1   BACKGROUND

1.1   Study of the Zincor iron removal process

Zincor Ltd. uses an integrated roast-leach-electrowinning circuit to produce high-grade zinc products as well as zinc-aluminium alloys from zinc sulphide concentrates [Meyer *et al.*, 1996]. Solution purification, specifically iron removal, forms an integral part of zinc refining circuits. Several processes, which include the hematite, jarosite, goethite and so-called para-goethite processes (ferrihydrite precipitation), have been developed to deal with iron in zinc-rich solutions, as discussed later.

At Zincor, iron is removed by means of the so-called Zincor Process, a process developed by Zincor over a period of nearly three decades. Most of the development work was done on a trial and error basis resulting in increased zinc losses, process disruptions and slow progress. However, early in 2000 a study of the Zincor process was initiated in order to speed up development work and minimise the impact of process changes on the circuit. This study by the authors aimed to characterise the Zincor Process and its residues and address soluble and insoluble zinc losses, which mainly result from the use of zinc calcine as a neutralising agent. In summary, it was found that [Claassen *et al.*, 2002; Claassen *et al.*, 2003(a)] the Zincor Process has a unique character and could be viewed as a process in its own right. This finding was based on the specific operating conditions employed in the process and the mineralogical composition of the residue produced (refer to section 1.2). Furthermore, soluble zinc losses could be reduced through improved pH and temperature control. The pH of the acid wash stage utilised in the process should be controlled at values between 2.7 and 2.9 due to silica gel formation at a pH below approximately 2.5 and to optimise particle growth. The study also indicated that the final pH of the iron removal step should be around 3.0.

It was also shown that insoluble zinc losses could be significantly reduced if a more reactive neutralising agent is used and/or a neutralising agent that contains no or little zinc. Finally, some basic work on the utilisation of seed material to improve the quality of the precipitated product also showed potential to reduce both soluble and insoluble zinc losses.

After completion of the study, several changes were made to the Zincor iron removal stage, such as changes to the operating set points, process controls and equipment. These changes assisted in stabilizing the process and reduced zinc losses associated with the iron residue. However, the inherent weakness of the Zincor Process, namely, the relatively high insoluble zinc loss associated with the final residue, was not adequately addressed. In order to reduce these losses, it was realized during the latter part of the study that more attention should be given to the factors that influence the two primary precipitation processes, nucleation and growth, i.e. a physical-chemical approach should be followed. It was proposed that the following important aspects should also be considered to improve the quality of iron precipitates:

- The rate-limiting step in the precipitation process.

- The influence of changes in the rate-limiting step on the quality of the precipitate.

- The impact of changes in the supersaturation level, which is the driving force for precipitation, on the quality of the precipitate.

- The influence and relative importance of operating parameters on the primary precipitation processes.

- Effective utilization of seed material to improve process stability and reduce zinc losses.

- The (meta)stability regions of the poorly crystalline phases present in the Zincor iron residue.

In an effort to address these aspects, a follow-up study, of which the detail is discussed in this document, was initiated early in 2003. The basis of this new study was the earlier work performed on the Zincor process since 2000. The determination of the mechanisms and phases formed during iron precipitation under the conditions specified by Claassen *et al.* [2002] is relevant to this follow-up study.

Since the speciation of phases involved in precipitation or crystallization processes could be seen as the first step to improve precipitate product quality, the process followed and findings of the earlier study on the characterization of the Zincor Process and its residues are discussed in more detail in section 1.2.

1.2   Speciation of iron phases

In precipitation systems, speciation of the phases present is done to determine the reaction mechanisms involved in the process, the relative stability of the phases present in the final product and the morphology of these phases.

Various analytical techniques were used to determine which phases are present in Zincor's iron residue. Firstly, results obtained from chemical and XRD analyses indicated that about 50% of the iron present in the residue could be associated with poorly crystalline phases. This was established by performing an elemental balance using the data obtained from these two techniques. The XRD study indicated the presence of crystalline iron-bearing phases, of which the most abundant were franklinite ($ZnO.Fe_2O_3$), plumbo jarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$) and argento jarosite ($AgFe_3(SO_4)_2(OH)_6$).

