# CRYSTALLIZATION OF CALCIUM SULFATE AND UPTAKE OF IMPURITIES



# G.J. WITKAMP

4 for 1ge JIZGICO JA dissija)

ł

CRYSTALLIZATION OF CALCIUM SULFATE AND UPTAKE OF IMPURITIES

# CRYSTALLIZATION OF CALCIUM SULFATE AND UPTAKE OF IMPURITIES

7

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, Prof. Drs. P.A. Schenck, in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen op donderdag 22 juni 1989 te 16.00 uug TECHNISC

door



# Geert Jan Witkamp

doctorandus in de chemie, geboren te Kerkrade

Gedrukt bij Offsetdrukkerij Kanters bv, Alblasserdam 1989

> TR diss 1743

Dit proefschrift is goedgekeurd door de promotor Prof. Dr. Ir. G.M. van Rosmalen

Het onderzoek beschreven in dit proefschrift werd gefinancierd door DSM en de ministeries van VROM, Economische Zaken, Landbouw en Visserij en Verkeer en Waterstaat.

Ter nagedachtenis aan mijn moeder Aan Mieke Mijn vader

/

ì

## CONTENTS

1.	INTRODUCTION	1
1	.1, General	1
1	2. Phosphoric acid production	3
1	3. Objective of this study	4
1	.4. Scope of the investigation	5
1	.5. Remark	8
2.	GROWTH OF GYPSUM I:KINETICS	9
2	.1. Introduction	9
2	2.2. Theory	10
	2.2.1. The driving force for gypsum growth	10
	2.2.2. The growth rate	11
2	.3. Experimental	12
	2.3.1. Chemicals and equipment	12
	2.3.2. Experimental procedure	13
2	.4. Results and discussion	14
	2.4.1. Analysis of the measurements	14
	2.4.2. Results	16
	2.4.3. Shape of outgrowth curves	18
	2.4.4. Effect of growth affinity	
	and electrolyte concentration	21
	2.4.5. Influence of the temperature	28
2	.5. Conclusions	29
2	.6. References	30
2	.7. Appendix	31
2	.7.1. Pitzer equations	31
	2.7.1.1. Equations	31
	2.7.1.2. Solubilities and $\beta$ values	36
	2.7.1.3. Activity coefficients	36
2	2.7.2. Conductivity	37
3.	GROWTH OF GYPSUM II: INCORPORATION OF CADMIUM	39
3	.1. Introduction	39
3	.2. Theory	40
	3.2.1. Thermodynamics	40
	3.2.2. Kinetics	44
3	.3. Experimental	47
	3.3.1. Constant composition suspension growth	47
	3.3.2. Continuous crystallization	47
	3.3.3. Precipitation experiments	47
	3.3.4. Sampling and analysis	47
	3.3.5. Adsorption experiments	48
3	.4. Results and discussion	48
	3.4.1. Precipitation experiments	48
	3.4.2. Constant composition experiments	51
	3.4.2.1. Influence of supersaturation	
	and electrolyte concentration	51
	3.4.2.2. Influence of the temperature	55

-

	3.4.2.3. Effect of higher Cd <sup>2+</sup> -concentrations	56
	3.4.2.4. Effect of initial surge in outgrowth curve	58
	3.4.3. Continuous crystallization experiments	59
	3.4.4. Adsorption experiments	60
	3.5. Conclusions	61
	3.6. References	62
4	. CONTINUOUS CRYSTALLIZATION OF HEMIHYDRATE IN PHOSPHORIC	ACID
	4.1. Introduction	64
	4.2. Experimental	65
	4.3. Results and discussion	68
	4.3.1. The hemihydrate crystals	68
	4.3.2. Incorporation of phosphate ions	68
	4.3.3. Incorporation of cadmium ions	73
	4.4. Conclusions	77
	4.5. References	78
5	. INCORPORATION OF CADMIUM AND ALUMINUM FLUORIDE IN CALCI	UM
	SULFATE	79
	5.1. Introduction	79
	5.2. Experimental	81
	5.3. Results and discussion	81
	5.4. Conclusions	87
	5.5. References	87
6	BATCHWISE RECRYSTALLIZATION IN PHOSPHORIC ACID I	
Ŭ	FORMATION OF GYPSIM AND ANHYDRITE	88
	6.1. Introduction	88
	6.2. Phase diagram and conversion rate	91
•	6.3. Experimental	96
	6.4. Results and discussion	98
	6.4.1. Recrystallization of hemihydrate and dihydrate	
	into anhydrite	98
	6.4.1.1. Conversion curves and	
	expressions for Cd uptake	98
	6.4.1.2. Influence of seeding	103
	6.4.1.3. Influence of the $H_2SO_4$ content	106
	6.4.1.4. Influence of the temperature	108
	6.4.1.5. Influence of the $P_2O_5$ concentration	109
	6.4.2. Recrystallization of hemihydrate into dihydrate	109
	6.4.2.1. Influence of the seeds	109
	$6.4.2.2$ . Influence of the $H_2SO_4$ concentration	112
	6.4.2.3. Influence of the temperature	114
	$6.4.2.4$ . Influence of the $P_2O_5$ concentration	114
	6.4.2.5. Influence of impurities	115
	6.5. Conclusions	117
	6.6. References	118
	6.7. Appendix:calculation of cadmium uptake and conversion	119
	6.7.1. Distribution coefficient K(Cd)	119
	6.7.2. Partition coefficient D	120
	6.7.3. The conversion	123
	6.7.3.1. Calculation from the Cd concentration	

in the solution	123
6.7.3.2. Calculation from the Cd and Ca concentration	
in the solution	123
6.7.3.3. Calculation of the conversion from	
the crystal water content	123
7. BATCHWISE RECRYSTALLIZATION IN PHOSPHORIC ACID II:	
HEMIHYDRATE INTO DIHYDRATE CONVERSION DESCRIBED WIT	TH A MODEL
7.1. Introduction	125
7.2. Recrystallization of calcium sulfate	126
7.3. The batch recrystallization model	127
7.4. Experimental	129
7.5. Results and discussion	130
7.5.1. General approach	130
7.5.2. The slurry density	130
7.5.3. The $H_2SO_4$ -concentration	131
7.5.4. The $H_3PO_4$ -concentration	133
7.5.5. Temperature	134
7.5.6. The stirring rate	134
7.5.7. Impurities	136
7.5.8. The type of source and seed material	135
7.5.9. Secondary nucleation	13/
7.0. Conclusions	130
7.9 Deferences	130
7.9. References	120
8. CONTINUOUS RECRYSTALLIZATION IN PHOSPHORIC ACID	141
8.1. Introduction	141
8.2. Theory	142
8.2.1. Driving force	142
8.2.2. Unsteady continuous system	142
8.2.3. Steady continuous system	145
8.3. Experimental	146
8.3.1. Chemicals and equipment	146
8.3.2. Operation of the apparatus	148
8.4. Results and discussion	149
8.4.1. General	149
8.4.2. Influence of (re)crystallization conditions	152
8.5. Conclusions	156
o.o. References	150
9. REDUCTION OF CADMIUM UPTAKE BY COMPLEXING AGENTS	157
9.1. Introduction	157
9.2. Theory	158
9.3. Experimental	160
9.4. Results	161
9.4.1. Recrystallization of HH into DH	161
9.4.2. Continuous crystallization of HH	163
9.4.3. Constant composition growth experiments	166
9.4.4. Incorporation of halides	166
9.5. Conclusions	166
9.6. References	167

.

10.	UPTAKE OF IMPURITIES	168
10.1.	Introduction	168
10.2.	Modes of foreign ion incorporation	170
10.2	.1. Interstitial incorporation	170
10.2	.2. Coprecipitation	171
10.2	.3. Isomorphous substitution	172
10.3.	Kinetical influence on incorporation	175
10.4.	Thermodynamical and kinetic parameters	177
10.5.	Experimental	180
10.6.	Results and discussion	181
10.7.	Conclusions	198
10.8.	Appendix	199
10.9.	References	202
11.	IMPURITY DISTRIBUTION IN A PHOSPHORIC ACID PROCESS	205
11.1.	Objective	205
11.2.	Distribution coefficients	205
11.3.	Impurity distribution in a phosphoric acid process	205
11.4.	Cd uptake	206
11.5.	Impurity disposal	208
	SUMMARY	210
	SAMENVATTING	213
	NAWOORD	216
	CURRICULUM VITAE	218
	LIST OF PUBLICATIONS	219

#### CHAPTER 1

#### INTRODUCTION

1.1. General

Crystallization is encountered in a large variety of industrial as well as natural processes. Its occurance ranges from concrete hardening for building purposes to growth of shells, from industrial production of chemicals to animal bone formation. Because of this diversity, crystallization is provoking interest in many fields of research.

In industrial processes crystallization is often applied as a separation technique, where the crystalline phase is either the main product or the byproduct. Successful operation includes a controlled acceptably fast crystallization rate, a high purity of the main product and/or the byproduct, as well as good filterability and washability of the crystals.

The purity of the crystals is often an important aspect in defining the product quality. But even in those cases where the crystalline phase is formed as an unwanted byproduct for disposal, its uptake of in particular toxic impurities is relevant in view of environmental protection.

In this thesis the emphasis lies on the incorporation of foreign ions in crystals of the three calcium sulfate modifications as well as on their crystallization rates and mechanisms, since both features are interrelated. The extent of incorporation of foreign ions in a host lattice depends on the thermodynamics of the system, reflected by the equilibrium state, but also on kinetic parameters such as the growth rate of the crystals. Impurity ions present at the crystal surface can become entrapped by oncoming growth layers, which propagate along the crystal surface. The degree of impurity entrapment depends on the adsorption/desorption rates of these impurities in relation to the growth rate of the crystals. The foreign ions, once buried in the

crystal surface, could obstruct the regular disposition of following growth layers. In this way the growth process could be hampered, which on its turn has an effect on the uptake of other impurity ions. То act as effective growth retarders, foreign ions have in fact to fulfill two requirements. They must have a strong affinity towards either of the ions in the crystal surface and thus become strongly the surface. At the same time the attached ions must attached to create a sterical hindrance for the deposition of the next growth units. This is especially the case for ions with a very low dehydration frequency, since for such ions their shield of water molecules or other ligands is almost permanently protruding from the crystal surface. Not both demands have to be fulfilled to the same extent.  $Cr^{3+}$  ions, for example which have an extremely low dehydration frequency do not have to be strongly attached to the crystal surface. For  $Ce^{3+}$  ions on the contrary, that are strongly attracted by e.g. sulfate or phosphate ions of a crystal surface, a high dehydration frequency is allowed. It has been demonstrated that minor amounts of trivalent metal ions even below the ppm range could have a significant kinetics of inorganic infuence on the growth and mixed inorganic/organic compounds.

In this work the uptake of foreign ions by the three calcium sulfate modifications as well as their influence on the crystallization kinetics of these salts have been studied.

The calcium sulfate modifications have been selected for this study, since during their crystallization as a byproduct in many industrial processes, impurities always play a dominating and unavoidable role. The approach used for this investigation is, however, applicable to other systems as well. Several trends observed for this system also appear to bear a more general character and are thus useful in a more general sense.

As mentioned, calcium sulfate is formed as a byproduct in many processes such as flue gas desulfurization, during production of fluorides and various organic acids as well as in phosphoric acid production, and in hydrometallurgical zinc and copper winning. The

-2-

impurities enter the processes with the raw materials or the ores, and their number is abundant. Especially in phosphoric acid production huge amounts of calcium sulfate are precipitated in the presence of a large variety of impurities.

1.2. Phosphoric acid production.

Phosphoric acid is produced mainly for application in the fertilizer industry ( $\sim 5 \cdot 10^7$  tons/year). Most of this acid is produced by so-called wet processes where the ore (fluorapatite) reacts with sulfuric acid to give phosphoric acid, calcium sulfate and hydrogen fluoride according to:

 $H_2O$ Ca<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>•CaF<sub>2</sub> + 10  $H_2SO_4$  → 10 CaSO<sub>4</sub>•xH<sub>2</sub>O↓ + 6  $H_3PO_4$  + 2 HFt

with x = 0 (anhydrite, AH), 0.5 (hemihydrate, HH) or 2 (dihydrate, DH or gypsum).

Sulfuric acid is usually chosen because it forms insoluble calcium sulfates that can be separated from the product acid. For each ton phosphate ore about two tons of calcium sulfate are formed. Mostly hemihydrate or dihydrate and only rarely anhydrite is formed. In some processes first formed hemihydrate is subsequently recrystallized into gypsum in order to lower the phosphate content of the gypsum crystals and to improve the filterability. Impurities, originating from the ore, are distributed between the phosphoric acid, the calcium sulfate and the gaseous phase. Since the waste calcium sulfate is often river water or at sea or piled in stacks, its disposed in contamination could lead to environmental problems. Most notorious impurities in this respect are cadmium, chromium and other heavy metals, fluoride and arsene, while also phosphates are disposed with the hemihydrate or gypsum. Until recently, phosphoric acid processes were optimized only with respect to phosphate uptake, but nowadays in the Netherlands restrictions imposed by the government in e.g. the amount of disposed cadmium are reason for additional optimization criteria. These restrictions have already led to a decrease from 15 to 5 tonnes per year of cadmium disposal in the Netherlands, encaptured in  $2\cdot10^6$  tonnes of calcium sulfate. This result has mainly been reached by use of ore mixtures with a low cadmium content.

further reduction can only be achieved by changes in the current Α processes, or by the application of Cd-free ores. The amount of such ores is, however, limited. These magmatic phosphates contain high concentrations of lanthanides, up to 1%, contrary to the sedimentary ores which contain up to 0.01% at most, being mainly cerium. These lanthanides hamper the (re)crystallization kinetics and therefore have large impact on the process performance, making application of а magmatic ores in this sense less attractive. Changes in current processes with the aim to minimize the cadmium uptake by hemihydrate as well as dihydrate are therefore intensively under investigation. Another often discussed impurity introduced by the ore is radium, which ends up entirely in the ore. Radium decays into radon gas, which is radioactive. This gas escapes from the the crystals and can accumulate in poorly ventilated rooms, when phosphogypsum is used as wallboard inside buildings. Since, however, also other properties of phosphogypsum hamper its aplicability, such as its phosphate content and its strength, radium uptake has not been part of this study. The awareness of the presence of other impurities and their impact on the environment is still increasing. For this reason the distribution of all kinds of impurities from the ore between the phosphoric acid and the calcium sulfate phases have been determined.

1.3. Objective of this study

The main effort of this research has thus been devoted to the next specific objectives:

- identification of the kinetic and thermodynamic parameters that determine the uptake of foreign ions in calcium sulfate modifications.

-4-

- determination of the (re)crystallization kinetics of the three modifications without and in presence of impurities.

This has been done in model experiments under well defined conditions as well as in experiments more resembling industrial circumstances. Many of the (re)crystallization experiments have therefore been performed in phosphoric acid solutions.

1.4. Scope of this thesis

In chapter 2 the kinetic equations governing the growth rate of gypsum in electrolyte  $(NaNO_3)$  solutions at various supersaturations and temperatures have been derived from constant composition experiments. In this way the growth order and plausible mechanisms could be determined under conditions where the solution composition is well defined and the activity coefficients could be calculated.

Chapter 3 describes the cadmium uptake occurring during the growth of gypsum under the well defined conditions prevailing in the experiments described in chapter 2, as well as during growth in other experiments continuous crystallization such as experiments from similar electrolyte solutions. All experiments were performed to study the influence of supersaturation, temperature and electrolyte concentration upon the cadmium uptake, and to compare results obtained from different types of experiments. Agreement should exist to allow the explanation and ultimately the prediction of uptake and crystallization behaviour under industrial conditions.

In chapter 4 industrial conditions are more closely imitated by performing continuous crystallization experiments in concentrated phosphoric acid solution at temperatures around 90 °C. Under such conditions calcium sulfate hemihydrate is formed. This hemihydrate not only contains cadmium, but also phosphate ions are incorporated. The uptake of both ions is investigated as a function of the sulfate

-5-

concentration in solution and the residence time, which determines the supersaturation, since these are dominating parameters in phosporic acid production.

In chapter 5 the uptake of  $AlF_3$  on the shape of the hemihydrate crystals and on the cadmium and phosphate uptake has been studied. The influence of  $AlF_3$  on the uptake of both ions has also been determined for gypsum and anhydrite crystals, formed at lower and higher temperatures respectively.

In chapter 6 the batchwise recrystallization of hemihydrate into anhydrite and gypsum and of gypsum into anhydrite has been investigated. Since during this solvent mediated conversion process impurities are redistributed between the solution and the newly formed phase, an opportunity is created to influence their uptake by an appropriate choice of conversion conditions. The recrystallization of hemihydrate into anhydrite has been studied as a function of temperature, phosphoric and sulfuric acid concentrations, of amount seed crystals and type of hemihydrate ( $\alpha$  or  $\beta$ ). For the conversion into gypsum also the role of a few impurities was considered. The conversion rate was measured by determination of conversion-time curves. The cadmium and phosphate uptake of the newly formed crystals were related to the conversion conditions.

The kinetics of batchwise recrystallization of hemihydrate into dihydrate were studied more systematically in chapter 7. A model was developed based on the dissolution rate of hemihydrate and the growth rate of dihydrate, both presented by a rate constant times the underand supersaturation respectively to the appropriate order. Once the effects of e.g. solution composition and temperature on these parameters are known, the recrystallization behaviour can be predicted in a wide range of operating conditions without and with impurities. The derived model has been extended to a continuous three-stage recrystallization section in chapter 8. Since similar rate equations were used, the continuous conversion behaviour can be predicted from rate constants obtained from batch experiments. By writing the recrystallization process as differential equations, the development of the process in time, following for example a perturbation, can be constructed. A few continuous experiments have been performed to verify this model.

In chapter 9 the reduction in cadmium uptake achieved by addition of complexing agents specific for cadmium has been studied. The effect of the halides in phosphoric acid solutions were tested in continuous crystallization and batch recrystallization experiments, while also constant composition dihydrate growth experiments were performed with halides as well as with thiosulfate in aqueous solution.

The extent of incorporation of a large scala of impurities, denoted by their partition or distribution coefficients, has been investigated in chapter 10. Attempts have been made to relate the uptake of in with their particular metal ions physical and chemical characteristics. there are the ionic radius, as the charge, complexing constants with other ions in the solution, solubilities of their sulfate salts, dehydration frequency and energy, and their polarizability. Also the uptake of other compounds has been studied.

In chapter 11 the formerly determined distribution coefficients have been used to calculate the distribution of many impurities over the phosphoric acid and the calcium sulfate modifications in a selected phosphoric acid process. In this process the initially formed hemihydrate is filtered and recrystallized into dihydrate. In the phosphoric acid recycle stream a small portion of 5% of the total amount of calcium sulfate is formed. If suitable process conditions are chosen, this AH captures a great deal of the cadmium ions from the stream, thus depleting the solution in the process with respect to cadmium.

#### 4.5. Remark

This thesis, which provides an attempt to improve the understanding of the uptake of impurities in camium sulfate crystals in relation to their crystallization kinetics, is composed of a series of chapters, some of which have already been published in the course of the investigation. A small overlap in the contents of the various chapters as well as some inconsistencies in the use of terms and symbols throughout the text could thus not be avoided. I apologize for these shortcomings, which hopefully do not cause any confusion.

#### CHAPTER 2

#### GROWTH OF GYPSUM I: KINETICS.

#### Abstract

A suspension of gypsum  $(CaSO_4 \cdot 2H_2O)$  crystals has been grown from electrolyte solutions using the constant composition technique. In pure water a parabolic rate law governs the growth kinetics, while in NaNO<sub>3</sub> solutions the order increases from 1 at low supersaturations up to 4 at higher supersaturations. In NaNO<sub>3</sub> solutions platelike crystals with some roughened faces develop under the given growth conditions. The higher growth rate in electrolyte solutions is partly due to the higher impingement rate and partly to a higher incorporation rate at the surface. The growth rate increases with increasing temperature.

# 2.1. Introduction

Crystallization of gypsum or other calcium sulfate modifications occurs in many industrial processes, such as flue gas desulfurization and the production of fluoride, zinc, organic acids or phosphoric acid [1].

Gypsum is mostly disposed in river water or at sea, or stored on a waste stack. Since impurities, originating from the raw materials, are incorporated in the gypsum, this disposal leads to environmental problems.

Both the crystallization process and the related uptake of impurities by gypsum are dependent on the crystallizing conditions and the concentration of the impurities. The uptake of cadmium, due to its toxicity one of the most notorious compounds in phosphoric acid production, is discussed in the next chapter. In an appendix the uptake of other impurities and their influence on the growth of gypsum will be described. The eventual aim of this work is to determine the interrelation between presence of impurities, growth kinetics and uptake of foreign ions in gypsum, at conditions resembling industrial circumstances. In this chapter the growth kinetics are investigated over a wide range of ionic strengths. On this subject many publications already exist [2-10], but most of these describe growth in dilute solutions at relatively low supersaturations, while only a few are performed at high ionic strengths but at further loosely defined conditions.

The constant composition technique was used here for studying the crystallization. An advantage of this technique is the sharp control of the driving force for growth. A disadvantage however, is that the choice of solution composition is restricted to those which allow monitoring of the  $Ca^{2+}$  or  $SO_4^2$ - concentration. As with any type of (semi) batch experiments, the obtained results are especially at the start influenced by the used seed crystals.

