GYPSUM PRODUCTION AND HYDROCHLORIC ACID REGENERATION BY REACTION OF CALCIUM CHLORIDE SOLUTION WITH SULFURIC ACID

Amani Lutfi Al-Othman

Department of Mining, Metals and Materials Engineering

McGill University
Montreal, Canada

August, 2004

A Thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Engineering

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 0-494-12578-0
Our file Notre référence
ISBN: 0-494-12578-0

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Abstract

One critical issue in chloride hydrometallurgy is the regeneration of the lixiviant HCl that is commonly achieved by pyrohydrolysis. It is the scope of this thesis to investigate a low temperature HCl regeneration process, which regenerates HCl and produces saleable gypsum. Experiments were performed to determine the optimum conditions of the chemical reaction that involved the reactive mixing of calcium chloride ($CaCl_2$) solution with sulfuric acid (H_2SO_4) solution at low temperature and atmospheric pressure.

The results showed that the crystallization chemistry of the $CaCl_2$ – H_2SO_4 reaction can be controlled in such away that favors the production of well grown gypsum crystals with the simultaneous regeneration of practical strength HCl. High strength HCl (= 4 M) was regenerated by the reaction of (3.5 M) $CaCl_2$ leach solutions with (8 M) sulfuric acid in the temperature range of 20–60°C. Acid addition in stages to simulate the titration procedure, seeding and recycling, and increasing temperature were found to favor crystal growth and filterability. Finally, this research showed that there is negligible metal uptake with the exception of lead, making the production of marketable gypsum possible.

Résumé

Un point critique de l'hydrométallurgie en milieu chloré consiste à régénérer l'acide chlorhydrique (HCl) qui est utilisé comme agent lixiviant. Cette étape est communément réalisée par pyrohydrolyse. L'objet de cette thèse était d'investiguer un procédé de régénération du HCl à basse température qui, tout en régénérant le HCl, permettrait la production de gypse vendable. Des expériences ont été réalisées pour déterminer les conditions optimales de la réaction chimique impliquant le mélange réactif de solutions de chlorure de calcium ($CaCl_2$) et de solutions d'acide sulfurique (H_2SO_4) à basse température et à pression atmosphérique.

Les résultats ont démontré que la chimie de la réaction de cristallisation $CaCl_2 - H_2SO_4$ peut être contrôlée de telle sorte que la production de cristaux de gypse bien développés et la régénération simultanée de HCl de concentration adéquate soient favorisées. Du HCl de concentration élevée (4M) a été régénéré par la réaction de lixiviats de $CaCl_2$ (3.5M) avec de l'acide sulfurique (8M) dans le domaine de températures 20–60°C. Il a été découvert que l'addition d'acide par étapes pour simuler la procédure de titrage, le «seeding» et le recyclage ainsi que l'augmentation de la température favorisent la croissance des cristaux et la filtrabilité. Finalement, cette étude a démontré que l'incorporation de métaux est négligeable, à l'exception du plomb, ce qui rend possible la production de gypse vendable.

Acknowledgments

First of all, I would like to express my deepest thanks for my supervisor Prof. George Demopoulos for his guidance, patience and supervision over the past two years, during which I have learned a lot about hydrometallurgy. Without his continuous guidance and help, this work would not have been possible. I would like also to thank the following for their generous contribution and financial support: Hatch, Noranda Inc. , Process Research Ortech and the Natural Sciences and Engineering Research Council of Canada (NSERC).

I am also very grateful for the people who helped me to complete this work during the results analysis, Helen Campell for helping me in the SEM image analysis, Ed Siliauskas for his help in ICP analysis and Monique Riendeau for her assitance in XRD and Particle Size analysis.

I would like also to express my thanks for my dearest loving husband, Muhammad for his encouragement all over the past years, and my family in Jordan for their support, care and unconditional love. Special thanks for my friends in the hydromet group, Terry, Georgiana, Cinziana, Marie-Claude, Seref, Vincent, Felipe, Yuanbing and Zhibao for their help whenever I needed, the nice talks we had, their help in my thesis and being my great colleagues since I started in McGill as a student. I would like also to thank my dear friend, Neda in Jordan for her prayers to me always, Maria and Helin for the nice times we had together.

Table of contents

List of Figures

List of tables

CHAPTER 1: INTRODUCTION

1.1 What is this research about

Calcium chloride ($CaCl_2$) solutions are produced in various chemical industries from geothermal brines to spent leach solutions after the leaching of ores with hydrochloric acid (HCl) and the employment of lime neutralization. Sulfuric acid, on the other hand, is a major by-product from the non-ferrous metallurgical industry that becomes increasingly more abundant and difficult to sell.

Chloride hydrometallurgy involves the dissolution of minerals and metals by HCl. Examples of chloride metallurgical processes are the refining of nickel, platinum-group metals, steel pickling and the processing of non-ferrous metal sulfide concentrates. A critical issue in chloride metallurgy is the regeneration of the lixiviant HCl. This in most of cases is accomplished by the process of pyrohydrolysis. This process however, is capital and energy intensive. On the other hand, it is not applicable to regeneration of HCl from calcium chloride solution. An alternative to pyrohydrolysis HCl regeneration process is investigated in this work.

This research, in particular, investigates a new low temperature HCl regeneration process with simultaneous production of saleable gypsum through the reaction of $CaCl_2$ solutions with H_2SO_4 solutions at low temperature and atmospheric pressure. Successful development of such a process is expected to enable the industry in using the preferred neutralization agent (Lime) and making a wider use of chloride processing of metal sulfides and dusts.

1.2 Research elements

The research objectives were sought to be fulfilled through the study of the following elements:

1. Evaluate and improve the properties of the produced gypsum crystals in terms of settling /filtration rate, % solids density and crystals morphology/purity.

2. Study the effect of sulfuric acid addition /concentration, titration rate, seed/recycling , co-existing metal chlorides and equilibration time on the crystal quality

3. Determine HCl strength in regenerated chloride solutions and the residual calcium sulfate content after crystallization.

1.3 Thesis outline

- Chapter 2 presents a literature review with two sections, the first section is devoted to HCl regeneration processes and the second section is devoted to precipitation processes and gypsum crystallization.

- Chapter 3 consists of a description of the experimental procedures and experimental setup used throughout this work.

- Chapter 4 of this thesis presents systematic description of the results obtained from the crystallization tests under different conditions.

- Chapter 5 presents the conclusions from this work.

CHAPTER 2 :LITERATURE REVIEW

In the first section of this chapter, a literature review on the properties of hydrochloric acid, its applications, production and regeneration methods in industry, with the emphasis on the issue of HCl regeneration in chloride metallurgy is presented. The second section of this chapter aims to present the basic concepts of crystallization/precipitation theory including nucleation and crystal growth along with some studies focused on the precipitation of gypsum under different conditions.

2.1 Hydrochloric acid regeneration

2.1.1 Hydrochloric acid properties

In chemical industries, HCl (Hydrogen Chloride) lies the second in rank to sulfuric acid in its uses and applications. Hydrogen chloride gas is highly soluble in water to give hydrochloric acid solution that is highly corrosive and has the ability to attack and dissolve most minerals and metals. HCl solution is colorless to slightly yellow, with sharp and irritating odor. HCl is also corrosive to the body organs mainly the eyes, the skin and the mucous membranes. Skin contact may result in sever burns, whereas, inhalation can cause respiratory problems such as coughing, chest pain and the damage of the mucous membrane [1].

Commercially, HCl can be found under different grades, these are as follows [2]:
18^0 Be 27.9 (wt.%) HCl of sp.gr. = 1.1417
20^0 Be 31.5 (wt.%) HCl of sp.gr. = 1.1600
22^0 Be 35.2 (wt.%) HCl of sp.gr. = 1.1417
23^0 Be 37.1(wt.%) HCl of sp.gr. = 1.1600
where Be is Baumé degree and its used in industry to determine the concentration of a solution [3].

The main physical properties of HCl, for concentration = 34%(wt. %) at 20 °C are shown in Table 2.1 below [4].

Table 2.1: Physical Properties of HCl [4].

Molecular Weight	36.46 g/mol
Color	Colorless to Pale
Odor	Pungent
Density	1.16 g/L
Viscosity (15 °C)	1.9 mPa.s
Freezing Temperature	- 30 °C
Boiling Temperature	108 °C
Decomposition Temperature	1782 °C
Vapor Pressure	7 kPa
Solubility	Soluble in Water at any Portion

The storage, handling and transportation of hydrochloric acid should be done with care because it is extremely corrosive. It must be kept in tightly closed, plastic coated containers that are clearly labeled. It should also be transported with care to prevent spillage or breakage of the containers and stored away from flammable or oxidizing materials [5].

In industry, stainless steel and titanium are not recommended as materials for HCl handling/processing. On the other hand, storage tanks and pipes can be made of fiber reinforced polyester with an inner plastics coating such as polyvinyl chloride (PVC). Rubber lined steel can be also used but once this coating is damaged, steel will corrode readily. Gaskets, valves and pumps can be made of Teflon [2, 6,7].

2.1.2 HCl uses and applications

Hydrochloric acid is used in a wide range of industries, in the manufacture of fertilizers, dyes textiles and rubber. It is also used in electroplating and in food industry such as the production of glucose and maltose. HCl is also used to adjust the pH of some basic effluents in some industries. Nowadays, HCl is also being used in various chemical industries such as : phosphoric acid production, phenol production , production of vinyl chloride, steel pickling and in pharmaceutical industries [4].

HCl is also employed in a wide range of metallurgical industries in order to recover the most useful metals that occur in mixtures of other undesirable constituents in the ore because of its strong leaching power, especially with the development of corrosion resistant materials and equipment that made chloride hydrometallurgy more attractive and effective than before. This interest towards chloride metallurgy is due to HCl characteristics as a strong lixiviant and the fast leaching rates obtained with higher Cl^- concentrations due to the increase in proton activity, solubility of the metal chlorides and the production of elemental sulfur instead of SO_2 or H_2SO_4 [8].

Examples of chloride leaching processes in hydrometallurgy that prove the significance of HCl as a lixiviant are: (i) the UGS process developed by QIT to upgrade its TiO_2- containing slag to synthetic rutile specification [9], (ii) the Magnola process involving the leaching of serpentine material to produce $MgCl_2$ [10], (iii) the Noranda HCl–O_2 process for the leaching of complex Zn–Pb sulfide concentrates [11] and (iv) the Jaguar Nickel Inc. process for the HCl leaching of laterite ores in $MgCl_2$ brine solution [12]. In addition to these examples, HCl has proved to be effective in removing zinc present in Electric Arc Furnace (EAF) dust in the form of zinc oxide and zinc ferrite. Studies showed that hot leaching with HCl around 95 °C exceeded 90 % of zinc recovery in this case [13].

HCl is also used in the steel pickling industry. During the steel processing, an oxide layer is formed. This scale layer consists of ferrous and ferric oxides and prevents further processing and must be removed because it affects steel quality. HCl has showed to be more effective than H_2SO_4 acid because of its advantages in obtaining cleaner and brighter surfaces. The commercial grade used is 30 wt.% followed by rinsing using water [14].

2.1.3 HCl production

HCl can be produced by various methods in industry. Following are examples of these methods:

1) Salt – Sulfuric Acid Method

HCl can be produced by several methods but the classical method is the salt-sulfuric acid method. In this regard, HCl is known as 'Muriatic acid' which means , from the sea, referring to the process by which HCl was historically produced from the reaction of NaCl with H_2SO_4 according to the following equation [15] :

$$2NaCl_{(s)} + H_2SO_{4(l)} \rightarrow Na_2SO_{4(s)} + 2HCl_{(g)} \qquad (2.1)$$

this process has a yield of 98 %[16].

2) Combustion of Hydrogen and Chlorine

HCl can be produced directly from the reaction of Hydrogen and Chlorine gases. The reactants are fed to the combustion chamber but hydrogen is introduced in excess to ensure that all the toxic and corrosive chlorine has converted into HCl gas. This reaction is described by the following equation:

$$\tfrac{1}{2} H_{2(g)} + \tfrac{1}{2} Cl_{2(g)} \rightarrow HCl_{(g)} \qquad (2.2)$$

Since HCl has a high affinity to water, this step is followed by HCl absorption to obtain HCl acid solution. HCl produced by this method is very clean and pure, and the yield is from 90-99% [16].

3) As a By-product in the Production of Sodium Carbonate [17]

This process of sodium carbonate production and HCl as by product is called the Leblanc process that was developed in 1787. It is represented by the following reaction:

$$2NaCl_{(s)} + H_2CO_{3(l)} \rightarrow Na_2CO_3(s) + 2HCl_{(g)} \quad (2.3)$$

Then HCl gas can be absorbed in water to produce HCl acid solution that can be further concentrated and sold.

The presence of azeotrope is one of the important issues in HCl regeneration. Figure 2.1 shows the T-x diagram for HCl/H2O system. The Figure shows the HCl- H_2O azeotrope. Azeotrope refers to the condition which the gas and the liquid phase have the same composition at constant boiling. For this system, the azeotrope occurs at 20.3 wt.% and at 108 °C. Such diagram is useful in HCl distillation, at low HCl concentration, water will end up in the distillate since it has a higher vapor pressure than HCl. On the other hand, at higher HCl concentrations (above the azeotrope), HCl will end up in the distillate since it is the one with the higher vapor pressure. These aspects are extremely important to be considered in the plant water balance [18].

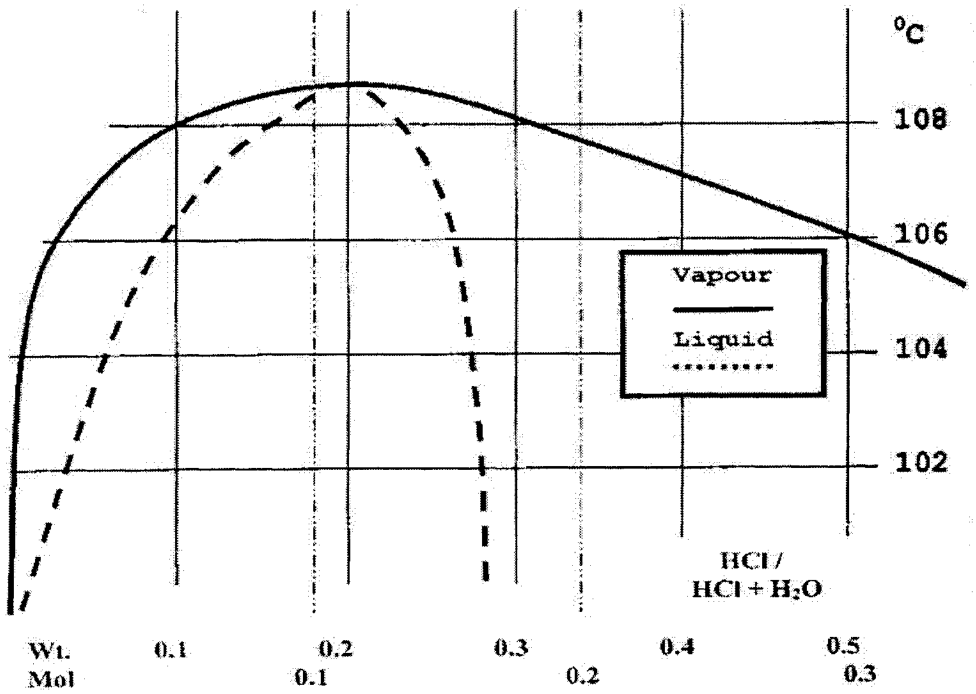


Figure 2.1 : Liquid and vapor equilibria in the HCl/H_2O system [18].

2.1.4 HCl regeneration in chloride metallurgy

As mentioned earlier in section 2.1.2 chloride metallurgy has become more attractive in recent years due to its unique properties. However, the regeneration of the lixiviant HCl represents a crucial aspect in chloride hydrometallurgy and there are several ways for HCl regeneration. One example is the Magnola process for magnesium production from serpentine. In this process, hydrochloric acid is recovered as a by-product when chlorine gas that is produced through electrolysis is combined with hydrogen gas to produce HCl that is reused in the leaching step and the feed chlorination step [19]. Pyrohydrolysis on the other hand, is the most widely used method for HCl regeneration which involves thermal decomposition of metal chlorides at high temperatures according to the following reaction [20]:

$$MeCl_n + \frac{1}{2}nH_2O \rightarrow MeO_{(s)} + nHCl_{(g)} \qquad (2.4)$$

Most metal chlorides (with the exception of calcium) in the form of aqueous solution or crystals behave similarly and decompose through pyrohydrolysis with an excellent recovery for HCl [20]. Pyrohydrolysis is finding new applications in chloride metallurgy; for example, it is used in the decomposition of nickel chloride crystals in the Falconbridge Matte Leach Plant [21] and in the decomposition of $FeCl_2$ or $FeCl_3$ steel pickling plants [22]. The pyrohydrolyzer is usually in the form of spray roaster or a fluidized bed reactor and operates at the temperature range from 600 – 800 °C [20].

Figure 2.2, which was constructed with the aid of FactSage software [23], shows the pyrohydrolysis of some metal chlorides. This figure also shows that the thermal decomposition of $CaCl_2$ is not feasible even up to 1500 K.

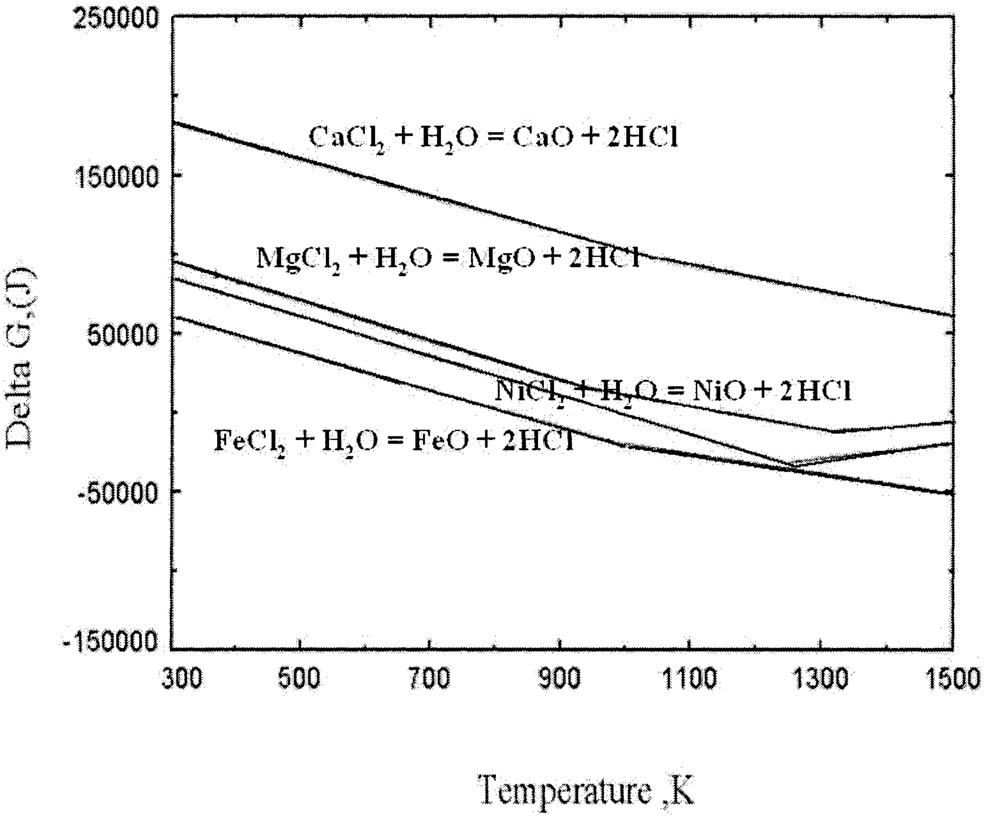


Figure 2.2: Change of ΔG for the pyrohydrolysis reactions for some metal chlorides obtained by FactSage[23].

There are approximately 400 plants all over the world that operate with pyrohydrolysis to regenerate HCl, 300 of them use spray roasters and the other 100 are using fluidized bed reactors [24].

The process can be briefly described as follows (refer to Figure 2.3): The spent pickle liquor goes to the preconcentrator where a part of the solution is evaporated before it enters the pyrohydrolyzer where a combustion gas with a certain amount of air is supplied in excess to provide heat for the pyrohydrolysis reaction. The gas leaving the reactor is separated from the oxide formed by a cyclone and the HCl gas formed is absorbed to form HCl acid solution that is used in the leaching step.

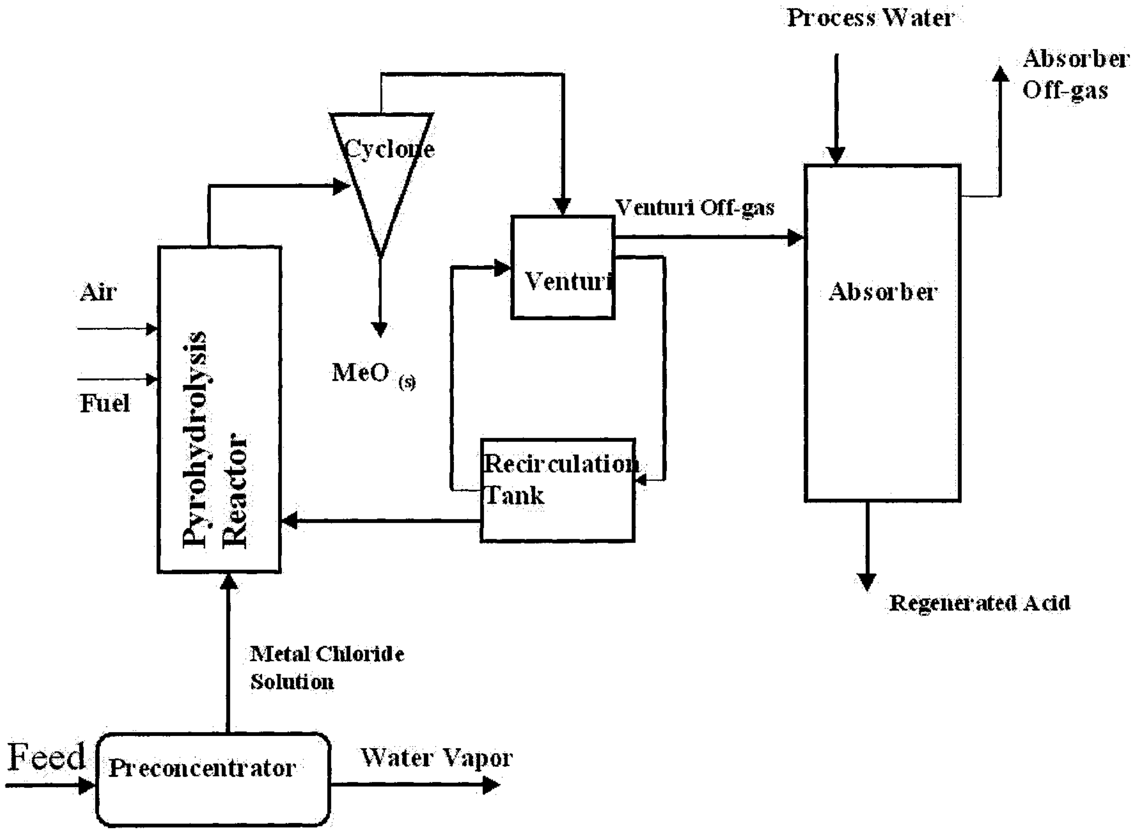


Figure 2.3: Simplified Flow Sheet for Pyrohydrolysis (adapted from Ref. [25]).