A SEM-EDX study of the residue confirmed the presence of one or more poorly crystalline phase in the form of oxy-hydroxides and oxy-hydroxy sulphates. The difference in the morphology of the phases present was also indicated by the SEM backscattered images, i.e. dense crystalline particles and smaller poorly crystalline particles with relatively large surface areas. The images also clearly indicated that the poorly crystalline oxy hydroxide phase(s) contained significantly more zinc than the hydroxy salts, which include basic iron sulphates and jarosites.

To identify the poorly crystalline phases present was more difficult. Several techniques including FT-IR spectroscopy, Raman spectroscopy, X-ray Photoelectron spectroscopy (XPS) and Mössbauer effect spectroscopy (MES) were used. Of these techniques, MES gave the best results. Samples were analyzed at room ($\approx$ 300 K), liquid nitrogen ($\approx$ 77 K) and liquid helium temperature ($\approx$ 5 K) as the different iron
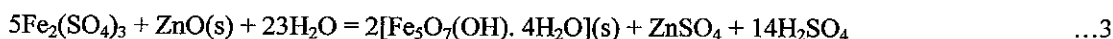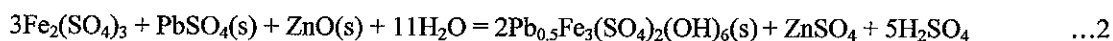
phases expected to be present are magnetically ordered at different temperatures, giving the opportunity to identify phases through a process of elimination. The data obtained fitted the spectra of franklinite, jarosite, schwertmannite, a poorly crystalline oxy-hydroxy sulphate, and ferrihydrite, reasonably well.

Furthermore, MES indicated that neither goethite nor any of its polymorphs were present in the residue samples and it was therefore proposed that the oxy-hydroxide phase found during the SEM-EDX study, could be ferrihydrite. To confirm this, a number of synthetic samples were produced using the same conditions employed in Zincor's iron removal process. The simulation focused on the hydrolysis of ferric iron in the absence of alkali elements, i.e. no franklinite was present and no additional chemicals were added to simulate jarosite precipitation. MES, XRD and wet chemical analyses were again utilized to analyze the precipitates produced. The results obtained using these techniques all confirmed that schwertmannite and ferrihydrite should be present in the iron residue. The iron phases therefore proposed to be present in the Zincor iron residue and their abundances are shown in Table 1.

Table 1. Iron phases expected to be present in Zincor's iron residue [Claassen *et al.*, 2002].

Phase	Formula	Abundance (%)
Schwertmannite	$Fe_8O_8SO_4(OH)_6$	50
Ferrihydrite	$Fe_5O_7(OH).4H_2O$	
Jarosite(s)	$Pb[Fe_3(SO_4)_2(OH)_6]_2$,	20
	Plumbo jarosite and solid solution phases	
Franklinite	$ZnO.Fe_2O_3$	25
Unknown	--	5

The reactions involved in the formation of these phases, were proposed to be:

$$4Fe_2(SO_4)_3 + ZnO(s) + 13H_2O = Fe_8O_8(OH)_6SO_4(s) + ZnSO_4 + 10H_2SO_4 \qquad ...1$$

$$3Fe_2(SO_4)_3 + PbSO_4(s) + ZnO(s) + 11H_2O = 2Pb_{0.5}Fe_3(SO_4)_2(OH)_6(s) + ZnSO_4 + 5H_2SO_4 \qquad ...2$$

$$5Fe_2(SO_4)_3 + ZnO(s) + 23H_2O = 2[Fe_5O_7(OH). 4H_2O](s) + ZnSO_4 + 14H_2SO_4 \qquad ...3$$

From this investigation, it should be highlighted that :

- 50% of the iron present in Zincor's iron residue is in the form of poorly crystalline ferrihydrite and schwertmannite, which are metastable towards goethite.

- Approximately 70% of the iron removed from the hot iron solution is in the form of these two phases. Any further study into the factors that influence the quality of iron precipitates should therefore focus on these phases.

- Ferrihydrite and schwertmannite form through a hydrolysis process in the absence of alkali and other elements. The iron and hydroxide concentrations are expected to play an important role in their formation as indicated in equations 1 and 3.

- Ferrihydrite and schwertmannite were found to have different morphologies and impurity levels. The relative stability and the factors that influence the stability and morphology of these phases should therefore be investigated.