### 2.2. Theory

#### 2.2.1. The driving force for gypsum growth

A measure for the driving force is the relative supersaturation, often denoted as  $\sigma = \frac{(c-c_{eq})}{c_{eq}}$ , where c is the actual concentration and c the saturation value. For non-stoichiometrical calcium sulfate solutions the following expression can be used, where the brackets refer to concentrations in moles per liter.

$$\sigma = \sqrt{\frac{[Ca^{2+}] \cdot [SO_4^2-]}{([Ca^{2+}] \cdot [SO_4^2-])_{eq}}} - 1$$
(2.1)

where the subscript eq refers to saturated solutions, and the given concentrations are total concentrations in the solutions. A better parameter for the driving force for growth is the growth affinity  $\beta$ , defined as [11]:

$$\beta = \frac{\Delta \mu}{RT}$$

(2.2)

where  $\Delta \mu$  is the difference in chemical potential of one mole of building units in the solution and in the crystals. For gypsum eq. (2.2) becomes:

$$\beta = \ln \frac{(Ca^{2+}) \cdot (SO_4^2 -) \cdot (H_2O)^2}{(Ca^{2+}) \cdot (SO_4^2 -) \cdot (H_2O)^2)}_{eq}$$

Quantities between parentheses indicate activities. The equilibrium activities only depend on the temperature and pressure. Since, however, it is not always possible to determine the activities of  $H_2O$ ,  $Ca^{2+}$  or  $SO_4^2-$ , often the supersaturation  $\sigma$  is still used. For very small supersaturations  $\beta \approx 2 \sigma$  if the activity coefficients are independent of the concentration. In our systems, however, this condition is not fulfilled as follows from the calculation described in the appendix.

The activities of  $Ca^{2+}$  and  $SO_4^2$  ions and  $H_2O$  in electrolyte solutions can in principle either be measured potentiometrically or be calculated with semi-empirical equations [12-17]. In the same way the solubilities can be determined experimentally or calculated from these activity coefficients (see appendix 1) [18,19]. Since the accuracy of solubility measurements is high, the calculation procedure of activities has been verified by comparison of both types of solubility data.

### 2.2.2. The growth rate

The linear growth rate  $R_{lin}$  basically depends on the particular (hkl) crystal face, the growth affinity and the solution composition.  $R_{lin}$  is, however, in the type of experiments performed here, somewhat obscured by:

- (i) the fact that only overall growth rates are obtained;
- (ii) starting effects such as changes in habit of crystals and in reactivity of the crystal faces of the seeds.

The overall growth rate R that is obtained, is given by the relative increase in total crystal mass with time:

$$R = \frac{d m(t)/m(o)}{dt} (s^{-1})$$
(2.3)

This R is used throughout this paper to characterize the growth rate as a function of supersaturation, electrolyte concentration and temperature. R is a function of surface averaged the sum of the linear growth rates of all crystal faces of all crystals in the suspension. This implies that R is proportional to  $R_{lin}$ , but additionally depends on the habit and size of the crystals i.e. on the available surface areas of the crystal faces. This geometrical effect will be discussed in the results.

#### 2.3. Experimental

#### 2.3.1. Chemicals and equipment

Merck p.a.  $NaNO_3$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Na_2SO_4$ , Chemicals used were  $Cd(NO_3)_2 \cdot 4H_2O$ . The solutions, containing 0.5 to  $1.0 \cdot 10^{-3}$  M  $Cd^{2+}$ , were made of doubly distilled water and filtered over a 0.22 µm millipore filter before use. The apparatus is drawn schematically in fig.2.1. The 1 liter double walled glass crystallizer was thermostated within approximately 0.05 °C by a Braun 1480 thermomix bath/pump. To prevent evaporation and  $CaCO_3$  formation, a small stream of N<sub>2</sub>, containing H<sub>2</sub>O at approximately the saturation pressure as expected in the experiment was passed over the solution. The lid was kept 1-2 °C higher to prevent condensation. The stirrer was a glass propeller blade type, and the impeller rate was adjusted so that the crystals remained in suspension.

The Ca-concentration was measured by a Ca-electrode (F2112, Radiometer) combined with a calomel reference electrode through a mV meter. The analogous output signal of the mV meter was fed to an Olivetti M24 PC through an A/D convertor (5712, Labmaster). The conductivity was measured with a modified Philips electrode with a Wayne-Kerr universal bridge or a Philips conductometer, connected to the A/D interface. For estimation of the conductivity as a function of calcium sulfate and sodium perchlorate concentrations the diagram



Figure 2.1. Scheme of the crystallizer.

presented in the appendix has been used.

The Ca-electrode could not be used in  $ClO_4$ - containing solutions due to its extreme sensitivity towards this ion. This is also the case for other types of electrodes (Orion, Philips) and is probably common for such membrane type electrodes. The Ca<sup>2+</sup> electrodes are also very sensitive towards lanthanide ions and Y<sup>3+</sup>, a property not documented by the producers. A non PVC-membrane electrode [20] might work better.

The data were processed by a program in Turbo Pascal (Borland), controlling the two Metrohm burettes (type 665), operated in pulse mode and equipped with double walled glas 50 ml reservoirs.

#### 2.3.2. Experimental procedure

The experiments were initiated by the addition of a suspension of seed crystals (about 300 mg in a 5 ml pycnometer) to the crystallizing solution (300 ml) of the appropriate composition.

The seed crystals were prepared according to a procedure of Nancollas et al. [7], and were used after at least several months of ripening. The total mass of added seed crystals in the suspension was calculated from the weight of the calibrated pycnometer within 3% accuracy according to

$$m_{s} = \frac{m_{p}(t) - m_{p}(\phi) + V_{p} \cdot \rho_{air} - V_{p} \cdot \rho_{\ell}}{1 - \rho_{\ell} / \rho_{g}}$$
(3.1)  
$$m_{p}(t) = mass of filled pycnometer$$

 $p_{p}^{P}(\phi)$  = empty mass of pycnometer  $v_{p}$  = inside volume  $\rho_{1}$  = density of solution of seed crystals  $\rho_{g}$  = density of gypsum

After addition of the seeds to the supersaturated solution their growth starts. The resulting decrease in Ca-concentration or conductivity is compensated by suppletion of  $Ca^{2+}$  and  $SO_4^2$ in solution. This can be achieved by adding a solution with a very high supersaturation, or by adding  $Ca(NO_3)_2$  and  $Na_2SO_4$ solutions simultaneously. The advantage of the first method is that the crystallization can easily be performed in pure water, while with the second method high supersaturations in background electrolyte can be obtained.

The amount of solutions needed to reach the setpoint was calculated from the known relationship between the conductivity and the calcium sulfate concentration, or by the Nernst law when the Ca-electrode was used. The added volume thus corresponds with a certain increase in mass of the crystals.

At the end of the experiment the slurry was poured over a 0.22  $\mu$ m filter and washed three times with a saturated gypsum solution in the appropriate electrolyte concentration and subsequently three times with saturated gypsum solution in water. The crystals were dried at 40°C.

# 2.4. Results and discussion

### 2.4.1. Analysis of the measurements

By registering the added volume vs. reaction time a so called V(t) curve is obtained which is processed into a kinetical curve of overall growth rate vs. outgrowth of the crystals.

As an example, exp. 33 from table 2.1 (2.4.2) has been worked out. The relative supersaturation is 0.15 in a solution of 1 M NaNO<sub>3</sub> at 35 <sup>o</sup>C. The amount of seed crystals is 327 mg. The burettes are filled with 0.2 M  $Ca(NO_3)_2/0.8$  M  $NaNO_3$  and 0.2 M  $Na_2SO_4/0.8$  M  $NaNO_3$  respectively, which are added in equal amounts. The added volume vs. time curve (V(t)) is given in fig. 2.2.

The overall growth rate, related to the slope of the curve seems to be about constant in time, but in order to be able to compare experiments under different conditions the data need to be further processed.

The V(t) curve is first fitted by a function of the form  $V(t) = \frac{i \Xi^5}{i \Xi^0} a_i f_i(t)$ , which has no physical meaning and yields for this example (t in s)  $V(t) = -189.14105 + 0.0383529.t - 7.750843 - \sqrt{t} + 72.42344.t^{1/4} + 338.7805/(\sqrt{t+1})$  (ml) (4.1)

by applying the Marquard fitting procedure taken from Bevington [21]. The added volume is related to the growth mass of the crystals m by:

$$m(t) = M_{CaSO_4.2H_2O}V(t) . ([CaSO_4] (added solution) - [CaSO_4] (crystallizing solution)) (4.2)$$

 $M_{CaSO_{4},2H_{2}O} = 0.172 \text{ kg.mole}^{-1}$ 

The normalized overall growth rate R is calculated from eq. (4.3).

Since the observed reaction time t depends on m(o) (with more seeds the reaction proceeds faster), the normalized outgrowth of the crystals m(t)/m(o) is used as a measure for the development of the reaction.

Both ordinates,  $\frac{d m(t)/m(o)}{dt}$  on the vertical axis and  $\frac{m(t)}{m(o)}$  on the horizontal axis can easily be obtained by using the fitted function



Figure 2.2. Added burette volume vs. reaction time (exp. 3).

m(t) and its analytical derivative respectively for various reaction times:

 $R = \frac{d m(t)/m(o)}{dt}$ outgrowth = m(t)/m(o)  $\begin{cases} 0 \le t \le t \\ end \end{cases}$  (4.3)

In the used example the expressions are:

$$\frac{d\mathbf{m}(t)/\mathbf{m}(o)}{dt} = \frac{d\mathbf{V}(t)}{dt} \cdot \frac{\mathbf{m}(t)}{\mathbf{m}(o) \cdot \mathbf{V}(t)}$$
(4.4)

with V(t) according to (4.1).

# 2.4.2. Results

In table 2.1 the experimental conditions are listed, together with the driving force  $\beta$ . In these experiments the electrolyte (NaClO<sub>4</sub> or NaNO<sub>3</sub>) concentration was varied as well as the supersaturation. In all

experiments the temperature was 25 °C, except for exp. 9,33,34 and 35, where the temperature was 35-60 °C. From the supersaturation and electrolyte concentrations the growth affinity  $\beta$  was calculated. The resulting overall growth rate appeared to depend on the degree of outgrowth (see 4.3.). For each condition one overall growth rate is given at a selected corresponding outgrowth (m(t)/m(0)-1).

Exp.	background	σ	β	$\frac{dm(t)/m(o)}{dt}$	outgrowth
<u>nr.</u>	<u>electrolyte</u>			x 10 <sup>5</sup>	m(t)/m(0)-1
1	-	0.13	0.15	0.7	1
2	-	0.16	0.18	1.0	1
3	-	0.17	0.19	1.2	· 1
4	-	0,20	0.22	2.2	1
5	-	0.32	0.34	5.2	1
6	-	0.10	0.12	0.6	1
7	-	0.19	0.214	1.3	1
8	- `	0.07	0.082	0.3	1
9	-, 40°C	0.10	-	4.0	1
10	0.1 M NaClO <sub>4</sub>	0.11	0.15	4.6	1
11	n	0.24	0.30	8.6	1
12	17	0.33	0.40	12.6	1
13	"	0.39	0.46	17.1	1
14	0.1 M NaNO <sub>3</sub>	0.15	0.20	10	5
15	"	0.30	0.37	20	5
16	n	0.50	0.59	40	5
17	n	0.70	0.72	120	5
18	11	1.00	0.93	330	5
19	D	1.20	1.06	650	5
20	0.3 M NaNO <sub>3</sub>	0.20	0.23	24	5
21	11	0.50	0.59	55	5
22	11	0.80	0.88	430	5
23	**	1.00	0.99	600	5

Table 2.1 Experimental conditions and results

24	11		1.20	1.10	1300	5
25	11		1.40	1.28	2200	5
26	п		1.60	1.32	2200	5
27	"		1.80	1.41	2800	5
28	1 M Nal	NO 3	0.15	0.22	80	5
29	**		0.30	0.41	1.60	5
30	н		0.50	0.64	310	5
31	н		0.70	0.80	600	5
32	**		0.90	0.89	1580	5
33	••	35°C	0.15		100	5
34	"	45°C	0.07		100	5
35	**	60°C	0.33		1000	5

The outgrowth for the experiments in water is not higher than approximately 2, so for these measurements the growth rate is given at outgrowth 1. Before discussing the influence of background electrolyte, supersaturation and temperature, the shape of the growth rate vs. outgrowth curve is treated.





2,4,3, Shape of outgrowth curves

For various supersaturations in  $1 \text{ M} \text{ NaNO}_3$  the overall growth rate has been plotted versus the outgrowth in figure 2.3. The curves consist of fast declining parts followed by slowly rising parts. The initial sharp decrease in growth rate has earlier been assigned to either a fusion of cooperating spirals or to disappearance of dislocations [10]. It can, however, also result from a poisoning of the surface by inevitably present impurities adsorbing on the crystal surface.

Since some outgrowth is required before the seed crystals have adopted a shape imposed by the crystallizing conditions, a shift in growth rate is anyway expected. Originally rouded crystals show after outgrowth by a weight factor of two flat well defined crystal faces (see figure 2.4).

The shape of the rising part of the outgrowth curve is partly determined by the developed geometry of the crystals. Indeed if all faces retain the same growth rate during outgrowth, i.e. if the geometry remains unchanged, the surface area and therefore the growth rate is proportional to  $m(t)^{2/3}$ . The order of the outgrowth curve then equals 2/3. When on the other hand one or more crystal faces are strongly retarded in growth with respect to other faces, either by poisoning or just by the altered conditions imposing a different crystal shape, the order of the outgrowth curve will be lower than 2/3. In general,  $\alpha$  can be derived from the slope of a log (R) vs. log (outgrowth) curve, since

$$R = \frac{d m(t)/m(o)}{dt} \sim (m(t)/m(0))^{\alpha}, \qquad (4.5)$$

For  $\alpha = 0$  needle growth prevails, while  $\alpha = 1/2$  is indicative for growth in two directions, yielding platelets and  $\alpha = 2/3$  means that the geometry is retained. A higher  $\alpha$ -value would be caused by an increasingly active surface. The  $\alpha$ -values obtained range from 0.4 to 0.5, for an outgrowth higher than 4. This is consistent with the shape of the obtained platelike crystals as can be seen from a SEM micrograph (figure 2.5).

Because of the various slopes in the growth curve, it is essential to



Figure 2.4. a:seed crystals (photo size  $90x110 \ \mu\text{m}$ ), b: seed crystals (photo  $30x40 \ \mu\text{m}$ ) and c:crystals after 200% outgrowth ( $450x550 \ \mu\text{m}$ ).

compare growth rates at the same degree of outgrowth. An outgrowth value of 5 seems a reasonable choice for the electrolyte solutions, but since for the experiments in water the outgrowth is not higher than about 2, a value of one was selected. In table 2.1 the calculated growth rates are listed, at the corresponding outgrowth values. Using these data, the growth rate is determined as a function of supersaturation for several electrolyte solutions.

#### 2.4.4. Effect of growth affinity and electrolyte concentration

In fig. 2.6a-d R has been plotted versus  $\beta$  and  $\sigma$  for various electrolyte solutions. In table 2.2 the best fitting growth equations of the form  $R = k \cdot \sigma^n$  or  $R = k' \cdot \beta^{n'}$  are given with the ranges in which these equations are valid. First the reaction orders n and n' will be discussed, and thereafter the rate constants k and k'.

solution	$\sigma_{range}$	n	-log k	$\beta_{range}$	n'	-log k'
pure water	0.07-0.32	2.0	3.36	0.08-0.34	2.1	3.40
0.1 M NaClO <sub>4</sub>	0.08-0.30	1.0	3.40	0.08-0.46	1.4	3.26
0.1 M NaNO <sub>3</sub>	0.15-0.50	1.2	3.05	0.20-0.60	1.3	3.13
	0.50-1.20	2.9	2.50	0.60-1.06	2.8	2.30
0.3 M NaNO <sub>3</sub>	0.15-0.50	1.0	3.00	0.23-0.60	1.0	3.10
	0.50-1.80	2.4	2.15	0.60-1.41	4.0	2.10
1.0 M NaNO <sub>3</sub>	0.15-0.50	1.1	2.17	0.22-0.60	1.1	2.32
	0.50-0.90	2.7	1.7	0.60-0.89	5.0	1.55

# Table 2.2 Overall growth equations in several solutions, $R = k \cdot \sigma^{n} = k' \cdot \beta^{n'}$

The order of growth n or n'

The second order growth in pure water at low supersaturation is in accordance with literature data [4, 10] and is consistent with a BCF spiral growth mechanism [11, 22, 23, 24, 25].

In the presence of an electrolyte the order is approximately 1 in  $\sigma$  or 1.0-1.4 in  $\beta$  at supersaturations or  $\beta$ -values up to 0.5 and 0.6



Figure 2.5. Crystals grown in 0.3 M NaNO<sub>3</sub> solution,  $\sigma=120\%$  (450x500 $\mu$ m)

respectively. This cannot be explained by diffusion limitation, since at higher supersaturations, where under similar conditions bulk diffusion should also be rate limiting, the order of growth increases to 3 or 5. Besides, the actual mass fluxes towards the growing surface can be calculated to be much smaller than those resulting from diffusion alone. The increasing growth order suggests an exponential relationship, but these curves could not be fitted by an acceptable exponential function.

Growth according to a BCF mechanism could be of the first order in  $\beta$ if the dislocation density is high enough to allow cooperating growth spirals to develop. Observation of this first order behaviour might only become noticeable at the high outgrowth values reached in these experiments, leading to a dominant contribution to the total growth rate by those crystal faces that fulfill the requirement of high dislocation densities. In the pure water experiments the outgrowth is not sufficient to reach this state and to expose this effect. Such a suggestion has been done in [10] to explain the decrease in growth order from 2 at outgrowth 0.1 to an order of 1.5 at outgrowth 0.5 for gypsum grown in pure water. There are, however, a few arguments against this explanation. The first is that in exp. 1 to 8 with an





Figure 2.6. Overall growth rate vs. relative supersaturation  $\sigma$  and vs. growth affinity in several solutions.

outgrowth of 1.0 this order of 1.5 has not been found, but instead an order of 2 was obtained. The second is that addition of electrolyte leads to an increase in solubility and therefore a decrease in edge free energy. Such decrease would lead to a decoupling of cooperating spirals.

Another explanation for first order growth is that surface roughening of the fastest growing top faces occurs, even at low supersaturations. Presence of NaNO<sub>3</sub> reduces the surface free energy and therefore the roughening temperature and the critical  $\beta$ -value for kinetical surface roughening.

With higher supersaturations the order increases to 3-5. This has, however, only a small effect on the resulting growth rate here, because the  $\sigma$  and  $\beta$  values hardly exceed unity. It is questionable whether at higher supersaturation this high order will continue. A transition around a  $\beta$  value of 0.6 might occur between two linear growth processes.

Also additional reactive surface area by the roughened crystal faces, might be formed due to overhangs. In figure 2.7a-d the roughened crystal faces can be seen.

Another explanation for the high growth order could be that impurities, inevitably present in the solution, cannot adsorb on the fast growing faces at high growth rates. At low growth rates the adsorbed impurities hamper the growth. Chernov [26] describes such behaviour for growth of  $Na_5P_3O_{10} \cdot 6H_2O$  with small concentrations of sodium dodecylbenzyl sulfonate in solution.

#### The rate of growth

The -log k and -log k'values in the given range of  $\sigma$  or  $\beta$  values are also presented in table 2.2. A high value implies a low rate at fixed  $\sigma$  or  $\beta$ . Clearly the growth proceeds the fastest in the most concentrated electrolyte solution. This can also be seen from fig. 2.8, where R is plotted versus  $\beta$  in various electrolytes. The curve obtained for a 1 M NaNO<sub>3</sub> solution lies above the curve for a 0.3 M, which in turn lies above the 0.1 M curve. To determine whether this is







Figure 2.7. Crystals grown in 0.3 M NaNO<sub>3</sub> solution at a  $\sigma$  value of 80% (a,b), 120% (c) and 180% (d, seen along the edge).Photo size a:450x500  $\mu$ m, b:150x160  $\mu$ m, c:80x90  $\mu$ m., d:90x100 $\mu$ m.



Figure 2.8. Overall growth rate vs.  $\beta$  in various electrolyte solutions



Figure 2.9. Overall growth rate divided by the difference in actual concentration and the saturation values  $R_{corr}$ , vs.  $\beta$ .

caused by the larger amount of available calcium sulfate in the solution, or that the incorporation reaction at the crystal surface proceeds faster, a corrected  $R-\beta$  curve is presented in figure 2.9. Corrected means that R is extrapolated to outgrowth 5 for exp. 1-13, as well as divided by  $\Delta CaSO_4$ , the actual total calcium sulfate concentration in the solution minus the concentration in a saturated solution. The curve for pure water lies below the other curves,

indicating that here the surface reaction of the growth is the slowest. At higher  $\beta$ -values the difference between the curves for pure water and for 0.1 M NaNO<sub>3</sub> becomes smaller, and it would require additional experiments to see whether there is a point where the corrected growth rates coincide. The curves for 0.1 M NaClO<sub>4</sub> and 0.1 and 0.3 M NaNO<sub>3</sub> coincide, while the corrected growth rate in 1 M NaNO<sub>3</sub> solution is more than three times higher. Apparently the incorporation reaction is promoted by background electrolyte in the solution.

The electrolyte might also influence the surface charge of the crystals, thus facilitating the transport of either  $Ca^{2+}$  or  $SO_4^{2-}$  ions towards the surface.

An explanation for the influence of electrolyte on the growth rate and the order of growth is not possible without additional data.

It would for example contribute to the understanding of the growth mechanism if the active species of the electrolyte in the solution could be identified as such. Electrolyte in the solution has the effect of screening the  $Ca^{2+}$  and  $SO_4^2$ - ions and of lowering the  $H_2O$  activity by their hydration (salt effect).

The ions also have their specific interaction with the calcium or the sulfate ions. Both effects result in a change in the activities of the  $Ca^{2+}$  and  $SO_4^2$ - ions. The free ion activity coefficients have been calculated with Pitzer's semi-empirical specific ion interaction model, using the appropriate interaction constants (see appendix).