The pyrohydrolyzer can be either a fluidized bed such as the one used in the Enhanced Acid Regeneration Process (EARS) for the manufacture of high grade synthetic rutile by HCl leaching of ilmenite [26], or a spray roaster that requires only solution feed and limited to the production of sub-azeotropic acid. Furthermore, it is responsible for the production of fine oxides that result in hygiene problems in the plant [18].

Pyrohydrolysis is a highly intensive process in terms of energy and capital, and recent research has focused on energy optimization. These efforts lead to the partial recovery of the both roasters off-gas and hot oxides sensible heat [25] .

A new method for energy optimization has been proposed by Altair Nanomaterials Inc. in relation to low cost production of a nano-sized TiO_2 · HCl in this process is recovered by pressure swing distillation that uses two distillation columns one of them is operating at 5 bars and 157 °C and the second one is operating under vacuum of 0.5 bar and 56 °C to overcome the problem encountered in the distillation of the azeotropic mixture of HCl obtained. The recovered HCl gas is used in the leaching step[27].

Another new process is proposed by the Office of Industrial Technologies, U.S. Department of Energy. This method regenerates HCl from steel pickling liquors using H_2SO_4 to produce ferrous sulfate heptahydrate crystals through a crystallization process and regenerated HCl [28].

Berrie and Woolie [29] have described a process that involves the reaction of $CaCl_2$ with H_2SO_4 to produce HCl and hemihydrate at 90°C, but the process dealt with dilute solutions; hence, no high strength HCl was produced while the process was poorly controlled.

2.1.5 The issue of this research

Figure 2.4 shows an example of a chloride hydrometallurgical process that involves alternative HCl regeneration approach. This process involves the leaching of zinc sulfide material using HCl and O_2 to produce zinc oxide [11]. It also involves precipitating zinc oxide from the leach solution using magnesium oxide (MgO) as a neutralizing agent to produce $MgCl_2$, which is subsequently pyro-hydrolyzed to regenerate HCl so that the latter can be recycled to the leaching step.

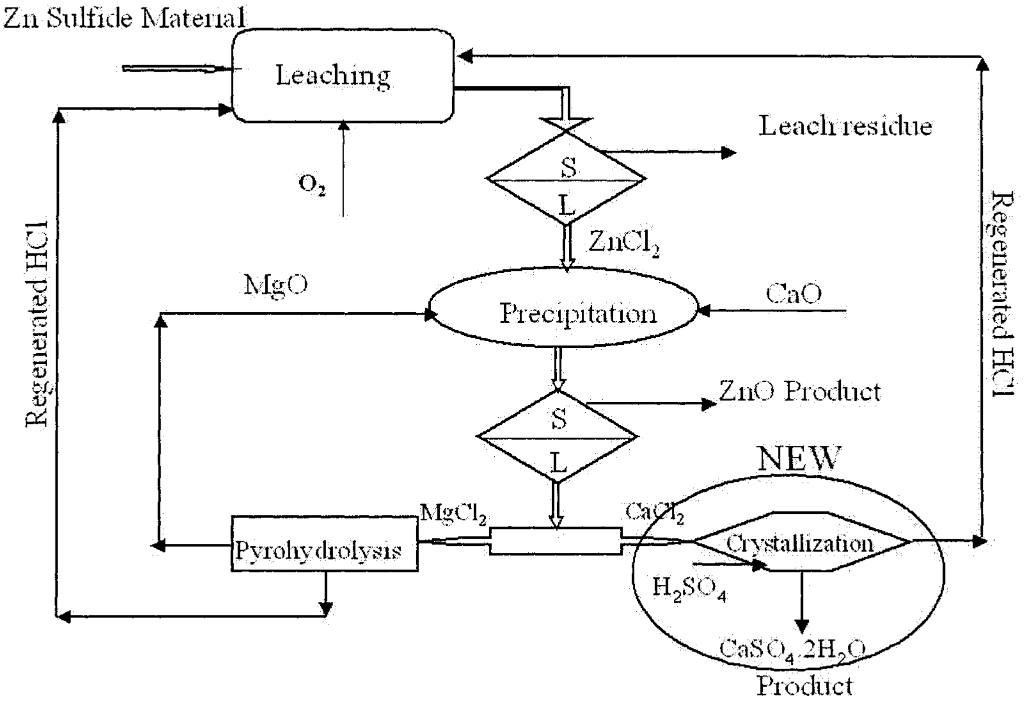


Figure 2.4: Flow sheet of ZnO production with incorporating the alternative approach for HCl regeneration (adapted from Ref. [11]).

In the precipitation stage, lime (CaO), which is the preferred neutralizing agent, cannot be used because of the formation of $CaCl_2$, the pyrohydrolysis of which is not thermodynamically feasible as mentioned earlier in section 2.1.4. Moreover, pyrohydrolysis is characterized by high cost and difficulties in water recovery [18]. For these reasons, a new process is being studied at McGill where the spent $CaCl_2$ leach solution is reacted with sulfuric acid (H_2SO_4) to regenerate HCl at low temperature. This process does not only regenerate HCl, but also potentially produces clean gypsum, or high value alpha-$CaSO_4$ hemihydrate [30] according to the following reaction:

$$CaCl_{2(aq)} + H_2SO_{4(aq)} + n\, H_2O \rightarrow CaSO_4{\cdot}nH_2O_{(s)} + 2HCl_{(aq)} \qquad (2.5)$$

Such reaction can take place readily and under atmospheric pressure at modest temperature.

This alternative low temperature process of HCl regeneration is expected to contribute to wider acceptance of chloride hydrometallurgy, by significantly lowering the cost of HCl regeneration which in turn enables the industry to take the advantage of the unique properties of chloride chemistry. In the same time the process promises to decrease the generation of wastes through the production of high quality saleable gypsum by crystallization. The present thesis aims to study in depth this process concept.

2.2 Gypsum crystallization

2.2.1 Precipitation chemistry

In this section, precipitation is viewed as a crystallization process. Precipitation is widely used in hydrometallurgy for the purposes of solution purification, product recovery and effluent treatment. Examples of precipitation in hydrometallurgy are iron precipitation as jarosite, geothite and hematite, alumina precipitation through crystallization and in zinc electrolyte purification through cementation, and the removal of arsenic through the precipitation of crystalline scorodite [31]. Before proceeding in the specific discussion of gypsum crystallization, the basic principles of precipitation are examined.

* Saturation and nucleation: The solution that is in equilibrium with the solute concentration is said to be saturated and the equilibrium relationship for bulk crystals is the solubility curve. Supersaturation is the solute concentration that exceeds the equilibrium concentration and it is the driving force for precipitation.

The formation of crystals involves the birth of new particles called nuclei [32]. In an aqueous solution, ions move randomly in such away that they may associate together to form what is called the cluster. After enough ions are associated together, the embryo is formed. The embryos are not stable and have a very short lifetime. However, if the supersaturation is very high, the embryo grows in size to form the nucleus, which will grow in turn to form the crystal. This type of nucleation is called primary homogeneous and it describes the mechanism by which nuclei are produced when no suspended crystals are present, i.e. nucleation from a single-phase system.

The rate of production of new nuclei per time per unit volume of solids-free mother liquor is called the nucleation rate (J), and this can be expressed by the following equation [33]

$$J = A \exp(-\Delta G/KT) \qquad (2.6)$$

where ΔG is the free energy change which it is given by the equation:

$$\Delta G = -RT\ln(\alpha/\alpha^*) = -RT\ln(S) \qquad (2.7)$$

where S is the saturation ratio and α is the activity of the solute. The saturation ratio may be also approximated as the following:

$$S = C/C^* \qquad (2.8)$$

Where C is the concentration in molarity and * denotes the equilibrium state.

Supersaturation is the most important parameter in the precipitation process that can be presented as an irreversible chemical reaction:

$$b\,A^{a+}{}_{(aq)} + a\,B^{b-}{}_{(aq)} \rightarrow A_bB_{a(s)} \qquad (2.9)$$

The saturating ratio can be also defined in the case of a salt such as gypsum as follows:

$$S = C_A{}^b\,C_B{}^a / Ksp \qquad (2.10)$$

where Ksp is the solubility product.

Thermodynamics predict that solids formation occurs when S >1. However, from kinetics point of view, S >> 1 is required to initiate the precipitation process.

Primary nucleation refers to the formation of nuclei when no suspended crystals are present. It can be homogeneous where the nucleation occurs spontaneously when no suspended crystals are present in the supersaturated system as described earlier or heterogeneous that is induced by the presence of foreign surfaces in the system. The secondary nucleation on the other hand, is induced in the presence of existing crystals and can be in the form of Surface on the suspended crystals, Contact (on reactor walls), Shear (fluid flow), Fracture and Attrition (Crystals fragmentation) or Needle due to particle disruption [33,34]. These nucleation mechanisms are summarized in Figure 2.5.

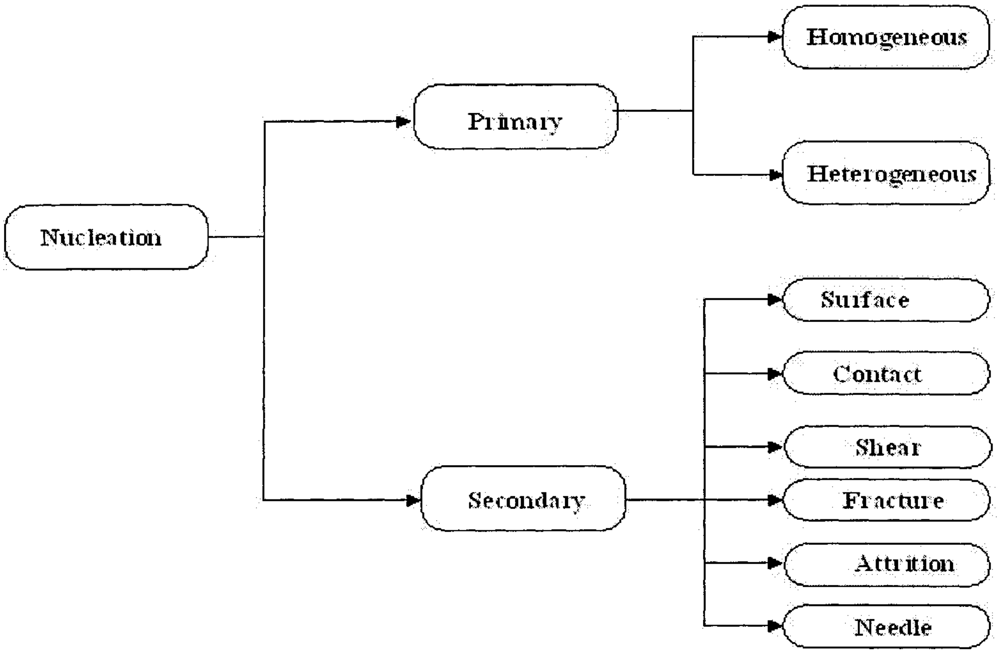


Figure 2.5: Nucleation mechanisms [33].

* Crystal growth: Crystal growth is a diffusional process that will not proceed until the solution is supersaturated and nuclei have formed in it. It consists of the following steps:
Step (1) : Mass transfer of solute to the crystal surface by diffusion through the liquid phase boundary layer.

Step (2) : Surface integration of the solute ions into the crystal lattice. This step also involves solute adsorption on the crystal surface then diffusion occurs through the adsorption layer. Subsequently or simultaneously desolvation (loss of water) occurs followed by solute integration.

* Growth mechanisms [34, 35] These are shown in Figure 2.6.

a). Continuous growth model: This model implies that the surface integration of the growth unit occurs at a kink site where the energy demand is the lowest and the crystal growth continues until the deformities heal over.

b). Birth and spread model: In this model, two dimensional nucleation occurs by the formation and subsequently the growth of the critical nucleus that rapidly spreads.

c). Screw dislocation model: This model was developed by Burton (1951) and assumes that crystals grow through continuous spiral dislocations. The growth occurs at the edge of defects where the angular velocity near the corner is faster.

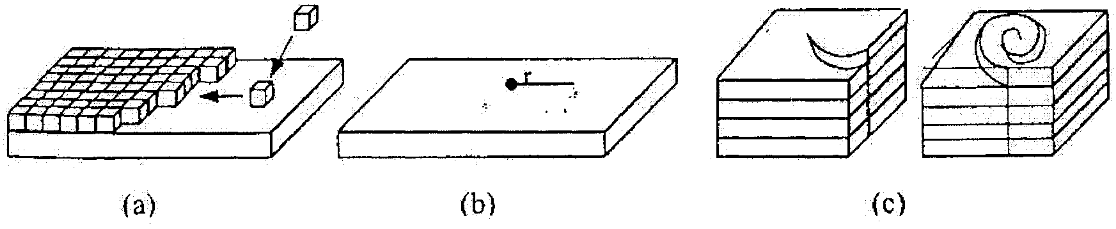


Figure 2.6: Growth mechanisms: a) Continuous growth model, b) Birth and spread Model , c) Screw dislocation model [35].

* Seeded growth: Based on the industrial need for the production of free settling product and well grown crystals out of the precipitation process, and according to the crystallization theory which states that deliberate introduction of crystals (seed) will

induce nucleation at lower degrees. Spontaneous nucleation can be blocked and crystal growth favored [35].

* Stranski's rule or Ostwald Step rule: According to Stranski's rule [33, 35], " the least stable phase will nucleate first when homogenous nucleation determines the rate". One example of this rule is the ferric ion hydrolysis reaction that leads first to the formation of the amorphous phase of hydroxide which is converted by aging to the most stable crystalline phase:

$$\mathrm{Fe(III)}_{(aq)} \rightarrow \mathrm{FeOOH.xH_2O(amorphous)} \rightarrow \text{a-FeOOH or b-FeOOH} \rightarrow \text{a-}\mathrm{Fe_2O_3} \quad (2.11)$$

2.2.2 Production of well grown crystalline compounds

The main factor in obtaining crystalline product and avoiding the formation of amorphous product is the operation at low supersaturation conditions. Low supersaturation leads to the avoidance of homogenous nucleation and the formation of the undesirable metastable phases as well as the minimization of impurity uptake. Supersaturation can be controlled via various methods and these are: stepwise addition of the precipitating agent, metal complexation and dissociation, solvent dilution and redox reactions [33].

The stepwise addition method involves the slow addition of the precipitating agent. Slow releasing of the chemicals instead of adding all the chemicals at once showed to be effective in obtaining well grown crystals. This approach has been successfully applied to neutralization-based precipitation processes in McGill and shown in Figure 2.7.

An example for this method is the production of scorodite from concentrated chloride solutions under ambient pressure [36]. Another example of the supersaturation control method is the precipitation of nickel hydroxide from sulfate solutions at various pHs and temperatures [37].

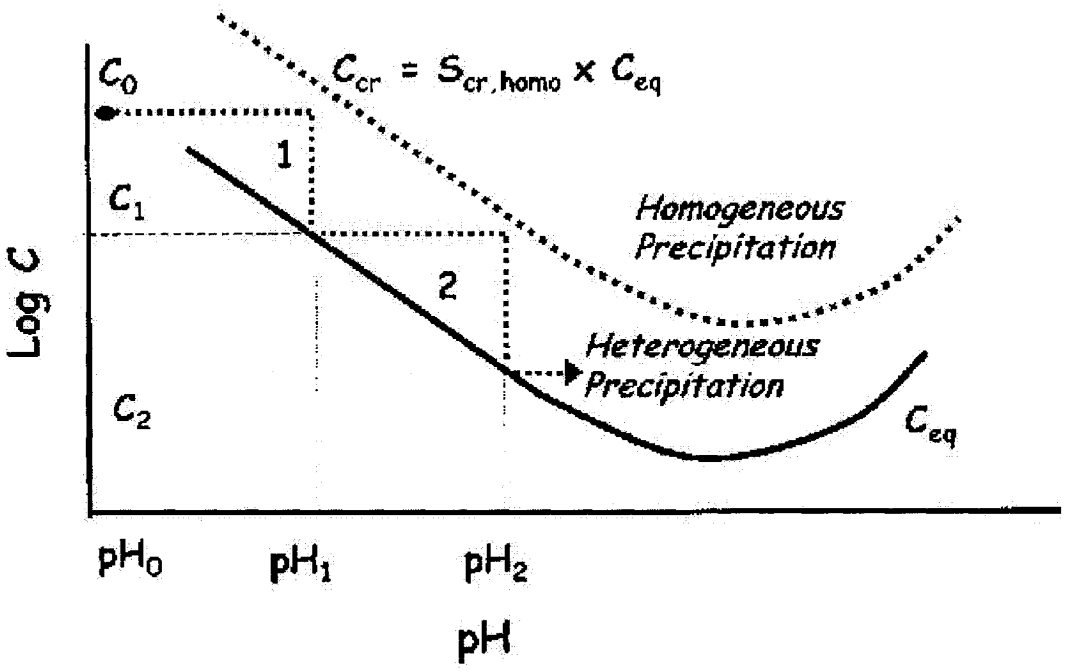


Figure 2.7 : Supersaturation control by neutralization (method developed at McGill)[37].

2.2.3 Precipitation process diagram

The properties of the produced crystals by any precipitation process can determine the energy consumption in the following solid – liquid separation operation. These properties are mainly the crystal size, shape and modification or purity. Careful control of the precipitation process and proper design of the crystallizer lead to obtainment of the desired product quality [38] .

If two or more precipitators are connected in series to form a cascade, great changes on the product quality will be achieved. The output from reactor 1 will be the input for reactor 2 and so on. For equal size tanks, the mean residence time is the same for each one. The level of supersaturation will be continuously reduced allowing more crystal growth. Figure 2.8 shows a typical precipitation process diagram.

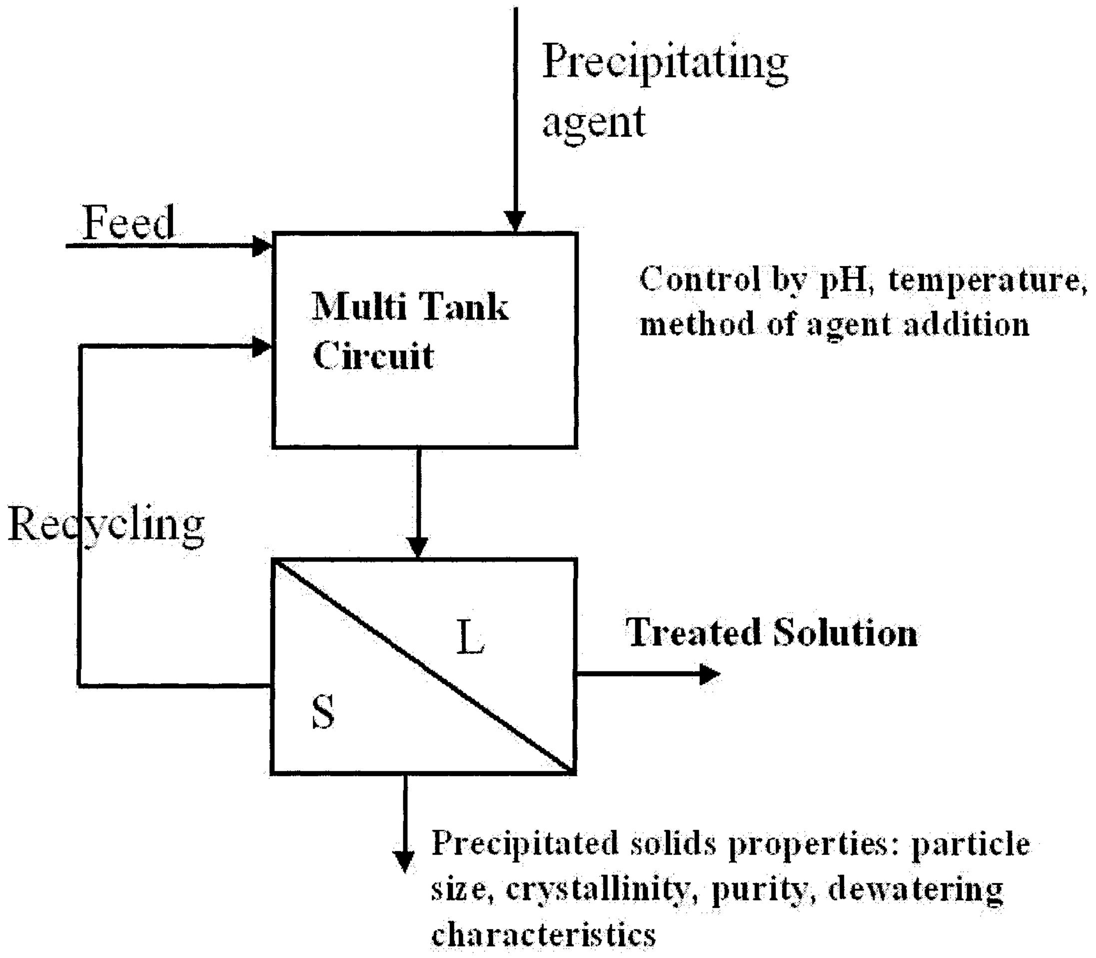


Figure 2.8 : Typical precipitation process diagram [33].

2.2.4 Impurity uptake in precipitation

The presence of impurities can affect the particle morphology and the growth rate. Small traces of impurities are enough to make significant changes in the crystal habit during the process of crystallization by mainly reducing the specific surface energy and slowing the growth rate [39]. Mullin [35] states that the presence of impurities is responsible for the suppression of the primary nucleation and the occurrence of secondary nucleation at significant impurity uptake.

The incorporation of impurities in the precipitation systems can occur through various mechanisms: through co-precipitation as a distinct phase such as in the case of the precipitation of arsenic as scorodite during the removal of iron(III) as jarosite in acid media, or by surface adsorption such as the pH dependent adsorption of cations(Cu^{2+}, Ni^{2+}, Zn^{2+}), and anions (As, Sb, Se, Ge)[33].

The control of adsorptive incorporation of impurities can be accomplished by several ways and these are [33]: (1) Reduction of the specific surface area by promoting the growth of large, well grown crystals; (2) enhancing the crystallinity and supression of the aggregation by the proper control of the supersaturation environment; (3) the modification of the pH or the redox potential of the media to change the character of the troublesome impurity and surface charge; and (4) the complexation of the troublesome cation.

2.2.5 Gypsum production

Gypsum occurs naturally as a crystalline mineral and has the chemical formula: $CaSO_4 \cdot 2H_2O$. It is called calcium sulfate dihydrate and it is usually white in color, however, it can be gray, yellow, pink and even brown [40]. Calcium sulfate has several phases, and it is also found in the form of anhydrite AH ($CaSO_4$) and hemihydrate HH($CaSO_4 \cdot 1/2H_2O$). The latter can be found as α- HH that has a very high strength and can be used as industrial and dental plaster or β- HH. β- HH is also called Plaster of Paris or the gypsum plaster, and it is most widely used as a building material and was found to be used as a building material in the old Egyptian pyramids [41]. Gypsum is used as premier fire resistant material and has applications in agriculture by being a source of calcium and sulfur and a neutralizing agent to reduce the soil acidity, hence improving the plant rooting [42]. Gypsum also finds an application in medicine as a source of calcium ions

[43]. Gypsum plaster is used to prepare pellets that are used to deliver antibiotics and anti-flammatory drugs.