- Due to their poor crystalline nature, these two phases contain high impurity levels as shown in the SEM-EDX study.

- Industrial processes where iron is removed at elevated temperatures, a pH range between about 2.5 and 3.5, and without significant amounts of alkali elements such as Na and K, probably all produce ferrihydrite and schwertmannite.

In previous paragraphs the need to determine the factors that influence the quality of poorly crystalline iron precipitates, such as ferrihydrite and schwertmannite, produced in the Zincor and probably other industrial processes where a sulphate leach medium is used under similar conditions, were indicated. In the present work the factors that

influence the quality of these poorly crystalline iron phases were studied. The steps used in this investigation could be summarized as follows:

- Speciation of the iron phases and the determination of the reaction mechanisms responsible for their formation. The initial work done on the Zincor iron removal process and its residues were used as basis, as summarized in sections 1.1 and 1.2.
- Study the differences in the morphology of the phases present.
- Determine the relative stability of ferrihydrite and schwertmannite.
- Study the role of supersaturation in the precipitation of ferrihydrite and schwertmannite.
- Determine the influence of typical operating conditions on the quality of ferrihydrite and schwertmannite precipitates.
- Determine the rate-limiting step in iron precipitation processes.
- Study the influence of changes in the mixing environment on precipitate quality.
- Study particle growth and specifically the factors that influence the agglomeration of iron precipitates.

2 INTRODUCTION

2.1 Precipitation in hydrometallurgy

Crystallization and precipitation are widely used industrial processes in the chemical and hydrometallurgical industries. Vast quantities of crystalline and poorly crystalline materials are manufactured commercially. These include the production of products such as pigments, dyestuffs, pharmaceuticals, fertilizers, plant protection agents and metallic products with varying metal contents and purities. All of these products are produced in one or more steps that include separation, purification, concentration and crystallization. The type of crystallization referred to here is generally known as "mass" or "bulk" crystallization where large numbers of particles are formed and grown at the same time in large industrial reactors. The specific method of crystallization employed to bring about the bulk removal of crystallites or precipitates from a solution or melt is a function of the properties of the solute. These include the sensitivity to thermal changes and the solubility of the crystallized product. Figure 1 indicates some criteria that could be used to choose the method of crystallization suitable for a specific application.
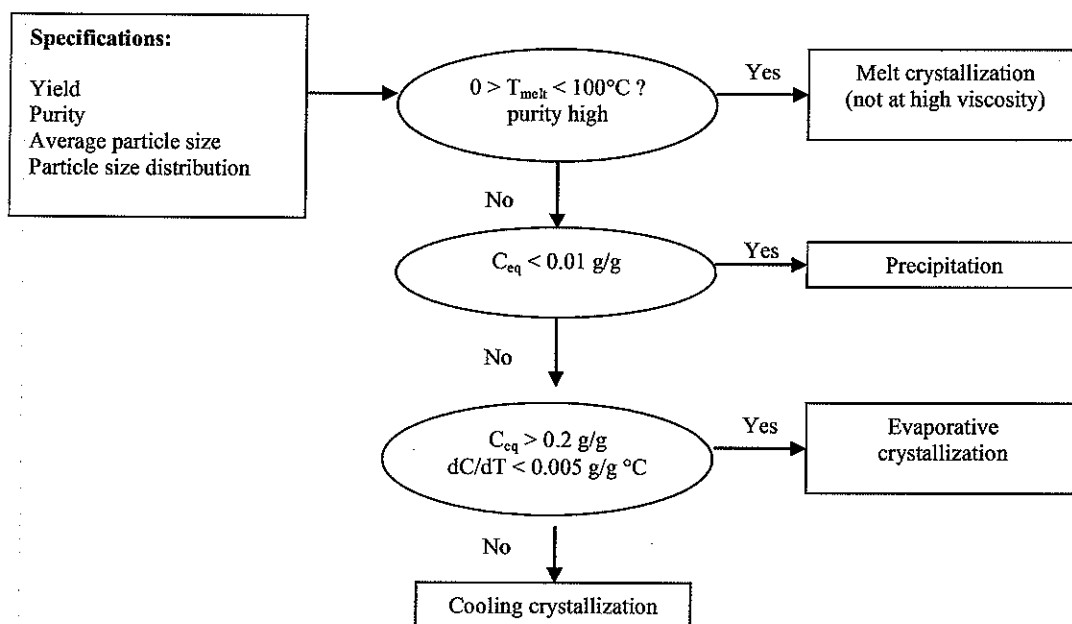

Figure 1: Decision diagram to choose the method of crystallization [After Rosmalen Van and Kramer, 1998]. C_{eq} = equilibrium solution concentration of element being removed.