From these calculations, it follows that in NaNO<sub>3</sub> and NaClO<sub>4</sub> solutions the activity coefficient of Ca<sup>2+</sup> is higher than that of SO<sub>4</sub><sup>2-</sup>, probably due to an interaction of Na<sup>+</sup> with SO<sub>4</sub><sup>2-</sup>. The growth process thus proceeds non-stoichiometrically. This probably has no effect upon the growth rate. Nielsen [27] reported that in a wide range of nonstoichiometry the growth rate of sparingly soluble salts only depends on the activity product. The effect of electrolyte on the growth rate could also be imposed through the influence of the ions on the rate of bulk or surface diffusion transport along the steps and the final incorporation of the building units at the kink sites. These rates depend on the rate of exchange of the ligands, such as H<sub>2</sub>O, NO<sub>3</sub>- and
$SO_4^2$ - for  $Ca^{2+}$  or  $H_2O$ ,  $Na^+$  and  $Ca^{2+}$  for  $SO_4^2$ -, and on the mobility of the complexes. During growth the ligands (except the  $Ca^{2+}$ - $SO_4^2$ - and two  $Ca^{2+}$ - $H_2O$  bonds) have to be disconnected. It is for instance known that the hydration number of  $Ca^{2+}$  varies from 10 in an aqueous solution to 5.5 in a strong background electrolyte solution [28, 29]. Since dehydration of  $Ca^{2+}$  is a very fast process (>10<sup>8</sup> s<sup>-1</sup>) [30, 31] only  $Ca^{2+}$ - $NO_3$ - complexes could limit the growth of gypsum. In a 0.9 M  $Ca(NO_3)_2$  solution however, only about 10% of the  $Ca^{2+}$  is directly connected to  $NO_3$ - [32], so this effect is not likely to be very large. The same applies to  $ClO_4$ - ions. The observed faster growth in electrolyte solution also makes a retarding effect by such complexation effect unlikely.

As mentioned,  $Na^+-SO_4^2$ - complexes are stronger and probably have a longer lifetime. Crystals formed in 0.1 M NaClO<sub>4</sub> contain about 0.1 w% Na<sup>+</sup>. This Na<sup>+</sup> might become incorporated as a complex. Such complex might also affect the growth rate.

Since, however, data on the influence of electrolyte concentration on the ligand exchange rates are scarce, it is hard to predict the effect of salts on the growth reaction, and so far no conclusive explanation for the salt effect can thus be given.

# 2.4.5. Influence of the temperature

To investigate the effect of a higher temperature, exp. 8 was performed in pure water at 40°C, beside exps. 33,34 and 35 in 1 M NaNO<sub>3</sub> at 35, 45 and 60°C respectively. The resulting growth rates are also plotted in fig. 2.9. The threefold increase in pure water corresponds with an activation energy of about 60 kJ/mol, which agrees with literature data [7]. The experiments in 1 M NaNO<sub>3</sub> yield lower values. The calculated activation energies are 20 kJ/mol between 25 and 35°C, 43 kJ/mol between 25 and 45°C and 41 kJ/mol between 25 and 60°C. The  $\beta$ -values needed to position these growth rates on figure 2.8 are not measured or calculated, but assumed to be equal to  $\sigma$ . This is not unreasonable, because in other experiments at 25°C the  $\sigma$ -values do not differ much from  $\beta$  and because the curve in fig. 2.8 is almost flat in the given range of  $\beta$ . Whether these higher growth rates are entirely due to a faster reaction with a constant activation energy or additionally result from changes in e.g. association equilibria in the solution, could be determined by calculating or measuring the association as a function of temperature, which has not been attempted here.

For a proper description of the influence of temperature both thermodynamic and kinetic parameters should be taken into account Since at high  $\beta$ -values around 0.6 a change in growth mechanism possibly occurs, determination of the activation energy below and above this value may reveal the nature of the effect of temperature.

### 2.5. Conclusions

- The curves of the overall growth rate vs. outgrowth consist of fast declining parts followed by slowly rising parts.
- The slope of the rising part of the outgrowth curve follows a power of 0.4-0.5, which is consistent with the observed platelike outgrowth of the crystals.
- In pure water the growth rate is proportional to the square of the relative supersaturation  $\sigma$  or the growth affinity  $\beta$ . This parabolic rate is consistent with a BCF spiral growth mechanism.
- In 0.1 M NaClO<sub>4</sub> or 0.1-1 M NaNO<sub>3</sub> the order of growth in  $\sigma$  or  $\beta$  is 1.0-1.4 below  $\sigma$  or  $\beta$  values of 0.6, and 2.8-5.0 above these values. This might be explained by surface roughening of a larger number of crystal faces, by higher surface reactivity or by the occurance of another linear rate law at higher supersaturations.
- The growth rate is higher in solutions with higher electrolyte concentrations. This is partly due to a higher solubility, giving more impinging growth units, and partly due to an effect on the incorporation reaction.
- The growth rate increases with temperature. The activation energy calculated from this increase varies between 20 and 45 kJ/mol in 1 M NaNO<sub>3</sub>, and is 60 kJ/mol in pure water.

# 2.6. References

- [1] Wirsching, F., Chemie in unserer Zeit <u>4</u> (1985) 137-143.
- [2] Hünger, K.L., O. Henning, Cryst. Res. Tech. 23 (1988) 1135-43.
- [3] Randolph, A.D., D.E. Vaden, AIChE Symp. Ser. <u>80</u> (19..) 110-121, Advances in crystallization from solutions.
- [4] Liu, S.T., G.H. Nancollas, Talanta <u>20</u> (1973) 211-16.
- [5] Brandse, W.P., G.M. van Rosmalen, G. Brouwer, J. Inorg. Nucl. Chem. <u>39</u> (1977) 2007-10.
- [6] Kagana, M., M.E. Shehan, G.H. Nancollas, J. Inorg. nucl. chem. <u>43</u> (1981) 917-20.
- [7] Nancollas, G.H., M.M. Reddy, F. Tsai, J. Cryst. Growth <u>20</u> (1973) 125-34.
- [8] Simon, B., M. Bienfait, Acta Cryst. <u>19</u> (1965) 750-6.
- [9] Klima, W.F., G.H. Nancollas, Crystallization and precipitation processes, AIChE Symp. Series <u>83</u> (1987) 23-30.
- [10] Christoffersen, M.R., J. Christofferson, M.P.C. Weijnen, G.M. van Rosmalen, J. Cryst. Growth <u>58</u> (1982).
- [11] Bennema, P. and G.H. Gilmer, Kinetics of crystal growth, in: Crystal growth: an introduction. P. Hartman, ed. North Holland Publ. Co. (1973).
- [12] Pitzer, K.S., J. Phys. Chem. <u>77</u> (1973) 268-77.
- [13] Pitzer, K.S., G. Mayorga, J. Phys. Chem. 77 (1973) 2300-08.
- [14] Pitzer, K.S., G. Mayorga, J. Sol. Chem. <u>3</u> (1974) 539-46.
- [15] Pitzer, K.S., J.J. Kim, J. Am. Chem. Soc. <u>96</u> (1974) 5701-7.
- [17] Pitzer, ACS Symp. Ser. 133 (1980) 451-66.
- [18] Harvie, C.E., J.H. Weare, Geochim. Cosmockim, Acta 44 (1980) 981
- [19] Pabalan, R.T., K.S. Pitzer, Geochim. Cosmochim. Acta <u>51</u> (1987) 2429-43.
- [20] Oehme, M., M. Kessler, W. Simon, Chimia <u>30</u> (1976) 204-6.
- [21] Bevington, P.R. Data reduction and error analysis (1969). McGraw-Hill, New York.
- [22] Nielsen, A.E., Pure & Appl. Chem. 53 (1981) 2025-39.
- [23] Chiang, P.P. and M.D. Donohue, J. Colloid and Interface Science <u>122</u> (1988) 2025-39.
- [24] Nielsen, A.E. J. Cryst. Growth 67 (1984) 289-310.
- [25] Bennema, P., J. Cryst. Growth 69 (1984) 182-97.
- [26] Chernov, A.A., Modern Crystallography III:Crystal Growth, Springer Series in Solid-State Sciences, Springer Verlag 1984.
- [27] Nielsen, A.E. and J.M. Toft, J. Cryst. Growth 67 (1984) 278-88.
- [28] Hunt, J.P., H.L. Friedman, Prog. Inorganic Chem <u>30</u> (1983) 359-387.
- [29] Hewish, N.A. G.W. Neison, J.E. Enderby, Nature <u>297</u> (1982) 138-9.
- [30] Friedman, H.L., Chemica Scripta 25 (1985) 42-48.
- [31] Merbach, A.E., Pure & Appl. Chem. <u>59</u> (1987) 161-72.
- [32] Nicholas, A.M. de P., R.E. Wasylishen, J. Phys. Chem. <u>89</u> (1985) 5446-50.
- [33] Pitzer, K.S., Pure & Appl. Chem. 58 (1986) 1599-1610.
- [34] Rosmalen, G.M., Thesis (1981) Delft University, The Netherlands.

#### 2.7. Appendix

# 2.7.1. Pitzer equations

2.7.1.1. Equations.

The following equations, taken from [33], have been used to calculate the activity coefficients.

In a mixture of solutes in a solvent a deviation from ideality occurs due to interactions between the species in the solution.

The excess free Gibbs energy resulting from these interactions cnosists of a term containing the Debye-Huchel contribution (I) and terms representing the interactions between each combination of species.

$$G^{\text{exc}}/\text{RT} = f(I) + \sum_{i} \sum_{j} m_{i}m_{j} \lambda_{ij}(I) + \sum_{i} \sum_{j} \sum_{k} m_{i}m_{j}m_{k} \mu_{ijk} + \dots, \quad (A.1)$$

where  $m_{i,j}$  are the molalities of the species i, j, ... in solution and  $\lambda_{ij}$  the second virial coefficient,  $\mu_{ijk}$  the third etcetera. I is the ionic strength, defined as:

$$I = \frac{1}{2} \sum_{i} m_{i} z_{i}^{2}$$
(A.2)

with  $z_i$  the change of particle i; Surprisingly, in most cases it is sufficient to use only the first two series or even the first only. f(I) in (A.1) is approximated by:

$$f(I) = -(4 I A_{\phi}/b) \ln (1 + bI^{1/2})$$
(A.3)
where b = 1.2 kg^{1/2} \cdot mole^{-1/2}

 $A_{\phi}$  is the Debye-Huckel parameter

$$A_{\phi} = \frac{1}{3} \left( 2\pi N_0 d_w / 100 \right)^{1/2} \left( e^2 / 4\pi \epsilon_0 \epsilon kT \right)^{3/2}$$
(A.4)

 $\varepsilon$  is the relative permittivity of the solvent,  $d_{_{\bf W}}$  the density.

In an electrically neutral solution  $\lambda_{ij}$  or  $\mu_{ijk}$  can not be determined separately. Instead neutral combinations are evaluated, such as:

$$B_{ca} = \lambda_{ca} + \left| \frac{z_a}{2z_c} \right| \lambda_{cc} + \left| \frac{z_c}{2z_a} \right| \lambda_{aa}$$
(A.5)

$$C_{ca} = \frac{3}{2} \left( \frac{\mu_{cca}}{|z_c|} + \mu_{caa} |z_a| \right)$$
(A.6)

$$\phi_{cc'} = \lambda_{cc'} - \frac{z_{c'}}{2z_c} \cdot \lambda_{cc} - \frac{z_c}{2z_{c'}} \cdot \lambda_{c'c'}$$
(A.7)

$$\psi_{cc'a} = 6 \ \mu_{cc'a} - \frac{\frac{3z_{c'}}{z_{c}}}{z_{c}} \cdot \ \mu_{cca} - \frac{\frac{3z_{c}}{z_{c'}}}{z_{c'}} \cdot \ \mu_{c'c'a}$$
(A.8)

c, c' are cations, a, a' anions.

In addition:

$$B'_{ca} = \frac{d}{d} \frac{B}{I}$$
(A.9)

.

and

$$\phi_{ca}' = \frac{d \phi_{ca}}{d I}$$
(A.10)

are needed.

The activities are calculated according to:

- for water:

using the osmotic coefficient  $\phi$ 

$$a_{H_20} = \exp\left(-\phi \frac{\sum_{i=1}^{\infty} m_i}{55.6}\right)$$
 (A.11)

where:

$$(\phi - 1) = \frac{2}{\sum_{i=1}^{\infty} \left[\frac{-A_{\phi} I^{3/2}}{1 + b I^{1/2}} + \sum_{c a} \sum_{m c a}^{m} (B_{ca} + Z C_{ca}) + \right]} + \sum_{c > c'} \sum_{m c c'}^{m} (\phi_{cc}^{\phi}, + \sum_{a} m_{a} \psi_{cc'a}) + \sum_{a > a'}^{\infty} \sum_{a' a}^{m} (\phi_{aa}^{\phi}, + \sum_{c} m_{c} \psi_{caa'})]$$
(A.12)

- for cations M:

$$\ln \gamma_{M} \approx z_{M}^{2} F + \sum_{M} m_{a} (2 B_{Ma} + Z C_{Ma}) + \sum_{C} m_{c} (2 \phi_{Mc} + \sum_{A} \psi_{Mca})$$

$$+ \sum_{a>a'} \sum_{m} m_{a'} \psi_{Maa'} + |Z_{M}| \sum_{C} \sum_{a} m_{c} m_{a'} C_{ca} \qquad (A.13)$$

- analogously for anions X:

$$\ln \gamma_{\rm X} = z_{\rm X}^2 F + \sum_{\rm c} m_{\rm c} (2 B_{\rm cX} + Z C_{\rm cX}) + \sum_{\rm a} m_{\rm a} (2 \phi_{\rm Xa} + \sum_{\rm c} \psi_{\rm cXa})$$
$$+ \sum_{\rm c>c'} m_{\rm c} m_{\rm c}, \psi_{\rm ccX'} + |Z_{\rm X}| \sum_{\rm c} \sum_{\rm a} m_{\rm c} m_{\rm a} C_{\rm ca} \qquad (A.14)$$

In (A.13) and (A.14):

$$F = -A_{\phi} \left[ \frac{I^{1/2}}{1 + b I^{1/2}} + \frac{2}{b} \ln (1 + b I^{1/2}) \right] + \sum_{c a} \sum_{c a} m_{c} m_{a} B_{ca}^{\prime}$$
$$+ \sum_{c > c'} \sum_{c = c} m_{c} m_{c}, \psi_{cc'} + \sum_{a > a'} \sum_{a = a'} m_{a} m_{a'} \phi_{aa'}^{\prime}$$
(A.15)

$$Z + \sum_{i} m_{i} |z_{i}|$$
(A.16)

$$B_{ca}^{\phi} = B_{ca} + I B_{ca}^{\prime} \tag{A.17}$$

$$\phi^{\phi}_{cc'} = \phi_{cc'} + I \phi'_{cc'} \tag{A.18}$$

b = 1.2

In (A.13) and (A.15) it is implicitly assumed that C  $_{\rm ij},~\psi_{\rm ijk}$  are independent of I.

$$B_{MX}^{\phi} = A_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2})$$
 (A.19)

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g (\alpha I^{1/2})$$
 (A.20)

$$B'_{MX} = \beta_{MX} \frac{(1) g' (\alpha I^{1/2})}{I}$$
(A.21)

with: 
$$g(X) = \frac{2[1 - (1 + X) \exp(-X)]}{X^2}$$

$$g'(X) = \frac{-2[1 - (1 + X + \frac{X^2}{2}) \exp(-X)]}{X^2}$$

with:  $\alpha = 2 \text{ kg}^{1/2} \cdot \text{mole}^{1/2}$  for 1-1, 2-1 and 3-1 electrolytes.

١,

For 2-2 electrolytes a better result is obtained using:

$$B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_2 I^{1/2})$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(-\alpha_2 I^{1/2})$$

$$B_{MX}' = \frac{[\beta_{MX}^{(1)} g'(\alpha_1 I^{1/2}) + [\beta_{MX}^{(2)} g'(\alpha_2 I^{1/2})]}{I}$$

with:  $\alpha_1 = 1.4 \text{ kg}^{1/2} \text{ mole}^{-1/2}$   $\alpha_2 = 12 \text{ kg}^{1/2} \text{ mole}^{-1/2}$ and  $\beta_{MX}^{(2)} = -\frac{K}{2}$ , K the association constant of the 2-2 electrolyte.

Pitzer also includes terms obtained from asymmetrical mixing such as 1-1 with 2-1 salts. At the relatively low concentrations applied here it is not necessary to take these into account. Also up to to I=2 evaluation of the  $C_{MX}$  terms is not necessary. The following coefficients have been used to calculate the activities:

# Coefficients used in Pitzer equations.

compound	β <sup>(0)</sup>	$\beta^{(1)}$	β <sup>(2)</sup>	С
HNO <sub>3</sub>	0.1190	0.3206		0.0005
NaNO3	0.0068	0.1783		-0.00036
NaClO <sub>4</sub>	0.0554	0.2755		-0.00118
Na <sub>2</sub> SO <sub>4</sub>	0.0181	1.0559		0.00202
$Ca(NO_3)_2$	0.2108	1.4093		
Ca(ClO <sub>4</sub> ) <sub>2</sub>	0.4511	1.7565		
CaSO4	0.2000	2.6500	-55.7	0.0000

All equations were evaluated with a computerprogram in Turbo Pascal (Borland). The activities in pure water solutions agree within 1% with those in [34], while in  $NaNO_3$  solutions a deviation of up to 15% occurred. This deviation was found by comparing the calculated activities in saturated calcium sulfate solutions containing  $NaNO_3$  with those in pure water. Since the activity products in saturated solutions are all equal to the thermodynamical solubility product, solubility data can be used to verify either the calculated activities or the coefficients from the Pitzer equations.

# 2.7.1.2. Solubilities and $\beta$ values

In fig. 2.10 the measured solubilities and the calculated values at  $25^{\circ}$ C are plotted as a function of the NaNO<sub>3</sub> and NaClO<sub>4</sub> concentrations. The calculations were done by an iterative procedure, in which the calcium sulfate concentration is gradually increased and the ion activity product is computed, until this product equals the value in pure water:  $(Ca^{2+}) \cdot (SO_4^2-) \cdot (H_2O)^2$ . The derivation in calculated and measured solubility is at most 15%, i.e. for 1 M NaNO<sub>3</sub>. The error in  $\beta$ -values is much less, since for those calculations were performed with such equilibrium value that  $\beta$  equalled zero in saturated solution. This means that a great part of the error is cancelled out.



Figure 2.10. Solubility of gypsum as a function of  $\rm NaNO_3$  concentration at 25  $^{\rm O}C.$  Measured and calculated values.

#### 2.7.1.3. Activity coefficients

Using the described procedure of calculation, the activity coefficients  $\gamma$  of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> at concentration zero are determined as a function of the NaNO<sub>3</sub> concentration up to 1.5 M at 25°C. The result is given in fig. 2.11. From  $\gamma=1$  at zero electrolyte

concentration  $\gamma$  decreases steeply to less than 0.5 at 0.5 M NaNO<sub>3</sub>. The sulfate activity coefficient is lower than for calcium in the whole range, and in 1 M NaNO<sub>3</sub> the difference is a factor 2. Qualitatively this can be ascribed to complexation of SO<sub>4</sub><sup>2</sup>- with Na<sup>+</sup>, reducing the amount of free sulfate.

# 2.7.2, Conductivity.

When the seeds crystals are added, the electrolyte in the vessel is diluted by the aqueous solution of the suspension. To anticipate to the change in conductivity  $\lambda$ ,  $\lambda$  should be known as a function of the calcium sulfate concentration and electrolyte. Since  $\lambda$  is used as a monitor for supersaturation only for pure water and 0.1 M NaClO<sub>4</sub> solutions, only these have been investigated.

In fig. 2.12 the conductivity  $\lambda$  is given as a function of the solution composition. The values can be represented by the following equation:

 $\lambda = [CaSO_4] \cdot (301.4 - 801.5/[CaSO_4] - 101.5/[NaClO_4]) + [NaClO_4] \cdot (159.4 + 6.984/[CaSO_4] - 92.17/[NaClO_4]) + 0.004084$ 



Figure 2.11. Calculated activity coefficients of  $Ca^{2+}$  and  $SO_4^2-vs$ . NaNO<sub>3</sub> concentration. Cadmium activity is used in chapter 3.



Figure 2.12. Conductivity of NaClO4 and gypsum solutions at 25  $^{\rm o}C.$ 

#### CHAPTER 3

#### GROWTH OF GYPSUM II: INCORPORATION OF CADMIUM

#### Abstract

The cadmium uptake in gypsum has been investigated using the techniques of constant composition, simple precipitation and continuous crystallization. The partition coefficient D increases from 4-8.10-3 at low supersaturations  $\sigma$  to 5.10-3 at  $\sigma$ =1.5. D is slightly higher in solutions with a higher electrolyte (NaNO<sub>3</sub>) concentration, partly due to a higher activity coefficient of  $Cd^{2+}$ . A higher also result in a higher uptake. temperature From adsorption experiments follows that the affinity of  $Cd^{2+}$  to  $SO_4^2$  at the crystal surface is not larger than for  $SO_4^2$  - in the solution.

# 3.1. Introduction

In chapter 2 the growth rate of gypsum has been described as a function of crystallizing conditions such as supersaturation, concentration of background electrolyte and temperature. The aim of chapters 2 and 3 is as has been mentioned to establish a relationship between crystallizing conditions and the uptake of cadmium, one of the most important impurities. Since kinetical as well as thermodynamical parameters can play a role, it is crucial to investigate the influences of both type of parameters separately.

The kinetics of uptake are studied by varying the growth rate, while the thermodynamics have to be derived from the equilibrium situation at zero growth rate, obtained by extrapolation.

To verify whether translation of observed results to a more practical situation is allowed, several types of experiments with a different set-up were performed.

In simple precipitation experiments streams of  $Ca(NO_3)_2$  and  $Na_2SO_4$ solutions containing 10-3 M Cd<sup>2+</sup> were added simultaneously to the crystallizer. By variation of the feed rate, temperature and stoichiometry a rough indication of the influence of these parameters on the Cd<sup>2+</sup> uptake was obtained under conditions where primary nucleation was followed by growth.

These influences were investigated under better defined conditions with constant composition growth experiments. Subsequently, for comparison, the same conditions were applied in continuous crystallization, where secondary nucleation and outgrowth of the crystals occurs simultaneously.