* Methods of gypsum production: As mentioned earlier in this section, gypsum mineral occurs naturally. However, a lot of gypsum is produced industrially as either a by-product or a waste. Gypsum can be produced as a by-product from Flue Gas Desulfurization (FGD gypsum)[44] . FGD gypsum can be produced by the capture of SO_2 with limestone according to the following reaction:

$$CaCO_3 + SO_2 + \frac{1}{2} O_2 + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O + CO_2 \qquad (2.12)$$

The production of saleable gypsum in hydrometallurgical processes via neutralization is not widely practiced. Waste gypsum produced is disposed in tailing ponds. An exception to this is Akita Zinc Co. plant in Japan which produces saleable quality gypsum by neutralization of zinc process solutions with limestone[45].

2.2.6 Crystallization of gypsum

In industrial practice, the crystallization process will be followed by solid–liquid separation in order to obtain the final product. The energy consumption in such operation is a decisive factor, and depends on the properties of the crystals produced. When it comes to gypsum crystallization, the control of the crystal size and the settling or the filtration characteristics are important to improve the total S/L separation economics.

Mersmann [38] studied the influence of the operational conditions on the crystallization of $CaSO_4$ in a continuous and a batch system. The results of this study in the continuous system showed that the mean crystal size in the precipitation process is affected mainly by primary nucleation which increases strongly with supersaturation. The increase in the reactant concentration and the decrease in the residence time increase the nucleation rate. Furthermore, crystal growth is favored by decreasing both residence time and the power input in the continuous system. The results of this study for the batch system also showed that the supersaturation decreases and approaches the solubility, thus favoring the crystal growth. A decrease in the median crystal size with the rise in the power input was also observed. The batch time on the other hand, seemed to have no effect on the median particle size.

Girgin and Demopoulos [30] showed in a study for the production of the high value material, alpha calcium sulfate hemihydrate out of spent calcium chloride solutions by reaction with sulfuric acid that this material can be successfully produced at 80 °C. Omelon [46] has showed on the other hand that the quality, shape and size of the gypsum crystals produced by the neutralization of dilute H_2SO_4 solution depends on the quality of the starting seed.

The effect of impurities on gypsum precipitation was investigated by Verbann [47], and the study showed that impurity uptake increases as the precipitation rate increases. Al-Sabbagh [48] has studied the influence of sodium chloride on the rate of phase transition during the crystallization of calcium sulfate, and the results of the study showed sodium chloride to increase this rate because it changes the driving force of recrystallization. Furthermore, it was observed that the conversion from gypsum to hemihydrate was strongly increased in the presence of sodium chloride. Kruger et al [49], studied the effect of some ionic contaminants on gypsum crystallization in the wet process phosphoric acid, in terms of their effect on the filtration rates, and these contaminates were Na^{+}, K^{+}, Mg^{2+}, Al^{3+}, F^{-} and Fe^{3+}; the results showed that filtration rates decreased at higher impurity levels.

CHAPTER 3: EXPERIMENTAL

3.1 Introduction

In this chapter, a description is given for the experimental procedure, the different chemicals and reagents, the experimental set-up, and the characterization techniques used throughout this work.

3.2 Chemicals

All the solutions were prepared using deionized water. Furthermore, all the chemicals used were of A.C.S analytical reagent grade. Table 3.1 shows the various chemicals and reagents that were used in this work.

3.3 Experimental set-up

The crystallization tests were done using the experimental set-up shown in Figure 3.1. The set-up consisted of a glass semi-batch reactor of 1 Liter volume where the calcium chloride solution was initially located. The top of the reactor was covered with a four hole cover, through one of which the reagent used (sulfuric acid solution in this case) was added to the calcium chloride solution. The other openings were for the stirrer, the thermometer and for sampling. These openings were not used, so they were closed to prevent losses from the solution due to evaporation.

The sulfuric acid solution was added using a glass burette of 100 mL volume. A Teflon stirrer was used and the speed was varied between 400 – 600 rpm. First, the reactor was unbaffled and then teflon baffles were added inside with the dimensions chosen based on standard chemical engineering principles [50], and shown in Appendix 1.

Table 3.1: Chemicals employed in the present work

Name	Formula	Provider	Purity (wt%)
Sulfuric Acid	H_2SO_4	Fisher Scientific	95-98
Hydrochloric Acid	HCl	Fisher Scientific	36.5-38
Sodium Hydroxide	$NaOH$	Fisher Scientific	98
Calcium Chloride Dihydrate	$CaCl_2.2H_2O$	Fisher Scientific	100.3
Calcium Sulfate Dihydrate	$CaSO_4.2H_2O$	Sigma Aldrich	98
Sodium Chloride	$NaCl$	Fisher Scientific	99
Magnesium Chloride	$MgCl_2.6H_2O$	Fisher Scientific	99.4
Zinc Chloride	$ZnCl_2$	A & C Chemicals Ltd.	97
Cupric Chloride	$CuCl_2.2H_2O$	Anachemia Chemicals Ltd.	99
Lead Chloride	$PbCl_2$	Anachemia Chemicals Ltd.	99
Ferrous Chloride	$FeCl_2.4H_2O$	Fisher Scientific	101.33
Nickel Chloride	$NiCl_2.6H_2O$	Fisher Scientific	97
Aluminum Chloride	$AlCl_3.6H_2O$	Fisher Scientific	95-102

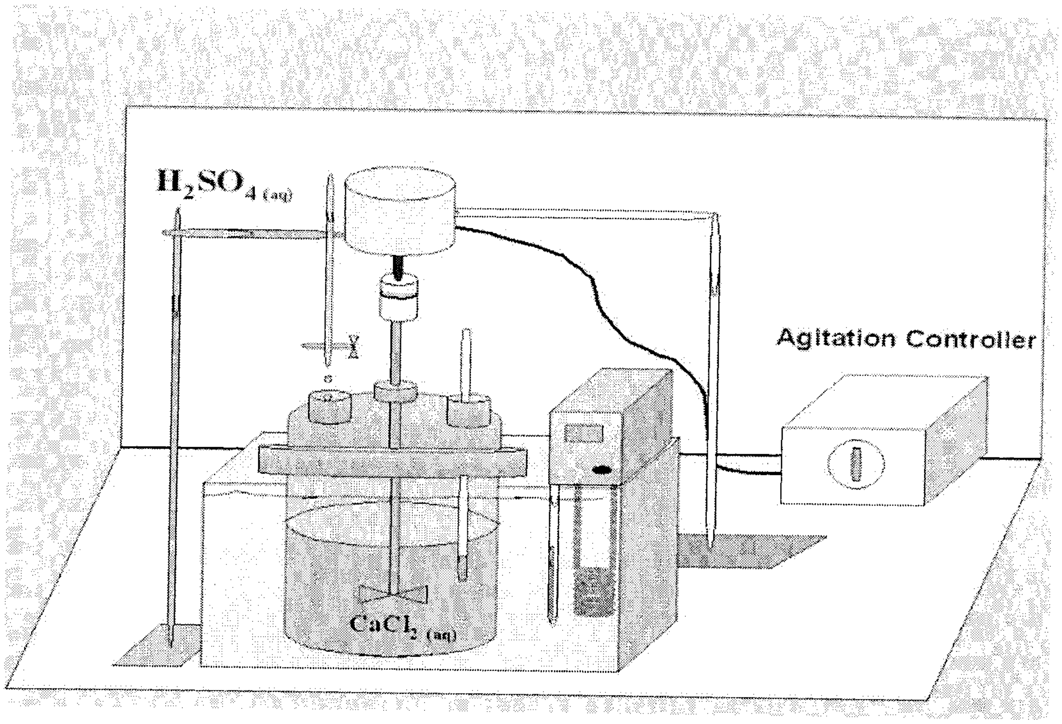


Figure 3.1 Experimental set-up used in the crystallization tests

The solutions were heated to the desired temperature that was kept constant using a water bath from Cole-Parmer with a circulator of model 1268-36. The temperature inside this bath and inside the reactor was also measured using a thermometer.

3.4 Experimental procedure

3.4.1 Standard tests

The gypsum crystallization experiments were performed at constant temperature at the range of 20 – 60 °C. Sulfuric acid solution was always the limiting reactant and added with different conditions: Variable addition rates; variable concentrations at the range of 2.66 to 8.0 M; different total molar ratios of $[SO_4]/[Ca]$ from 0.33 to 0.8, whereas calcium chloride solution was either 3.0 or 3.5 M. These conditions were chosen to keep always an amount of unreacted calcium chloride in the final solution to suppress the solubility of $CaSO_4$ in the regenerated solution [51]. When different sulfuric acid concentrations were used, the acid was added in different volumes to ensure always the same amount of solids were produced in each experiment. These acid volumes are shown in Table 3.2.

Table 3.2: Sulfuric acid volumes used (conditions: Acid was added to 300 mL of 3.5 M $CaCl_2$ at a ratio $[SO_4]/[Ca]=0.8$).

Sulfuric Acid Concentration (M)	Sulfuric Acid Volume (mL)
2.66	315.79
5.32	157.89
6.65	126.32
8.0	105

The addition time of the acid was varied between the case that all the acid was added at once and up to 4 hours of acid addition and either by titration during this time or acid addition in small doses over certain time periods. The agitation time provided for the crystals after the reaction was completed is called the equilibration time and this was also varied from the case when no equilibration time was provided to up to 6 hours of equilibration.

Another set of experiments was conducted to study the effect of seed/recycling using A.C.S calcium sulfate dihydrate purchased from Aldrich as a seeding material. The seed loading was varied as follows:15, 25, 30 and 60 g/L seed. This seed load was calculated based on the initial calcium chloride solution volume. The recycling tests performed were also based on filtering the solids in a Buchner funnel flask connected to a vacuum pump and using Fisher brand filter paper, quantitative Q5 and the liquid obtained was clear in all the experiments and drying the solids 60 °C for 24 hours in the oven, then taking first seed load using them as seed for the next recycle.

After the crystallization test was completed, samples were taken from the obtained solution for the analysis of calcium and sulfur content in the regenerated solution in order to find the soluble sulfate content. Samples were also taken to measure the HCl strength in the final solution and this was simply done by titration using NaOH. The settling rate of the produced solution, the % solids density and the filtration rates were also measured.

3.4.2 Impurity uptake tests

In order to study and evaluate the metal uptake by the produced solids, solutions of 3.5 M $CaCl_2$ with 0.1 M of various metal chlorides: NaCl, $MgCl_2$, $ZnCl_2$, $FeCl_2$, $CuCl_2$, $AlCl_3$, $NiCl_2$ and $PbCl_2$ were prepared. First NaCl, $MgCl_2$ and $ZnCl_2$ were studied separately while the other chlorides were studied in a mixed solution. Seeding was employed using Calcium Sulfate Dihydrate A.C.S 15 g/L load, and recycling was performed twice. From these tests, the filtration rate of the produced solids and the regenerated HCl strength were measured. The latter was done by titration with NaOH solution up to pH equal 2 to prevent the hydrolysis of the present metals. Samples were also taken from the regenerated solutions, filtered using Millex syringe filters of 0.22 μm pore size, diluted and analyzed for sulfur and calcium content. According to solubility data published in this regard [51], the maximum solubility of $CaSO_4$ as a function of HCl concentration and at room temperature of 22.2 °C is obtained at 3 M HCl and equals to 19 g/L. Based on this, 1.8 g of the produced solids from each test were dissolved in 100 mL solution of 3 M HCl to obtain samples that were analyzed for their metal concentration to determine the metal uptake level of the solids. The sulfur and calcium content of the dissolved solids was also measured using ICP.

3.5 Handling of the solid product

Upon the completion of each of the crystallization tests, the slurry was collected and after all the solids settled down, the clear liquid was separated and the remained thickened slurry was filtered using a Buchner funnel flask connected to a vacuum pump and using Fisher brand filter paper, quantitative Q5 and the solution was obtained. For the measurement of the filtration rate, different procedure was followed as will be described later in this chapter.

The produced solids cake was then washed using boiling distilled water to remove any retained acid by the cake. The washing volume was always equal to two volumes of the filtrate and this hot water washing was followed by acetone washing to further dry the cake and displace any retained moisture.

The washed solids were dried at 60 °C for 24 hours and the produced solids were placed in sealed plastic bags to be used either for characterization or as a seed in the recycling test.

3.6 Property measurements methods

3.6.1 Measurement of the solids settling rate

The settling rate of the produced solids is important to the design of the thickener, and it determines the solids concentration in the thickener underflow. The settling rate in this

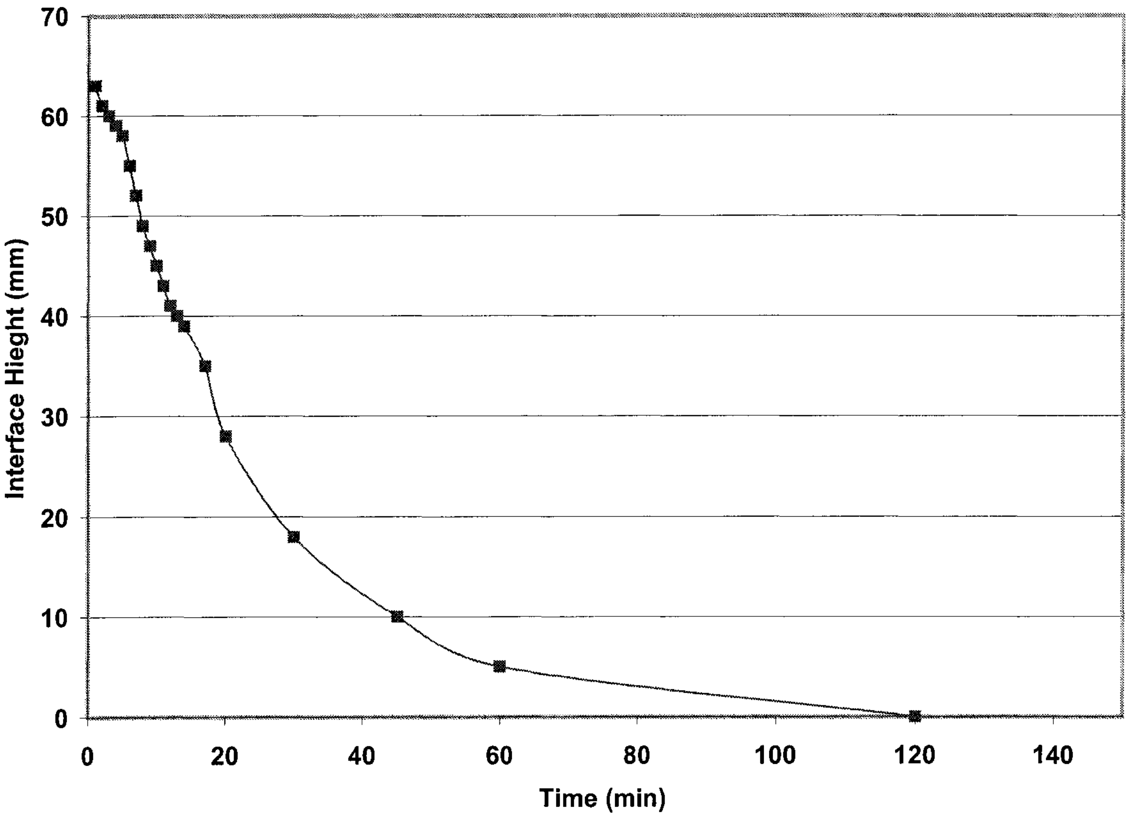


Figure 3.2: Settling rate curve(conditions: 5.32 M H_2SO_4 added to3.5 M $CaCl_2$ at 40 °C, for 2 hours followed by 2 hours of equilibration).

work was measured by a batch sedimentation test using 500 mL graduated cylinder provided with a scale and a stopwatch to measure the height of the interface with time.

When the solution was obtained after gypsum crystallization, it was poured in the cylinder, the solids suspended in it started to settle to give a zone of clear liquid with variable depth called the interface height. Figure 3.2 shows a typical plot of the interface height with time obtained from one of the experiments done in this context. The settling rate was measured based on the linear part of the curve and the results were reported as cm/hour.

3.6.2 Measurement of the solids density

After all the solids settled down for 24 hours, the clear liquid was removed and the weight of the remained solution was measured. Then the samples were filtered and dried for 24 hours at 60 °C. The weight of the dry solids was measured and the % solids density was calculated based on the following equation:

$$\text{Solids density (\%)} = (\text{dry sample mass}) / (\text{wet sample mass}) * 100 \qquad (3.1)$$

3.6.3 Measurement of filtration rate

The filtration rate of the produced solids was measured using a press filter, under 20-psi pressure and at room temperature. The filter paper used was Whatman No. 1 (> 11 micron) of 0.142 m diameter and using slurry that contained 30 % of the solids produced.

The time until all the filtrate volume collected was measured, the solids deposited were washed, dried and weighed. The filtration rate was reported as the mass of dry solids deposited on the filter paper per unit area per time in hours.

3.7 Analytical and characterization techniques

After the crystallization test was completed, solution samples were taken, diluted using deionised water and kept in special containers to be titrated with NaOH solution to measure the strength of the regenerated HCl. The standard titration procedure involved titration with 0.1 M NaOH and the following indicators: Methyl Orange and Phenolphthalein. In the case of the test that involved the metals chlorides, titration was done until a pH 2 as the end point to prevent metals hydrolysis. This procedure yielded lower than expected results(~3.4 vs 4.1 M), hence, some of the solutions were re-titrated but this time using Phenolphthalein as an indicator. Further samples were also taken, filtered with syringe filters (0.22 μm), diluted and kept to be tested by Inductively Coupled Plasma Spectroscopy (ICP) for the calcium and sulfur content, from which the residual sulfate in the regenerated solutions was calculated.

ICP was performed in the Department of Chemical Engineering, using Thermo Jarrel Ash Trace Scan machine, and standard solutions for sulfur and calcium from Fisher of 50 and 100 ppm [52].

XRD analysis was performed using a Philips PW 1710 machine to determine the phases of calcium sulfate present in the produced samples.

Scanning Electron Microscopy (SEM), was performed using a Joel JSM 840A scanning microscope of 10 kV.

Finally the particle size of gypsum crystals was measured using a Horiba Laser Scattering Particle Size Analyzer model LA 920.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

The research work described in this thesis was undertaken with the overall goal of determining the optimum conditions for the regeneration of HCl from concentrated $CaCl_2$ solutions (simulated spent chloride leach liquor) by reaction of H_2SO_4 under relatively mild conditions (20 – 60 °C) with simultaneous production of well grown and clean gypsum. The investigated process is described by the following chemical reaction:

$$CaCl_2 + H_2SO_4 + xH_2O \rightarrow CaSO_4{\cdot}xH_2O_{(s)} + 2HCl_{(aq)} \qquad (4.1)$$

The process parameters studied and optimized were: (1) The method of sulfuric acid addition; (2) the equilibration time; (3) the effect of acid concentration; (4) the effect of temperature;(5) the effect of seeding/recycling and (6) the effect of co-existing chlorides. The effect of these parameters was evaluated on the basis of the quality of the produced solids and the composition of the regenerated HCl solution; more particularly, the settling rate, % solids density, filtration rate, particle size, crystal morphology and crystal purity.

Sulfuric acid was chosen to be the limiting reactant, so that a portion of $CaCl_2$ solution was always present in the regenerated solution to suppress the calcium sulfate solubility [51], hence, lower the potential for scaling upon the recycling of the regenerated HCl solution in the process plant.

4.2 The effect of the titration and step-wise addition of acid

The rationale for performing tests at different titration rates and stages stems from observations that are well documented in literature according to which the method of addition of the precipitating agent (in this case H_2SO_4) has a great impact on supersaturation, hence, on the quality of the produced crystals [53] .

4.2.1 Titration method

In these experiments, 112 mL of 5.32 M H_2SO_4 were added to 300 mL total of 3 M $CaCl_2$ at the total molar ratio of $[SO_4] / [Ca] = 0.66$, where $[SO_4]$ and $[Ca]$ are the moles of total sulfate and calcium respectively. The experiment was performed at 40 °C. The time of acid addition was variable between adding all the acid at once, or up to 4 hours of acid addition, followed by 2 hours of equilibration after each test except for the first test when no equilibration followed for reasons that will be mentioned later in this section.

The experimental results in the form of settling rate and % solids of the resultant settled slurry are shown in Figure 4.1. It was noticed that when all the acid was added at once, a colloidal suspension (gel-like) was obtained that exhibited no settling and had very poor dewatering characteristics and was difficult to agitate. However, by gradual increase in the addition time starting with 1 , 2 and 4 hours of addition, i.e., slower titration rate, the settling rate started to increase as well as the % solids density. For example, the % solids content increased from 16 % when all the acid was added at once to 27 % at 4 hours of addition. The settling rate nevertheless (despite its improvement) remained slow.

The effect of acid addition method was further evaluated through the examination of the SEM images taken for the different solids obtained and shown in Figure 4.2. The difference in crystal growth can be observed in each case.

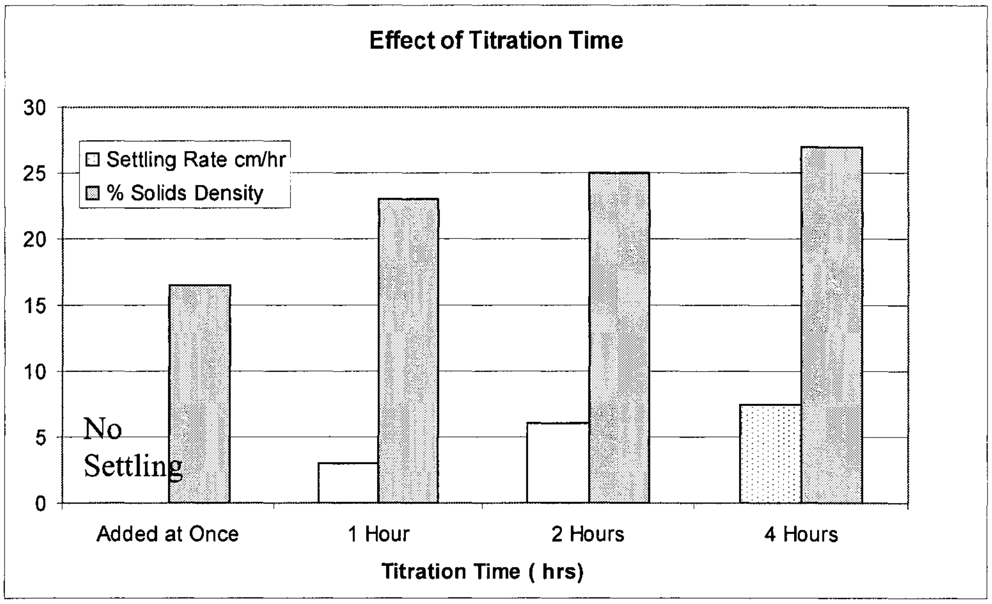
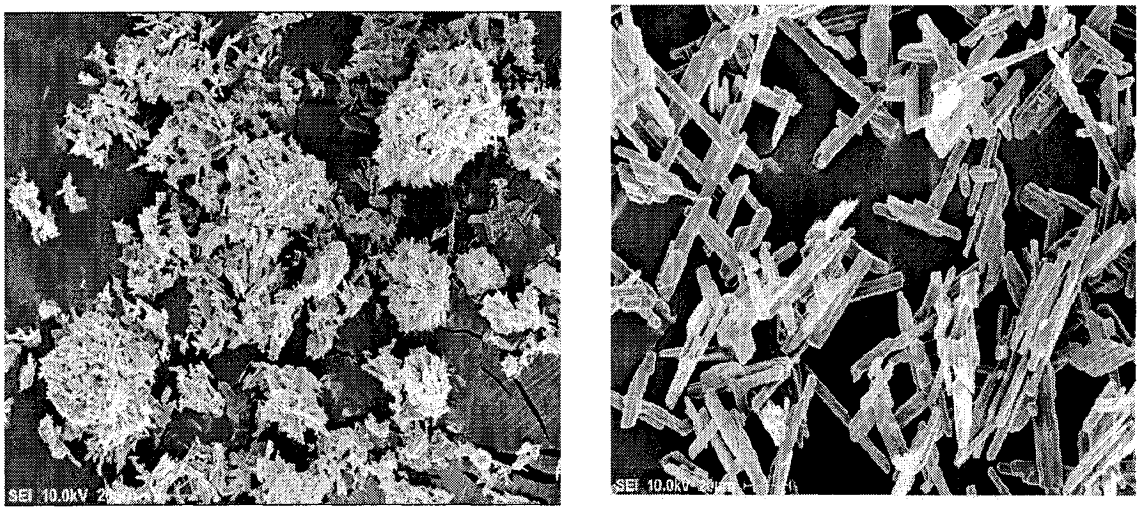


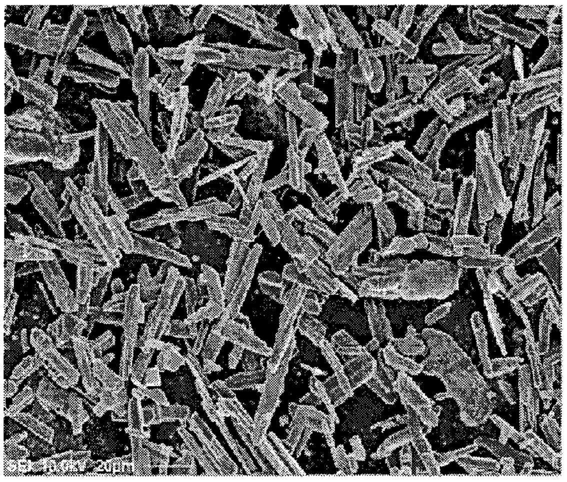
Figure 4.1 : Effect of titration time on the solids properties at constant equilibration time of 2 hours except for the test involving the acid addition at once. (5.32 M H_2SO_4 were added to 300 mL of 3 M $CaCl_2$ at the total molar ratio of $[SO_4] / [Ca] = 0.66$ at 40 °C.)