In precipitation processes, the driving force, i.e. the change in the supersaturation level, for the phase change is provided by a chemical reaction. Under these conditions a solid with a relatively low solubility of ca. 1% is formed compared to ca. 20% for solids formed in crystallization processes, i.e. the equilibrium concentration in solution of the element being precipitated is low (Refer to Figure 1). This indicates that a relatively high supersaturation is present during precipitation processes. Despite this fact and the impact the high driving force has on product quality, precipitation, or reactive crystallization is widely used in the minerals and metals industry. Reactive crystallization is used to produce metal sulphides, phosphates, hydroxides and carbonates, to name a few. Table 2 gives a summary of some compounds produced from precipitation processes.

Table 2. Summary of ionic and hydrolytic precipitation methods [Habashi, 1999].

Precipitate	Precipitating agent	Example
Oxides, hydrated oxides and hydroxides	H_2O OH^-	TiO_2, $Al(OH)_3$, $Be(OH)_2$ Cu_2O, $Mg(OH)_2$, $Co(OH)_2$
Hydroxy salts	OH^- + Anion	$Cu(OH)_2.CuCO_3$, Jarosites, Iron hydroxy sulphates
Polyacids and their salts:		
Vanadates	H^+	$Na_4V_6O_{17}$, $(NH_4)_4[V_4O_{12}]$
Molybdates	H^+	$(NH_4)_4[H_2 MO_6 O_{21}].3H_2O$
Tungstates	H^+	$Na_2 W_{12} O_{41} .28H_2O$
Uranates	OH^-, MgO	$(NH_4)_2 U_2O_7$, $Na_2 U_2O_7$, $Mg U_2O_7$
Dialuminates	OH^- + Cation	$LiAl_2(OH)_7. 2H_2O$
Sulfides	S^{2-}	CuS, NiS, CoS, ZnS
Carbonates	CO_3^{2-}	Li_2CO_3
Chlorides	Cl^-	CuCl, $(NH_4)_2 PtCl_6$, K_2TiCl_6
Cyanides	CN^-	CuCN
Fluorides	F^-	PuF_3, $UF_4. nH_2O$
Oxalates	$(C_2O_4)^{2-}$	$Th(C_2O_4)_2$, $Li_2(C_2O_4)_3$
Peroxides	O_2^{2-}	$UO_4. 2H_2O$, PuO_4
Sulfites	$(NH_4)_2SO_3$	Copper ammonium sulfites
Metalloids	H^+	Se from selenosulfate solution

Most of the compounds listed in Table 2 contains the sought after element whereas an element such as iron is in most cases precipitated as part of a purification step, i.e. it is treated as an impurity. Iron, one of the most abundant elements on earth, mostly ends up in leach solutions and typically needs to be eliminated prior to the final product removal step.

This is also true for the hydrometallurgical processing of zinc concentrates. These concentrates generally contain between 1% and 10% iron with some concentrates that can contain up to 18% [Chen and Cabri, 1986]. Initial attempts to remove iron from leach solutions as a hydroxide resulted in poorly filterable, voluminous and gelatinous precipitates [Tainton and Leyson, 1924]. This was a direct result of the high supersaturation levels present during the precipitation of iron from ferric ion solutions. Later attempts focused on the establishment of processes where precipitates can be formed using more dilute solutions, i.e. the level of supersaturation is kept low to improve the quality of nucleates and promote particle growth rather than nucleation.

