and metastability region, which is the region between the metastability limit and the solubility limit, were determined for the case where metastable iron phases such as ferrihydrite and schwertmannite are formed from hot dilute ferric iron solution. The relative supersaturation present during the precipitation of these phases and its influence on the quality of the final product was also studied. It was shown that:

- The metastability ranges between a pH of about 2.0 at 50°C and 1.6 at 90°C.
- Therefore, most industrial processes where iron is precipitated from ferric iron solutions, operates well above the metastability limit in the region where rapid nucleation occurs and poor quality precipitates are produced.
- The width of the metastable zone was reduced to between 0.2 and 0.3 pH units, mainly by the presence of seed material and intensive mixing. In crystallization processes operation within the metastable zone is encouraged as it promotes growth rather than nucleation. Low molecular growth rates at low solute concentration make this approach less attractive for iron precipitation. Nonetheless, it was found that precipitating iron in a stagewise fashion even above the metastability limit improved the quality of the final product significantly.
- Ferrihydrite and schwertmannite precipitated over a range of relative supersaturation levels between pH values of about 1.65 and 3.5 and temperatures between 50°C and 90°C, but the quality of ferrihydrite and schwertmannite produced were dependent on the supersaturation level.
- Two-line ferrihydrite was precipitated at relative supersaturation levels between approximately 10,000 and 30,000.
- Six-line ferrihydrite was precipitated at relative supersaturation levels between approximately 2,500 and 25,000.
- Schwertmannite was precipitated at relative supersaturation levels between approximately 1,000 and 20,000.

- Relative supersaturation levels lower than about 1,000 are required for the production of goethite. It is known that goethite precipitation is achieved when the ferric iron concentration is controlled at very low levels by the slow rate of ferrous iron oxidation at elevated temperatures and low pH values as a result of the poor solubility of oxygen under these conditions.
- Schwertmannite could be produced at lower supersaturation levels than ferrihydrite and therefore is of a better quality. The sulphate content of schwertmannite varied between about 14% at a pH of about 2.20 and a temperature of 50°C to approximately 7% at a pH of about 2.45 and a temperature of 90°C. For ferrihydrite, the sulphate content varied between about 10% and 6.5% at pH and temperatures values of 2.7 at 50°C and 3.05 at 90°C, respectively.
- Low supersaturation levels effective at higher temperatures and lower pH values, generally support the production of precipitates with lower impurity levels (moisture, sulphate and zinc content). Exceptions to this are the increase in the zinc content of the precipitates, with an increase in temperature, and an increase in moisture and sulphate values in precipitates formed at low pH values. At low pH values fine precipitates were produced, with a higher relative surface area, resulting in higher sulphate and moisture levels. It was proposed that the increase in temperature results in increased surface diffusion rates and rates of precipitation of iron species, which could entrain unleached ZnO or $ZnSO_4$ solution.

6.2 Mixing and precipitation

It is known that high supersaturation levels are present during ferric iron precipitation with the result that the timescales of the chemical reactions and nucleation are much lower than the timescales of macro, meso and micromixing. Ferric iron precipitation processes are therefore mixing controlled, and any change in the rate-limiting step is therefore expected to influence the quality of the precipitates. The study into the influence of changes to the mixing environment on the quality of iron precipitates, indicated the following:

- The three-zone model approach was used effectively to indicate that the quality of iron precipitates, expressed in terms of its filterability and purity, is sensitive to changes in the macro and micromixing environments.
- The filterability of the precipitates is more sensitive to changes in cation/ferric mass transfer, in the region of the inlet points, than mass transfer of the neutralizing agent. An increase in dilution of the hot iron solution had a significant impact on product quality.
- The specific filter resistance of the solids was reduced by about 50% by using the three-zone model approach to precipitate poorly crystalline iron phases. Furthermore, the water and acid soluble zinc values in the precipitate were reduced by 14% and 75%, respectively.
- The reactivity, expressed in terms of particle size, of the neutralising agent had a significant influence on the weak acid soluble zinc values associated with the precipitate. The use of a coarser neutralising agent resulted in increased zinc losses.
- The pumping capacity of an impeller should be selected in such a manner that mixing times below about 5 minutes are avoided.
- In iron precipitation systems, agitators are generally running at lower speeds and high mixing times, i.e. precipitation is macromixing controlled. In such systems the macrofluid is poorly mixed whereas the microfluid is well mixed. When this is the case, it is known that the reactor geometry and position of the feed points could influence product quality.
- The controlling mixing environment, i.e. macro or micromixing controlled, generally indicates where feed points should be placed. In a well-mixed

macrofluid, as in a DTB reactor, feed points should be placed far away from the agitator. In a CSTR, where the macrofluid is less homogeneous, feed points need to be placed close to the agitator.

- Feed points, the hot iron solution and neutralising agent in this case, should be placed on opposite sides of the reactor to increase mixing time.
- An optimized DTB reactor should give precipitates with superior quality compared to the traditional CSTR.
- When precipitation is either micromixing or macromixing controlled, a precipitate with poor filterability is produced. A balance between the agitator speed and agitator pumping capacity for a specific type of reactor therefore needs to be found.
- Any change to the mixing environment in a precipitation system needs to be carefully considered before implementation, as it could have a significant influence on the final product quality, especially the filterability of the precipitate.

6.3 Agglomeration

Supersaturation, the driving force for precipitation, not only influences the nucleation process but also particle growth. It is known that particle growth in precipitation systems typically takes place in the form of agglomeration. Particle growth is required to ensure that down stream processes, such as thickening and filtration, are viable. However, if the agglomeration process is not well controlled, it could lead to the formation of particles with high relative surface areas and increased impurity levels. It is therefore necessary to determine the influence as well as the relative importance of typical operating variables on product quality parameters such as the filterability, particle size and purity of the precipitates formed. In this part of the study it was found that:

- A Hadamard matrix could be used to indicate that the degree of agglomeration is influenced by, in order of importance, seed addition, temperature, solution viscosity and pH. In the same way, it was shown that the filterability of iron precipitates is sensitive to pH, seed addition, hot iron solution iron concentration and temperature. When the impact of the variables on iron removal efficiency was evaluated, it was found that pH, hot iron solution iron concentration, temperature and seed addition were most important. Overall, pH is the most important parameter, followed by seed addition, temperature and iron solution iron concentration.
- Every effort needs to be made to optimize 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 through its influence on supersaturation.
- Seed addition is essential to ensure good quality iron precipitates. However, it is often not considered, or even neglected in industrial processes. It was found that seed addition supported agglomeration, and that up to initial seed concentrations of about 25g/L, it resulted in lower sulphate and zinc levels and stabilized the process.

- Higher seed concentrations require higher solute concentrations to ensure that growth takes place.
- Agglomeration was found to be optimum for initial seed sizes between 5 and 6μm.
- Agglomeration should be controlled to ensure that the change from orthokinetic to perikinetic agglomeration takes place.
- Higher solute concentrations support growth at higher seed concentrations, which gives a coarser final product.
- Changes in the physico-chemical parameters were of greater importance than changes in the hydrodynamic environment, for the range of each operating parameter explored.