As can be seen, in the SEM pictures, the method of acid addition results in different morphologies of the gypsum crystals. Thus, when all the acid was added at once into the calcium chloride solution, very fine needle crystals were clustered together with a "glass-wool" appearance. On the other hand, crystals obtained with gradual addition of the acid (by titration for 2 hours as can be seen from Figure 4.2 (b) and at 4 hours titration (Figure 4.2 (c)) were well developed with dimensions approximately 50 μm length and 5 μm thickness.



a) Acid added at once

b) Acid added for 2 hours



c) Acid added for 4 hours

Figure 4.2 : SEM images for the produced gypsum during the titration tests; (a) when all the acid was added at once; (b) when the acid was titrated for 2 hours; and (c) when the acid was titrated for 4 hours (for conditions see Figure 4.1).

Such differences in crystal growth characteristics can be attributed to the supersaturation environment that can be also influenced by the rate of addition of the precipitant agent (H_2SO_4) in this case. The supersaturation can be expressed by the following equation that gives the saturation ratio S (refer to equation 2.10):

$$S = \frac{a_{Ca} . a_{SO4} . a^2_{H2O}}{Ksp} \approx \frac{C_{Ca} . C_{SO4}}{Ksp} \qquad (4.2)$$

Where a is the activity of each species and Ksp is the solubility product of gypsum. As can be deduced from equation 4.2, as the acid addition rate increases(which is equivalent to the increase of the sulfuric acid activity), the supersaturation also increases, hence, primary fast homogeneous nucleation occurs with limited growth of crystals (refer to Figure 4.2 (a)). It is also clear that slow addition of the acid through the titration procedure is preferred in this context.

4.2.2 Step-wise addition method

From an industrial point of view, the titration procedure is equivalent to step-wise addition of sulfuric acid to a number of reactors connected in series, where each reactor receives a certain dose of the acid as shown in Figure 4.3, the upper part shows the change of unreacted calcium chloride portion with each dose of the acid added with reaction time and the lower part describes a continuous operation of a step-wise addition method.

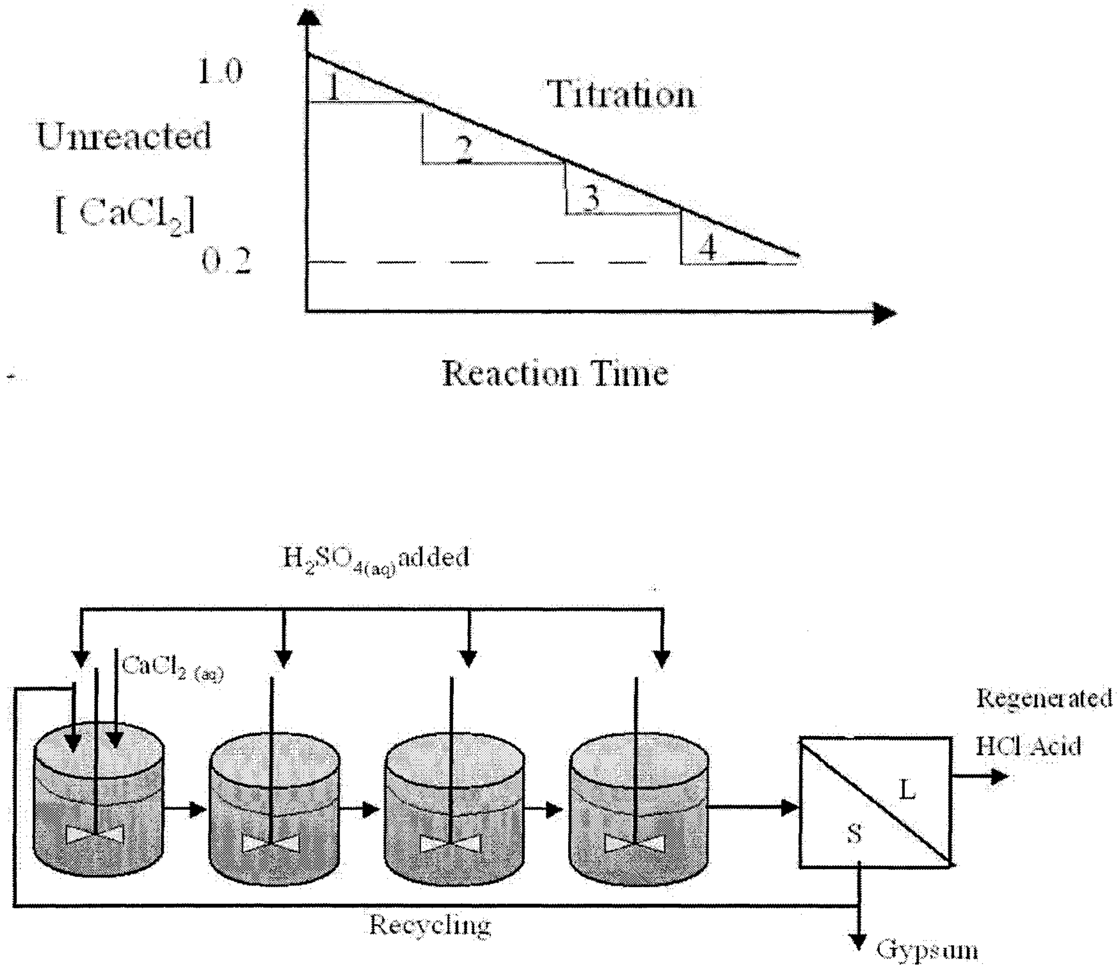


Figure 4.3 : Step wise addition of the acid; (a) the change of unreacted $CaCl_2$ portion with reaction time and (b) a continuous circuit incorporating the step-wise addition of acid and recycling

With the dual purpose of: (i) verify that the step-wise addition of the acid is equivalent to titration and (ii) determine the optimum number of steps (or stages) required to approximate the titration procedure, a new set of tests were conducted. In this series of tests, a total volume of 126.3 mL of 6.65 M H_2SO_4, was added to 300 mL of 3.5 M $CaCl_2$ solution, over a period of 2 hours. The total amount of acid added corresponded to the molar ration , $[SO_4] / [Ca] = 0.8$, at certain doses at 4, 6 and 8 stages and at 40 °C . In each experiment, 2 hours of equilibration were provided after the limiting reactant was consumed. The experimental results in terms of the settling rate and the % solids are shown in Figure 4.4.

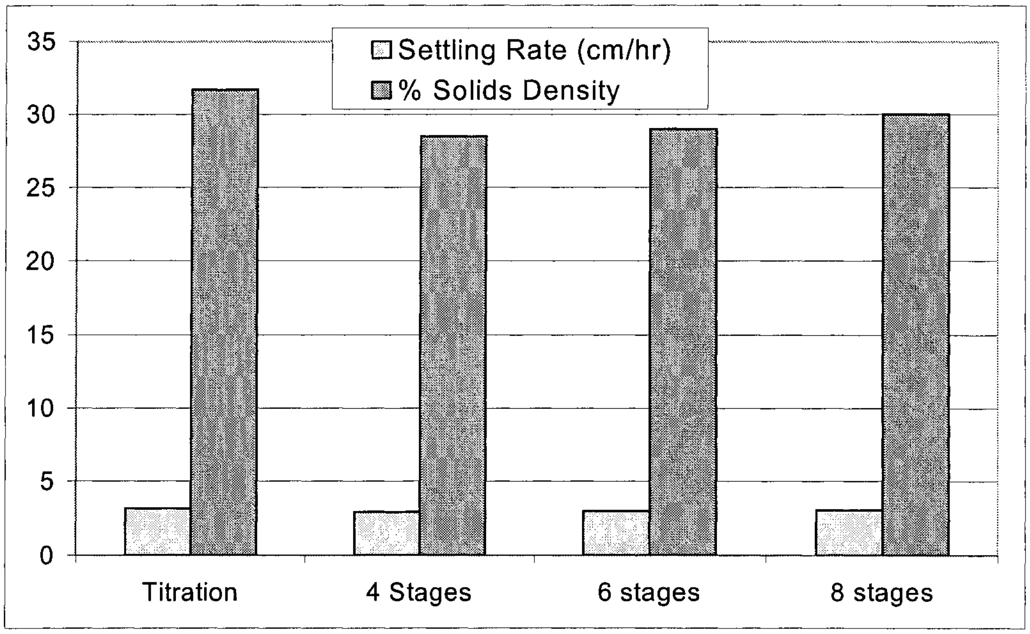


Figure 4.4: Titration vs staged addition of the acid.(126.3 mL of 6.65 M H_2SO_4, was added to 300 mL of 3.5 M $CaCl_2$ solution, over a period of 2 hours. The total amount of acid added corresponded to the molar ration , $[SO_4] / [Ca] = 0.8$, at certain doses at 4, 6 and 8 stages at 40 °C).

From Figure 4.4 above it is evident that titration is equivalent to step-wise addition of the acid in terms of the settling rate of the produced solids and the solids density. Moreover, it appears that the four stages gives reasonable approximation of the titration procedure.

4.3 The effect of equilibration time

The objective of performing these tests was to determine the effect of equilibration time on the produced solids properties. Equilibration time refers to the agitation time provided for crystals after the limiting reactant is consumed (sulfuric acid in this case).

The effect of this parameter was studied using 5.32 M H_2SO_4 that was added to 300 mL of 3 M $CaCl_2$ at a constant addition rate over 2 hours and constant temperature of 40 °C. The equilibration time was varied from 0 hours and up to 6 hours. The results are shown in Figure 4.5 .

It can be clearly seen from this figure that the crystals settling rate and the % solids density increases with the increase in the provided time. SEM analysis (see Figure 4.6 revealed that gypsum crystals undergo ripening, i.e., larger crystals grow in size at the expense of the smaller crystals that are slowly disappear, and this is a spontaneous process that is well documented in literature [54].

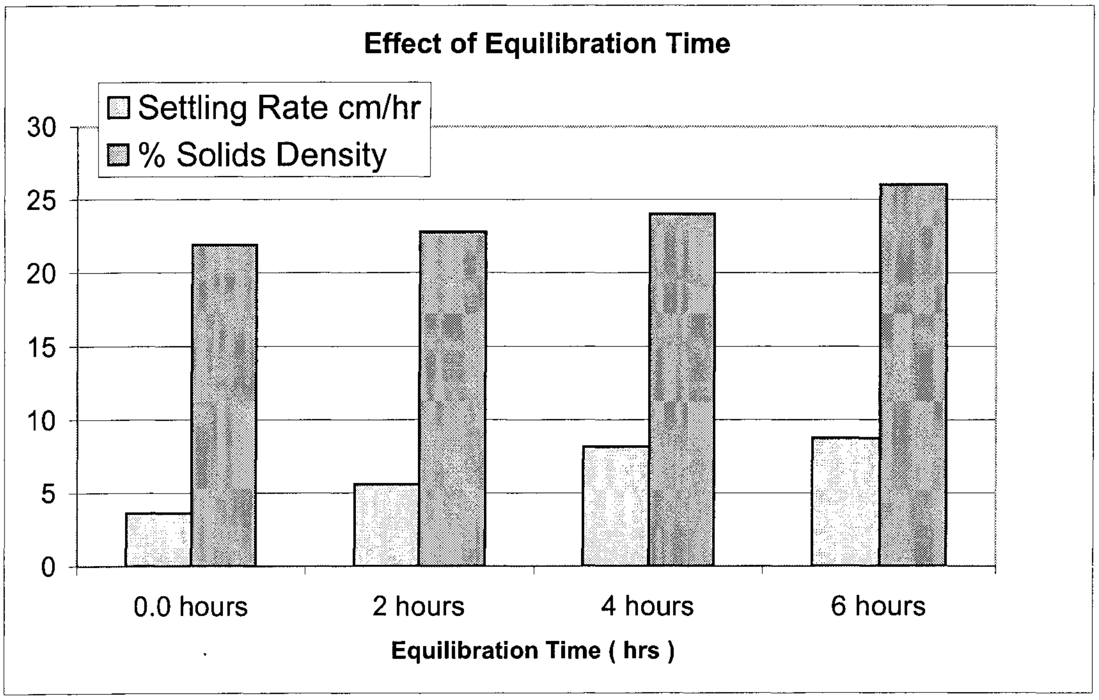
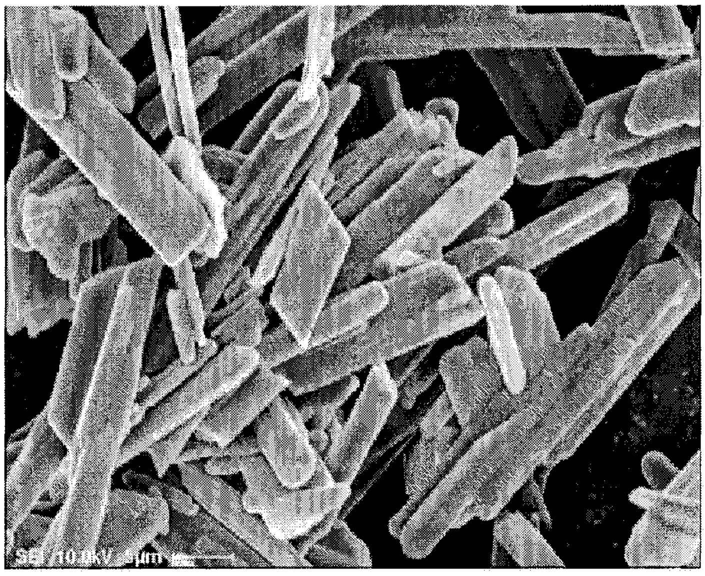
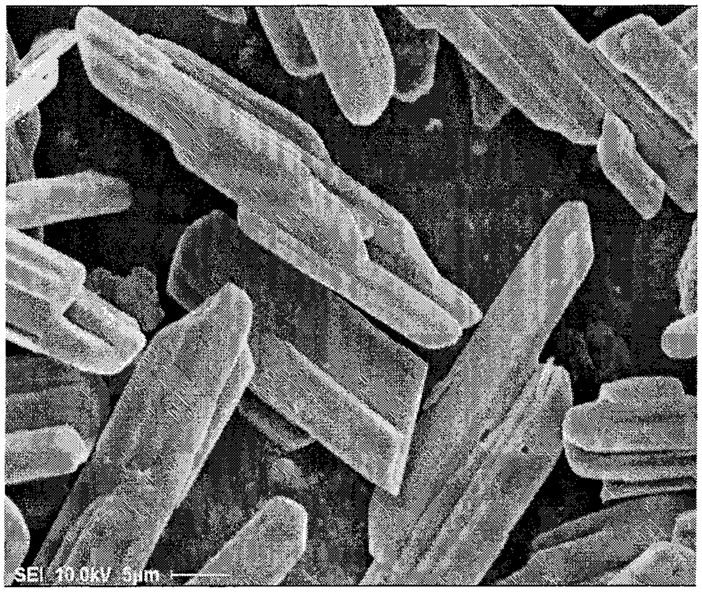


Figure 4.5 : Effect of equilibration time on the produced gypsum settling rate and % solids density.



(a) when no equilibration time was provided



(a) after 6 hours of equilibration

Figure 4.6: SEM images for the produced gypsum under variable equilibration time;(a) no equilibration time was provided and (b) after 6 hours of equilibration (conditions: 5.32 M H_2SO_4 that was added to 300 mL of 3 M $CaCl_2$ at a constant addition rate over 2 hours and constant temperature of 40 °C).

4.4 The effect of acid concentration

One of the objectives of this work is the regeneration of HCl out of $CaCl_2$ solution. For a given concentration of $CaCl_2$ solution, it is obvious that H_2SO_4 should be used as concentrated as possible, because this will increase the strength of the resultant HCl. High sulfuric acid concentration on the other hand, is responsible for producing high supersaturation (refer to equation 4.2) which induces fast primary nucleation and the production of small crystals of poor dewatering characteristics [55].

Different acid concentrations 2.66 M, 5.32 M,6.65 M and 8.0 M H_2SO_4 were used. Acid was titrated over a time period of 2 hours, to 300 mL of 3.5 M $CaCl_2$ and at 40 °C wit the $[SO_4] / [Ca]$ ratio = 0.8, followed by an equilibration time of 2 hours.

4.4.1 Gypsum crystallization

The impact of acid concentration on the settling rate and the % solids density is shown in Figure 4.7. The same tests were run for a second time to verify the degree of reproducibility, and the results are shown in Figure 4.8. According to these results, excellent reproducibility was obtained. It is clearly evident that as the acid concentration increases, the settling rate of the produced gypsum crystals decreases. This may be attributed to the fact that higher acid concentration results in higher supersaturation (see equation 4.2),hence, fast primary nucleation that favors the formation of smaller particles that settle slower. However, the settling rate is not a definitive indication for the increase in the gypsum particle size, because it is a function of the solids content. For this reason SEM image analysis and particle size analysis were performed to check the crystals morphology and their mean particle size. These results are shown in Figures 4.9 and 4.10 respectively.

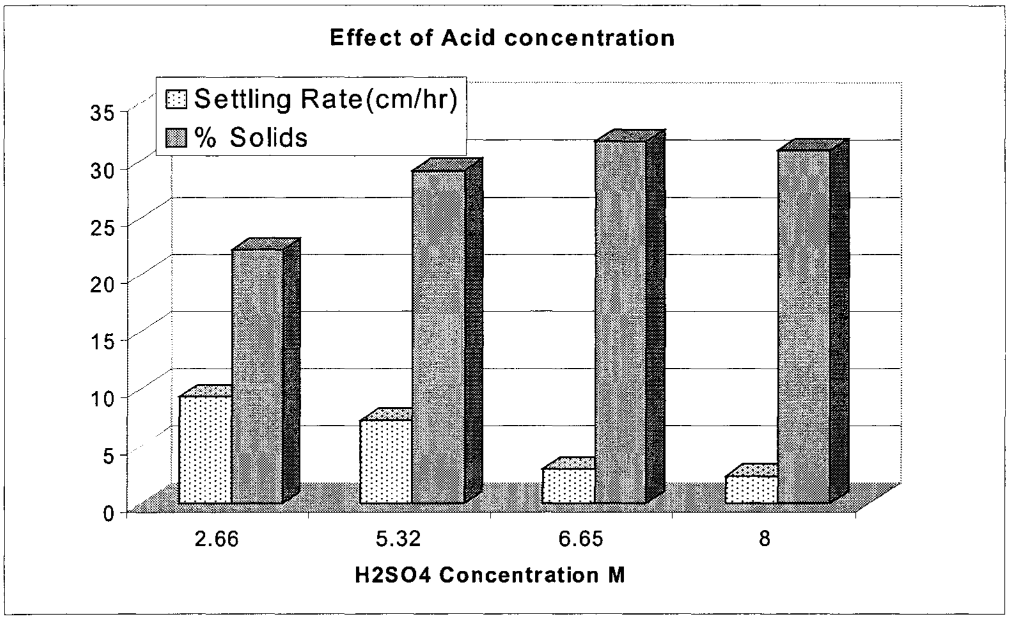


Figure 4.7: Effect of H_2SO_4 acid concentration used as a titrant on gypsum settling rate and % solids(conditions: 3.5 M $CaCl_2$, 40 °C , $[SO_4] / [Ca]$ ratio = 0.8, followed by an equilibration time of 2 hours).