This principle is used in two of the precipitation processes developed to control and remove iron from zinc-rich process solutions, *i.e.* the goethite (FeOOH) and the so-called para-goethite processes [Gordon and Pickering, 1975]. During more or less the same period, the hematite (Fe_2O_3) process [Tsunoda *et al.*, 1973; Onozaki et al., 1986] was developed and implemented at the Iijima Zinc Refinery in Akita, Japan. It was also recently shown [Claassen *et al.*, 2002] that the Zincor Process discussed earlier, which is similar to the para-goethite process [Patrizi *et al.*, 1985; Cubeddu *et al.*, 1996; McCristal and Manning, 1998], produces mainly iron hydroxy sulphates in the form of schwertmannite ($Fe_8O_8SO_4(OH)_6$) and plumbo-jarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$). The establishment of these processes in the zinc industry was preceded by the development of the jarosite process ($AFe_3(SO_4)_2(OH)_6$) where A is typically Na^+, K^+ or NH^+. These processes, excluding the Zincor Process, are shown in Figure 2.
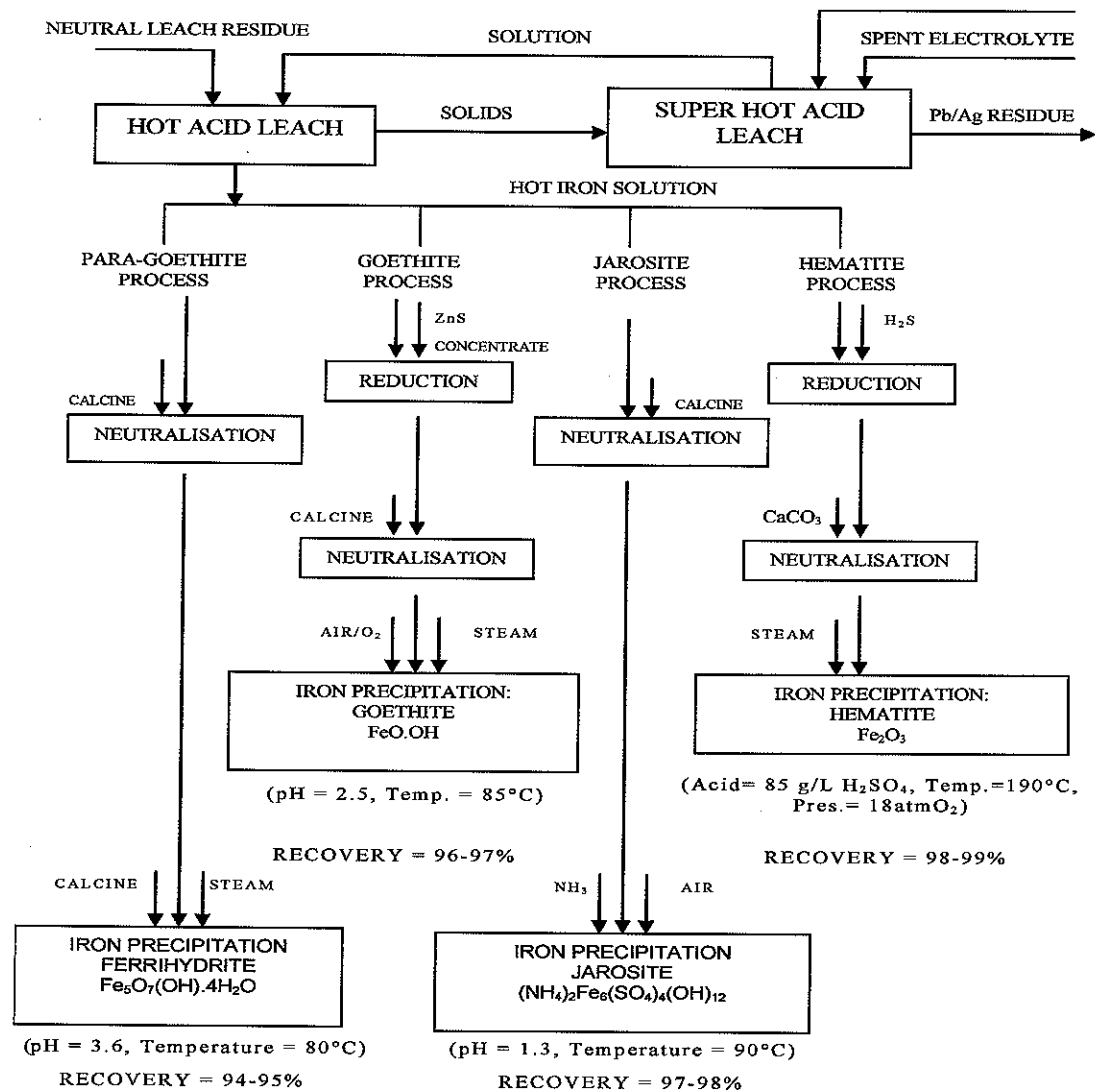
Figure 2. Iron removal processes used in the zinc industry to purify zinc-rich process solutions [After Claassen *et al.*, 2003(b)].