# 3.2. Theory

# 3.2.1 Thermodynamics

Uptake of  $Cd^{2+}$  in calcium sulfate proceeds by isomorphous substitution of  $Ca^{2+}$  ions, as will be elucidated in chapter 10. The degree of uptake is given by the partition coefficient D, that takes into account the competition of  $Cd^{2+}$  and  $Ca^{2+}$  for the same lattice site. D is defined as:

$$D = \frac{[Cd^{2+}]/[Ca^{2+}]}{[Cd^{2+}]/[Ca^{2+}]}$$
(1)

A constant D-value implies that the resulting  $Cd^{2+}$  concentration in the crystals can be influenced by either the  $Cd^{2+}$  or the  $Ca^{2+}$  concentration in the solution. A thermodynamical expression has been derived for D (see chapter 10):

$$D = \frac{\gamma(Ca^{2+})s}{\gamma(Cd^{2+})s} \cdot \frac{\gamma(Cd^{2+})\ell}{\gamma(Ca^{2+})\ell} \cdot \frac{Ksp(CaSO_4)}{Ksp(CdSO_4)} \cdot exp(-\epsilon_{e1}/RT) \cdot exp(-\Delta\mu(CdSO_4 \to CaSO_4)/RT)$$
(2)

D comprises the activity coefficients  $\gamma$  of Cd<sup>2+</sup> and Ca<sup>2+</sup> in the solution ( $\ell$ ) and in the solid phase (s), the thermodynamical solubility products of calcium and cadmium sulfate, the energy of elastic lattice deformation  $\epsilon_{el}$  and the free energy required to make a CdSO<sub>4</sub> lattice isomorphous with the corresponding CaSO<sub>4</sub> lattice. The activity coefficients represent in fact the deviation from ideality, which can also be expressed as an excess free energy  $\Delta G = -RTln\gamma$ . Changes in energy affecting the activity coefficients can thus also be written as an exponent. For pure calcium sulfate  $\gamma(Cd^{2+})$ s equals 1, while  $\gamma(Cd^{2+})$ s is related to the bonding energy of Cd<sup>2+</sup> in the calcium sulfate lattice.

If all parameters in (2) were known, D could be calculated. Mostly, however, the values of these parameters are not available, which hampers the use of eq. 2 for prediction of the D-value. An error of only 6 kJ/mol in one of the energies determining D already gives rise to an error in D of a factor of 10. Assuming the bonding energies in the lattice to be of the same order of magnitude as the hydration energy, being several hundred kJ/mol, already indicates that a small error in the bonding energy of 6kJ/mol could easily happen. It is therefore hard to make an a priori prediction of the D-value on basis of (2), but under certain conditions the effect of some parameters can become visible. For instance, at constant temperature and pressure the exponential terms as well as the solubility product remain constant. If in addition the uptake does not exceed a value of about 1%, the activity coefficients in the solid are also unaltered. In that case the D-value only depends on the activity coefficients in the solution and thus solely on the solution composition.

Although an a priori prediction of D is as said not possible, the observed D-values may be understood by comparing the physical and chemical properties of  $Cd^{2+}$  and  $Ca^{2+}$ . Therefore in table 3.1. some characteristics of these two ions are listed.

The radii of  $Cd^{2+}$  and  $Ca^{2+}$  are almost equal, enabling replacement of  $Ca^{2+}$  by  $Cd^{2+}$  without introducing much lattice strain. It is therefore expected that the  $\epsilon_{e1}$  term in eq. (2) is small.

-41-

Table 3.1. Some properties of  $Ca^{2+}$  and  $Cd^{2+}$ 

	Ca <sup>2+</sup>	Cd <sup>2+</sup>	unit	ref.
radius				
(8-coordination)	112	107	pm	[1]
hydration enthalpy	- 1602	- 1833	kJ/mol	[2]
hydration enthalpy				
sulfate salt	18	52	kJ/mol	[3]
Pitzer constant				
sulfate salt				
(appendix, chapter 2):				
$\beta^{(0)}$	0.20	0.2053		
$\beta^{(1)}$	2.65	2.62		
$\beta^{(2)}$	-55.7	-48.07		[4]
hydration number	10 (dilute)	6		[5,6]
	5.5 (conc.)			
hydration type	isotropic	octaeder		[5,6,7]
specific conductivity				
at infinite dilution, $\Lambda^0$	119	108	S.m <sup>2</sup> .mol	-1 [8]
(de)hydration frequency	10 <sup>8</sup> -10 <sup>9</sup>	10 <sup>8</sup> -10 <sup>9</sup>	s-1	[9]
constant for $SO_4^2$ -	204	195-204		
complex formation		71		[10-14]
solubility of				
sulfate salt	2.10-2	6	molal	

The hydration enthalpy (a negative value) according to Marcus [2] is about 200 kJ/mol lower for Cd<sup>2+</sup> than for Ca<sup>2+</sup>. For the anhydrous salts, however, this difference is only about 30 kJ/mol according to Vieillard and Jenkings who gathered hydration enthalpies data of many types of salts [3]. They derived formulas from these data describing these enthalpies with a few parameters. Since these parameters are almost equal for Ca<sup>2+</sup> and Cd<sup>2+</sup>, the hydration enthalpies of Cd<sup>2+</sup> and Ca<sup>2+</sup> must be about the same, and the difference of 30 kJ/mol is probably typical for sulfates.

The Pitzer constants ( see appendix chapter 2) are also about equal for cadmium and calcium sulfate, which indicates similar hydration behaviour. The existence of more hydrated phases such as  $CdSO_4 \cdot {}^8/_3H_2O$  and  $CdSO_4 \cdot {}^7H_2O$  contrary to the highest hydration number of 2 in gypsum makes a stronger hydration of  $Cd^{2+}$  nevertheless more likely.

A difference in hydration behaviour is expected, because a higher electric field is induced by the smaller radius of  $Cd^{2+}$  and owing to its tendency to form slightly covalent bonds with preferential directions.  $Cd^{2+}$  ions in solution are surrounded by 6 H<sub>2</sub>O, while  $Ca^{2+}$ ions accomodate up to 10 H<sub>2</sub>O. The  $Ca^{2+}$  - H<sub>2</sub>O bond must therefore be weaker. Despite the smaller hydration number of a  $Cd^{2+}$  ion in solution, its specific conductivity and therefore its mobility is smaller than of  $Ca^{2+}$ . This might be caused by the more rigidly shaped hydration mantle of  $Cd^{2+}$ , but not by a difference in exchange rate of water molecules, since the (de)hydration frequencies are in the same order for both ions.

These data on hydration suggest that hydration of  $Cd^{2+}$  is somewhat stronger than of  $Ca^{2+}$ . This is in accordance with the much higher solubility of the sulfate salts of  $Cd^{2+}$ . Since the complexing constants for formation of sulfate complexes are equal to about 200 for  $Cd^{2+}$  and  $Ca^{2+}$ , this difference in solubility cannot be explained from the interaction with sulfate. The lower value of complex constant of 71 is probably erroneous. Leden and Hellwege [13,14] report multiple Cd-sulfate complexes. The overall complexation constants are  $\beta_{1\ 2\ 3} = 8$ , 10, 110 and 1.3, 10, 50 respectively ( see also the calculations with complexing constants in chapter 9). These constants are lower than the already mentioned value of 200 because in this higher value multiple complexation is included as if it were single complexation. Whether  $Ca^{2+}$  is also able to form multiple complexes cannot be verified because of the low solubility of the calcium sulfates.

The cadmium-sulfate complexes are not contact pairs, as has been concluded from the absence of a significant NMR shift in  $CdSO_4$ solutions [15]. This means that for incorporation of a  $Cd^{2+}$  ion dissociation of the complex has to take place. In solutions where the degree of complexation is higher, the uptake is then lower. If, however, also  $Ca^{2+}-SO_4^2$ - complexes are not contact pairs as well, this effect also cancels out. It is, however, despite the literature data [15], questionable whether the relatively strong complexes of  $Cd^{2+}$  and  $Ca^{2+}$  with  $SO_4^2$ - are not directly bonded.

Conclusively, the main difference between  $Ca^{2+}$  and  $Cd^{2+}$  probably lies in their hydration behaviour, but this cannot be quantified.

From the much higher solubility of cadmium sulfate, the product of activity coefficients in the solution and the thermodynamical solubility product is estimated to be much higher for  $CdSO_4$  than for  $CaSO_4$ , which gives a contribution of about  $10^{-5}$  to the D-value. Since, as mentioned, the other parameters cannot be estimated, the actual D-value may be different from this value, but will probably be lower than 1.

# 3.2.2 Kinetics

The incorporation of an impurity takes place at the surface. Uptake is therefore mostly influenced by surface processes as growth. Two extreme cases can be distinguished:

The first is that the growth rate is so high that any  $Cd^{2+}$  or  $Ca^{2+}$  near the crystal surface has an equal chance to become incorporated

with equal diffusion coefficients for these two ions. The resulting Dvalue is equal to 1. For  $Cd^{2+}$  in gypsum where D is smaller than 1 this means an increase with respect to the equilibrium situation, due to entrapment at the surface. For  $Cd^{2+}$  in  $CaCO_3$  on the other hand, where D is larger than 1 the uptake becomes lower [16] at increasing growth rates because the time available for adsorption restricts the amount of  $Cd^{2+}$  that can become attached to the surface and incorporated.

The second situation is equilibrium without growth, but with an exchange of ions between the solid state and the solution. Since this will only occur at a very large time scale, equilibrium partition coefficients can only be obtained by extrapolation to growth rate zero.

In practice, D will lie between the thermodynamical value and the value determined by the diffusion rates, i.e. approximately 1.

In the literature many examples are found of the dependency of uptake on the growth rate, e.g. for  $Ce^{3+}$  in  $K_2SO_4$  [17], for  $Fe^{3+}$  and  $Ce^{3+}$  in potassium acid phtalate [18], for  $Cd^{2+}$  in  $CaCO_3$  [16] (see also chapter 10), for  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Na^{2+}$  in gypsum [19] and for  $Mn^{2+}$  in  $CaCO_3$ [20]. For  $Cr^{3+}$  in  $K_2SO_4$  [21] the uptake was found to be not only dependent on the growth rate but also on the crystal face by which the growth takes place. Faces of  $K_2SO_4$  with D > 1 showed a decrease, and faces with D < 1 an increase in uptake at increasing growth rate. Earlier [22], using radiotracer techniques, funnel shaped concentration profiles of impurities in crystals have been shown, indicating a different uptake for the various crystal faces and therefore a kinetically determined uptake.

These examples show that the kinetical aspects have long been recognized. In the above mentioned examples, and also in studies done by Chernov [23], efforts are made to explain the trapping of impurities as a function of growth rate. For a proper explanation the reactions occuring during growth of the crystals and uptake should be considered for each case separately. By comparing the respective reaction rates of, in this case,  $Cd^{2+}$  and  $Ca^{2+}$  some prediction of the

kinetical behaviour of uptake may be done. The reactions that can be considered bulk diffusion, adsorption desorption, are surface diffusion, transport along a step, bonding at the kink site, or direct attachment from the solution. Since during these reactions dehydration occurs, the reaction rates are somehow related to well-known processes as ligand exchange, dehydration and diffusion. Nielsen [24] related the growth rate of electrolytes to the dehydration frequency of the cations. Such an approach might be applied to incorporation of  $Cd^{2+}$  or  $Ca^{2+}$  in calcium sulfate. The (de)hydration frequencies of these ions are, however, about equal ( see table 3.1) so there is no reason to expect special effects. A further refinement could involve the mechanism of exchange of water ligands, which can be either dissociative or associative. Merbach [9] makes this distinction on the basis of exchange rate measurements as a function of pressure. If rate increases with pressure, formation of the the activated intermediate complex induces a decrease in volume and therefore in hydration number of the complex (dissociative). An associative exchange means that the hydration number of the activated complex is higher. A dissociative mechanism possibly makes the uptake in the crystal lattice easier, since during incorporation the coordination of the cation changes from 6-10 H<sub>2</sub>O in solution to 2H<sub>2</sub>O and 4 sulfates in the lattice (see chapter 10). It is, however, unknown whether the exchange of  $H_2O$  of  $Cd^{2+}$  and  $Ca^{2+}$  takes place according to a dissociative or an associative mechanism because this has not been measured yet and this can not be estimated from the chemical properties of these ions. Perhaps experiments with ions as Fe<sup>2+</sup>, Fe<sup>3+</sup> and other transition elements for which the exchange mechanism has been measured [9] can give a clue. Conclusively, it can only be remarked that for an explanation of observed uptake values based on molecular reactions more data are needed.

### 3.3. Experimental

# 3.3.1 Constant composition suspension growth

These experiments have been detailed in chapter 2.  $Cd^{2+}$  was added as nitrate to each solution in concentrations of  $5\cdot 10^{-4}$  to  $10^{-2}$  M. In some experiments the outgrowth of the crystals occured partly in absence of  $Cd^{2+}$ .

#### 3.3.2 Continuous crystallization

These were performed by computer controlled simultaneous addition of 1 M Ca(NO<sub>3</sub>)<sub>2</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub> both containing  $10-^3$  M Cd<sup>2+</sup>, to a 1 liter crystallizer. By continuous, unclassified withdrawal of slurry (10% solids), the level was kept constant. The level control was achieved by conductivity measurement with two platinum wires hung partly in the solution. The signal of the conductivity meter controls, with an adjustable hysteresis, the peristaltic withdrawal pump. The total reaction time was 10 residence times, each lasting 15 to 180 minutes. The equipment is further described in chapter 4. In some experiments also lanthanides were added to the solution for purposes not described in this thesis.

#### 3.3.3 Precipitation experiments

Here 300 ml of a  $Ca(NO_3)_2$  and 300 ml of a  $Na_2SO_4$  solution of varying concentrations were added simultaneously to 300 ml of a  $NaNO_3$  solution. The addition rate ranges from 0.1 to 1 ml/min per solution.

# 3.3.4 Sampling and analysis

Samples were taken from the solutions and filtered over a G4 glass filter. The solutions were diluted about two times to prevent precipitation. The crystals were washed three times with a saturated gypsum solution in the corresponding electrolyte, and three times with a saturated gypsum solution in water. Solution and crystals were analysed by ICP or INAA (instrumental neutron activation analysis). The Ca<sup>2+</sup> concentration was sometimes determined by EDTA titration.

### 3.3.5 Adsorption experiments

These experiments were done using <sup>109</sup>Cd as a tracer to allow very low concentrations to be measured. To a solution of  $10^{-9} - 10^{-7}$  M <sup>109</sup>Cd<sup>2+</sup> in H<sub>2</sub>O up to 10 w% gypsum (Merck, p.a.) was added and left for a period up to several days. After filtration the residual <sup>109</sup>Cd<sup>2+</sup> concentration was measured by counting.

# 3.4. Results and discussion

#### 3.4.1. Precipitation experiments

These experiments have been performed to obtain a first insight on the effect of supersaturation, stoichiometry, pH and temperature upon the cadmium uptake. The cadmium concentration in the crystals is expressed as a distribution coefficient K(Cd), defined by:

$$K(Cd) = \frac{[Cd^{2+}]}{[Cd^{2+}]} \quad (crystal) \quad (3)$$

The conditions and the resulting Cd-uptake are given in table 3.2. In table 3.2 the composition and rates of the feed streams are listed as well as of the starting solutions. The resulting concentrations in the solution have not been analyzed. Only the  $Cd^{2+}$  concentrations in the crystals and in the solutions were measured. Their ratio, K(Cd), is also given in the table.

In exps. 1 and 2 the feed rate was 0.1 and 1.0 ml/min respectively. The higher rate resulted in a 2.5 times higher uptake. This is an indication that supersaturation plays a role in the cadmium uptake, as has also been reported earlier [25,26,27,28].

exp.	strea [Na <sub>2</sub> SO <sub>4</sub> ][]	m 1 NaNO <sub>3</sub> ]	stream [Ca(NO <sub>3</sub> ) <sub>2</sub> ][	2 NaNO <sub>3</sub> ]	feed rate stream	start [NaNO <sub>3</sub> ]	remark	K(Cd)
_	(M)	(M)	(M)	(M)	ml/min	(M)		
1	0.5	0	0.5	0	0.1	0.5	low rate	0.10
2	0.5	0	0.5	0	1.0	0.5	high rate	0.26
3	0.2	0.8	0.2	0.8	1.0	1.0	standard*	0.10
4	0.2	0.6	0.4	0.8	1.0	1.0	Ca>S04	0.13
5	0.4	0.8	0.2	0.6	1.0	1.0	Ca <so<sub>4</so<sub>	0.23
6	0.2	0.8	0.2	0.8	1.0	1.0	pH = 1,no	pre-
							cipit	ation
7	0.2	0.8	0.2	0.8	1.0	1.0	pH = 2	0.16
8	0.2	0.8	0.2	0.8	1.0	1.0	pH = 3	0.07
9	0.2	0.8	0.2	0.8	1.0	1.0	pH = 4	0.07
10	0.2	0.8	0.2	0.8	1.0	1.0	pH = 6.3	0.09
11	0.2	0.8	0.2	0.8	1.0	1.0	$T = 35^{\circ}C$	0.10
12	0.2	0.8	0.2	0.8	1.0	1.0	$T = 45^{\circ}C$	0.12
13	0.2	0.8	0.2	0.8	1.0	1.0	$T = 60^{\circ}C$	0.24

Table 3.2. Cd-uptake in precipitation experiments

\* further conditions are: pH = 5,  $T = 25^{\circ}C$ .

In the other experiments a background concentration of 1 M NaNO<sub>3</sub> was applied. The Ca<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup> content was about 0.2 M to limit the supersaturation while maintaining a high feed rate. In this way it is possible to vary the pH and the stoichiometry without affecting the ionic strength too much.

In the standard experiment, nr. 3, a solution containing 0.2 M  $Na_2SO_4$ and 0.8 M  $NaNO_3$  is added simultaneously with a 0.2 M  $Ca(NO_3)_2$  / 0.8 M  $NaNO_3$  mixture both with a rate of 1.0 ml/min to the reactor prefilled with 1 M  $NaNO_3$  solution. The produced crystals are long flat needles up to 1 mm long. K(Cd) is 0.1, from which it can be calculated that the decrease in Cdconcentration of the crystallizing solution due to uptake is negligible. The D-value is about 10-3, which is comparable to the value in phosphoric acid (chapter 6).

In exps. 4 and 5 the feed streams are not stoichiometric but contain excess  $Ca^{2+}$  and  $SO_4^2$ - respectively. With excess  $Ca^{2+}$  K(Cd) equals 0.13. D can not be calculated because the  $Ca^{2+}$  concentration in the solution is not known but since  $[Ca^{2+}]$  is probably higher than in standard exp. 3, the D-value is higher than in exp. 3. From the lower  $[Cd^{2+}]/[Ca^{2+}]$ ratio in solution a lower D-value is expected. This higher D-value can thus only be explained by a kinetical effect through the higher supersaturation caused by growth retardation under these nonstoichiometrical conditions. A high D-value at high  $Ca/SO_4$  ratios was also found in phosphoric acid [29].

In exp. 5, with excess  $SO_4^2-$ , K(Cd) is 0.23. Again D can not be calculated, but from exps. 4 and 5 it can be concluded that the stoichiometry has an effect on the observed Cd-uptake.

At pH 1 no precipitation occurs. This is due to the high solubility (0.06 M) of gypsum (see fig. 3.1.) which makes the supersaturation too low (about 10%) to cause nucleation within two days. The higher solubility is due to formation of  $HSO_4$  with a pK value of about 2. At a pH of 2-4, K(Cd) decreases from 0.16 to 0.07, while at a pH of 5 and 6.3 the K-values are almost equal (~ 0.10). The K-value of 0.16 at pH 2 implies a higher D-value than at pH 5, since with an unaltered D K(Cd) would be lower due to the higher solubility at this low pH. It requires additional experiments under better defined conditions to explain this higher uptake.

In exp. 3 and 11-13 the temperature varies from 25 to  $60^{\circ}$ C, yielding an increase in K(Cd) from 0.10 to 0.24. Since the slightly lower solubility at higher temperature can lead to higher supersaturations, this might be partly a kinetical effect. It is on the other hand also



Figure 3.1. Solubility of gypsum at 25  $^{\rm o}C$  as a function of pH in several NaNO3 solutions

possible that a change in activity coefficients causes this higher uptake.

Since in these experiments the conditions during growth are not well defined and not constant, it is necessary to conduct other types of experiments that provide more information. The constant composition experiments will be discussed first, followed by the continuous crystallization experiments. The adsorption of  $Cd^{2+}$  will be treated separately.

# 3.4.2 Constant composition experiments

3.4.2.1 Influence of supersaturation and electrolyte concentration.

These experiments have been described in more detail in the previous chapter. Variables are the relative supersaturation  $\sigma$  (defined in chapter2, eq. 2.1), the electrolyte concentration and the temperature. In fig. 3.2 the uptake of Cd<sup>2+</sup> as D(Cd) is plotted versus  $\sigma$  for solutions of 0-1 M NaNO<sub>3</sub> and 0.1 M NaClO<sub>4</sub>. D(Cd) increases linearly with  $\sigma$  from about 3-8  $\cdot$  10-<sup>4</sup> at low  $\sigma$  (0.05 - 0.10) to 5  $\cdot$  10-<sup>3</sup> at  $\sigma$  =

1.8. The latter high  $\sigma$ -value is only obtained in 0.3 M NaNO<sub>3</sub> solution. In less concentrated solutions the relatively low Ca<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup> concentrations in the feed streams limits the maximally attainable supersaturation when they are mixed, while in stronger NaNO<sub>3</sub> solutions excessive nucleation prevents application of such high  $\sigma$ -values. The higher uptake at high  $\sigma$ -values is in accordance with a model where Cd<sup>2+</sup> is entrapped on the gypsum surface.