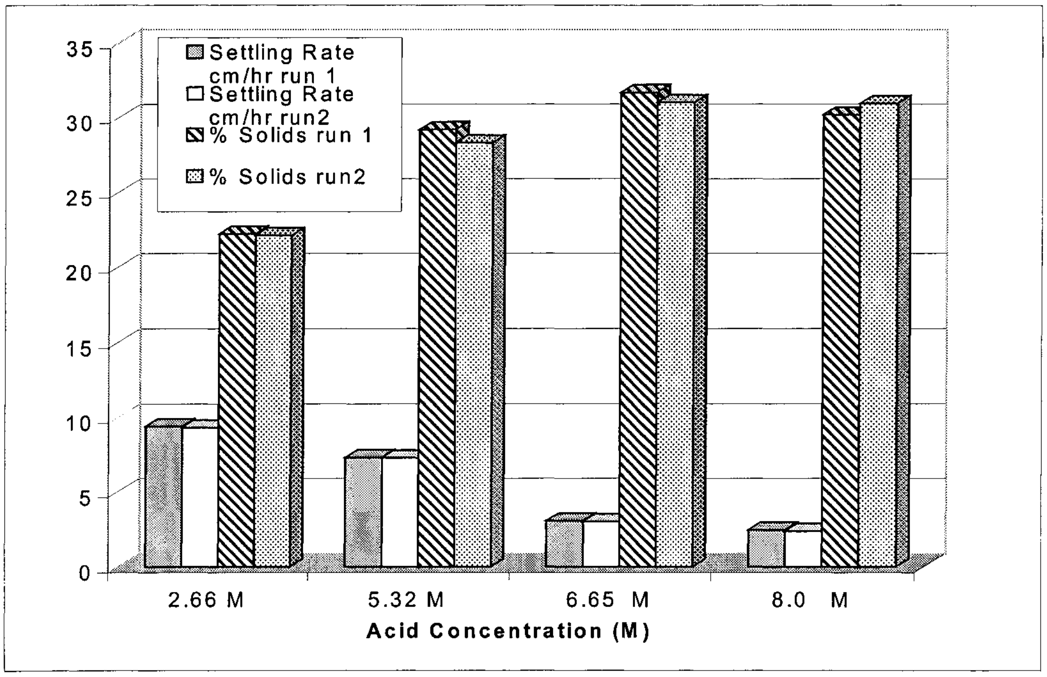
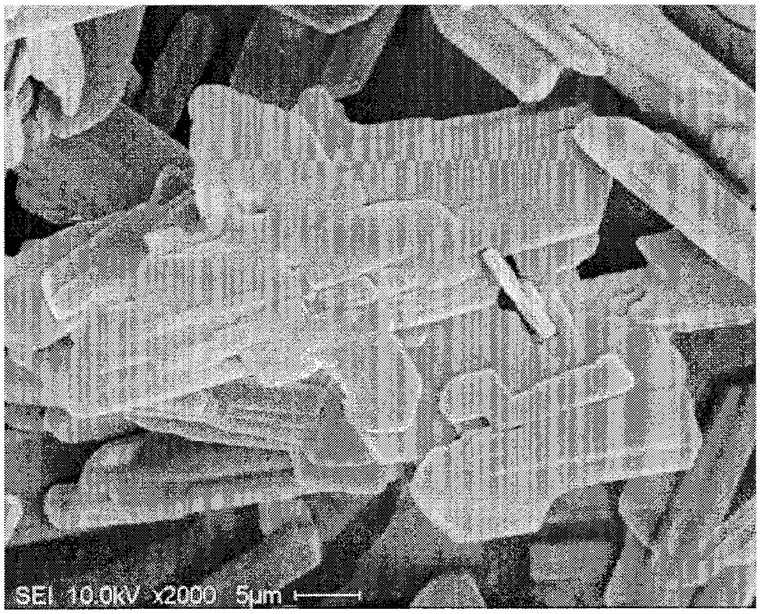
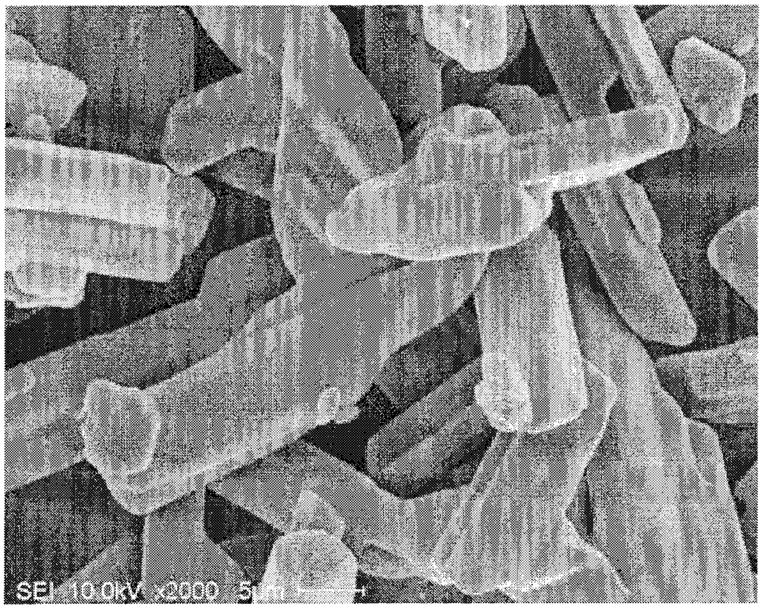


Figure 4.8: Duplication tests to check the reproducibility of the results(for conditions see Figure 4.7).



(a) 2.66 M H_2SO_4 used as a titrant



(b) 6.65 M H_2SO_4 used as titrant

Figure 4.9 : SEM analysis of the produced gypsum when (a) 2.66 M H_2SO_4 used as a titrant and (b) 6.65 M H_2SO_4 used as titrant(for conditions see Figure 4.7).

As can be seen from the SEM pictures above, the crystals were well formed in both cases with some evidence of the occurrence of small spherical crystals of approximately 5 μm in diameter in the case of the higher acidity , which indicates the occurrence of homogeneous nucleation and the lack of supersaturation control. These differences in particle size are better seen with the particle size analysis presented in Figure 4.10.

Upon the increase of acid concentration, smaller crystal size was obtained. As it can be seen in Figure 4.10, the mean particle size was found to be as follows: 25.4 μm at 2.66 M H_2SO_4, 21.0 μm at 5.32 M H_2SO_4, 20.2 μm at 6.65 M H_2SO_4 and 19.9 μm at 8.0 M H_2SO_4, hence, the settling rate decreased upon the increase in acid concentration again, and this is attributed to the formation of smaller particles at higher acid concentration.

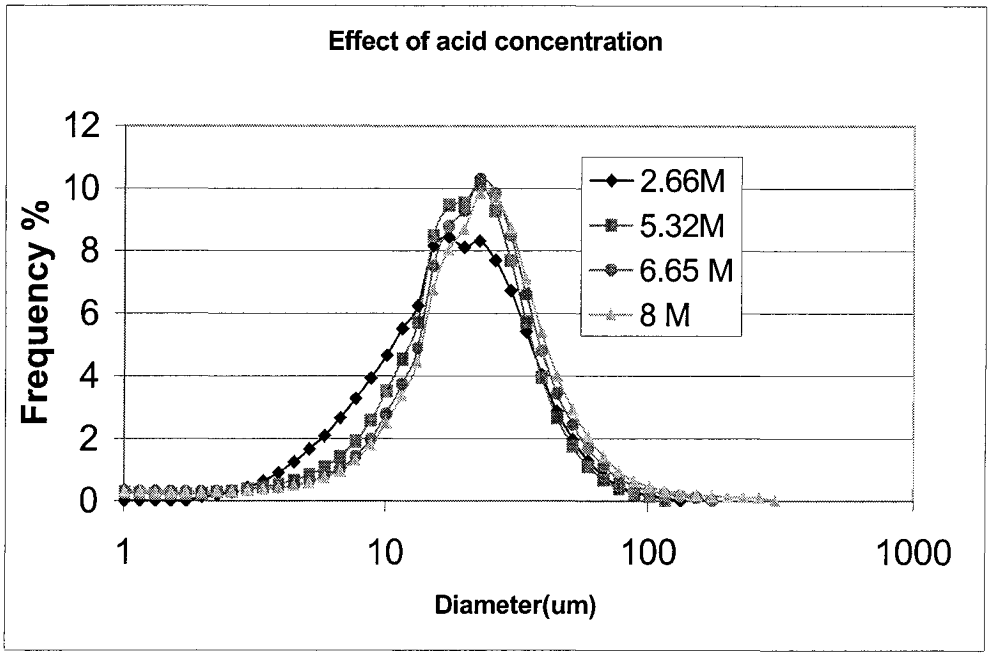


Figure 4.10: Particle size analysis for the gypsum produced using different sulfuric acid concentrations at 40 °C(for conditions: see Figure 4.7).

On the other hand, the % solids density was found to be increasing with the increase in the acid concentration from 22 % at 2.66 M H_2SO_4 up to 30 % at 8.0 M H_2SO_4. One possible explanation for this increase is that the same amount of solids were produced in each test, since the reaction ratio $[SO_4] / [Ca]$ was kept constant, in such a way that the same solids were produced but in less volume of solution as the acid concentration increased. Additionally, the crystals morphology and the size distribution have resulted in greater degree of agglomeration and better compaction at higher acid concentrations.

The settling rates measured were rather slow despite the certain improvements obtained when supersaturation was controlled via the regulation of the acid concentration. On the other hand, the % solids was relatively high, around 30 %. This means that thickening of the slurry can be replaced by direct filtration in this context. Hence, filtration rate measurements were made as described Chapter 3 , and the filtration rate values obtained are tabulated in Table 4.1

Table 4.1: Filtration rate of gypsum produced using different acid concentrations (for conditions: see Figure 4.7).

H_2SO_4 Concentration M	$CaCl_2$ Concentration M	Filtration Rate: kg solids deposited/m^2.hr
2.66	3.5	2398
5.32	3.5	3657
6.65	3.5	4078
8.0	3.5	4594
Commercial reference material	**Reagent grade gypsum added (30 wt.%) in 4 M HCl and 0.5 M $CaCl_2$**	530

It can be clearly seen that the material exhibited increasing filtration rates with increasing sulfuric acid concentration used. No explanation for this behavior can be offered apart from the observation that as the acid concentration used increased, the total volume of the slurry produced was lower. According to an industrial source [56] , those filtration rates obtained are satisfactory to make the solid/liquid separation method cost effective in the present system.

4.4.2 HCl regeneration

Figure 4.11 compares the theoretical HCl strength with the actual one obtained from different sulfuric acid concentrations used to treat 3.5 M $CaCl_2$ at 40 °C and a molar ratio of $[SO_4]$ / [Ca] equal to 0.8. The theoretical concentration was calculated based on the stiochiometry of the chemical reaction presented in equation 4.1 assuming that all the sulfuric acid was reacted and taking into account the dilution brought by the addition of the sulfuric acid.

It is clearly seen that HCl strength in the regenerated solution increased with the increase in the concentration of sulfuric acid used as expected. However, the theoretical HCl concentrations predicted from the chemical equation were somewhat higher than those obtained from titration. One possible explanation for this difference is the experimental error resulted from the formation of the bisulfate ion in solution :

$$SO_4^{2-} + H^{+} = HSO^{4-} \quad (4.3)$$

Nevertheless, a 4 M of HCl strength that was regenerated appears to be feasible to obtain.

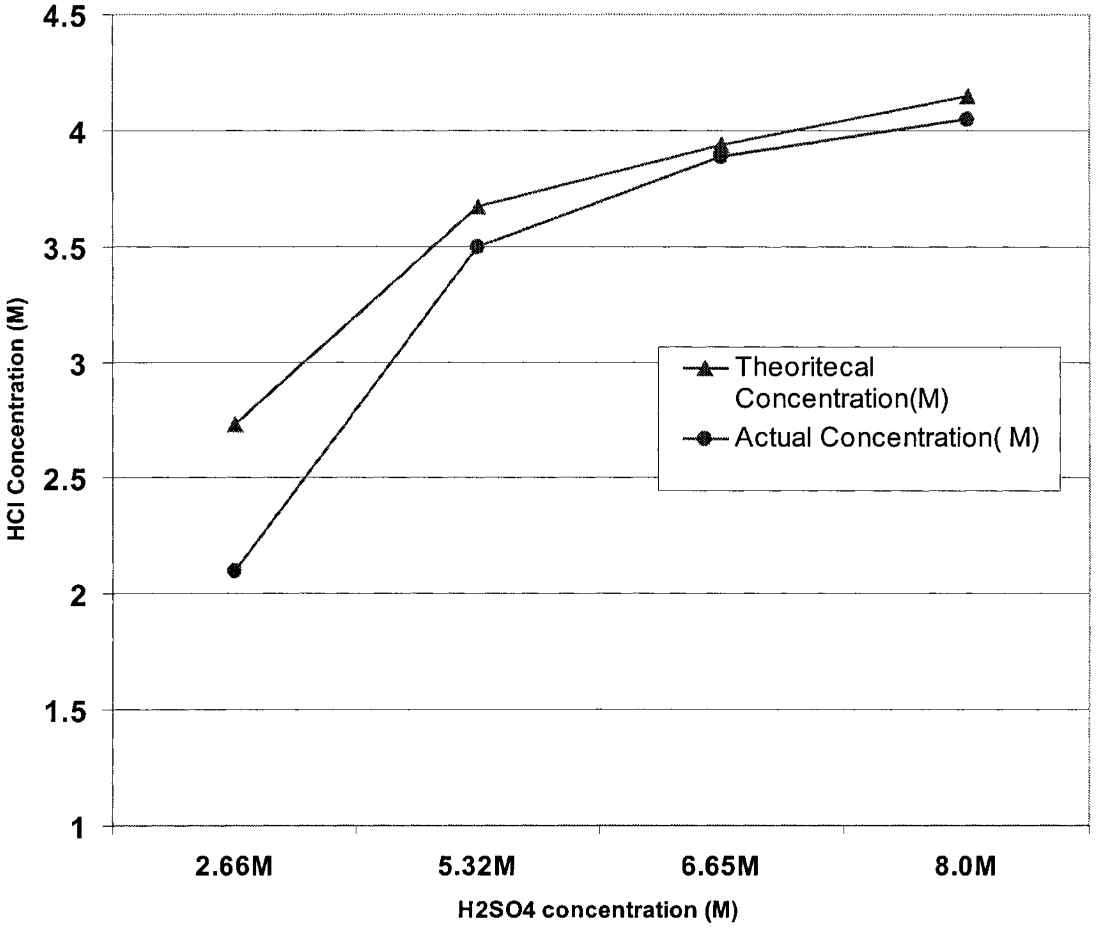


Figure 4.11: Actual and theoretical HCl strength in the regenerated solutions(for conditions, see Figure 4.7).

An attempt was made to perform a test with 8 M H_2SO_4 but this time using higher $CaCl_2$ concentration (5 M) so as to produce HCl strength higher than 4 M. The conditions employed were: Titration for 4 hours at 60 °C , $[SO_4]/[Ca]$ ratio equal to 0.8 and equilibration time of 2 hours. Unfortunately, the result of the test was the formation of a very thick concentrated suspension (gel – like) product that was difficult to settle or filter. Hence, further concentration of HCl should be achieved via evaporation.

4.4.3 Residual sulfate

The same final regenerated solutions were analyzed to determine the residual calcium sulfate content and compare it with the one expected from equilibrium (solubility) [5]. The results are presented in Figure 4.12. It can be noticed that as the amount of sulfuric acid increases, the residual sulfate concentration decreases and this is because of the increase of the unreacted $CaCl_2$ concentration in the final solution, which suppresses the solubility of dissolved $CaSO_4$ due to the common ion effect. The unreacted $CaCl_2$ concentration increases with increasing the added sulfuric acid concentration due to the less dilution that occurs as the total volume of the added acid is lower with the increase in its concentration at the same molar ratio.

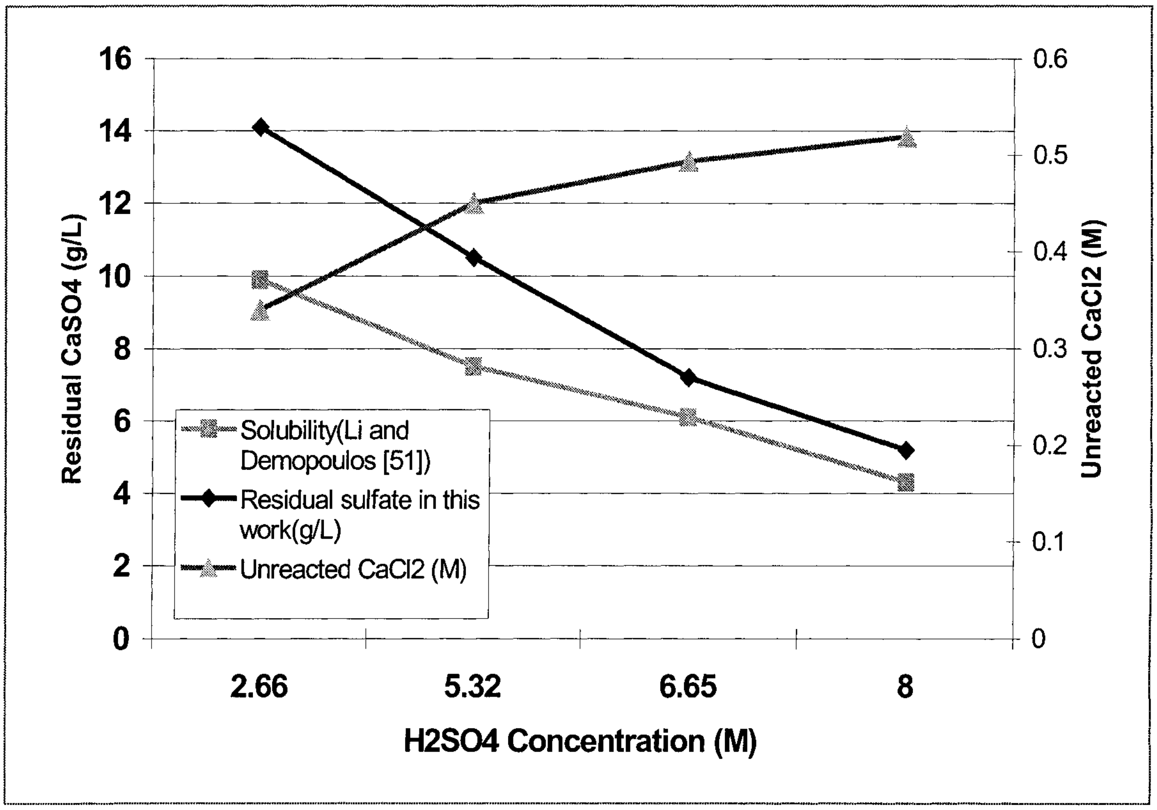


Figure 4.12: Residual calcium sulfate content in the final regenerated solutions using different sulfuric acid concentrations compared with the equilibrium concentrations (for conditions: see Figure 4.7).

4. 5 The effect of temperature

The objective of the following crystallization tests is to determine the temperature effect on the solids quality, because this parameter has a great influence on the growth rate of crystals. The growth rate constant k_G depends on temperature and can be expressed by the well known Arrhenius equation [34]:

$$k_G = k_{G0} \exp\left[-\frac{\Delta E_G}{RT}\right] \tag{4.4}$$

where k_{G0} is a constant and E_G is the activation energy for growth.

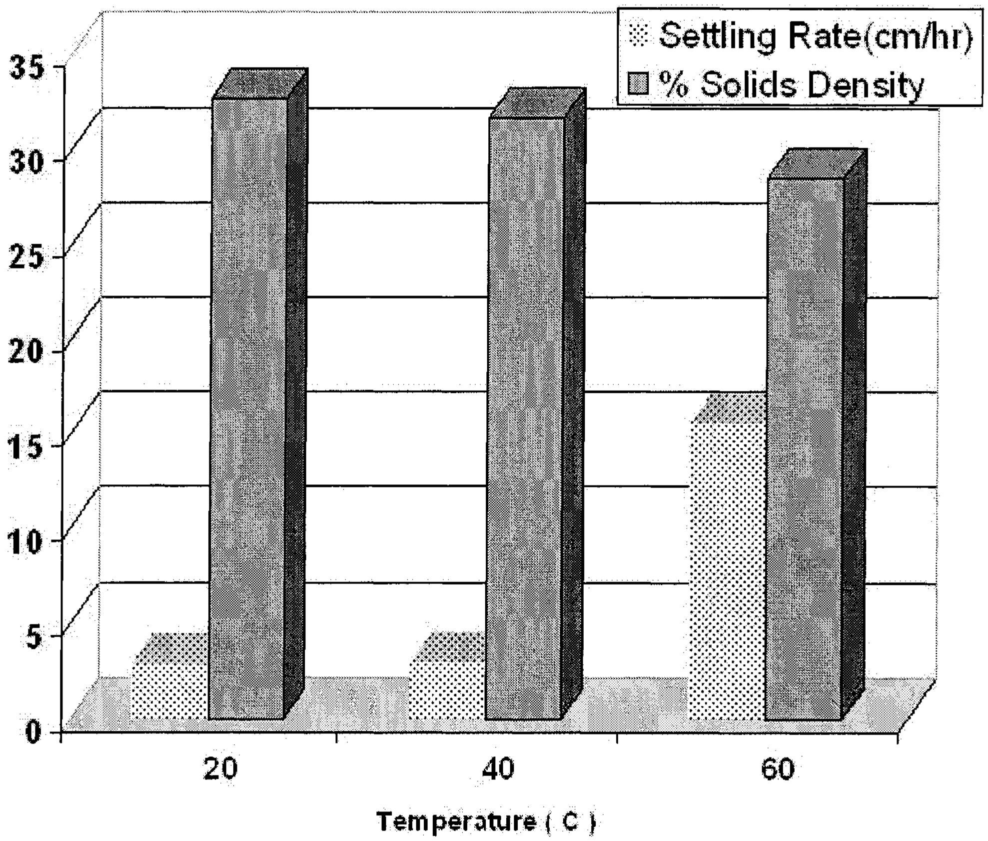
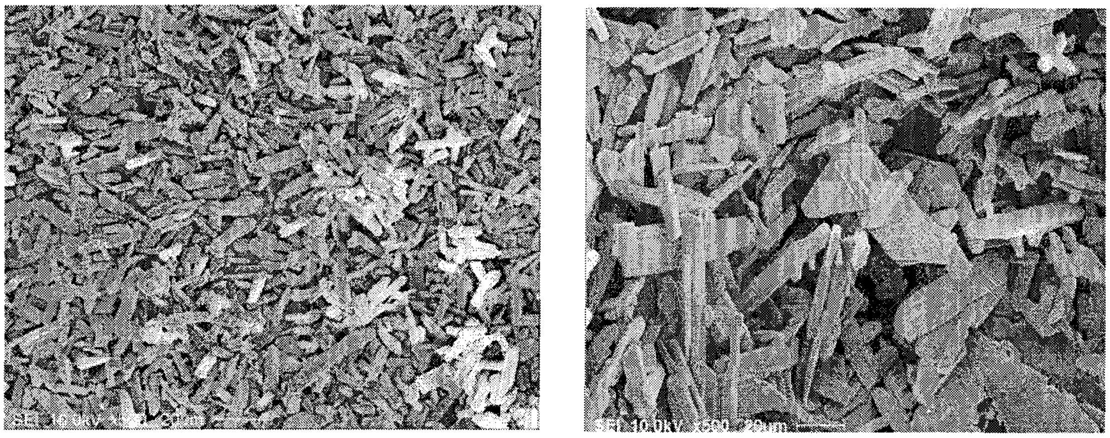


Figure 4.13: Effect of temperature on the produced gypsum crystals settling rate and % solids density at different temperatures(conditions: 6.65 M H_2SO_4 were added to 300 mL of 3.5 M $CaCl_2$ for 4 hours followed by 2 hours of equilibration, and a partial reaction $[SO_4] / [Ca] = 0.8$ at 20, 40 and 60 °C respectively).

Figure 4.13 shows the effect of temperature on the settling rate and the % solids density as a function of temperature. No higher temperatures were tried as it is known that elevated temperatures favor the conversion of calcium sulfate dihydrate to hemihydrate or anhydrate [30].