The advent of the jarosite process reduced the complexity of the early treatment of the zinc containing neutral leach residues dramatically. It was the first iron removal process that allowed the production of a filterable residue on a commercial scale and is still the most widely used iron precipitation process used in the zinc industry today [Pammenter *et al.*, 1986; Uusipaavalniemi and Karlman, 1996]. A simplified flowsheet of the jarosite process is shown in Figure 3.

Zinc Calcine   Spent Electrolyte

NEUTRAL LEACH

Solids Separation ⟶ Solution to Purification

Spent
Electrolyte
⟶

Conc. H_2SO_4 **HOT ACID LEACH**

Solids Separation ⟶ Pb/Ag Residue

Solution

Calcine ⟶ **JAROSITE PRECIPITATION**

NH_4, Na, K

Return Solution

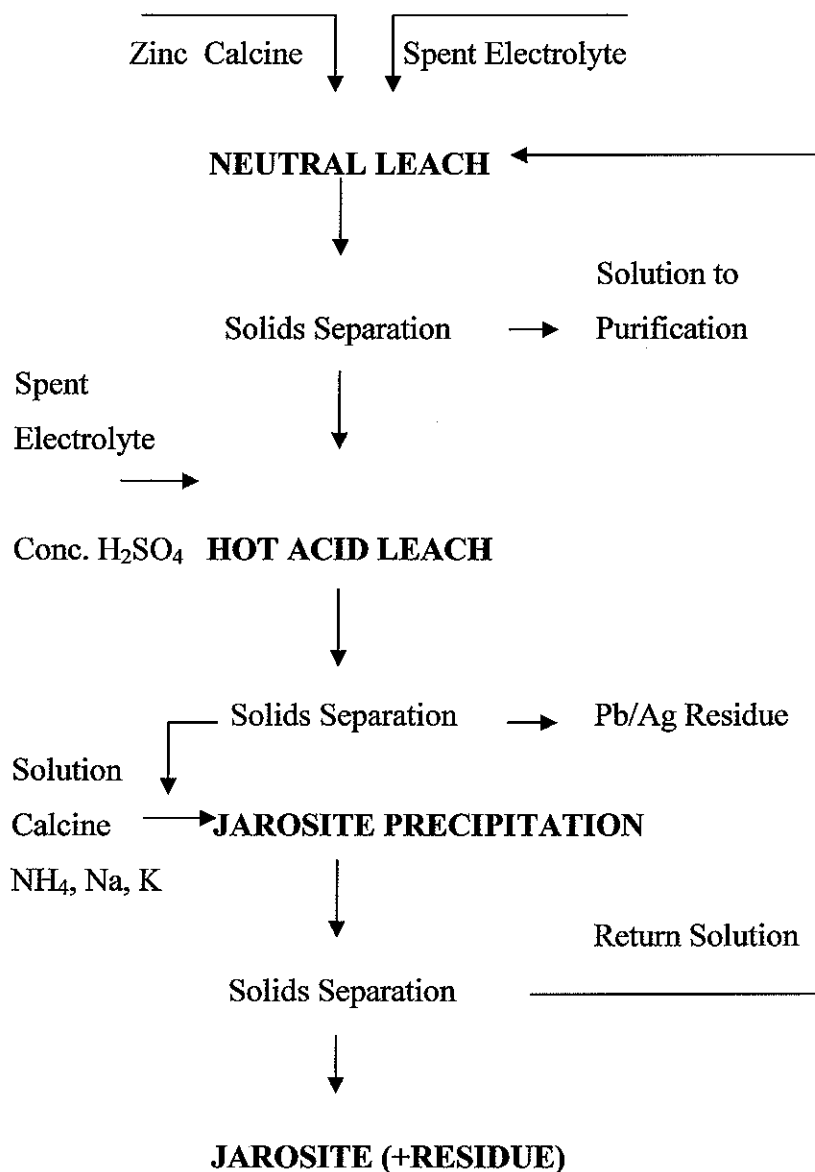Solids Separation

JAROSITE (+RESIDUE)

Figure 3: Simplified jarosite precipitation flowsheet [Arregui *et al.*, 1980].