The relative supersaturation  $\sigma$  is, however, not a proper measure for the rate of growth. Instead the linear growth rate should be taken but since in these experiments only overall growth rates are obtained, expressed as the relative increase of mass per second,

d (m(t)/m(t=o)) /dt (eq. 2.3, chapter 2), the exact linear growth rate is not known. The overall growth rate R is proportional to the linear growth rate  $R_{lin}$  only if the geometry is retained during outgrowth. This assumption is found to be qualitatively true for the experiments after sufficient outgrowth of the seed crystals. This means that the overall growth rate is more or less a measure for the linear growth rate.

For the given crystals an R-value of  $10^{-2}$  s<sup>-1</sup> corresponds with a mean linear growth rate of  $3 \cdot 10^{-8}$  m.s<sup>-1</sup>, based on spherical crystals. For the platelets formed here a deviation of a factor 10 is possible for the various crystal faces.

Bearing in mind this possible source of error, the overall growth rate R has been used as a measure for the linear growth rate by lack of an alternative. In fig. 3.3 D(Cd) is plotted as a function of R in 0.1, 0.3 and 1.0 M NaNO<sub>3</sub> solutions. The curve rises steeply at low R-values to become almost flat at higher growth rates. Without more quantitative data on the rate determining steps in the process of incorporation and growth of the various crystal faces it is not possible to give a proper explanation for the shape of the curve. Kushnir [19], who found similar shapes for the uptake of  $Mg^{2+}$  in gypsum, suggests that a limiting value for the partition coefficient is caused by a competition between foreign ions and  $Ca^{2+}$  for the



Figure 3.2. Partition coefficient of  $Cd^{2+}$  in gypsum versus relative supersaturation in various solutions at 25 °C.

available adsorption sites. At extremely high growth rates the number of available sites for the foreign ion then decreases. Whether this limiting value lies at the observed flat part of the D-R curve can not be estimated. At very high growth rates a D(Cd) of 1 is expected. The D-value seems to be 2 times higher in 0.3 and 0.1 M NaNO<sub>3</sub>. If this small difference by a factor 2 is be due to differences in surface reaction or adsorption/desorption rate, measurements of the uptake of  $Cd^{2+}$  by the (hkl) crystal faces separately as a function of linear growth rate will probably be needed to unravel the mechanism of the kinetical effect of electrolyte concentration. If on the other hand this difference in uptake is imposed by the thermodynamics, also the



Figure 3.3. Partition coefficient of  $Cd^{2+}$  as a function of overall growth rate at 25 °C, in solutions of 0.1 M NaNO<sub>3</sub> (o), 0.3 M NaNO<sub>3</sub> (x) and of 1 M NaNO<sub>3</sub> (o).

uptake at zero growth rate should be different for the various electrolyte solutions. Assuming that extrapolation is allowed, the equilibrium D-value probably lies between  $3 \cdot 10^{-4}$  and  $10^{-3}$  in the various solutions. The lower values are obtained from 0, 0.1 M NaNO<sub>3</sub> or 0.1 M NaClO4 while the higher values result from experiments in 0.3 or 1.0 M NaNO<sub>a</sub>. This difference in D-value can partly be explained by the faster increasing activity coefficient  $\gamma$  of Cd<sup>2+</sup> with respect to Ca<sup>2+</sup> with increasing NaNO<sub>3</sub> concentration. These  $\gamma$ -values are calculated with the Pitzer equations (see appendix chapter 2). The other part might be due to an error in the extrapolation of the D-σ curve. Such an error can be reduced by applying another method of crystallization, allowing extremely low supersaturations be to This can be done by slowly evaporating a small part of a applied. large volume of saturated gypsum solution containing Cd<sup>2+</sup> with a very small amount of gypsum seed crystals. Since evaporation can be well controlled by leading e.g. a thermostated dry air or  $N_2$  flow through the solution this method should work.

### 3.4.2.2 Influence of temperature

In a few constant composition experiments the temperature was higher than  $25^{\circ}$ C. The conditions and the resulting growth rates (see previous chapter) and D(Cd) values are given in table 3.3. For comparison some experimental data at  $25^{\circ}$ C are listed. All experiments are done in a 1 M NaNO<sub>3</sub> solution.

T (°C)	σ	R (10- <sup>3</sup> s- <sup>1</sup> )	D(Cd) (10- <sup>3</sup> )
25	0.15	0.8	1.2
25	0.30	1.6	1.2
25	0.50	3.1	1.9
25	0.70	6.0	1.8
25	0.90	1.6	2.0
35	0.15	1.0	1.1
45	0.07	1.0	1.8
60	0.33	10	3.3

Table 3.3. Influence of temperature

At comparable supersaturations the D-value is higher for 45 and  $60^{\circ}C$  than for 25°C. Since the growth rate also increases with temperature. comparison of the uptake at the same growth rate is more realistic. At 45°C with  $\sigma = 0.07$  the growth rate is almost equal to that obtained at 25°C with  $\sigma = 0.15$ , but the D-value is 1.5 times higher. Also the higher uptake at 60 °C is only partly caused by the higher growth rate. This can be concluded from the only weak dependance of uptake on the growth rate in this range.

This temperature effect can be either kinetical or thermodynamical. If the effect were entirely thermodynamical, the change in uptake as a function of temperature is expected to be more gradual because of the exponential term in eq. 2. A reasonable value for the sum of the energies in the exponential term would then be about 20 kJ/mol, as can be calculated from the temperature dependancy of the uptake. A kinetical effect may include a change in the growth mechanism and thus in incorporation.

The acquired D(Cd) values agree with the K(Cd) values of the precipitation experiments (table 3.2). The corresponding K-values of these constant composition experiments are approximately 0.1, 0.2 and 0.3 at 35, 45 and 65°C respectively. This accordance in K-values means that the D-values are also not much different. Therefore, the thermodynamical effect seems to be rather dominant, since it is unlikely that the kinetics are exactly the same in the constant composition as in the precipitation experiments. To investigate the thermodynamical and kinetical effects separately, experiments should be performed at these higher temperatures at various supersaturations, including very low ones, so that again by extrapolation the D-value at equilibrium at higher temperatures can be determined as well as the dependance on the growth rate.

# 3.4.2.3 Effect of higher Cd<sup>2+</sup>-concentrations

It is crucial to know whether the data obtained for Cd-uptake are also valid when higher concentrations are present in the solution. The Cdconcentration can affect the activities of all ions in both solution and solid. This could lead to other observed D-values according to eq. 2.

By complexation and an ionic strength effect the calcium sulfate activity and therefore the driving force for growth of gypsum may also change. By specific interaction with sulfate the effective stoichiometry changes. In the solid the activities of ions can change when there are foreign ions present in the lattice. At high concentrations (> few %) formation of Cd neighbour pairs could alter the bond types in the gypsum lattice.

A gradual decrease in K(Cd) from 48 to 35 has been observed for recrystallization of calcium sulfate hemihydrate into anhydrite from concentrated phosphoric acid/sulphuric acid at  $90^{\circ}$ C, when the Cdconcentration in solution was increased from  $3 \cdot 10^{-5}$  to  $3 \cdot 10^{-2}$  mol per kg solution. This type of experiment is described in chapter 6. The crystals contained up to several percents of Cd<sup>2+</sup>. Since the solution composition in those experiments was hardly affected by Cd<sup>2+</sup>, this effect was probably due to the altered composition of the solid state. Since the decrease in K-value in AH seems not so drastic, the influence of the Cd-content in the solid on the partition coefficient in gypsum is also not suspected to be large. Especially in systems with a low partition coefficient such as counts for Cd<sup>2+</sup> in gypsum, effects of concentration are mainly imposed through the solution.

Addition of  $Cd(NO_3)_2$  was compensated for by a reduction in  $NaNO_3$  or  $NaClO_4$  to an extent that the total concentration background electrolyte remained constant at the chosen value.

Due to complexation with  $SO_4^2-$ , addition of  $Cd^{2+}$  (as  $Cd(NO_3)_2$ ) in 0.1 M NaClO<sub>4</sub> leads to an enhanced solubility of gypsum.

With  $4.10^{-4}$  M Cd<sup>2+</sup> the solubility is  $2.09 \cdot 10^{-2}$  M CaSO<sub>4</sub>, while with  $9.10^{-3}$  M Cd<sup>2+</sup>  $2.33 \cdot 10^{-2}$  M calcium sulfate is dissolved. It could be calculated that using the complexation constants for Cd<sup>2+</sup> - SO<sub>4</sub><sup>2</sup>- (K  $\approx$  200) and Ca<sup>2+</sup> - SO<sub>4</sub><sup>2</sup>- (K  $\approx$  200) the product of free Ca<sup>2+</sup> and SO<sub>4</sub><sup>2</sup>- is equal with and without Cd<sup>2+</sup>. Application of Pitzer equations yield a similar result.

The growth rate is not affected by  $Cd^{2+}$ , provided that the higher solubility is taken as equilibrium value. For a solution containing 2.94·10-<sup>2</sup> M CaSO<sub>4</sub> the relative supersaturation  $\sigma$  is  $\frac{2.94 \cdot 10^{-2}}{2.33 \cdot 10^{-2}} = 0.26$ 

and not  $\frac{2.94 \cdot 10^{-2}}{2.09 \cdot 10^{-2}} = 0.41$ . The observed growth rate is  $\frac{d m(t)/m(o)}{dt} = 11 \cdot 10^{-5}$  s<sup>-1</sup>, which is a reasonable value (see previous chapter) for  $\sigma = 0.26$ , and which would have been much too low for a  $\sigma$  value of 0.41.

Apparently the effect of  $Cd^{2+}$  on the growth rate only works through the complexation with  $SO_4^2$ -. For the low cadmium concentration applied in the former sections its influence on the growth rate was negligible.

The reason of this experiment was to verify whether k-values for Cduptake were not concentration dependent. The D-value of  $4.7 \cdot 10^{-4}$  is similar to those obtained from  $10^{-4}$  M Cd<sup>2+</sup> containing solution. A concentration effect is therefore likely to be absent in the given range.

3.4.2.4 Effect of initial surge in outgrowth curve.

Since the uptake is a strong function of the growth rate, one may wonder whether the initial fast growth as it occurs in each experiment (see previous chapter) leads to excessive Cd-uptake and possibly obscures the real D-value.

For experiments with an outgrowth factor of 50 this is not likely, but for the experiments in pure water and 0.1 M NaClO<sub>4</sub> with only a small outgrowth (2-3 times) such effect may play a role.

For this reason experiments have been performed where during the first phase of growth no  $Cd^{2+}$  was present in the solution.

In some of these experiments gypsum was grown ( $\sigma = 0.15$ ) to approximately 150% of the original mass in a Cd-free environment (0.1 M NaClO<sub>4</sub>), followed by growth to about 300%. The resulting D-value, corrected for the Cd-free seed crystals was  $3.0 \cdot 10^{-4}$ . A similar experiment, but with Cd<sup>2+</sup> present in the solution during the whole outgrowth, yielded D =  $3.6 \cdot 10^{-4}$ .

Apparently the uptake is slightly higher during the initial fast outgrowth, but not so much as to make a correction necessary. For this reason all other experiments were performed in solutions containing cadmium from the start.

#### 3.4.3 Continuous crystallization experiments.

The crystals obtained from continuous crystallization experiments with a residence time of 30 minutes are agglomerates of platelets of a few hundred  $\mu$ m maximal. In principle the growth rate can be calculated from the crystal size distribution CSD (see chapter 7), but with such agglomerates the physical meaning of the CSD is not straightforward. Variations have been made in the Ca<sup>2+</sup> over SO<sub>4</sub><sup>2</sup>- ratio in the crystallizing solution and in the mean residence time. In two other experiments a mixture of lanthanides was added for a purpose not described here, but since also Cd<sup>2+</sup> was added D(Cd) is reported here. In table 3.4 the conditions and results are listed.

From table 3.4 it can be concluded that:

- a longer residence time gives rise to a lower D-value;
- non-stoichiometry influences the K-value, but has hardly an effect on D(Cd);
- presence of lanthanides does not affect D(Cd).

The lower uptake at longer residence times can be explained by a lower supersaturation due to the lower feed rates. This supersaturation, however, could not be determined very accurately because of the lack of very accurate  $Ca^{2+}$  and  $SO_4^2$ - analyses in concentrated electrolyte solutions. Therefore the  $\sigma$ -values in table 3.4 are not very reliable, but are merely an indication of the  $\sigma$  range. The D-values around  $10-^3$ correspond with those in constant composition experiments for  $\sigma$ -values up to 0.40. The higher D-value of  $3.10-^3$  at 900 s residence time corresponds with a  $\sigma$  of at least 0.50 in constant composition experiments, which is higher than the measured but probably erroneous  $\sigma$  value of 0.19.

Variation in stoichiometry has some effect on the D-value, probably through the growth kinetics. When the  $Ca^{2+}$  over  $SO_4^2-$  ratio changes from 0.3 to 2 D(Cd) decreases from 1.5 to 1.0, while K(Cd) goes from 0.25 to 0.09. This greater effect on K points at a competition between  $Ca^{2+}$  and  $Cd^{2+}$ , which was also found for crystallization of calcium

residence time (10 <sup>3</sup> s)	[Ca <sup>2+</sup> ] (M)	[S0 <mark>4</mark> -] (M)	σ	K(Cd)	D(Cd) (10- <sup>3</sup> )
7.2	0.090	0.030	0.08	0.05	0.8
7.2*	0.065	0.055	0.25	0.14	1.2
1.8	~ 0.06	~ 0.06		0.20	~ 2.0
1.8	0.035	0.030	0.35	0.25	1.5
1.8	0.08	0.030	0.19	0.09	1.0
1.8*	0.067	0.030	0.26	0.15	1.3
0.9	0.067	0.030	0.19	0.32	3.0

Table 3.4. Conditions and results of continuous crystallization experiments

\* with lanthanides

sulfate from phosphoric acid solutions (chapter 4, 5).

The drastic effect of lanthanides on the growth kinetics are described in the chapters 6 and 7. Due to a strong adsorption onto the growing surface they hamper the growth at low supersaturations. The Cd uptake is apparently not affected. This may be caused by the fact that lanthanides are not so effective at these supersaturations, but it is more likely that the D-value of about 10-3 is close to thermodynamical equilibrium and can hardly be influenced by growth retarding agents.

# 3.4.4 Adsorption experiments

The amount of gypsum was up to 10 w% in the slurry, while the  ${}^{109}Cd^{2+}$ -concentration was varied from  $10-{}^9$  to  $10-{}^6$  M. Assuming that  $5.10^{18}$  adsorption sites per m<sup>2</sup> gypsum are available, and a specific surface area of 0.5 m<sup>2</sup> per gram of gypsum, the number of sites was  $2.5 \cdot 10^{20}$  per kg suspension. This means that the surface coverage could be  $10-{}^9 \cdot 6.10^{23} = 2.4 \cdot 10-{}^6$  at the lowest Cd<sup>2+</sup> concentration. Since no

decrease in  $Cd^{2+}$  concentration was detected on the addition of gypsum, the surface coverage is less than  $10-^6$ .

This absence of adsorption can be explained from the large number of  $SO_4^2$ - ions in the solution competing with those at the surface for the available  ${}^{109}Cd^{2+}$  ions. In the solution  $1.5 \cdot 10^{-2} \cdot 6 \cdot 10^{23} = 9 \cdot 10^{21} SO_4^2$ - ions are present, which is more than thirty times the number of available sites at the surface.

Since no adsorption of  $Cd^{2+}$  on gypsum could be detected in the whole range of conditions it has to be concluded that the affinity of  $Cd^{2+}$ to the crystal surface is not greater than its interaction with the saturated gypsum solution.

Apparently the energy gain on adsorption is not much greater than the complexing energy with  $SO_4^2$  – in the solution. All  $Cd^{2+}$  that is incorporated during crystal growth is just statistically present at the surface without preferential adsorption.

#### 3.5. Conclusions

- The incorporation of Cd<sup>2+</sup> in gypsum is determined by thermodynamical and kinetical parameters. The D-value increases from  $3-8\cdot10-^4$  at a low relative supersaturation  $\sigma$  to  $5\cdot10-^3$  for  $\sigma = 1.5$  in 0.3 M NaNO<sub>3</sub>. At a given growth rate the uptake is higher in solutions with a higher NaNO<sub>3</sub> concentration, partly due to a higher activity coefficient of Cd<sup>2+</sup> in the solution.
- The D-values in  $NaNO_3$  solutions are almost equal to those in  $H_3PO_4$  at higher temperatures.
- Results of precipitation experiments, constant composition and continous crystallization experiments are in reasonable agreement.
- At a given supersaturation the Cd-uptake increases with temperature.
- The effect of higher  $Cd^{2+}$  concentrations in the solution is mainly imposed by complexation with  $SO_4^2-$ , but at high uptake an effect through the solid is expected, just as for  $Cd^{2+}$  uptake by anhydrite.

- The affinity of  $Cd^{2+}$  for  $SO_4^2-$  at the crystal surface is not larger than for  $SO_4^2-$  in the solution.
- 3.6. References.

<ul> <li>[2] Y. Marcus, Vhem. Soc. Far. Trans. I, <u>83</u> (1987) 339-49.</li> <li>[3] P. Vieillard and H.D. Jenkins, J. Chem. Res. (M) (1986) 3701-</li> <li>[4] K.S. Pitzer and G. Mayorga, J. Sol. Chem. <u>3</u> (1974) 539-46.</li> <li>[5] J.P. Hunt and H.L. Friedman, Prog. Inor. Chem. <u>30</u> (1983) 359-</li> <li>[6] N.A. Hewish, G.W. Nelson and J.E. Enderby, Nature <u>297</u> (1987)1</li> <li>[7] S. Aslanian and C. Balarew, Kristall und Technik <u>12</u> (1977)435</li> <li>[8] P.H. Rieger, Electrochemistry, Prentice Hall (1987)</li> <li>[9] A.E. Merbach, Pure &amp; Appl. Chem. <u>59</u> (1987) 161-72.</li> <li>[10] K.B. Yatsimirskii and V.P. Vasitey Instability constant</li> </ul>	-69. -87. -38-9 5-46.
complex compounds. Pergamon Press 1960.	
[11] J. Kragten, Atlas of Metal-Ligand equilibrium in aqu solution. Ellis Horwood Ltd., Chichester.	ieous
[12] H.L. Schlafer, Complexbildung in Losung, Springer Verlag 1961	
[13] I. Leden, Acta Chem. Scand. <u>6</u> (1952) 971-87.	
[14] H.E. Hellwege and G.K.J. Schweitzer, J. Inorg. Nucl. Chem. <u>27</u> (1965) 99-104.	
[15] H. Kruger, O. Lutz, A. Schwenk, G. Strieker,	
Z. Physik. <u>266</u> (1974) 223-37.	
[16] R.B. Lorens, Geochim. Cosmochim. Acta <u>45</u> (1981) 553-61.	
[17] I.V. Melikhov, Growth of Crystals, <u>11</u> (1979) 309-21.	
[18] M. Hottenhuis, Thesis, Nijmegen Catholic University,	The
Netherlands, 1988.	
[19] J. Kushnir, Geochim. Cosmochim. Acta <u>44</u> (1980) 14/1.	
[20] W. Heijnen, Thesis, Utrecht State University, The Netherla	inds,
[21] Z.I. Zhumurova, V.I. Khaimov-Malkov, K.S. Bagdasarow,	
E.M. Akulenok, Adsorption et Groissance Gristalline, R. Kern	ea.
UNKS PARIS (1903) 329	
[22] N.A. bonner and M. Kann In: Radioactivity applied to chemistr	у,
Eus. A.C. wain and N.A. bonner, John writey Sons, N V 1051 $p$ 102,178	
N.I. 1991, P. 102-170 [23] Charney A A Modern Crystallography III:Crystal Gro	wth
[25] Unernov, A.A., Modern Orystallography intorystal of	wen,
[26] A F Nielsen and I M Toft I Crystal Growth 67 (1984) 278-8	 1 R
$[24]$ A.E. Miersen and S.H. 1910, S. Orystar Growth $\underline{o_{f}}$ (1904) 270 c [25] T.T. Tijoe H. van der Woude J. Verbiest P.F.M. Durville	
and G M, van Rosmalen, Cryst. Res. Techn. 21 (1986) 1287-97	
(26) C. Rinaudo, M. Franchini-Angela and R. Boistelle. J. Cryst.	
Growth 89 (1988) 257-66.	
[27] chapter 4.	
[28] chapter 6.	
[29] G.J. Witkamp and G.M. van Rosmalen, abstract submitted to	ACS
symposium on PACICHEM '89, December. Honolulu, Hawaii.	

#### CHAPTER 4

### CONTINUOUS CRYSTALLIZATION OF HEMIHYDRATE IN PHOSPHORIC ACID

### Abstract

In a continuous crystallization procedure calcium sulfate hemihydrate (HH) crystals were formed by feeding a calcium dihydrogen phosphate (CDHP) solution in concentrated phosphoric acid (5.6 and 6.6 mol  $H_3PO_4$ per kg), simultaneously with a sulfuric acid solution, into a 1 litre crystallizer at 92°C. The slurry removal occurred unclassified. Residence times of 20 to 80 min were maintained. The solid over liquid weight ratio depended on the calcium content of the CDHP solution. By slight adjustment of the feed streams the molar calcium over sulfate ratio in the solution was varied between about 0.05 and 8. A cadmium concentration of 30 ppm was maintained in the crystallizing solution. of the HH crystals varied with increasing sulfate The shape concentrations from mainly aggregates to mainly needles. During crystallization of the HH crystals, cadmium as well as phosphate ions are incorporated into the lattice. The degree of uptake strongly depends on the operating conditions. The phosphate uptake decreases with increasing sulfate concentrations in the crystallizer, while the cadmium uptake increases. The molar phosphate over sulfate ratio in the crystals is found to be proportional to the same ratio in the solution. A comparable linear relationship is also observed for the molar cadmium over calcium ratios at a residence time of 20 min. At high sulfate concentrations. long residence times and high temperatures (about  $92^{\circ}C$ ), the stable anhydrite modification (AH) tends to develop next to the metastable HH phase. The cadmium uptake in AH is at least 10 times higher than in HH, while the phosphate uptake is not influenced by a small amount of AH in the crystals. The cadmium incorporation in the HH lattice can be reduced by adding halogenides to the solution.
During the production of phosphoric acid for fertilizer applications, huge amounts of calcium sulfate are precipitated as a by-product. This by-product not only tends to incorporate phosphate ions, but also cadmium ions, originating from the phosphate ore [1, 2]. Uptake of phosphate lowers the efficiency of the process [3], while the incorporation of cadmium hampers the disposal of the by-product due to environmental restrictions. In order to obtain hydrated calcium sulfate with a low cadmium and phosphate content from concentrated phosphoric acid, a new process has been developed.