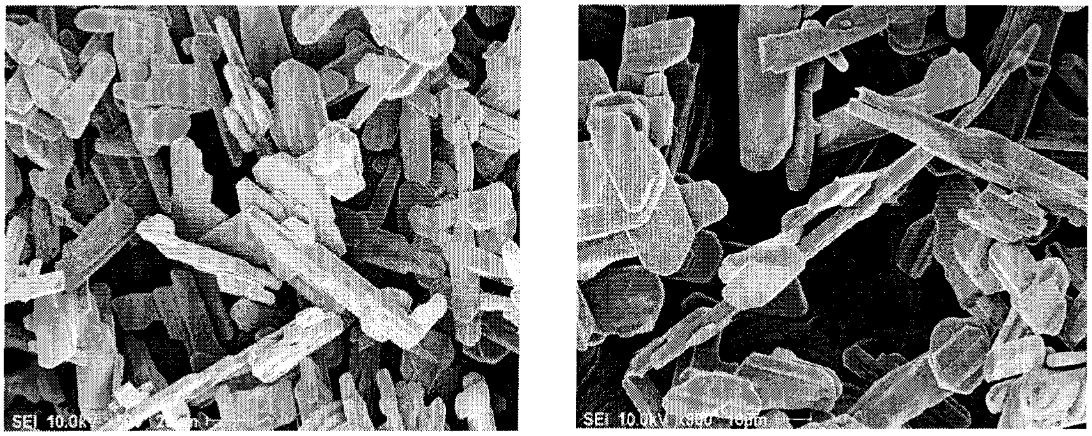
In these tests, 6.65 M H_2SO_4 was added to 3.5 M $CaCl_2$ for 4 hours followed by 2 hours of equilibration, and at a $[SO_4] / [Ca]$ ratio equal to 0.8. From Figure 4.13 above, it can be seen that as the temperature increases, the settling rate also increases from 2.5 cm/hr at 20 °C to 15 cm/hr at 60 °C, with a % solids density ranging from 31 % at 20 °C to 27 % at 60 °C. This increase in the settling rate may be due to the increase in the particle size because of increase in growth with temperature. Temperature is known to affect the diffusion rates and the surface integration steps, hence promoting crystal growth [57]. As can be seen from the SEM images shown in Figure 4.14, the size and shape improved with increasing the temperature and the pictures also revealed some elongated crystals.

This increase in the crystal size was also confirmed by the particle size analysis and the results are shown in Figure 4.15. Furthermore, XRD analysis confirmed the formation of calcium sulfate dihydrate with the exception of the test done at 60 °C which revealed the presence of calcium sulfate hemihydrate as a minor phase. See Figure 4.16.



(a) gypsum obtained at 20 °C

b) gypsum obtained at 40 °C



c) gypsum obtained at 60 °C

d) gypsum obtained at 60 °C

Figure 4.14 : SEM images for different gypsum crystals obtained at different temperatures (a) at 20 °C , (b) at 40 °C and (c) ,(d) at 60 °C (for conditions : see Figure 4.13).

The mean particle size increased from 10.9 μm at 20 °C , 22.9 μm at 40 °C to 47.3 μm at 60 °C. This particle size increase seems to be associated with crystal growth as well as with crystal morphology change (see Figure 4.14). Plate like crystals formed at 40 °C but at 60 °C, some elongated, needle-like, crystals appear to be present. Needle-like crystal morphology is a characteristic of α - Hemihydrate [30]. It appears that some of the dihydrate converted to hemihydrate at 60 °C.

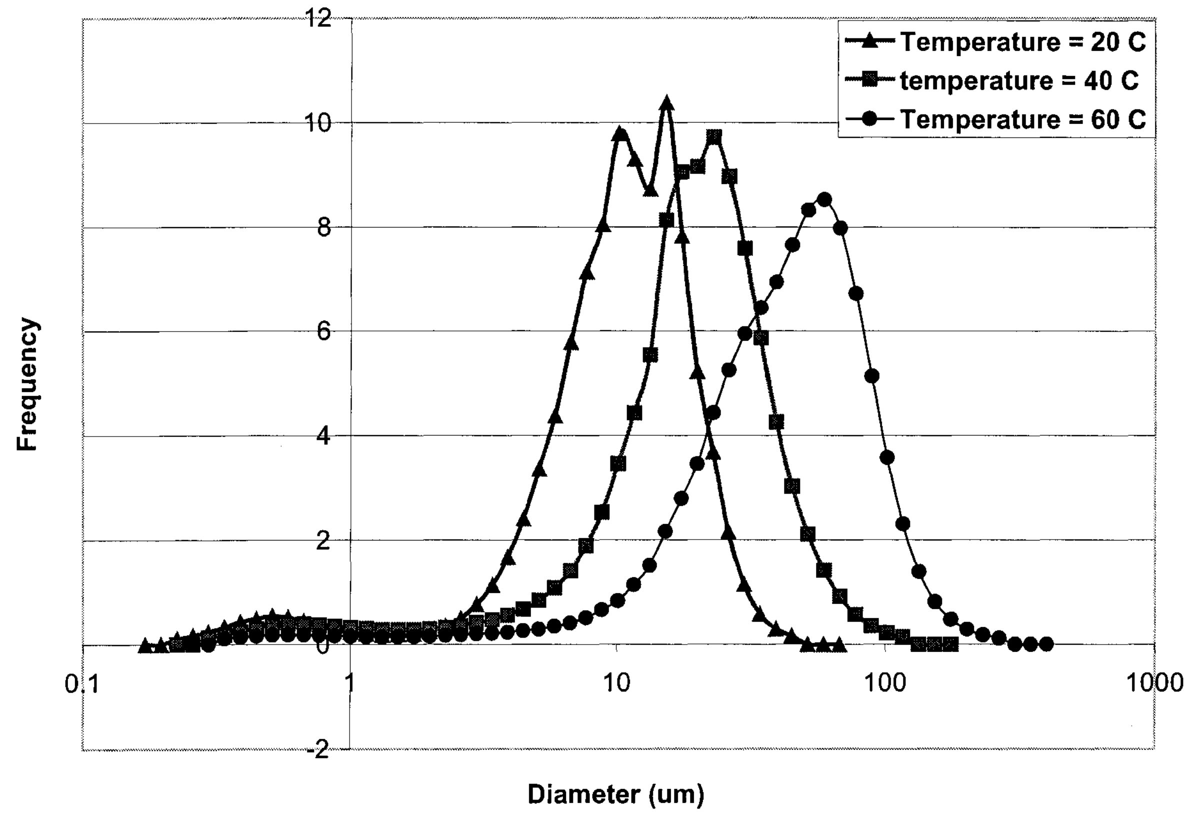


Figure 4.15: Particle size analysis for gypsum crystals obtained from crystallization tests at different temperatures(for conditions: see Figure 4.13).

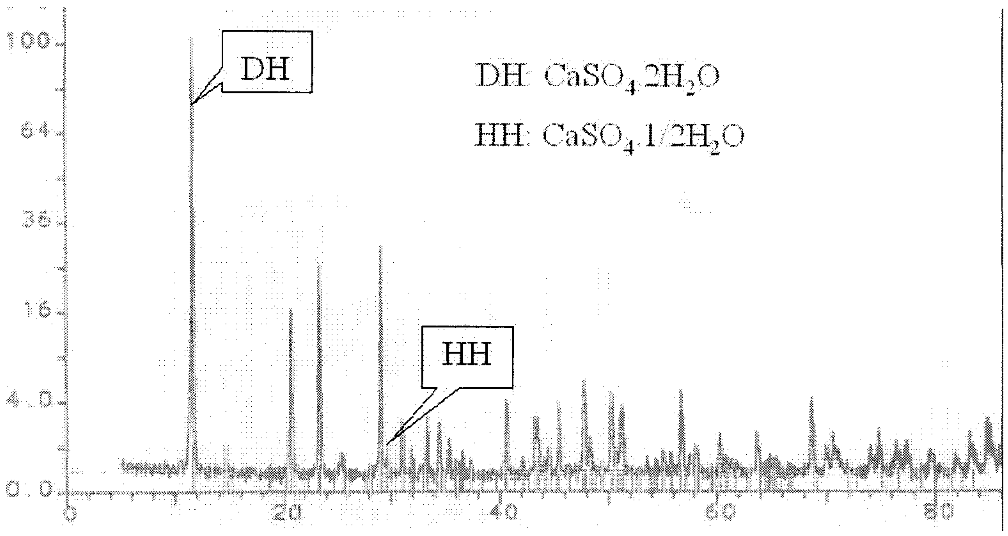


Figure 4.16: XRD analysis for the gypsum obtained at 60 °C from the reaction of 6.65 M H_2SO_4 and 3.5 M $CaCl_2$ with [SO4] / [Ca] = 0.8 (for conditions: see Figure 4.13).

Despite the improvements achieved in the settling rate with temperature increase, the obtained values are still rather low. However, the filtration rates obtained for these were considered to be acceptable and theses values are shown in Table 4.2.

Table 4.2: Filtration rate data for gypsum slurry produced at different temperatures (for conditions see Figure 4.13).

Temperature °C	Filtration Rate : Kg Solids deposited /m^2.hr
20	4106
40	5460
60	6626

The results show an increase in the filtration rate with the increase in temperature, and the best value of filtration was for the solids obtained from crystallization test at 60 °C. The filtration rate numbers obtained above are considered to be very good from an industrial point of view [56].

A comparison among the three reaction temperatures in terms of theoretical and actual dissolved sulfate content and the regenerated HCl strength is shown in Figure 4.17.

It can be noticed from Figure 4.17 that as the temperature increases, the amount of $CaSO_4$ dissolved also increases this is because the solubility of $CaSO_4$ increases with temperature [51]. It was also observed that the actual sulfate dissolved was higher than that of the equilibrium concentration because of the high supersaturation conditions under which precipitation occurred . When it comes to HCl strength, the concentration was from 3.98 to 4.1 M at 40 and 60 °C respectively which are close to the theoretical values.

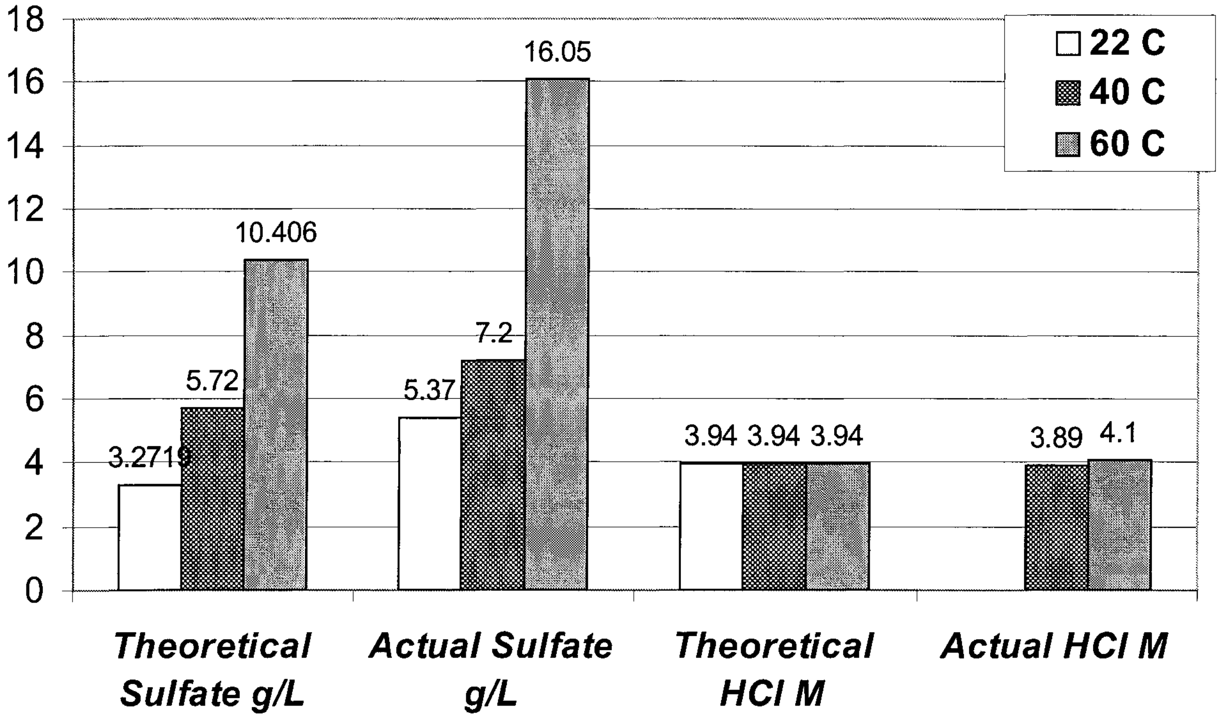


Figure 4.17: A comparison between the theoretical and the actual residual sulfate, and the regenerated HCl strength obtained at different temperatures :20, 40 and 60°C(for conditions: see Figure 4.13).

4.6 The effect of seeding / recycling

The objective of this section is to investigate the effect of seeding / recycling on the produced crystal properties. Several tests were performed in this section to evaluate the effect of seed loading / recycling on the gypsum settling rate, % solids, particle size and crystal morphology at 40 and 60 °C. Tests were done at 40 °C and 60 °C using 2.66 M and 6.65 M of H_2SO_4. The addition time was for 2 hours, followed by 2 hours of equilibration. Different gypsum seed loadings were used, 25 and 50 g/L of the initial solution volume. Recycling was done up to 10 recycles.

The seed used in these experiments were A.C.S calcium sulfate dihydrate of 98 % purity and purchased from Aldrich .

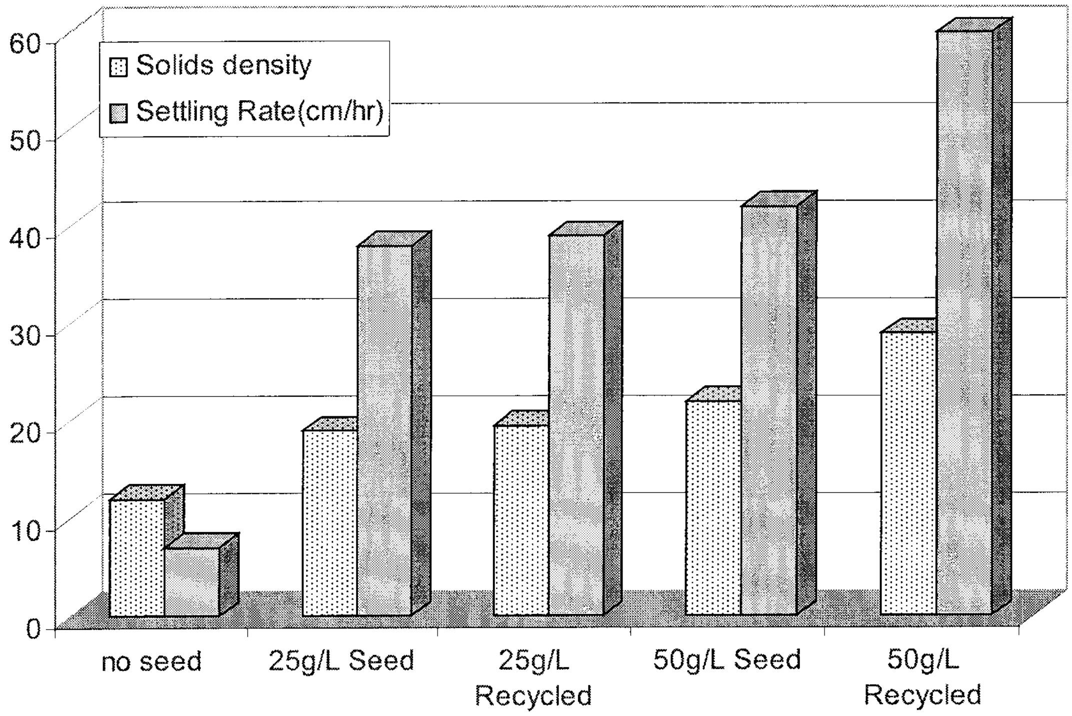
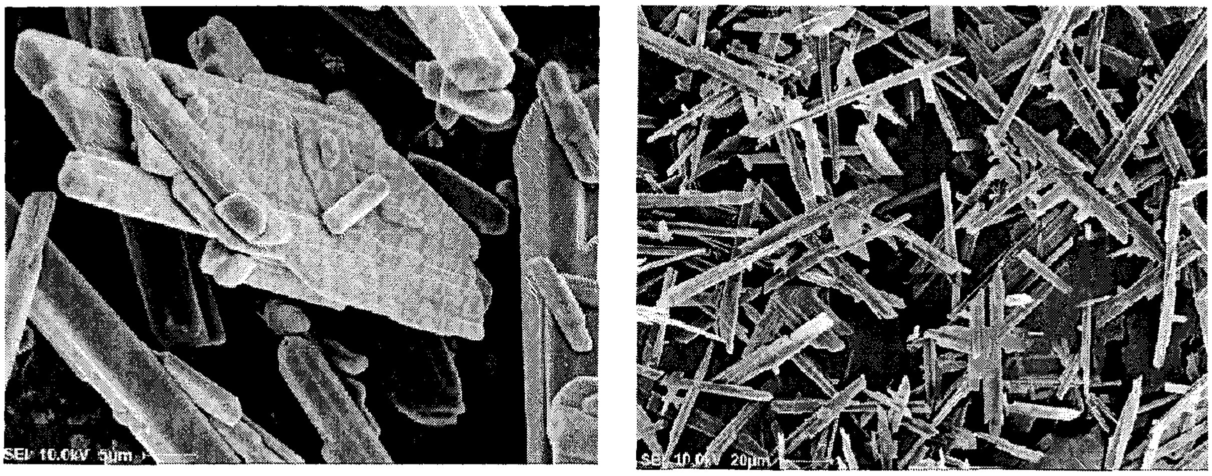
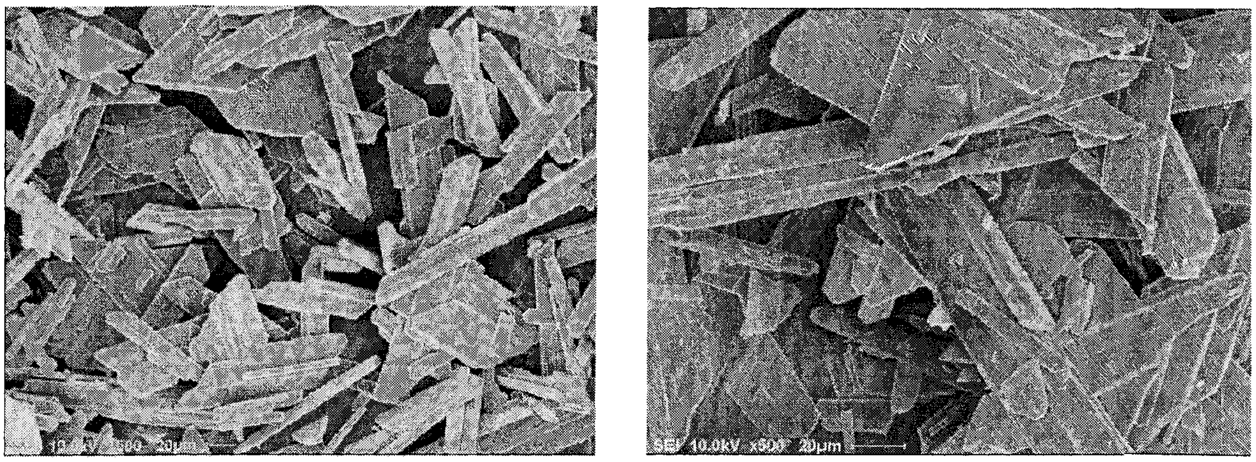


Figure 4.18: The effect of seed loading on the settling rate and the % solids density of the produced gypsum at 40 °C(conditions: 2.66 M H_2SO_4 added for 3.5 M $CaCl_2$, $[SO_4]/[Ca] = 0.33$, for 2 hours titration and 2 hours equilibration at 40 °C).



(a) gypsum seed used (b) gypsum produced when no seed was added



(c) when 50 g/L seed were added (d) when the 50 g/L seed recycled once

Figure 4.19: SEM images for the gypsum particles obtained with seeding /recycling : (a) seed crystals used, (b) crystals when no seed was added, (c) crystals obtained when 50 g/L seed was used and (d) crystals obtained when the 50 g/L seed was recycled once(for conditions see Figure 4.18).

Figure 4.18 shows the results obtained from preliminary series of different seed loadings where the effect of seed on the solids settling rate and the % solids density was evaluated. The results showed that the settling rate increases significantly from 6 cm/hr when no seed is present up to 38 cm/hr at 25 g/L seed loading and to 42 cm/hr at 50 g/L seed loading. Recycling also brought an increase in the settling rate up to 60 cm/hr when 50 g/L seed was recycled once. The effect of seeding / recycling was also studied through SEM image analysis as shown in Figure 4.19.

The SEM pictures above revealed various gypsum crystal shapes, hence, explaining the difference in the behavior between seeded and unseeded tests. While the unseeded tests produced elongated crystals, (typical dimensions are ~ 60 μm in length, 3-5 μm in thickness), the seeded tests produced plate-like crystals. The crystals appear to have grown via surface nucleation as a result of the low supersaturation environment induced by the slow addition of the acid. Recycling resulted in further growth (up to 100 μm length and ~ 20 μm thickness). The increased crystal growth by seeding is therefore responsible for the increase in the settling rate. The % solids content also increased from 10 % when no seed was used to 28 % when the 50 g/L seed load was recycled once as can be noticed again from Figure 4.18.

It was decided to perform a longer recycling series (up to 10 times), but this with higher sulfuric acid concentration (6.65 M) and $[SO_4]/[Ca]=0.8$, as this is preferred from an HCl regeneration point of view (See section 4.4). The results in terms of settling rate and % solids are shown in Figure 4.20. In this figure, there is a comparison between the case when no seed was added to the system and when 25 g/L seed were added and recycled. Unfortunately, the results showed no significant improvement in the settling rate up to the tenth recycle. This is in contrast to the observation made from the previous recycling series (Figure 4.18). The difference between the two series is in the product yield and the dilution brought by the added acid. Thus, while in the first series of recycling, 2.66 M sulfuric acid was used, with a $[SO_4]/[Ca] = 0.33$, this gives a yield 51 g of gypsum in a total volume of 0.411 L solution , i.e., 124 g/L and ~ 12 % solids content; in the second series of recycling, 6.65 M sulfuric acid was used, with a $[SO_4]/[Ca] = 0.8$; this gives a yield of 144.56 g of gypsum in a total volume of 0.426 L solution , i.e., 339 g/L and ~ 30 % solids content. This higher solids content results apparently in a high frequency of fragmentation for the soft gypsum crystals which interferes the settling process.

In view for the poor settling rate observed from seeding/recycling tests observed at 40 °C, a new set of series were conducted but this time at higher temperature of 60 °C. Since the data in section 4.5 showed an improvement in the crystals quality at this temperature. In this set of tests, 6.65 M of H_2SO_4 was added over a period of 4 hours to 3.5 M $CaCl_2$ at a ratio $[SO_4] / [Ca]$ equal to 0.8 and at 60 °C. This was followed by 2 hours of equilibration. Once more 15 , 30 and 60 g/L seed was used, and the results are shown in Figure 4.21.