Whereas volumes have been published on the jarosite and goethite processes, little is known about the para-goethite and Zincor processes, that mainly produce ferrihydrite [Loan *et al.*, 2001] and schwertmannite [Claassen *et al.*, 2002] respectively. These phases were reported to be poorly crystalline with high surface areas and are metastable towards goethite [Bigham *et al.*, 1990, 1994, 1996; Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998; Dutrizac, 1999]. As such, the iron-bearing residues produced in the para-goethite and Zincor Processes is less filterable, more voluminous and contains more zinc than goethite, jarosite and hematite residues

[Dutrizac, 1985]. Even though the para-goethite and Zincor Processes are relatively simple and easy to operate, higher zinc recoveries than what these processes can achieve are required in an extremely competitive industry.

However, precipitation of sparingly soluble substances from solution, such as iron, has not been studied to the same extent as most crystallization processes. This probably indicates that these processes are difficult to study as reaction crystallization (precipitation) generally involves the simultaneous and rapid occurrence of primary processes in the presence of secondary processes [Söhnel and Garside, 1992]. The primary processes involve mixing on macro, micro and molecular scale, the chemical reaction (sometimes with a complex mechanism), nucleation and growth of the particles. Secondary processes playing a role during reactive crystallization include agglomeration, ageing and ripening of the precipitates. As a result very little information is available in the literature on reaction crystallization. The general approach in studying these systems is therefore to apply classical crystallization theory to a specific system and make adjustments where necessary through empirical observations.

The main drive for studying crystallization and precipitation processes is to enable the engineer to design and control these processes with the emphasis on the production of a suitable quality product, i.e. optimum recovery and materials handling properties, at the required rates and as economical as possible. However, if precipitation processes are not well understood and controlled, gelatinous phases could form which would severely hamper downstream processes such as liquid-solid separation, which include filtration, thickening and bulk storage.

2.2 Precipitate product quality

In general the type of precipitate, the purity of the precipitate, density of the particles, particle size and size distribution influence the economics of a precipitation process. These factors are all strongly influenced by the primary and secondary precipitation processes mentioned earlier. This is discussed in detail for crystallization systems by Nielsen [1964, 1967], Walton [1967, 1969], Nyvlt [1971, 1982], Nyvlt *et al.* [1985], Mullin [1972, 1976], Pamplin [1975], Garside [1977], Söhnel and Garside [1992], Mersmann [2001] and David and Klein [2001].

However, as far as product quality of iron precipitates is concerned, very little information is available. Reference is made in the literature to iron precipitate product quality parameters, such as particle size, size distribution and porosity [Cornell and Schwertmann, 1996], but little attention is paid to the factors that influence product quality and the importance of controlling the supersaturation to obtain the desired product [Demopoulos, 1993].

A proper understanding of the stability of iron phases formed in the precipitation process as well as the kinetics of precipitation (nucleation and growth) and all the factors, such as hydrodynamics, temperature, supersaturation/pH, and seeding, that impact on iron precipitate product quality, are therefore required. In order to address all these issues, the results obtained from the study were summarized in three sections. In the first chapter, the chemical aspects of iron precipitation is addressed, with the results obtained from the earlier study of the Zincor iron removal process and its residues as basis, by studying the influence of typical operating parameters on the stability of poorly crystalline phases as well as the influence of supersaturation, which is the chemical driving force for precipitation, on the quality of these precipitates. In the next two chapters attention is given to factors that influence the nucleation and growth processes with the emphasis on controlling the local supersaturation levels. This was done by studying, firstly, the impact of changes in the mixing environment on the quality of schwertmannite and ferrihydrite precipitates and secondly, the influence of operating parameters on agglomeration growth.