In this process [4] a clear calcium dihydrogen phosphate (CDHP) solution is obtained by digestion of the phosphate ore (fluoroapatite) in recycled phosphoric acid, enabling the removal of  $Cd^{2+}$  ions by, e.g. ion exchange [5]. Thereafter the major amount of calcium sulfate hemihydrate is precipitated from the CDHP solution by adding sulfuric acid. The incorporation of phosphate ions and of the remaining cadmium ions during this crystallization has to be minimized. The amount of foreign ions incorporated largely depends on the operating conditions, given by the  $H_3PO_4$  and  $H_2SO_4$  content of the solution, the temperature, and the supersaturation, which is, in our experiments, in its turn determined by the residence time and the solid over liquid weight ratio. Also, impurities originating from the ore or purposely added components affect the uptake of foreign ions by calcium sulfate. Components which are able to coordinate the cadmium ions in solution, like, e.g., halogenides [6,7], reduce the cadmium uptake. The nature of the precipitated calcium sulfate phase also influences the uptake of foreign ions. Depending on the temperature and the  $H_3PO_4$  and H<sub>2</sub>SO<sub>4</sub> content of the solution either calcium sulfate dihydrate (DH). hemihydrate (HH) or anhydrite (AH) will be formed [8], as shown in figure 4.1.

The solid lines in fig. 4.1 represent equilibrium curves, but since some of the modifications are metastable under the given conditions, these lines merely indicate which phase will initially precipitate.



Figure 4.1. The precipitated calcium sulfate phase as a function of the  $H_3PO_4$  content and temperature of the solution. Note that HH only exists as a metastable phase, and that AH is stable in a wide range of conditions. Our working conditions are indicated with a + sign.

The broken line in figure 4.1 separates the regions where either DH or AH is stable. The HH phase only exists as a metastable phase. The influence of  $H_2SO_4$  on the position of the curves in fig. 4.1 can be taken into account by assuming 1 mol of  $H_2SO_4$  to be equivalent with about 1.5 mol of  $H_3PO_4$  [1]. The working conditions in our process, where HH is produced, are indicated in figure 4.1.

The aim of the present study is to investigate the incorporation of both phosphate and cadmium ions in HH as a function of the above mentioned operating conditions during continuous crystallization. In addition a start has been made with the investigation of the influence of halogenides on the incorporation of cadmium ions.

## 4.2. Experimental

In all experiments chemically pure  $H_3PO_4$ ,  $H_2SO_4$ ,  $3CdSO_4 \cdot 8H_2O$  and ammonium halogenides were used. The CDHP solution was prepared by dissolving CaCO<sub>3</sub> in a concentrated  $H_3PO_4$  solution at about 92°C. The calcium content of the CDHP solution is restricted by its solubility and was about 1 mol/kg in a solution containing 5.6 mol H<sub>2</sub>PO<sub>4</sub>/kg 55 wt%  $H_3PO_4$ ) and approximately 0.6 mol/kg in a solution containing 6.6 mol  $H_3PO_4/kg$  (65 wt%  $H_3PO_4$ ). The CDHP solutions contained 3 x 10-4 mol  $Cd^{2+}/kg$ , which is the same as in the crystallizer. Concentrated sulfuric acid was added in the experiments where a solution containing 5.6 mol  $H_3PO_4/kg$  was fed into the crystallizer, while a solution containing 1.7 mol  $H_2SO_4/kg$  and 5.4 mol  $H_3PO_4/kg$  was added in experiments with 6.6 mol  $H_3PO_4$  per kg solution in the crystallizer. Fig. 4.2 shows the experimental arrangement. The 1 litre glass doublewalled crystallizer was provided with a six bladed polyvinylidenefluoride (PVDF) turbine stirrer. The CDHP and the sulfuric acid inlet tubes, as well as the drain outlet tube, served as baffles. The power input, generated by the stirrer, was calculated from the stirrer speed, the slurry density, and the geometry of both vessel and stirrer [1], and was normally approximately 1  $kW/m^3$  (stirrer speed 640 rpm). The supply vessels as well as the crystallizer were thermostated at about  $92^{\circ}C$  except the supply vessel for concentrated  $H_2SO_4$ , which was kept at room temperature. Peristaltic pumps were used, equipped with marprene or viton tubes.

At the start of each experiment, the crystallizer was filled with a solution of the desired composition and the requisite amount of HH from a former experiment. The continuous crystallization was performed by simultaneous addition of the CDHP solution and the sulfuric acid solution to the crystallizer. The slurry volume in the reactor was kept constant by continuous, unclassified, removal of slurry from the crystallizer. The residence time of the slurry, defined as the reactor volume divided by the slurry volume stream, was varied in the experiments from 20 to 80 min.

In each experiment a steady state was obtained after 8 to 10 residence times. For experiments were no HH was initially added, a longer runtime appeared to be necessary to obtain a steady state. In experiments where solutions were used containing 5.6 mol  $H_3PO_4/kg$ solution, the solid over liquid weight reaction was about 0.11, while



Figure 4.2. Schematic diagram of the crystallization apparatus

in case of 6.6 mol  $H_3PO_4/kg$  solution this ratio was 0.05. To vary the  $H_2SO_4$  content of the solution from 0.02 to 0.35 mol/kg at a given  $H_3PO_4$  concentration, corresponding with molar calcium over sulfate ratios between about 0.1 and 8, only small changes in the CDHP and  $H_2SO_4$  feed streams were needed. The influence of such small variations on the solid over liquid ratio was negligible. Also the residence time had hardly any effect on it.

After each residence time unclassified samples were taken from the crystallizer with a sample tube. This tube was connected with a G4-glass filter, placed on a reception tube under vacuum. The liquid was diluted with water and analyzed for its phosphate and sulfate content by X-ray fluorescence, its  $Ca^{2+}$  content by complexometric titration and its  $Cd^{2+}$  content by inductively coupled plasma spectroscopy (ICP) [9]. The crystals were washed twice with a saturated gypsum solution of about 90°C, three times with acetone and dried at 60°C. The HPO $_4^2-$  content of the crystals was determined by colorimetry while the  $Cd^{2+}$  content was measured by ICP. X-ray diffraction was used to identify the phase of the crystals.

## 4.3. Results and discussion

#### 4.3.1. The hemihydrate crystals

When hexagonal calcium sulfate hemihydrate crystals are precipitated from a solution containing 5.6 or 6.6 mol  $H_3PO_4/kg$ , where the calcium ions are in excess of the sulfate ions, aggregates are formed. Each aggregate consists of numerous needles originating from one point and growing out like the radii of a sphere (see fig. 4.3a). At increasing sulfate concentration in the solution, further referred to as  $[H_2SO_4]$ , mostly separate needles are grown, which are longer and relatively thinner. In addition some bundles of two or more needles are formed, which are often oriented in twin positions (see fig. 4.3b). At  $[H_2SO_4]$ beyond about 0.25 mol/kg many tiny needles are formed, beside needles with a length up to 2000  $\mu$ m (see fig. 4.3c). In 6.6 mol H<sub>3</sub>PO<sub>4</sub>/kg aggregate formation still occurs at much higher  $[H_2SO_4]$  than in solutions containing 5.6 mol  $H_3PO_4/kg$ . This might be caused by a restricted volume diffusion to the tops of the needles, due to the higher viscosity of the solution containing 6.6 mol  $H_{4}O_{4}/kg$ . In many of the long needles, however, hollow cores were observed in the direction of the c-axis (see fig. 4.3d).

Examination, by X-ray diffraction, of the crystals obtained revealed that some of the batches of crystals contained anhydrite. The detection limit for AH in the crystals is approximately 0.5-1 wt%. The amount of AH varied even at fixed operating conditions. In spite of this irreproducibility, it can be concluded that a combination of a prolonged residence time, dosage of concentrated sulfuric acid might locally induce AH nuclei. Once AH nulei are present, the residence time becomes very important.

## 4.3.2. Incorporation of phosphate ions

The predominant ions in the phosphoric acid solution are, according to Elmore et al. [10], the  $H^+$ ,  $H_5P_2O_8^-$  and  $HSO_4^-$  ions. In the crystals,



Figure 4.3. HH crystals obtained at 92  $^{\circ}C$  in 5.6 mol  $H_{3}PO_{4}/kg$  and a:0.05 mol  $H_{2}SO_{4}/kg$ , b:0.24 mol  $H_{2}SO_{4}/kg$  and c:0.32 mol  $H_{2}SO_{4}/kg$ . 4.3d: SEM photograph of hollow cores in HH crystals

however, it is more likely that  $HPO_4^2$ - ions replace  $SO_4^2$ - ions. The  $HPO_4^2$ - ion can easily substitute for a sulfate ion, since these two ions are almost similar in size and share an affinity towards calcium ions. The similarity of these an-ions is also reflected by the existence of two comparable salts:  $CaHPO_4 \cdot 2H_2O$  and  $CaSO_4 \cdot 2H_2O$ , which are both sparingly soluble in water and have the same molar volume [11].

First crystallization experiments were performed in a solution containing 5.6 mol  $H_3PO_4/kg$ , with residence times of 20 and 40 min, and  $[H_2SO_4]$  between 0.02 and 0.35 mol/kg. These conditions yielded a solid over liquid weight ratio of 0.11. In fig. 4.4 the  $HPO_4^2$ incorporation in the crystals, expressed as the molar  $[HPO_4^2-]$  over  $[SO_4^2-]$  ratio in the crystals, is given versus the molar  $[H_3PO_4]$  over  $[H_2SO_4]$  ratio in the solution. The phosphate uptake decreases with increasing  $[H_2SO_4]$  and a linar dependence between the molar phosphate over sulfate ratios in the crystals and in the solution appears to exist. The relationship between the molar ratios presented by the drawn line in fig. 4.4 for  $0.02 < [H_2SO_4] < 0.35$  mol/kg is given by eq. (4.1):

$$\frac{[\text{HPO}_4^2-]}{[\text{SO}_4^2-]} \text{ (crystal)} = 1.4 \text{ x } 10^{-4} \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{SO}_4]} \text{ (solution)}$$
(4.1)

where  $1.4 \ge 10^{-4}$  denotes the partition coefficient  $D(HPO_4^2-)$ . This linearity points to a competition between the two anions for the available adsorption sites at the crystal surface. An influence of the linear growth rate upon the phosphate uptake can therefore be expected, since at a higher growth rate more phosphate ions will be entrapped by the propagating steps. This growth rate is determined by the actual supersaturation. Measurement of the supersaturation is impossible because the differences between the calcium and sulfate concentrations in the solution and their respective saturation values are too small to be determined. Therefore, the production rate, defined as the amount of HH obtained per kg suspension per second, has been used as a yardstick for the linear growth rate, under the



Figure 4.4. The phosphate incorporation, expressed as the molar phosphate over sulfate ratio in the crystals, as a function of the same ratio in the solution at various residence times. The slope of the curve  $D(HPO_4^2-)$  is approximately  $1.4 \cdot 10^{-4}$ .

assumption that the specific surface area of the crystals remains constant. Although the specific surface area tends to increase at higher supersaturation, ít will never obscure the higher supersaturation inherent to the higher production rate. In the case of unclassified withdrawal the production rate is directly correlated to the solid over liquid weight ratio and the residence time. In all experiments the solid over liquid weight ratio is approximately and is determined by the calcium content constant, of the CDHP solution and by the sulfate concentration of the sulfuric acid solution. This is only true because the amount of calcium ions not precipitated is extremely low, due to the slight solubility of HH in phosphoric acid (about 0.07 mol/kg) [1]. At shorter residence times, the production rate is higher and therefore the supersaturation will be higher, and an enhanced phosphate incorporation is expected. Comparison of the results obtained for various residence times, as given in fig. 4.4, does not show this tendency, so the differences in supersaturation are apparently too small to cause a visible effect on uptake.

Additional experiments were performed, with a power input of either 0.04 or 11 kW/m<sup>3</sup> (stirrer speed 250 and 1570 rpm respectively). No effect on the phosphate uptake was noticed. This shows that either the film layer thickness is hardly effected by the change in power input or that volume diffusion is not a predominant growth barrier in our experiments.

In addition to the experiments in 5.6 mol  $H_3PO_4/kg$ , experiments were also performed in 6.6 mol  $H_3PO_4/kg$  to examine the effect of the  $H_3PO_4$ content. For 5.6 mol  $H_3PO_4/kg$  it was found that for changing  $[H_2SO_4]$ in the solution, the phosphate uptake in the crystals, given by the molar  $[HPO_4^2-]$  over  $[H_2SO_4]$  ratio, is ruled by the same ratio in the bulk of the solution. If this rule remains valid for varying phosphate concentrations in solution, no shift of the curve in fig. 4.4 is expected for different  $H_3PO_4$  concentrations. Experiments performed in a solution containing 6.6 mol  $H_3PO_4/kg$  yielded values lying on the line as obtained for solutions containing 5.6 mol  $H_3PO_4/kg$ . The same crystallizing solution, however, is quite different. A lower solid over liquid weight ratio and a lower solubility of calcium sulfate prevail, while due to the higher viscosity of the solution the diffusion coefficient is also lower. No estimation can therefore be made of the differences in supersaturation for experiments performed in either 5.6 or 6.6 mol  $H_3PO_4/kg$ . Since, however, all results obtained in 6.6 or in 5.6 mol  $H_3PO_4/kg$  for various residence times to the same line in figure 4.4, small changes contribute in supersaturation, due to variations in residence time and phosphoric acid concentration, apparently do not influence the uptake significantly.

Results formerly obtained from batch experiments [12] in 6.6 mol  $H_3PO_4/kg$ , where the production rate was varied over a much wider range, showed that the influence of larger increases in feed rates and thus in supersaturation can no longer be neglected. Therefore, if much

-72-

higher feed rates were applied, a higher uptake can be expected in our experiments.

In some of our experiments AH was formed. In the experiments where the AH percentage of the crystals remained below approximately 10 wt% no significant increase of the phosphate uptake was observed. A visibly higher uptake was noticed only for AH percentages above 15 wt%. Finally, a few experiments were performed where under further similar conditions either Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup> was added. Addition of halogenides did not influence the phosphate uptake.

#### 4.3.3. Incorporation of cadmium ions

Since the ionic radii of  $Ca^{2+}$  and  $Cd^{2+}$  are almost equal  $(r(Ca^{2+}) = 1.12 \text{ Å} \text{ and } r(Cd^{2+}) = 1.07 \text{ Å} [13]$ , both with 8-fold coordination [14,15]), the  $Cd^{2+}$  ions can replace the  $Ca^{2+}$  ions in the crystals without causing much lattice strain. The chemical properties of these ions, on the contrary, are quite different. Cadmium sulfate, as well as its hydrates, are very soluble in aqueous solution [11], so the interaction between the  $Cd^{2+}$  ions and the  $SO_4^2-$  ions at the crystal surface must be much weaker than between the  $Ca^{2+}$  ions and the  $SO_4^2-$  ions. This also counts for a solution containing 5.6 mol  $H_3PO_4/kg$  at 92°C, where the molar solubility of cadmium sulfate has been measured to be about 0.7 mol per kg solution, which is ten times higher than the molar solubility of HH.

For the experiments in 5.6 mol  $H_3PO_4/kg$  with sulfuric acid concentrations ranging from 0.02 to 0.35 mol/kg and residence times of 20 and 40 min, the cadmium concentration in the HH crystals was measured. In fig. 4.5 the cadmium uptake, expressed as the molar cadmium over calcium ratio in the crystals, is presented as a function of the sulfate concentration in the solution. The  $[H_2SO_4]$  in the solution can be converted to a molar cadmium over calcium ratio because the product of  $[Ca^{2+}]$  and  $[H_2SO_4]$  is approximately constant, and equal to  $5 \times 10^{-3} \text{ mol}^2/kg^2$  in 5.6 mol  $H_3PO_4/kg$ , while  $[Cd^{2+}]$  in the solution was  $3 \times 10^{-4}$  in all experiments. In fig. 4.5 the molar



Figure 4.5. The  $Cd^{2+}$  incorporation expressed as the molar  $Cd^{2+}$  over  $Ca^{2+}$  ratio in the crystals as a function of the same ratio and of the sulfate concentration in the solution. The star indicates the reduced level of incorporation that could be obtained by addition of halogenides to the solution (see text), e.g.  $0.7 \cdot 10^{-2}$  mol I<sup>-</sup> per kg.

cadmium over calcium ratio in the solution is also given on the horizontal axis. If, by analogy with the phosphate uptake, competition takes place between cadmium and calcium ions for the available adsorption sites at the interface, a linear relationship between the cadmium over calcium ratio in the crystals and in the solution is expected. For experiments performed with a residence time of 20 min this linearity indeed exists for sulfate concentrations of 0.1 up to 0.35 mol/kg. The partition coefficient for cadmium, expressed as:

$$D(Cd^{2+}) = \frac{([Cd^{2+}]/[Ca^{2+}])(crystal)}{([Cd^{2+}]/[Ca^{2+}])(solution)}$$
(4.2)

equals 1 x 10-3 for HH. Experiments with 40 minutes residence time could not be performed at sulfate concentrations beyond about 0.25 mol/kg, without excessive AH formation. For sulfate concentrations below 0.15 mol/kg the cadmium uptake is higher for 40 than for 20 min residence time. At present no explanation for this phenomenon can be given. An indication that, at sulfate concentrations below 0.05 mol/kg, the cadmium incorporation is lower than predicted by our experiments with 40 min residence time is given by the results of continuous operation of the phosphoric acid process on a laboratory scale. During this operation a small amount of HH is precipitated during the digestion of the ore. The solution contains in this case about 0.005 mol  $H_2SO_4/kg$ , and in the crystals only a very small amount of cadmium, corresponding to a molar cadmium over calcium ratio below  $3 \times 10^{-6}$  is found. This difference in cadmium uptake can hardly be resulting from a difference in residence time (120 versus 40 min) and in solid over liquid ratio (0.04 versus 0.11 or 0.05) only. It is therefore possible that for  $[H_2SO_4]$  below 0.05 mol/kg the actual cadmium uptake will decrease. The tendency of increasing uptake with increasing  $[H_2SO_4]$  is also found in batch experiments [16], although in that case the extent of the incorporation was higher [12].

A variation in power input from 0.04 to  $11 \text{ kW/m}^3$  did not have a visible effect on the cadmium uptake. In fig. 4.5 the strong influence of AH formation on the cadmium uptake is shown. The cadmium uptake in the AH at various sulfate concentrations could be estimated from experiments, where AH was formed, after correction for the amount of cadmium incorporated in the HH. These preliminary data make likely a linear relationship between the molar cadmium over calcium ratio in AH and the solution. The corresponding partition coefficient D is about 1 x  $10-^2$ . This linearity points to a competition between the cations for the available adsorption sites at the interface, which is also assumed occur for the phosphate and sulfate ions. Comparison of the to partition coefficient for cadmium ions in the HH phase, which for a residence time of 20 min equals  $1 \times 10^{-3}$ , with the partition coefficient for phosphate uptake, which equals  $1.4 \times 10^{-4}$  in HH, demonstrates that substitution of the  $Ca^{2+}$  ions by  $Cd^{2+}$  ions occurs about six times more frequently than replacement of  $SO_4^2$  - ions by HPO\_4^2ions.

Regarding the weak affinity of the  $Cd^{2+}$  ions towards the  $SO_4^2-$  ions at the interface and the much stronger affinity of  $HPO_4^2$  ions towards the  $Ca^{2+}$  ions at the interface, this high  $Cd^{2+}$  uptake is rather surprising. The preliminary partition coefficient for  $Cd^{2+}$  in AH, D =  $1 \times 10^{-2}$ , is substantially higher than  $D(Cd^{2+})$  HH and  $D(HPO_4^2-)$  HH. A possible reason for this enhanced uptake follows from the lower solubility (about twice) of AH, [Ca<sup>2+</sup>][H<sub>2</sub>SO<sub>4</sub>] is approximately  $mol^2/kg^2$  in 5.6 mol  $H_3PO_4/kg$ , which causes the х  $10^{-3}$ 2 supersaturation for AH to be much higher than for HH. This results in a higher  $Cd^{2+}$  uptake in AH due to a kinetic overgrowth effect. Also thermodynamic effects have to be considered as possible reasons for the enhanced cadmium uptake in AH compared to the uptake in HH. These thermodynamic effects on the partition coefficient can be taken into account by writing D, according to McIntire [17], and assuming the activity coefficients of  $Cd^{2+}$  and  $Ca^{2+}$  to be about equal, as:

$$D(Cd^{2+}) = \frac{K(CaSO_4)}{K(CdSO_4)} \exp\left(-\frac{\Delta\mu}{RT}\right)$$
(4.3)

Here the difference in chemical potential between  $Cd^{2+}$  and  $Ca^{2+}$  in the solution is assumed to be taken into account mainly by the quotient of the solubility products K, while  $\Delta \mu$  represents the difference in chemical potential between  $Cd^{2+}$  and  $Ca^{2+}$  in the crystal lattice. If  $\Delta \mu$  were similar for Cd<sup>2+</sup> uptake in AH and in HH, the partition coefficient for  $Cd^{2+}$  in HH is expected to be twice the value in AH, due to the lower solubility of AH. The observed D value for  $Cd^{2+}$  in AH at least ten times higher than its value in HH. Therefore, if we is assume eq. (4.3) to be valid,  $\Delta \mu$  can not be the same, and replacement of  $Ca^{2+}$  by  $Cd^{2+}$  possibly requires less energy in AH than in HH. This assumption is not unlikely because  $CdSO_4$  and  $CaSO_4$  are almost identical salts, while this is not true for their hydrates. Partition coefficients were also determined by Kushnir, who investigated the incorporation of many foreign ions in DH, HH and AH, precipitated from or recrystallized in seawater [18, 19]. A striking

difference between our results for Cd<sup>2+</sup> uptake and Kushnir's results

for  $Mg^{2+}$  uptake is that  $D(Mg^{2+})AH$  is two times smaller than  $D(Mg^{2+})HH$ , while we found  $D(Cd^{2+})AH$  to be more than ten times larger than  $D(Cd^{2+})HH$ . The partition coefficient for  $Mg^{2+}$  in AH from seawater is smaller than for  $Cd^{2+}$  in AH from phosphoric acid, although the solubilities of  $CdSO_4$  and  $MgSO_4$  in aqueous solutions are comparable. The apparent differences in  $\Delta\mu$  values of  $Mg^{2+}$  and  $Cd^{2+}$  in  $CaSO_4$  are probably caused by the larger differences, e.g. in ionic radii, between  $Mg^{2+}$  and  $Ca^{2+}$  compared to  $Cd^{2+}$  and  $Ca^{2+}$ , leading to a larger lattice mismatch for  $Mg^{2+}$ . The  $Mg^{2+}$  ions probably fit equally poorly in the HH as in the AH lattice, while  $Cd^{2+}$  ions fit better in the AH than in the HH lattice and apparently better than  $Mg^{2+}$  ions. Our  $Cd^{2+}$ incorporation results will be verified in the near future by recrystallization experiments.