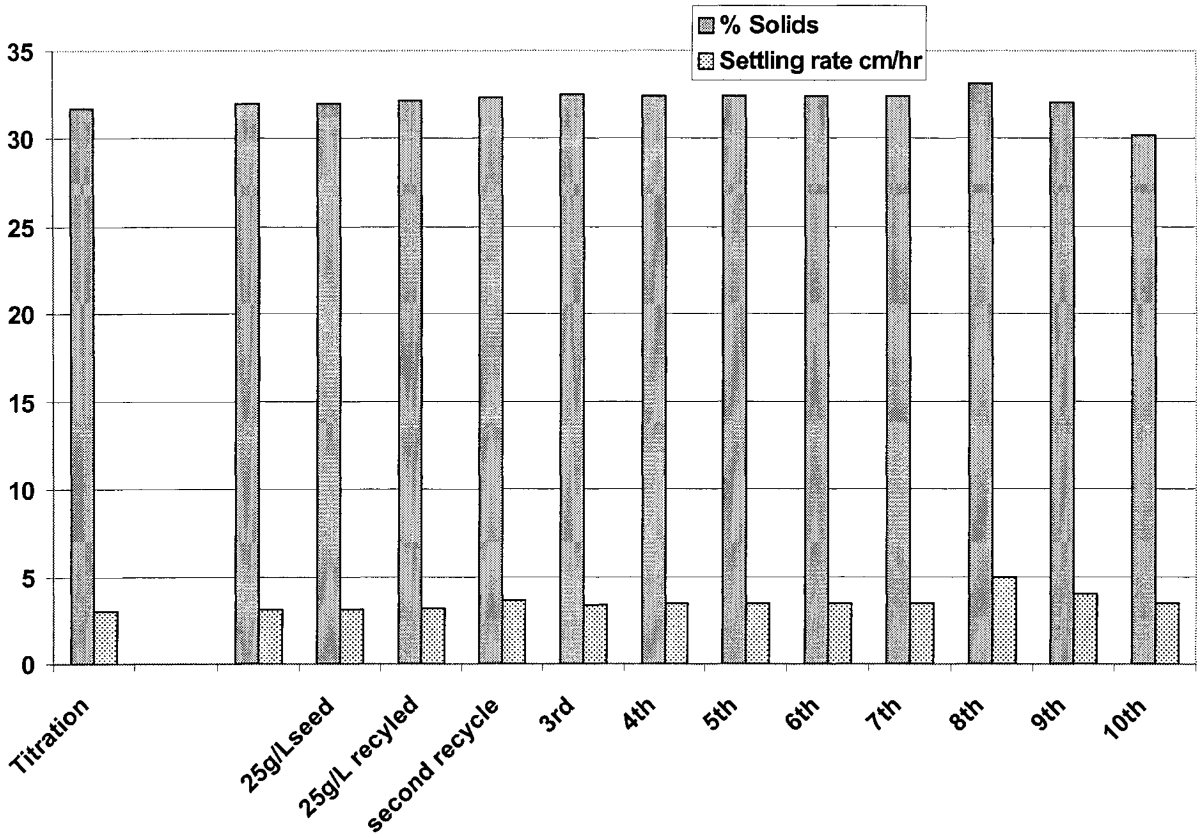


Figure 4.20: Effect of seed addition and recycling up to the tenth recycle on the solids settling rate and % solids density (conditions: 6.65 M H_2SO_4 added for 3.5 M $CaCl_2$, $[SO_4]/[Ca] = 0.8$, for 2 hours titration and 2 hours equilibration at 40 °C).

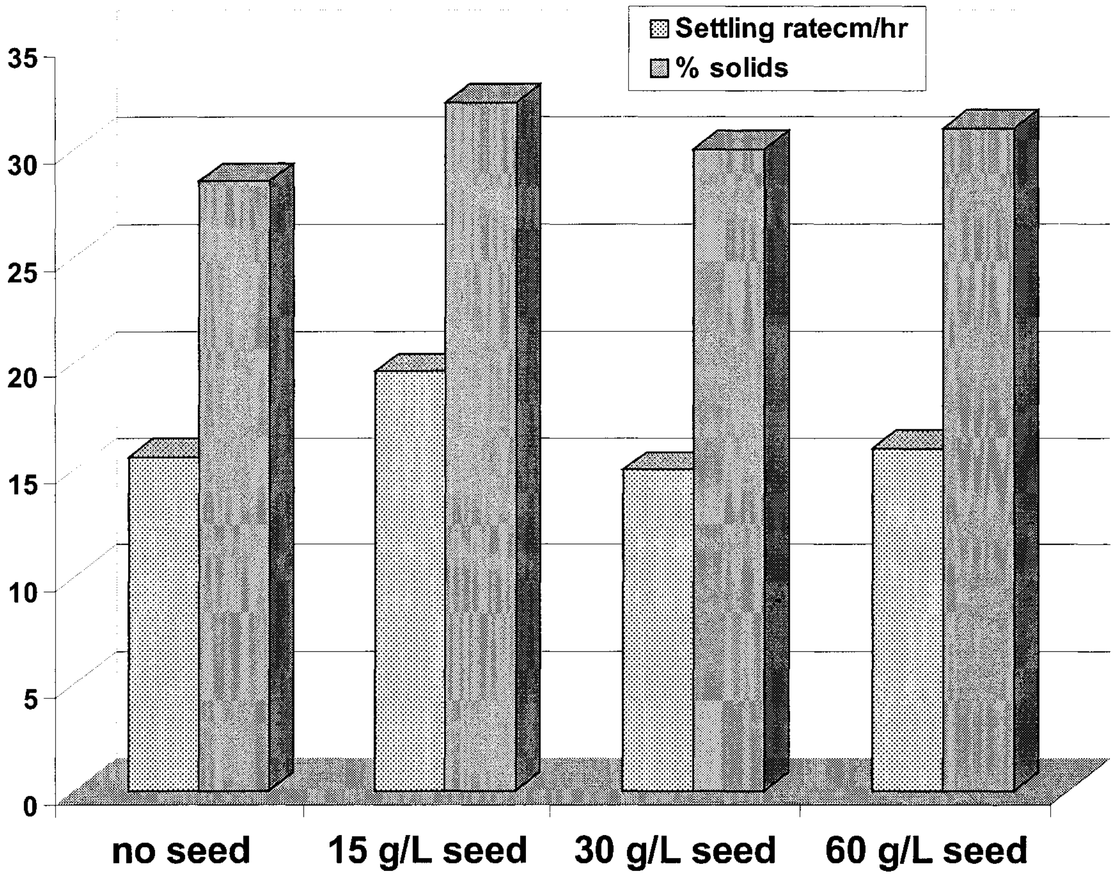


Figure 4.21: Effect of seed on crystals settling rate and % solids density (conditions: 126.315 mL of 6.65 M of H_2SO_4 that was added over a period of 4 hours to 3.5 M $CaCl_2$ following at a ratio [SO_4] / [Ca] equal to 0.8 and at 60 °C. This was followed by 2 hours of equilibration at 60 °C).

The results showed a slight increase in the solids settling rate from 14 to 18 cm/hr and the solids density, from 27 to 31 % with the addition of 15 g/L seed and basically no significant change with the addition of more seed. Based on this result, the 15 g/L seed loading was chosen to do the recycling test. The recycling test was performed by obtaining the solids from the first seeding test, filtering and drying them and then using them as a new seed load for the following test and so on. The results are shown in Figure

4.22. Again, there was no significant increase in the settling rate of the produced gypsum. In general, the settling was low and the solids density was in the range of 26 to 32 %.

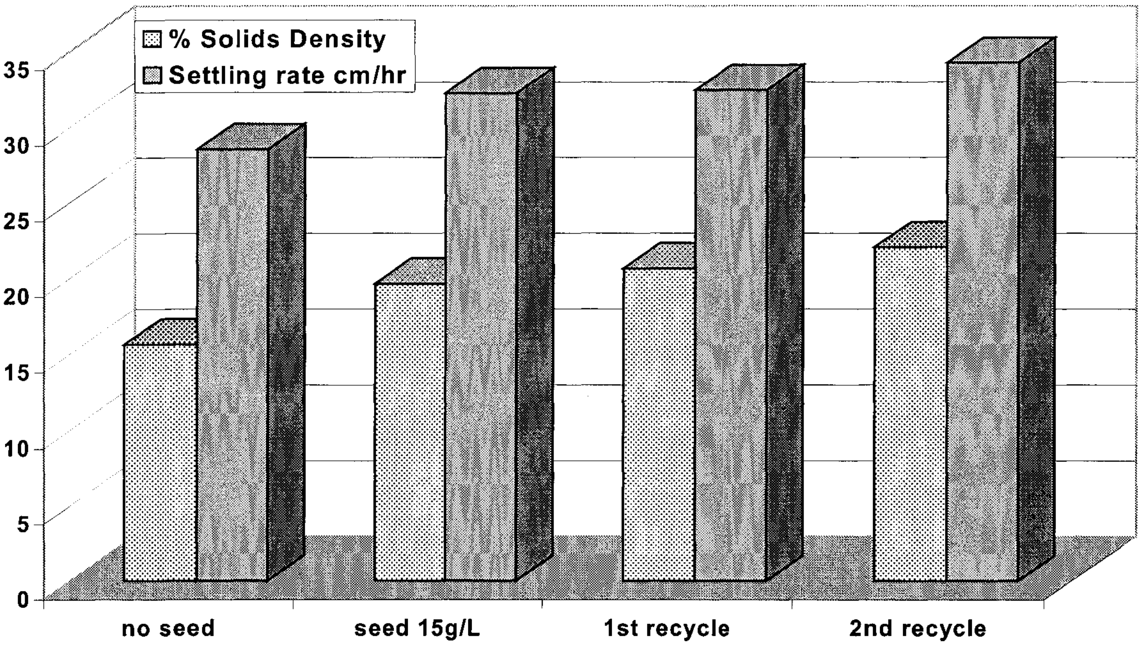
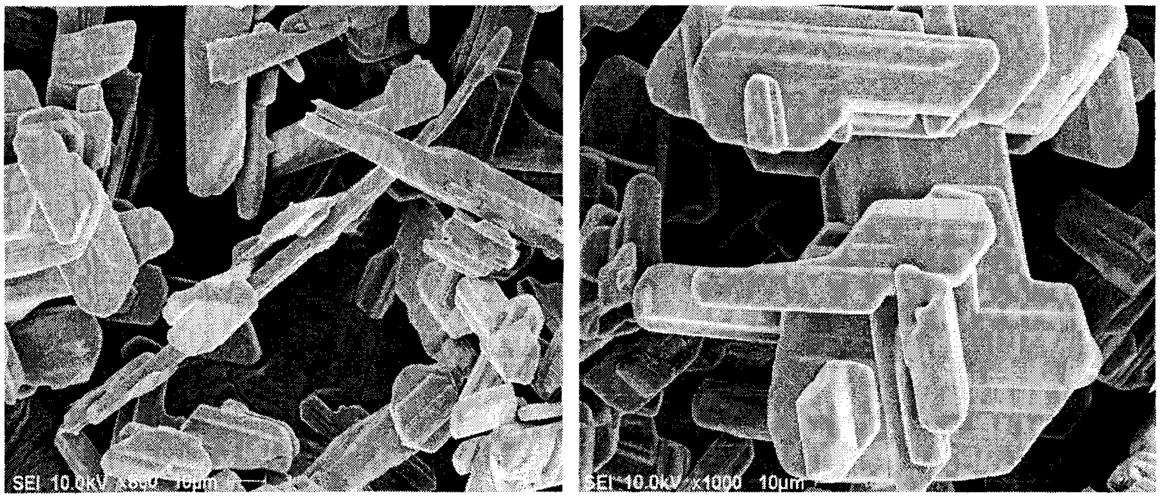


Figure 4.22: The effect of seed / recycling on the settling rate and solids density (for conditions: see Figure 4.21).

The lack of improvement of the settling rate upon recycling is the result of hindered settling due to the huge mass of solids obtained or simply , there was no crystal growth upon recycling. Hence, SEM image analysis and particle size analysis were done to evaluate the crystals characteristics. Figure 4.19 (a) shows the seed itself and Figure 4.23 shows the crystals obtained at 60 °C from the unseeded and the seeded tests.



(a) unseeded test (b) the second recycle

Figure 4.23: SEM images for crystals obtained at 60 °C (a) unseeded test and (b) from the second recycle (for conditions: see Figure 4.21).

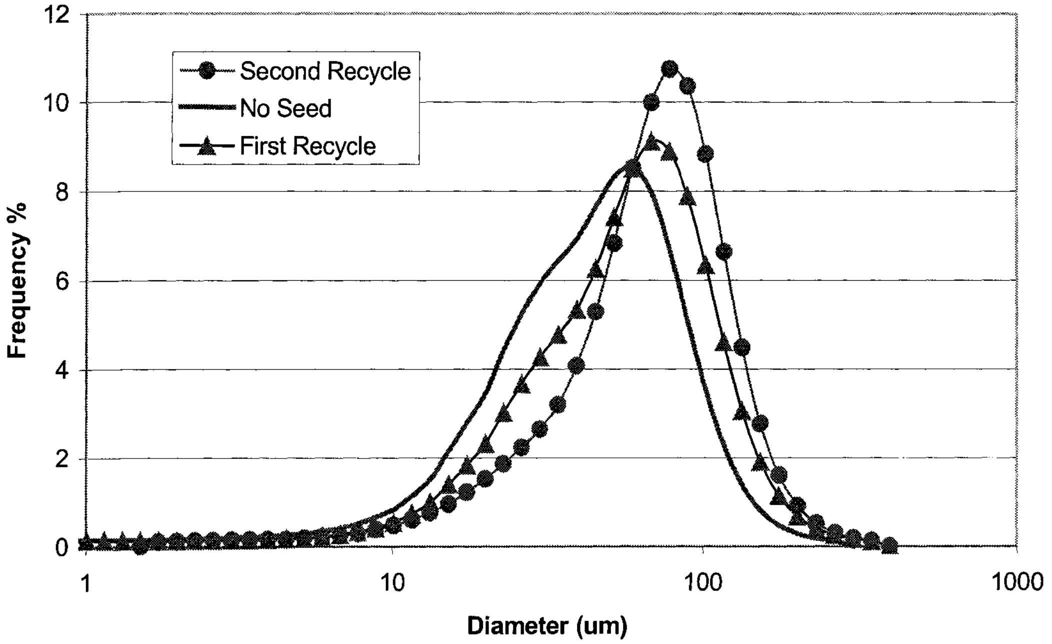


Figure 4.24: Particle size analysis of the different gypsum particles obtained: unseeded, first recycle and the second recycle (for conditions: see Figure 22).

The growth of crystals was confirmed through particle size analysis that is shown in Figure 4.24 below. It can be noticed from Figure 4.24 that the particle size distribution gets narrower upon recycling. Thus the mean particle size was 47.3 μm for the unseeded test, 60.1 μm for the first recycle and 80.3 μm for the second recycle. Hence, excellent growth obtained upon recycling with simultaneous narrowing in the particle size distribution.

4.7 Metal uptake

Spent CaCl2 solutions may contain a variety of metal ions. In this section, the effect of various metal chlorides on the crystallization of gypsum in terms of physical properties and uptake (purity) is evaluated. Various metal chlorides have been investigated; first NaCl, $MgCl_2$ and $ZnCl_2$ were evaluated separately; then a mixture of chlorides that included $FeCl_2$, $NiCl_2$, $CuCl_2$, $AlCl_3$ and $PbCl_2$ were investigated together.

In these experiments, 0.1 M of NaCl, $MgCl_2$ and $ZnCl_2$ was added to 3.5 M of $CaCl_2$, at 40 °C. Then 8 M H_2SO_4 acid was added in 8 stages over 2 hours, followed by 2 hours of equilibration. A.C.S. Calcium Sulfate Dihydrate of 98 % purity purchased from Aldrich was used as seed of 15g/L load followed by recycling twice. Then the same procedure was repeated but with a mixture of electrolytes, containing 0.1 M of each of $FeCl_2$, $NiCl_2$, $CuCl_2$, $AlCl_3$ and $PbCl_2$. In this case, the filter cake was washed several times with boiling water till all the color removed.

4.7.1 Gypsum crystallization

The crystals obtained were analyzed using XRD and the results are shown in Figure 4.25, the samples were chosen in such away that sample 1 consisted of the gypsum produced in the presence of NaCl, sample 2 for $MgCl_2$, sample 3 for $ZnCl_2$ and sample 4 for the mixture of the metal chlorides respectively. The results showed that the main phase present was gypsum (calcium sulfate dihydrate DH), however, the presence of calcium sulfate hemihydrate as a minor phase was detected in sample 1 and sample 4 which corresponds the gypsum produced in the presence of NaCl and the mixture of metal chlorides (of $FeCl_2$, $NiCl_2$, $CuCl_2$, $AlCl_3$ and $PbCl_2$) respectively.

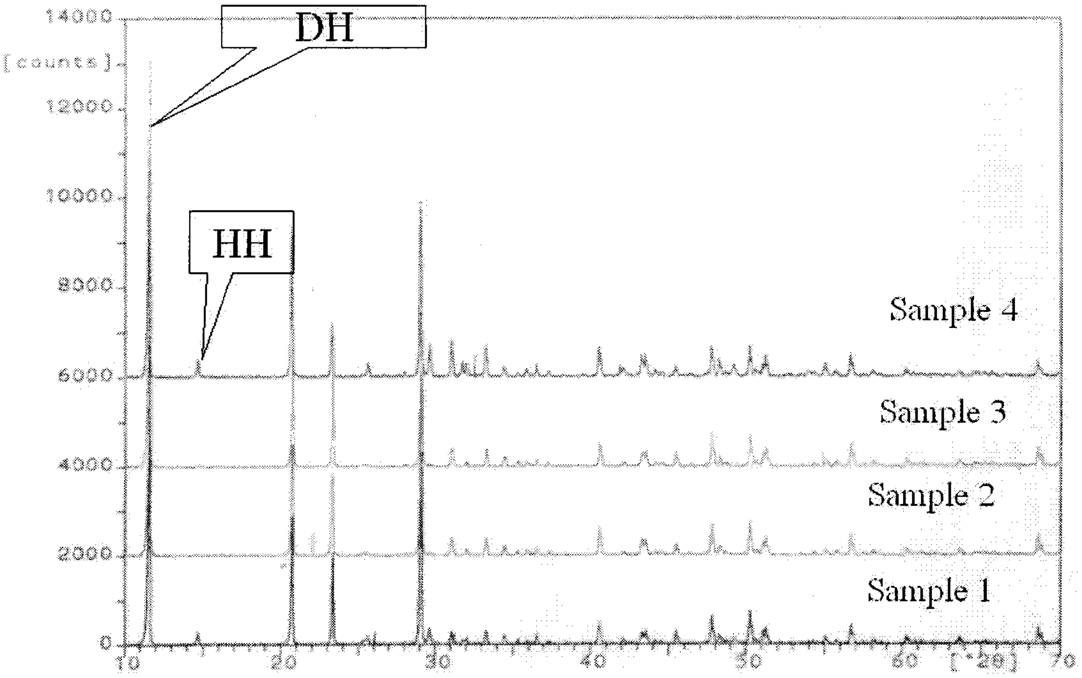


Figure 4.25: XRD analysis of the gypsum produced in the presence of metal chlorides (conditions: 8 M H_2SO_4 acid was added on stages of 8 over 2 hours, followed by 2 hours of equilibration to a solution containing 3.5 M of $CaCl_2$ and 0.1 M of NaCl (sample 1), $MgCl_2$ (sample 2), $ZnCl_2$ (sample 3) and a Mixture of $FeCl_2$, $NiCl_2$, $CuCl_2$, $AlCl_3$ and $PbCl_2$, at 40 °C with 0.1 M of metal chlorides at 40 °C (sample 4)).

In order to quantify the metal uptake by gypsum, the solids produced were dissolved in 3 M HCl to give 18 g/L concentration, and analyzed using ICP. The results are shown in Figure 4.26. This figure shows the uptake of each metal in ppm between the first seeded test and the second recycle. A comparison between the two cases shows that the metal uptake has slightly decreased upon recycling. It is clear from the results that the produced gypsum is practically free of metal impurities, hence, the product can potentially meet market specifications for sale. The only exception of this was lead (Pb) which was found to report a level ~ 80 ppm.

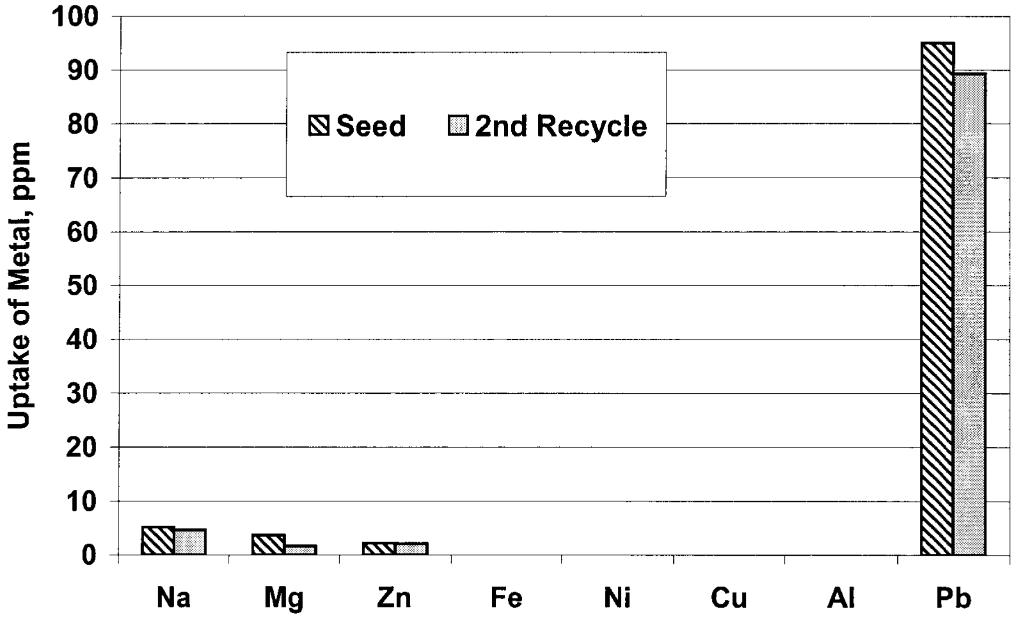


Figure 4.26: Metals uptake by gypsum in seeded and the second recycle tests (for conditions See Figure 4.25).

The filtration rates of the produced gypsum from the seeded tests, 1st recycle and the 2nd recycle were also measured using a press filter and at room temperature, under a vacuum pressure of 20 psi. The results are shown in Table 4.3.

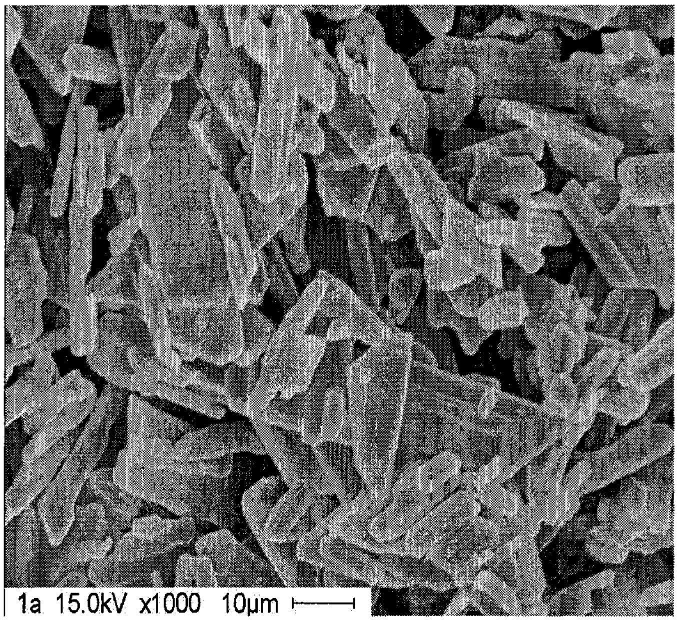
In General, the presence of seed and metal chlorides improved the filtration rate for all the solids with an exception for the case of the 2nd recycle in the crystallization test in the presence of 0.1 M NaCl. This reduced value for the filtration rate compared with the other values may be due to the change of morphology upon recycling that was only noticed in the case of NaCl upon the SEM analysis of the produced solids or the possibility of an experimental error. These results are shown in Figure 4.27.

Table 4.3: Values of filtration rates for the gypsum obtained from the seeded , 1st recycle and the 2nd recycle tests (for conditions see Figure 4.25).

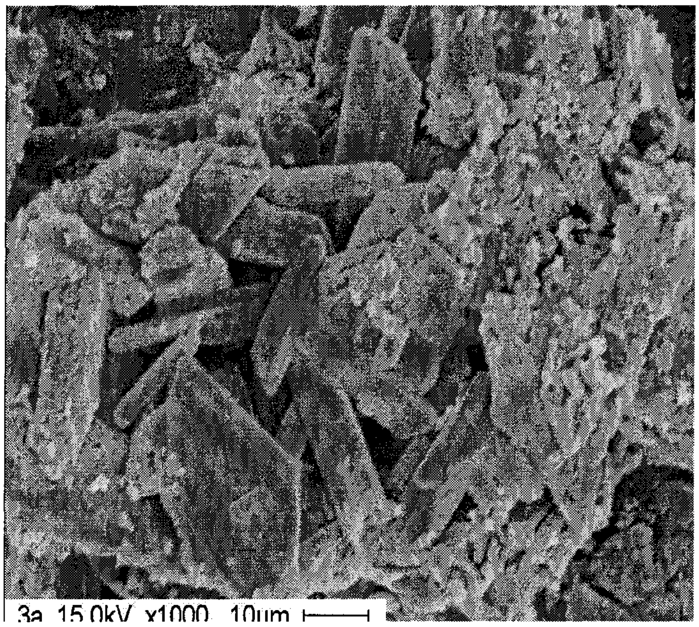
Experiment	**Filtration Rate: kg solid deposited/m^2.hr**
Gypsum produced in a pure system but by acid titration	4594
NaCl (Seed)	5118
NaCl (1st Recycle)	5500
NaCl (2nd Recycle)	2978
$MgCl_2$ (Seed)	5000
$MgCl_2$ (1st Recycle)	5380
$MgCl_2$ (2nd Recycle)	5487
$ZnCl_2$ (Seed)	5651
$ZnCl_2$ (1st Recycle)	5691
$ZnCl_2$ (2nd Recycle)	5700
Mixture (Seed)	6328
Mixture (1st Recycle)	6393
Mixture (2nd Recycle)	6473

4.7.2 HCl regeneration

The regenerated HCl strength was measured in all the experiments by samples dilution, then by titration with NaOH up to pH = 2, in order to prevent the metal ions present from hydrolysis.



a) 1st seed load in the case of NaCl



b) 2nd recycle in the case of NaCl

Figure 4.27: SEM analysis for the gypsum produced in the case of NaCl (for conditions see Figure 4.25).

Table 4.4: Regenerated HCl strength (for Conditions see Figure 4.25).

Experiment	HCl Concentration (M)
Regenerated HCl strength produced in a pure system	4.1
NaCl (Seed)	3.41
NaCl (1st Recycle)	3.4
NaCl (2nd Recycle)	3.4
$MgCl_2$ (Seed)	3.43
$MgCl_2$ (1st Recycle)	3.45
$MgCl_2$ (2nd Recycle)	3.44
$ZnCl_2$ (Seed)	3.47
$ZnCl_2$ (1st Recycle)	3.5
$ZnCl_2$ (2nd Recycle)	3.48
Mixture (Seed)	3.69
Mixture (1st Recycle)	3.71
Mixture (2nd Recycle)	3.7

It can be noticed from the Table 4.4 above that the values obtained upon titration were all around 3.4 M of the acid, taking into consideration that this value obtained is not the actual one because the titration stopped at pH 2. So, some of these samples were also titrated again using NaOH but this time using phenolphthalein as an indicator, the results in this case showed a strength around 4 M HCl .

4.7.3 Residual sulfate

The same final regenerated solutions were analyzed to determine the residual calcium sulfate content. The solubility of calcium sulfate in a pure system when 8 M sulfuric acid was added to 3.5 M $CaCl_2$ at 40 °C is 4 g/L [51], and the residual calcium sulfate under the same conditions was found to be 5 g/L. An analysis for the residual sulfate in the presence of each metal chloride was performed and the results are shown in Figure 4.28. It can be noticed that the residual calcium sulfate content decreased upon seeding. This shows that recycling helps the system to get near its equilibrium state. It can be also seen that the highest residual sulfate value was observed in the case of $MgCl_2$.

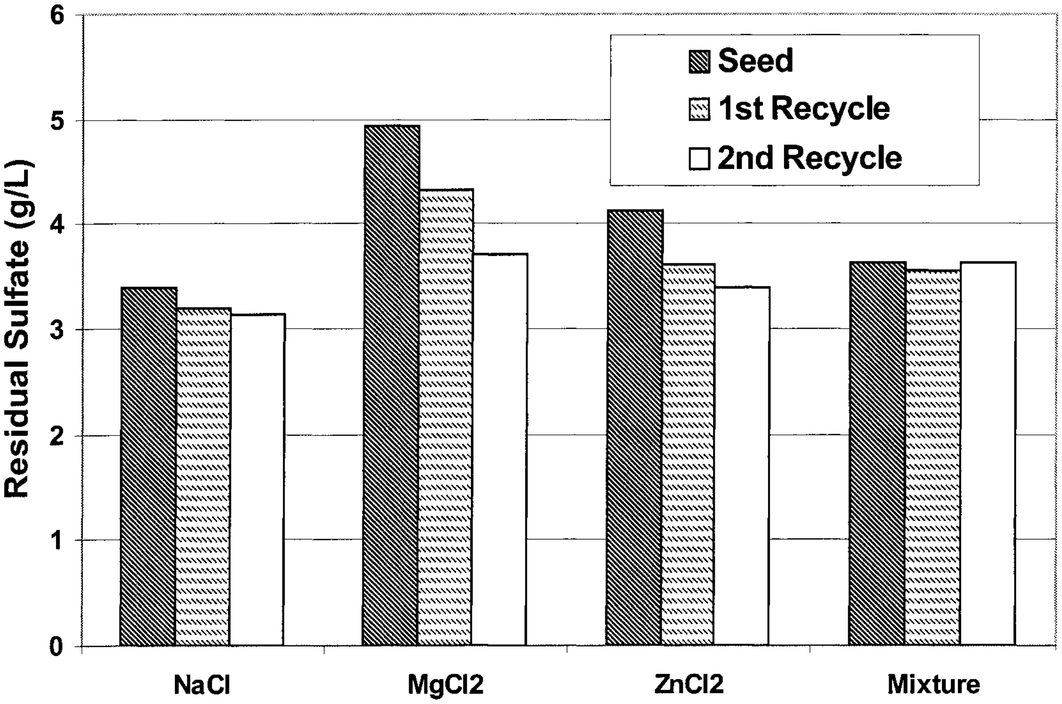


Figure 4.28: The effect of different metal chlorides on residual calcium sulfate content (for conditions: see Figure 4.25).

CHAPTER 5: CONCLUSIONS

It was found that the crystallization chemistry of the $CaCl_2$ – H_2SO_4 reaction can be controlled in such a way that favors the production of well grown and clean gypsum with the simultaneous regeneration of practical strength HCl.

The optimum crystallization results in terms of the production of high quality crystals can be achieved through supersaturation control. In this work, supersaturation was controlled by the method of sulfuric acid addition and it was found in the lab that the slower addition of the acid helped to produce large and more dense crystals. SEM analysis showed a visible difference in the morphology and size of the obtained solids and confirmed that larger particles were produced by the slower acid addition. It was also shown that the acid can be added in a series of stages that yielded results equivalent to those obtained by titration.

The equilibration time was also found to have an effect on gypsum particle size. SEM images presented for the samples obtained at various equilibration times under constant titration time and temperature showed more ripening for the crystals when more time of equilibration was provided.

The use of different and higher sulfuric acid concentrations showed that there was a decrease in the settling rate with the increase in the acid concentration due to the generation of higher supersaturation conditions that led to the formation of smaller particles. This was also confirmed via the SEM and particle size analysis. In general, it was possible to obtain a high solids density of 30 % and well grown crystals that separated easily. Experiments performed using higher reagent concentrations : 5 M $CaCl_2$ and 8 M H_2SO_4, showed that the gypsum produced has gel – like characteristics that was hard to filter. It was also concluded that the settling rate of the produced solids was low in general, however, filtration rates were very good in the order of 5000 $kg/m^2.hr$- rates that are considered to be industrially feasible.

The concentration of residual $CaSO_4$ in the regenerated HCl solution was found to be higher than the expected equilibrium concentration due to high supersaturation conditions. In order to minimize the soluble fraction of $CaSO_4$, it was decided to leave a certain amount of unreacted $CaCl_2$ to suppress the solubility of $CaSO_4$, hence, the potential of scale formation upon recycling of the regenerated acid. It was also shown that the HCl regenerated from this process can have a high strength (4 M) when 8 M of H_2SO_4 was reacted with 3.5 M of $CaCl_2$ at 40 °C.

The properties of the gypsum crystals produced were also affected by the temperature. It was noticed that the solids settling increased with temperature although it is still considered low, and the crystals mean particle size increased with the increase in the reaction temperature. SEM analysis has shown a visible difference in crystal growth with temperature. Concerning the solids density, a high of 32 % solids was obtained at 20 °C. The residual sulfate in the regenerated solution was also a function of temperature and increased with the increase in temperature because of the effect of temperature on $CaSO_4$ solubility. Finally, the filtration rates were very good and the highest value was obtained for the solids produced at 60 °C.

Seeding and recycling were also used to improve the dewatering characteristics of the produced gypsum. The crystal mean particle size was found to improve with the addition of seed and recycling.

The effect of metal chlorides on gypsum crystallization was also investigated using various metal chlorides including: NaCl, $MgCl_2$, $ZnCl_2$ and a combination of $FeCl_2$, $CuCl_2$, $NiCl_2$,$AlCl_3$ and $PbCl_2$. All the metals exhibited very low tendency for uptake except for the case of Pb. The higher reported uptake value was for Pb at the level of 127 ppm versus less than 10 ppm for the other metals. Once more, excellent, even better filtration rates and residual $CaSO_4$ levels were obtained, hence, the investigated process is highly attractive for further development to industry.

References

1. http://www.diet-and-health.net/Supplements/HydrochloricAcid.html

2. http://www.inchem.com.ph/hcl.htm

3. http://www.ilpi.com/msds/ref/baumescale.html

4. www.solvaychemicals.com

5. http://www.paleoresearch.com/MSDS/HYDROCHLORIC%20ACID.

6. http://c3.org/chlorine_knowledge_center/pvcbuild.html

7. H. Perry and D.W Green, "Perry's Chemical Engineers Handbook", 7th edition, McGraw Hill, New York, 2001,28-43.

8. J. Jansz , "Estimation of Ionic Activities in Chloride Systems at Ambient and Elevated Temperature", Hyrdometallurgy; Vol.11; 1983, p.13 – 31.

9. K. Borowiec, A.E. Grau, M. Gueguin and J-F. Turgeon, "Method to Upgrade Titania Slag and Resulting Product" , US Patent, No. 5,380,420, Nov. 3, 1998.

10. J.E. Dutrizac, T.T. Chen and C.W. White, "Leaching of Magnesium from Asbestos Processing Wastes" , in Waste Processing and Recycling in Mineral and Metallurgical Industries IV, S.R. Rao, L.M. Amaratunga, P.D. Kondos, G.G. Richards, N. Kuyucak and J.A. Kozinski, Eds., CIM, Montreal, Canada, 2001, 249-268.

11. C. Allen, P. Kondos, S. Payant, G. Van Weert and A. Van Sandwijk, "Production of Zinc Oxide from Complex Sulphide Concentrates using Chloride Processing" , US Patent, No. 6,395,242, May 28, 2002.

12. G.B. Harris, T.J. Magee and V.I. Lakshmanan, "The Jaguar Nickel Inc. Sechol Laterite Project – Atmospheric Chloride Leach Process" , in International Laterite Nickel Symposium 2004, W.P. Imrie and D.M. Lane, Eds., TMS, Warrendale, PA, USA, 219-241.

13. D.S. Baik and D.J. Fray, " Recovery of Zinc From Electric-Arc Furnace Dust by Leaching With Aqueous Hydrochloric Acid, Plating of Zinc and Regeneration of Electrolyte", Transactions of the Institution of Mining and Metallurgy-Section C-Mineral Processing.Dec, Vol. 109, 2000. C121.

14. R. Rituper," High Performance Effluent Free Pickling Plants With Fluid Bed Hydrochloric Acid Regeneration", Iron and Steel Engineer, Vol. 72, No. 11, 1995, p.50.

15. R. Chang and W. Tikkanen," The Top Fifty Industrial Chemicals," Random House Inc., New York, 1st Edition, 1988, 90-94.

16. W.L. Faith, D.B. Keyes and R.L. Clark,"Industrial Chemicals", John and Wiley Sons Inc. U.S.a, 3rd Edition, 1965, 420-426.

17. http:// www.psigate.com

18. G. Van Weert, "Some Observations on the Chloride Based Treatment of Nickel-Copper-Cobalt Mattes", Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds. Vol. 1, CIM, Montreal, Quebec, Canada, 2002,277-297.

19. http://www.metsoc.org/virtualtour/processes/magnola.asp

20. G. Van Weert, " Chloride and Nitrate Systems in Hydrometallurgy, Applications and Opportunities", Ph. D Thesis, Delft University of Technology, Delft NL.,1989, 71-101.

21. J. Markussen, E. Thune and G. Van Weert, "Pyrohydrolysis of Nickel Chloride Crystals in the Falconbridge Matt Leach Plant", in EPD Congress 1991, TMS, Warrendale, PA, USA, 1991, 405.

22. E.C. Eccleston and S.A.Bunk, "Development of Fluidized Bed Pyrohydrolysis Processes for Iron and Nickel Chloride Solutions", in Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds , Vol. 2, CIM, Montreal, Quebec, Canada, 2002, 713-725.

23. FactSage Software (http//www.factsage.com)

24. W. Steinbach and F. Baerhold, "Comparison of Spray Roasting and Fluidized Bed Granulation for the Recovery of Hydrochloric Acid from Metallurgical Processes through Pyrohydrolysis," Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds, Vol. 2 CIM, Montreal, Quebec, Canada, 2002, 643-655.

25. K. Adham and C. Lee, "Energy Recovery in the Metal Chloride Pyrohydrolysers", in Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds, Vol. 2, CIM, Montreal, Quebec, Canada, 2002, 657-671.

26. E. A. Walpole and J. D. Winter, "The Austpac ERMS and EARS Processes for the Manufacture of High-Grade Rutile by the Hydrochloroc Acid Leaching of Ilmenite", in Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds, Vol. 2, CIM, Montreal, Quebec, Canada, 2002, 401-415.

27. D. Verhulst, B. Sabacky, T. Spitler and W. Duyvesteyn, "The Altair TiO2 Pigment Process and its Extension into the Field of Nanomaterials", in Chloride Hydrometallurgy 2002, E. Peek and G. Van Weert Eds , Vol. 2, CIM, Montreal, Quebec, Canada, 2002, 417-431.

28. http://www.oit.doe.gov/nice3/factsheets/greentech.pdf

29. S. Berrie and G.E. Wooley, "Manufacture of Alpha Calcium Sulfate Hemihydrate", U.S. Patent No. 4,120,737, Oct. 17, 1978.

30. S. Girgin and G.P. Demopoulos, "Production of the High Value Material, Alpha-$CaSO_4$ Hemihydrate Out of Spent $CaCl_2$ Solutions by Reaction with H_2SO_4", in EPD Congress 2004, M.E. Schlesinger, Ed., TMS, Warendale, PA, USA, 2004, 627-639.

31. G.P. Demopoulos, Hydrochemical Processing Course notes, McGill Univesity, Montreal, Canada (2003).

32.A. Mersmann " Crystallization and Precipitation", Chemical Engineering Processing Vol. 38, No. 4, 1999, p.345

33. G.P. Demopoulos, Aqueous Processing Course notes, McGill Univesity, Montreal, Canada (2004).

34. A. J. Jones," Crystallization Process Systems", Butterworth – Heinemann Ltd, Oxford, 1st Edition, 2002, 123 – 214.

35. J.W. Mullin, "Crystallization," Third edition, Butterworth Heinemann Ltd, UK, 3rd Edition, 1997, 333 – 350.

36. G.P. Demopoulos, D.J. Dropert and G. Van Weert, "Precipitation of Crystalline Scorodite ($FeAsO_4 \cdot 2H_2O$) from Chloride Solutions", Hydrometallurgy, Vol. 38, 1995, p.245.

37. C. Sist," Precipitation of Nickel Hydroxide from Sulfate Solutions Using Supersaturation Control", M.Eng.Thesis, McGill University, Montreal, Canada, 2003.

38. J. Franke and A. Mersmann, "The Influence of the Operational Conditions on the Precipitation Process", Chemical Engineering Science, Vol. 50, No. 11 , 1995, p. 1737.

39. J.A. Dirksen and T.A. Ring,"Fundamentals of Crystallization," Chemical Engineering Scince, Vol. 46. No. 10, 1991, p.2389.

40. A. Coburn, E. Dudley and R. Spence,"Gypsum Plaster: Its Manufacture and Use", Intermediate Technology Publivcation, UK, 1989, 5-15.

41. http://www.dreamghar.com/bm-gyupsum.html

42. http://www.ars.usda.gov/is/np/agbyproducts/agbychap7.pdf

43. http://www.allcustom.net/ACGPDF/Medical%20Uses%20of%20Gypsum.pdf

44.K. H. Büchel, H.H. Moretto and P. Woditsch,"Industrial Inorganic Chemicals", Random House Inc., 1st Edition, Germany,1988, p. 90-421.

45. M. Matsumoto, H. Inoue, M. Abumiya and Y. Mitsune, "Extractive Metallurgy of Copper, Nickel and Cobalt(1993)," The Paul Queneau International Symposium, C.A. Landolt (Editor), TMS, Warrendale, Pa, 1993, 1599.

46. S. J. Omelon, " High Solids Density Gypsum Production Through an Improved Neutralization Process for Zinc Plant Effluent", M. Eng. Thesis, McGill University, Montreal, Canada, 1998.

47. C.M. Verbann, "The Uptake of Impurities During Gypsum Crystallization in Zinc Plant Waste Water Treatment", M. Eng. Thesis, McGill University, Montreal, Canada, 2000.

48. A. Al-Sabbag, A. Widua and H. Offermann, "Influence of Different Admixtures on the Crystallization of Calcium Sulfate Crystals",Chemical Engineering Community, Vol. 154, 1996,133.

49. A. Kruger, W. Focke , Z. Kwela and R. Fowles,"Effect of Ionic Impurities on the Crystallization of Gypsum in Wet Process Phosphoric Acid," Ind. Eng. Chem. Res., No. 40, 2001,p.1346.

50. W.L. McCabe, J.C. Smith and P. Harriot, "Unit Operations of Chemical Engineering", 5th Edition, McGraw –Hill,Singapore,1993, 243 – 1059.

51. Z. Li and G.P. Demopoulos, "Calcium Sulfate Solubilities in Concentrated Chloride Solutions", in Chloride Metallurgy 2002, Vol. 2, E. Peek and G. Van Weert, Eds., CIM, Montreal, Canada, 2002, 561-574.

52. E. Siliauskas, Dept. of Chemical Engineering, McGill University, Montreal, Canada, Personal Communication (2002).

53. M. Loffelmann and A. Mersmann, "How to Measure Supersaturation?", Chemical Engineering Science, Vol. 57, No. 20, 2002, p.4301.

54. R. Boistelle and J.P. Astier," *Crystallization mechanisms in solution*", Journal of Crystal Growth , No. 90 ,1988, p.14.

55. A. Mersmann, " Supersaturation and Nucleation," A Publication Chemical Engineering Research and Design, Vol. 74, No. 7 1996 p. 812.

56. Personal Communication with Dr. Bryn Harris, Hydrometallurgy Consultant, Montreal, Quebec , Canada, (2003).

57. O. Söhnel and J. Garside," Precipitation: Basic principles and industrial application", Butterworth – Heinemann Ltd, Oxford, 1992, 223 – 285

Appendix A Design of Reactor Baffles

Typical Ratios [51]: as illustrated in Figure A.1 shown, the dimensions of the reactor , impeller and their heights can be calculated;

$$\frac{Da}{Dt}=\frac{1}{3},\ \frac{E}{Dt}=\frac{1}{3},\ \frac{H}{Dt}=1$$

The diameter of the reactor of interest (D_t) = 0.0993 m (measured),it follows that Da = 0.0331 m.

E = 0.0331 m, H = 0.0993 m.

J(Baffle width) can be also calculated since: J/Dt = 1/12 , given Dt= 0.0993 m , then J = .00828 m

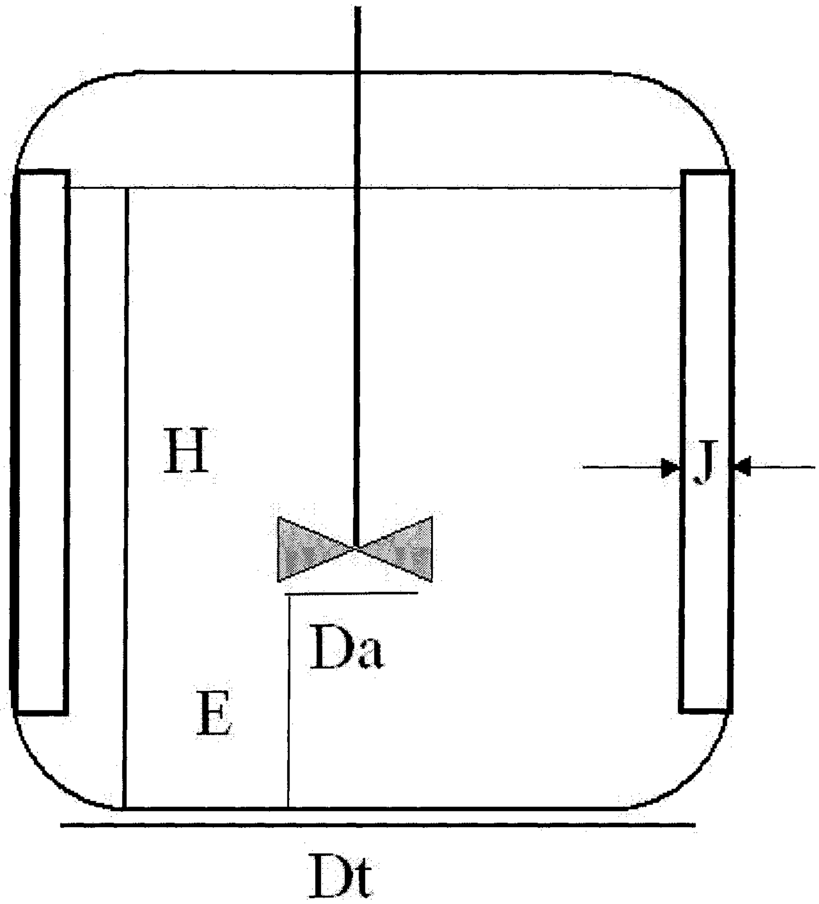


Figure A1: Typical Reactor and Baffle Ratios [50].