Finally a few experiments were performed where either Cl<sup>-</sup>, Br<sup>-</sup> or l<sup>-</sup> was added. The preliminary results presented in fig. 4.5 demonstrate that when 2.7 x  $10^{-2}$  mol Cl<sup>-</sup>, 1.3 x  $10^{-2}$  mol Br<sup>-</sup> or 0.7 x  $10^{-2}$  mol l<sup>-</sup> is added to 1 kg solution containing 3 x  $10^{-4}$  mol of Cd<sup>2+</sup>, a reduction in Cd<sup>2+</sup> incorporation in the crystals of about 40% is achieved. These results are in agreement with literature data concerning cadmium complexation by halogenides in aqueous solutions [6,7]. In these data a decrease in complexing activity is mentioned in the order I- > Br- > Cl-.

## 4.4. Conclusions

The habit of the HH crystals changes with increasing  $[H_2SO_4]$  from mainly aggregates to mainly needles.

The  $HPO_4^2$ - incorporation decreases with increasing  $[H_2SO_4]$  and is directly proportional to the phosphate over sulfate ratio in the bulk of the solution.

The  $Cd^{2+}$  incorporation increases with increasing  $[H_2SO_4]$  and is directly proportional to the molar cadmium over calcium ratio in the solution for residence times of 20 min and between about 0.15 and 0.35 mol  $H_2SO_4$  per kg solution. High  $H_2SO_4$  concentrations, high temperatures and long residence times stimulate the formation of AH.

Under identical operating conditions, the  $Cd^{2+}$  uptake in AH is at least 10 times higher than in HH.

Halogenides reduce the Cd<sup>2+</sup> uptake.

#### 4.5. References

- P. Becker, Phosphates and Phosphoric Acid, FertilizerScience and Technology Series, Vol. 3 (Dekker, New York, 1983).
- [2] V. Slack, Phosphoric Acid, Fertilizer Science and Technology Series, Vol. 1, Part 1 (Dekker, New York, 1968).
- [3] H. Gorecki, Indian J. Technol. 23 (1985) 51.
- [4] S. van der Sluis, Z. Murach, J.A. Wesselingh and G.M. van Rosmalen, The Predigestion Stage of a New Phosphoric Acid Process, submitted to World Congress III of Chemical Engineering, Japan, 1986.
  - [5] T.T. Tjioe, P. Weij and G.M. van Rosmalen, Removal of Cadmium by Anion Exchange in a Wet-Phosphoric Acid Process, submitted to World Congress III of Chemical Engineering, Japan, 1986.
  - [6] I.M. Kolthoff and P.J. Elving, Treatise on Analytical Chemistry, Vol. 3, Part 2 (Interscience, New York, 1961).
  - [7] R.J. Kostelnik and A.A. Bothner-By, J. Magnetic Resonance 14 (1974) 141.
  - [8] A.A. Taperova, M.N. Shulgina, J. Appl. Chem. (USSR) 23 (1950) 27.
  - [9] Klok, A., J.J. Tiggelman, P. Weij, J.P.J. van Dalen and L. de Galan. in: Proc. 24th Colloq. Spectrosc. Intern., 1986, p. 98.
- [10] K.L. Elmore, J.D. Hatfield, R.L. Dunn and A.D. Jones, J. Phys. Chem. 69 (1965) 3520.
- [11] R.C. Weast, Handbook of Chemistry and Physics, 59th ed. (CRC Press, Boca Raton, FL, 1978).
- [12] M. Jansen, A. Waller, J. Verbiest, R.C. van Landschoot and G.M. van Rosmalen, in: Industrial Crystallization 84, Eds. S.J. Jancić and E.J. de Jong (Elsevier, Amsterdam, 1984) p. 171.
- [13] J.E. Huheey, Inorganic Chemistry (Harper and Row, New York, 1975) p. 74.
- [14] G.A. Lager, Th. Armbruster, R.J. Rotella, J.D. Jorgensen and D.G. Hinks, Am. Mineralogist 69 (1984) 910.
- [15] N.N. Bushuer, Russion J. Inorg. Chem. 27 (1982) 344.
- [16] T.T. Tjioe, H. van der Woude, J. Verbiest, P.F.M. Durville and G.M. van Rosmalen, in: Proc. Intern. Conf. on Heavy Metals in the Environment, Athens, 1985, Vol. 1, Ed. T.D. Lekkas, p. 292.
- [17] W.L. McIntire, Geochim. Cosmochim. Acta 27 (1963) 1209.
- [18] J. Kushnir, Geochim. Cosmochim. Acta 44 (1980) 1471.
- [19] J. Kushnir, Geochim. Cosmochim. Acta 46 (1982) 433.

#### CHAPTER 5

#### INCORPORATION OF CADMIUM AND ALUMINUM FLUORIDE IN CALCIUM SULFATE

## Abstract

In phosphoric acid processes uptake of cadmium by the precipitated calcium sulfate modifications depends on the process conditions as well as on the presence of foreign ions or complexes in the solution, like e.g. aluminum fluoride. The influence of  $AlF_3$  on the Cd uptake and the shape of the crystals has been studied by continuous crystallization and batchwise recrystallization experiments. The noticed effects are related to the impact of  $AlF_3$  on the (re)crystallization kinetics.

## 5.1. Introduction

Phosphoric acid for applications in the fertilizer industry is usually produced by a so called wet process. The ore, which mainly consists of fluoroapatite, is treated with sulfuric acid diluted by a recycle stream of phosphoric acid. In this way a calcium sulfate modification is precipitated, according to:

 $Ca_9(PO_4)_6.CaF_2 + 10 H_2SO_4 \rightarrow 6 H_3PO_4 + 10 CaSO_4.nH_2O + 2 HF$ 

Depending on the phosphoric acid concentration and the temperature, either anhydrite (AH, n=0), hemihydrate (HH, n=0.5) or dihydrate (DH, n=2) is formed. In order to diminish phosphate loss following from  $HPO_4^2$ - uptake in the crystal lattice, and to improve the quality of the calcium sulfate crystals, the obtained calcium sulfate is often recrystallized, i.e. transformed into another modification.

It has long been recognized that not only the process conditions, like the phosphoric acid and sulfate concentration and temperature of the solution, but also various impurities in the crystallizing solution have a large impact on the quality of the obtained product. This quality also concerns incorporation of foreign ions. In Europe the attention is nowadays strongly focused on the uptake of heavy metal ions and particularly of cadmium in the product, since the

presence of these ions hampers its disposal for environmental reasons. Attempts are therefore made to control the cadmium incorporation in calcium sulfate precipitates.

In former studies the influence of the process conditions on the (re)crystallization kinetics and the cadmium uptake has been detailed [1,2]. Among the impurities, which have a large influence on the kinetics of calcium sulfate, aluminum fluoride belongs to the most notorious. In practice, for instance, often an aluminum containing clay is added to improve the filterability of the obtained crystals by shortening the needle length. The aluminum from the clay forms complexes with the fluoride, released by the ore during digestion. According to Glaziryna et al. [3], the effectivity of aluminum fluoride largely depends on the molar F:Al ratio in the solution. The most striking effect was found the Al and F ions in solution are present in such a ratio that  $AlF_3$  complexes can be formed in the phosphoric acid. From batch crystallization experiments the phosphate uptake in DH and the specific surface of the crystals were found to be at a minimum when  $AlF_3$  was present in the solution [3]. To a certain extent it is also possible to influence the nature of the precipitated phase (DH or HH) by addition of aluminum fluoride. Presence of  $AlF_{3}$ also retards the recrystallization rate of DH into HH and shortens the length of produced HH needles [4]. Thus, AlF<sub>3</sub> apparently changes the growth rate of the various faces of the crystals differently and thereby alters their habit.

These reported effects on crystal shape and the phosphate uptake make an effect of  $AlF_3$  on the cadmium uptake also likely. The main objective of this work is therefore to test the effect of  $AlF_3$  on the uptake of cadmium, and on the shape of the crystals during continuous crystallization and batchwise recrystallization of calcium

- 80 -

sulfate. In addition the uptake of aluminum and phosphate ions was measured.

## 5.2. Experimental

all experiments chemically pure reagents were used. The In recrystallization experiments were performed in a batchreactor and the crystallization experiments in a continuous MSMPR crystallizer. The recrystallization experiments were performed in a thermostated hard glass vessel [2]. This vessel was filled with the requisite amounts of reagents and AH or DH seed crystals, whereafter the experiment was initiated by the addition of HH or DH source material. During the conversion samples of the slurry were taken, and after filtration the crystals were washed with saturated gypsum solution and subsequently with acetone. The crystals and the filtrate were analyzed for the phosphate, aluminum and cadmium content, with ICP and AAS, while for determination of the fluoride an ion selective electrode was used. The experiments, described in [1], were continuous crystallization performed by adding a monocalcium phosphate solution simultaneously with a sulfuric acid solution to the crystallizer, which content was maintained at a level of 1 liter through unclassified removal of the After about 8 residence times of 20 to 60 minutes a steady slurry. state was obtained. Samples were taken after each residence time, and treated similarly as for the recrystallization experiments. The solid over liquid weight ratio was about 11 %.

## 5.3. Results and discussion

The conditions of the experiments, such as the composition of the solution and the temperature, are summarized in table 5.1. All solutions contain about 50 to 100 ppm  $Cd^2+$ . The residence time during the continuous crystallization is 20 minutes, unless stated otherwise.

Experiments 3, 5, 8, 10, 12 and 14 are performed as a blank, i.e. without Al or F present in the solution.

				solution composition							uptake by crystals			
exp nr.	•	react		 %Р <sub>2</sub> О <sub>5</sub>	%H2SO4	addi	tive	temp. (°C)	K(Al)	K(Cd)	D(Cd) (10- <sup>3</sup>	%P <sub>2</sub> O <sub>5</sub>		
1	нн	→ AH	recryst	:. 40	10	0.8%	AlF <sub>3</sub>	90	0.5	31	16	0.4		
2		"		40	10	0.3%	A1	90	0.01	32	20	0.4		
3				40	10	-		90	-	40	20	0.4		
4	нн	→ DH	recryst	:. 25	6	0.8%	AlF <sub>3</sub>	70	n.a.	0.4	1.3	0.4		
5		n		25	6	-		70	-	0.4	1.2	0.4		
6	HH	cont	. cryst.	40	3	0.8%	AlF <sub>3</sub>	90	0.25	1.1	7	0.5		
7		Ħ		40	3	0.2%	A1	90	0.01	0.4	1.5	0.2		
8		n		40	3	-		90	-	0.4	1.5	0.2		
9.	DH	cont	. cryst.	25	2	0.8%	AlF <sub>3</sub>	60	0.6	0.19	2.6	1.3		
10		11		25	2	-		60	-	0.3	2.0	1.0		
11		11		25	5	0.8%	AlF <sub>3</sub>	60	0.6	0.75	3.6	0.9		
12		11		25	5	-		60	-	0.4	1.4	0.6		
13	AH	cont	. cryst.	40	10	0.8%	AlF,	95	≈0.3	40	15	≈0.5		

Table 5.1. Experiments and results.

40

10

14

The shape of the obtained crystals is needle like, especially at high  $H_2SO_4$  concentrations of above a few %, while the length can be up to 2000  $\mu$ m (fig. 5.1). Often hollow cores are found in the HH or DH needles. The AH crystals are much smaller, only 100  $\mu$ m long, and develop in the form of needles or platelets. (see also fig. 5.1).

95

70

39

0.3

The respective Cd and  $P_2O_5$  levels in the crystals are also given in table 5.1. The incorporation of Cd is expressed as K(Cd), defined as the ratio of the Cd concentration in the crystals divided by the Cd concentration in the solution. K(Cd) is for AH much higher (40) then for HH or DH (0.4). In former experiments [1,2] it was found that K(Cd) largely depends on the calcium concentration in the



Figure 5.1. crystals of DH (a) and AH (b and c) from continuous crystallization in chemically pure acid.

solution which is known to be determined by the sulfate concentration and the solubility, and that a better description of the uptake is given by a partition coefficient D, defined as:

 $D = ( [Cd^2+]/[Ca^2+]) (crystal) / ([Cd^2+]/[Ca^2+]) (solution).$ 

In this expression a competition between Cd and Ca in the solution and at the interface is assumed to occur. In a wide range of process conditions D(Cd) was found to be equal to about  $1.5 \cdot 10^{-2}$  for AH and  $1.5 \cdot 10^{-3}$  for HH and DH [1,2]. At higher crystallization rates, however, an increase in the D-value can be expected [5]. The constancy of D at moderate crystallization rates is a strong indication for a cadmium uptake proceeding via an isomorphous substitution of the Ca ions in the crystal structure [6]. Such a substitution is possible because the ionic radii of  $Ca^{2}$ + and  $Cd^{2}$ + are almost equal (112 and 107 In this isomorphous pm respectively, in an 8-fold coordination). substitution mechanism the ionic radius plays an important role in the degree of incorporation [7]. The uptake of  $Al^3+$  is expected to be low, because its ionic radius is about half that of  $Ca^{2}+$ . In case of  $Al^{3}+$ incorporation, the charge of 3+ in addition requires compensation, which complicates the incorporation. It is thus not surprising that in experiments 2 and 7, where  $Al^3+$  is added to the solution, the corresponding D(A1) can be calculated to be much lower than D(Cd), i.e. less than  $10^{-5}$  for all three phases of calcium sulfate.

The presence of  $Al^3$ + up to 0.4 % does not have a visible effect on the crystal shape or on the cadmium uptake. Also in the literature only small effects of  $Al^3$ + upon the growth rate of DH are reported [8]. Therefore, any effect of  $AlF_3$  has to be assigned to Al-F complexes in the solution.

Addition of  $AlF_3$  to the solution gives rise to a drastic increase of the aluminium uptake by a factor of at least 30, for all three calcium sulfate modifications. Typical K(Al) values are e.g. 0.25 for the continuous crystallization of HH in phosphoric acid (exp. 6) or 0.6 for DH (exp. 9 and 10). This higher uptake in the presence of fluoride can be explained by the incorporation of  $AlF_5^2$ - ions substituting for  $SO_4^2$ - ions [9]. The molar Al:F ratio found in the HH





Figure 5.2. HH (a), DH (b) and AH (c) crystals from continuous crystallization in chemically pure acid with 0.8 w%  $\rm AlF_3$ 

crystals (exp. 6) is about 7 instead of the expected 5, but this deviation can be assigned to additional coprecipitation of CaF2. The effect of  $AlF_3$  is also visible on the habit of the obtained crystals. SEM views of the AH, HH and DH products of exp. 6, 9 and 13 are shown in figure 5.2, and it can be seen that 0.8 % AlF, in both cases gives rise to a strongly modified crystals shape. Instead of the needles of obtained in the absence of AlF<sub>3</sub>, now almost spherical aggregates of very short needles are produced. The size of the aggregates is maximally 200  $\mu$ m. The shape of the HH crystals reveals that the growth is strongly retarded in the direction of the c-axis. The top face is irregularly formed, indicating a change in growth mechanism. This is probably caused by the higher supersaturation as a result of the retarded growth of the crystals due to adsorption and uptake of aluminum fluoride at these faces. The DH crystals show comparable rough (111) faces. The habit modification of AH into AH also indicates an effect on one or more of the crystal faces.

A reduction in growth rate is also found during the recrystallization of HH into DH (exp. 4), where addition of 0.8 % AlF<sub>3</sub> gave rise to a 30 % slower conversion [2]. The influence of AlF<sub>3</sub> on the Cd uptake determined by continuous crystallization experiments (exp. 6, 9, 11 and 13) leads to a D-value of  $7 \cdot 10^{-3}$  for HH, of  $3 \cdot 5 \cdot 10^{-3}$  for DH and  $3.9 \cdot 10^{-2}$  for AH, while for the blanks lower D-values are obtained. An explanation for the increase in uptake probably lies in the higher supersaturation caused by the presence of AlF<sub>3</sub>. Although the top faces grow slower, their forced growth at the higher supersaturation leads to an irregular surface with an enhanced uptake of cadmium and phosphate. This explanation is supported by the observation that during batch recrystallization of HH into DH the Cd uptake is not influenced by AlF<sub>3</sub> (exp. 4). In these experiments the supersaturation is restricted by the solubility of HH , and thus more likely lower. 5.4. Conclusions

- The uptake of Al<sup>3</sup>+ in the three calcium sulfate modifications is much higher when present as AlF<sub>3</sub> in the solution, probably due to the incorporation of  $AlF_5^2$ - ions, and is about equal for AH, HH and DH.

- Presence of 0.8 w%  $AlF_3$  in the solution strongly retards the growth of HH and DH, especially on the top faces of the crystals.

- In continuous crystallization processes the growth retarding effect of  $AlF_3$  strongly affects the size and shape of the obtained crystals.

- In continuous crystallization experiments the cadmium and phosphate uptake is enhanced by the presence of  $AlF_3$ , probably due to a kinetic effect.

5.5. References.

- S. van der Sluis, G.J. Witkamp and G.M. van Rosmalen, J. Crystal Growth <u>79</u> (1986) 620
- [2] G.J. Witkamp and G.M. van Rosmalen, Proceedings of the Second International Symposium on Phosphogypsum, Miami 1986, ed. W.F. Chang, University of Miami.
- [3] L.N. Glaziryna E.I. Savinkova, A.V. Grinevitch and L.E. Akhmedova, Zh. Prikl. Khim. <u>56</u> (1983) 241

[4] A.A. Naret, R.Y. Zinyuk, B.D. Guller, G.M. Cherkeneva and M.E. Pozin, Zh. Prikl. Khim. <u>50</u> (1977) 2440

[5] J. Kushnir, Geochim. Cosmochim. Acta <u>44</u> (1980) 1471

[6] W.L. McIntire, Geochim. Cosmochim. Acta 27 (1963) 1209

[7] A.A. Chernov, Modern Crystallography III (Crystal growth),

Springer Series in Solid-State Sciences, Springer Verlag Berlin/New York 1984, p. 204.

[8] S. Zielinski, Industrial Crystallization 81, S.J. Jancic and E.J. de Jong (editors), North Holland Publishing Company (1982), p.329.

[9] D. Kitchen and W.J. Skinner, J. Appl. Chem. Biotechnol. 21(1971) 56

#### CHAPTER 6

# BATCHWISE RECRYSTALLIZATION IN PHOSPHORIC ACID I: FORMATION OF GYPSUM AND ANHYDRITE

Abstract

Calcium sulfate hemihydrate and dihydrate were batchwise recrystallized into anhydrite in a solution containing 40 w%  $P_2O_5$ , 2 to 12 w%  $H_2SO_4$  at temperatures ranging from 70 to 100 °C. Hemihydrate was converted into dihydrate in a solution of 15 to 25 w%  $P_2O_5$  with varying sulfate concentrations at temperatures from 40 to 70  $^{\circ}$ C. The rate of conversion and the Cd uptake by the formed crystals was determined in dependance of the type and amount of seed crystals and as a function of process conditions such as temperature, sulfate and phosphate concentration in the solution. The rate of both conversions was affected by the amount of seed crystals, while for anhydrite no induction period preceeded the recrystallization when no seed crystals were added. The Cd uptake appeared to be very sensitive to the process conditions and was much higher for anhydrite than for dihydrate. The rate of conversion into dihydrate was retarded by the presence of AlF<sub>3</sub> in the solution and even more by  $Ce^{3+}$  ions. Impurities in 'black acid', originating from the ore, hampered the conversion into dihydrate and promoted the Cd uptake in anhydrite. Comparison was made between the Cd uptake during batchwise conversion with the uptake obtained by continuous crystallization of dihydrate and anhydrite.

## 6.1. Introduction

Phosphoric acid for application in the fertilizer industry is usually produced via a so called wet process. The overall reaction ruling most wet phosphoric acid processes is the digestion of fluoroapatite ore and the precipitation of calcium sulfate by the addition of sulfuric acid, according to:

-88-

where, depending on the process conditions either dihydrate (x=2), hemihydrate (x=1/2) or anhydrite (x=0) is formed. Which of the three phases is formed, depends on the temperature as well as on the sulfate and phosphate concentration of the crystallizing solution, as will be discussed below. In current processes only DH or HH is precipitated, while formation of AH does not occur in any commercial phosphoric acid process.

During crystallization cadmium ions, originating from the ore, are incorporated in the calcium sulfate lattice due to isomorphous replacement of calcium ions. This happens because the ionic radii of these two ions are almost equal  $(r(Cd^{2+})=107 \text{ pm}, r(Ca^{2+})=112 \text{ pm}, \text{ both})$ for an 8-fold coordination [Huheeh, 1975]). Uptake of cadmium in the byproduct is problematic, because the calcium sulfate is usually disposed, and especially in Europe strong regulations are imminent against the disposal of cadmium in river water or even at sea. According to a similar substitution mechanism HPO42 ions can replace  $SO_4^{2^-}$  ions in the crystal lattice. This uptake should also be kept at the lowest possible level, because it reduces the phosphate efficiency of the process. Another unwanted impurity is radium. Radium is coprecipitated with the calcium sulfate due to the very low solubility of radium sulfate. When the calcium sulfate byproduct is used as a building material, the radium content is bound to strict limits. In poorly ventilated rooms radon gas, a decay product of radium, may build up to health-hazardous concentrations.

In order to improve product as well as process characteristics, such as the phosphate uptake and the quality of the crystals, recrystallization of one calcium sulfate phase into another under carefully controlled conditions is often applied in phosphoric acid processes. Examples are hemihydrate-dihydrate processes [3], where initially formed hemihydrate (HH) is transformed to dihydrate (DH). The reverse reaction, the DH to HH recrystallization, is applied in the Prayon process [Becker, 1983].

During the direct crystallization well as as during recrystallization the uptake of cadmium and phosphate are determined by the process conditions and by the nature of the precipitated phase (HH, DH or HH). Process conditions are for instance the  $P_2O_5$  and  $H_2SO_4$ concentration of the solution, the temperature and the production rate. In general minimization of uptake is pursued. There is, however, one example where the purposely incorporation of cadmium in AH, which is at least ten times higher than in HH or DH, has been patented as a method for the production of phosphoric acid with a low cadmium content [Weterings and Janssen, 1986]. In this process cadmium is removed from the recycled phosphoric acid stream by precipitation of a small amount of AH which contains most of the cadmium. The conditions of the AH precipitation depend on the required reduction in cadmium level of the phosphoric acid, but are e.g. 40 %  $P_2O_5$ , 10 %  $H_2SO_4$  and a temperature of 95°C.

In order to study the cadmium uptake by AH, recrystallization experiments were performed from DH or HH into AH under different conditions. Because in existing processes the cadmium uptake also becomes increasingly important, such data about the HH into DH recrystallization were also obtained.

More generally defined the objective of this work is to determine the relationship between the uptake of cadmium and phosphate and the nature of the precipitating phase as well as the process The conversion rate is also an important parameter to be conditions. not only because it determines the dimensions known. of the recrystallization equipment, but also because of its influence on the uptake of  $P_2O_5$  and Cd by the crystals through the growth kinetics. The effect of the linear growth rate of calcium sulfate upon the degree of incorporation of foreign ions like  $Mg^{2+}$  and  $Sr^{2+}$  has already been described in the literature [Kushnir, 1980]. For comparison of the Cd uptake during conversion with the uptake during continuous crystallization, a few DH and AH crystallization experiments were performed under almost identical process conditions.

6.2. Phase diagram and conversion rate

As mentioned, important parameters of the (re)crystallization process are the  $P_2O_5$  and  $H_2SO_4$  concentration of the solution and the temperature. In figure 6.1 the stability of the three phases is indicated as a function of the  $P_2O_5$  content of the solution and the temperature.



Figure 6.1.

Stability of the three calcium sulfate phases in phosphoric acid. Note that HH only exists as a metastable phase, and that AH is stable in the largest part of the diagram.

In this diagram the additional presence of  $H_2SO_4$  can be taken into account by taking 1 w%  $H_2SO_4$  equal to about 1 w%  $P_2O_5$ . The role of  $H_2SO_4$ and  $P_2O_5$  in the formation of the different phases can be explained by considering the activity of water as the determining factor in the stability of the three phases. The three phases contain different percentages of water, leading to a dependance of their stability on the activity of water. At higher acid concentrations, the amount of free water, and therefore the activity of water, is lower. This favours formation of a more dehydrated phase, i.e. AH or HH, with respect to a less dehydrated phase, i.e. DH. At higher temperatures, water tends to form looser bonds, in the crystal and also in the solution, thus favouring the vapour phase; the vapour pressure increases. This makes less water containing calcium sulfate modifications more stable at high temperatures. From the diagram AH appears to be stable in the largest

part of the diagram, that is above 40°C in pure water, and above lower temperature levels at increasing  $P_2O_5$  concentrations. Up to high temperatures and acid concentrations, however, metastable DH and HH can be formed in the stable AH region. This results from the fact that AH growth proceeds very slowly in a large part of the diagram. Eventually these metastable DH or HH phases will be transformed into AH, but this only occurs with measurable speed at high temperatures and acid concentrations. It can further be seen that HH only exists as a metastable phase. Conversion of HH into DH and vice versa can occur by crossing the DH-HH equilibrium line, i.e. by bringing HH into the metastable DH region, or by bringing DH into a solution which satisfies the metastable HH conditions. Any transition of the three phases into each other is possible, except the AH into HH conversion. This is because HH can only be formed in a region where AH is stable.

In the recrystallization reaction three steps can be distinguished:

- i) dissolution of the source material,
- ii) diffusion transport through film layers at the surface of the dissolving crystal and at the newly formed phase,
- iii) growth of the new phase. In case no or not sufficient seed crystals are present, the growth step is preceeded by a nucleation step.
  conversion rate (1) dissolution of source material

controlled by: (2) growth of seed crystals



Fig. 6.2a: degree of conversion and 2b: calcium concentration versus reaction time. Conversion rate controlled by:

(1) dissolution of source material or (2) growth of seed crystals

It is important to know which step is rate determining under various conditions, because such knowledge allows the conversion rate to be optimized. The rate determining step (r.d.s.) of the conversion can in principle be derived from the shape of the recrystallization curve obtained from batch experiments [ Cardew and Davey, 1985]. This curve is a plot of the percentage conversion versus the reaction time. If the dissolution of the source material is rate determining, the conversion proceeds faster at the start when the amount of source material is the largest. Curve (1) is then obtained, for which the conversion rate, given by the slope of the curve, decreases with time, as shown in figure 6.2a. If, on the contrary, the growth of the newly formed phase is rate determining, the increasing surface area of the growing crystals will give rise to an increasing conversion rate. The shape of the obtained curve is then given by curve (2). The two curves (1) and (2) represent two extremes, since one step is rate determining while the others proceed infinitely fast. It can, however, as well be assumed that in batch processes the growth is the r.d.s. at the start of the conversion, but that when the conversion is almost completed, the dissolution becomes rate limiting. During most of the conversion the situation is lying somewhere in between, i.e. the conversion rate is determined by both the dissolution of the source material and the growth of the newly formed phase. The obtained conversion curve then lies between (1) and (2), and it is hard to tell only from the shape of the curve to what extent dissolution and growth play a rate determining role.

During the recrystallization of the  $CaSO_4$  phases, the rate of dissolution must be lying rather close to the growth rate (both in kg/s), because the low solubility of DH, HH or AH does not allow any significant amount of calcium sulfate material to be stored by and removed from the solution, compared to the total amount of recrystallized calcium sulfate. At  $H_2SO_4$  concentrations of 5 to 10 w% the amount of calcium in the solution can be taken as a measure for the concentration of calcium sulfate in the solution, because the sulfate concentration can be considered constant during the experiment.

During recrystallization the calcium concentration of the solution will decrease in time, from the solubility value of the source material to the solubility of the newly formed phase. Thus, in the same way as the conversion versus time curve, the shape of the calcium concentration versus time curve enables us to derive information about the r.d.s. (see figure 6.2b). Additional evidence about the r.d.s. can be obtained by varying the relative amounts of seed and source material to see how the conversion rate responds to these variations.

rate at which a transition takes place depends, as mentioned The before, on the growth rate of the newly formed phase and on the rate of dissolution of the source material. Both rates have a driving force which directly depends on the relative supersaturation or undersaturation. i.e. on the differences between the actual CaSO, concentration and the solubilities of the respective phases. The CaSO, concentration is normally given in grams per kg solution. Often, however, in the different experiments the molar calcium over sulfate ratio in the solution is not equal to one, but varies from 1 to 1/200, depending on the sulfate concentration in the solution. It is therefore more convenient to use the square root of the product of the calcium and sulfate concentrations as a measure for the solubility and for the actual calcium sulfate concentration. This value equals the concentration of calcium sulfate given in grams/kg solution at stoichiometric calcium and sulfate concentrations. Since the sulfate concentration of the solution is known and remains about constant during the conversion, only the calcium content of the solution has to be measured for the calculation of the newly defined calcium sulfate concentration. The difference between the actual concentration and the solubility value now equals  $\sqrt{[Ca]*[H_2SO_4]} - \sqrt{[Ca]eq*[H_2SO_4]eq}$  and the relative supersaturation is given by:

/ ([Ca]\*[H<sub>2</sub>SO<sub>4</sub>]) / / ([Ca]eq\*[H<sub>2</sub>SO4]eq) - 1 In these formulas the charges of the ions are left out. The growth rate will increase when the supersaturation increases, which happens when the actual concentration is higher. Dissolution on the other hand, occurs faster when the actual calcium sulfate concentration is lower. So a large difference in solubilities of the newly formed phase and the phase of the source material favours a fast conversion. This situation can for the HH into DH or for the reverse recrystallization be reached by selecting the process conditions not too close to the HH-DH equilibrium line. In figure 6.3 as an example the solubilities of the three  $CaSO_4$ phases at 60°C are given as function of the  $P_2O_5$  concentration [ Slack, 1968].



Figure 6.3.

Solubility of calcium sulfate as a function of the phosphate concentration at 60  $^{\circ}$ C.

At all phosphate concentrations AH is the most stable phase and has thus the lowest solubility. Below 40 w%  $P_2O_5$  DH is more stable than HH and at further decreasing  $P_2O_5$  concentrations the relative difference in solubilities becomes greater. A low  $P_2O_5$  concentration therefore stimulates the HH into DH conversion. Analogously, it can be derived that high  $P_2O_5$  concentrations stimulate the DH into HH conversion. Also for the HH or DH to AH conversion the relative difference in solubility becomes greater which explains why this conversion is also stimulated by high  $P_2O_5$  concentrations. As mentioned above, the influence of  $H_2SO_4$  is the same as of  $P_2O_5$  in the phase diagram, and this is also true for the solubility.  $H_2SO_4$  has, however, not only an effect as an acid, like phosphoric acid, in affecting the solubility of the calcium sulfate, but also as a constituent ion of the calcium sulfate, influencing the molar  $Ca/SO_4$  ratio in the solution. It is known from literature data [Becker, 1983] that sulfate ions at low concentrations up to a few w%, generally enhance the conversion rate of any of these phase transitions. The effect of sulfate ions is therefore not unambiguous.

Next to the  $P_2O_5$  and  $H_2SO_4$  concentration and the temperature, impurities originating from the phosphate ore may influence the solubility or the difference in solubility between two phases. The influence of impurities is therefore not only directly noticeable on the growth kinetics, but also indirectly, via the solubility. For instance, AlF<sub>3</sub> can have considerable influence on solubility of HH and DH in a 35 w%  $P_2O_5$  solution at 95°C. [Glazyrina et al., 1980].

6.3. Experimental

In all experiments chemically pure  $CaSO_4.2H_2O$ ,  $H_3PO_4$ ,  $H_2SO_4$ ,  $3CdSO_4.8H_2O$ ,  $Ce(NO_3)_3.6H_2O$  were used. In the experiment with so called "black" acid, phosphoric acid from a Nissan H process was used. In case of the HH into DH conversions the experiments were performed in a thermostated double walled hard glass vessel. The experimental procedure is given schematically in figure 6.4.



Figure 6.4.

Setup of the recrystallization experiments.

The vessel was filled with a solution of the selected  $P_2O_5$  and  $H_2SO_4$ concentrations and a  $Cd^2$ + concentration of 100 ppm. First either AH or DH seed crystals were added, whereafter the experiment was initiated by addition of DH or HH source material free from or with a known the content of cadmium and  $P_2O_8$ . During at least one hour samples were taken from the slurry at regular intervals. After filtration of the sample over a G4 filter, the crystals were first washed three times with a hot saturated gypsum solution in water to remove the phosphoric acid, and subsequently three times with acetone to remove the adhering water from crystals. The filtrate was diluted with water in a sample flask to the avoid after-precipitation of the supersaturated solution. For the HH into DH recrystallizations p.a. gypsum from Merck was used as seed material for the first conversion. After this first conversion, the recrystallization was always repeated at least once, where in the second recrystallization the product of the first conversion was used as a seed material. So called  $\alpha$  HH, obtained during continuous crystallization (see below) was used as source material. For the conversion of DH or HH into AH the AH seed material was prepared by recrystallizing DH in a Cdfree 40 w%P<sub>2</sub>O<sub>5</sub>, 10 w%  $H_2SO_4$  containing solution at 90°C. The source material was either  $\alpha$  HH obtained from continuous crystallization or  $\beta$ HH obtained by drying p.a. gypsum (Merck) at 150°C during 24 hours, or the source material was p.a. DH (Merck). For this conversion a slightly modified set-up was used. In order to avoid evaporation of the solution at the necessarily high temperatures, a closed round bottom vessel placed in a thermostated bath was used. For only one of these experiments the conversion was repeated, using the AH from the former conversion as seeds.

A few continuous crystallization experiments were performed. The experimental procedure is described extensively in ref. [ Sluis et al., 1986]. In each experiment a solution of  $Ca^{2+}$  in phosphoric acid (about 1 mole  $Ca^{2+}/kg$ ) was added continuously together with concentrated  $H_2SO_4$  to the crystallizer, except for the experiment with 'black acid', where a stream of  $Ca(OH)_2$  slurry in water was added simultaneously with a stream of 'black acid', containing 20 w%  $H_2SO_4$ . The slurry volume in the

reactor is kept constant by continuous, unclassified removal of slurry from the crystallizer. The residence time of the slurry, defined as the reactor volume divided by the slurry volume stream, was varied from 20 to 60 minutes. In each experiment a steady state was obtained after 8 residence times. The solid over liquid weight ratio was about 11 %. Samples were taken each residence time, and treated similarly as for the batch experiments. For the production of AH temperatures of 90 to  $100^{\circ}$ C were maintained in a solution of 40 w%  $P_2O_5$  and 5 to 10 w%  $H_2SO_4$ , while the DH production took place at  $60^{\circ}$ C in a solution of 25 w%  $P_2O_5$  and 1 to 10 w%  $H_2SO_4$ .

The Ca and Cd contents of the solution as well as the  $P_2O_5$  and Cd contents of the crystals were measured by means of inductive coupled plasma spectroscopy (ICP). The crystals were dissolved in HCl and then diluted to about 1 gram calcium sulfate per 100 ml solution. Corrections were made for the initial impurity contents of the seed crystals. The  $H_2O$  content of HH/DH samples was determined by placing the samples overnight in an exsiccator dried over silicagel, followed by weighing and then by glowing at  $800^{\circ}C$  for two hours, and weighing again. In this way a reproducable value of about 6 w%  $H_2O$  for the otherwise varying water content of HH (0.1 - 7 w%) could be obtained.

6.4. Results and discussion

## 6.4.1. Recrystallization of hemihydrate and dihydrate into anhydrite

6.4.1.1. Conversion curves and expressions for Cd uptake.

The conditions at which the conversion takes place, are determined by the region of the phase diagram, where both DH and HH are unstable or where metastable HH rapidly transforms into AH. For most of the conversions into AH conditions were selected of  $90^{\circ}$ C, 40 w%  $P_2O_5$  and  $H_2SO_4$  concentrations above 5 w%. Some experiments were performed at slightly different conditions of temperature, w%  $P_2O_5$  and w%  $H_2SO_4$ . The amount of AH formed per kg solution was kept low in accordance with the patented process [Weterings and Janssen, 1986], mentioned in the introduction. Only 2 to 5 w% AH was formed in the solution of 40 w%  $P_2O_5$  and 10 w%  $H_2SO_4$  at 90°C. The amount of added AH seed material varied from 0 to 10%. All results are given in table 6.1.  $\tau$ (50%) indicates the time required for 50% conversion. In this table also results of the continuous crystallization experiments are given. As an example, the results of an experiment with 2 w% AH seeds will be discussed, where  $\alpha$  HH was used as a source material (exp. 3). In figure 6.5 the resulting Cd and Ca concentrations of the solution are plotted versus the reaction time.

solution						crystals						
exp nr	). con- . versio	%P <sub>2</sub> (	) <sub>5</sub> %H₂SO₄	ppm C	a % %seeds	sourc	e T(ºC)	K(Cd	) D(Cd) (10- <sup>3</sup> )	τ(50%) (min)		
1	∝HH→AH	40	10	200	0	2	90	40	27	5		
2	αHH→AH	40	10	195	1	2	90	60	40	4		
3	αНН→АН	40	10	180	2	2	90	62	40	3.5		
4	αHH→AH	40	10	160	5	2	90	48	26	3		
5	αHH→AH	40	10	145	10	2	90	39	19	1.5		
6	αHH→AH	40	5	475	1	5	90	18	29			
7	βНН→АН	40	5	215	1	5	80	27	20	17		
8	βНН→АН	40	5	425	1	5	90	18	26	12		
9	βнн→ан	40	5	375	1	5	100	27	28	5		
10	DH→AH	40	5	320	1	5	100	22	24	12		
11	AH cont	t 40	10	140	10%sc	olids	90	38	18	(chem.		
12	AH cont	t 40	11	170	10%sc	olids	90	65	38	(black		
13	DH→AH	35	12		5	5	90	23				
14	DH→AH	45	12		5	5	90	79				

Table 6.1 HH and DH into AH recrystallization


The Cd concentration decreases as a result of the high Cd incorporation in the newly formed AH. When the Cd concentration remains constant, the conversion is assumed to be completed. The still continuing slight decrease in Ca concentration can be calculated to contribute negligibly to the AH mass or to the conversion. It follows from figure 6.5 that the main part of the conversion is completed within 10 minutes. In this period the Ca concentration decreases from about 200 ppm at 2 minutes reaction time to 120 ppm. Comparison with figure 6.2b shows that the shape of the curve during this period is lying between curve 1 and 2. This implies that the conversion is at least to some extent controlled by the dissolution of the  $\alpha$  HH crystals. This also follows from the shape of the conversion curves presented in figure 6.7 (section 4.1.2.). This result is probably related with the quality of the  $\alpha$  HH crystals, which are prepared by continuous crystallization. These crystals are rather large with a length of up to 1000  $\mu$ m and dissolve rather slowly due to their low specific surface area. In another experiment (exp. 8), where 5 w%  $\beta$  HH was added to a 40 w%  $P_2O_5$ solution with 5 w% H<sub>2</sub>SO<sub>4</sub> and 1 w% AH, the Ca versus time curve remains more or less constant at a high level of about 400 ppm during most of

aggregates of tiny crystals with a high specific surface area. These crystals dissolve easily and the Ca versus time curve resembles curve 2 in figure 6.2b, where the conversion is growth determined. The higher Ca levels of this curve result from the lower  $H_2SO_4$  concentration in solution. The control by growth also follows from the shape of the conversion curves in figure 6.11 (section 4.1.4.). For the DH into AH conversion, where fine grained DH from Merck was used, similarly shaped Ca and Cd versus time curves were obtained as for the  $\beta$  HH into AH conversion. The DH into AH conversion process, however, proceeded significantly slower. This is also illustrated by comparing the two conversion curves at 100°C in figure 6.11, which will be discussed in section 4.1.4. (exp.9, 10)



Figure 6.6. Cd and Ca concentration in the solution during the recrystallization of  $\beta$  HH into AH.

In order to express the degree of conversion in a quantitative way several techniques are available. The simplest way, however, is to use the Cd concentration in solution as a measure. This method is feasible, since the Cd uptake in AH is high. The degree of conversion at time t can be calculated from the remaining Cd concentration at the given time, combined with the Cd concentrations at the start and at the end of the conversion. This leads to the following expression for the degree of conversion:

conversion (t) = mass of formed AH (t) / mass of formed AH (end)

$$= \frac{\ln ([Cd](0)/[Cd](t))}{\ln ([Cd](0)/[Cd](end))}$$
(1)

The derivation of this equation is given in the appendix. The Cd uptake can be expressed by a distribution coefficient K(Cd), given by:

$$K(Cd) = [Cd] (crystal)/[Cd](solution)$$
(2)

or by a partition coefficient D(Cd):

$$D(Cd) = [Cd]/[Ca] (crystal) / [Cd]/[Ca] (solution) (3)$$

Because in the batch experiments the Ca and Cd concentrations are not constant in time, K(Cd) and D(Cd) must be obtained by integration. The derivation is given in the appendix. K(Cd) is more for practical use, because this is the parameter that is directly measured, while D(Cd) gives a better description of the cadmium incorporation since e.g. variations in the Ca concentration in the solution are already taken into account. K(Cd) also depends on all process conditions, while in principle D only depends on the temperature, the supersaturation of the calcium sulfate and the nature of the precipitated phase (AH, HH or DH). In the example of figure 6.5 (exp. 3) the D-value is about  $4*10^{-2}$ . The calculation of D for this example is shown in the appendix. It has been mentioned in the introduction, that at higher already supersaturations or growth rates, the D value will increase, while at lower supersaturations a lower D is expected until a thermodynamically determined limit is reached. This implies, that during a batchexperiment D is not a constant, but decreases with reaction time, because the Ca concentration and thus the supersaturation in the solution decreases during the conversion. In the derivation of the expression for D, however, D has been assumed to be constant during the experiment (see

appendix). For the experiments, where the Ca concentration remains at the about same level during most of the reaction period, this assumption is almost valid. For the experiments where the Ca concentration decreases continuously, D is only an average value.

# 6.4.1.2. Influence of seeding

First the influence of the type of seed crystals was checked, since the conversion rate and the Cd and  $P_2O_5$  uptake could depend on the type of seed crystals used. It has formerly been observed that the use of seed crystals with or without incorporated phosphate ions during batch crystallization of HH from phosphoric acid solutions leads to different growth rates. This is caused by a different solubility of the seed crystals due to the presence or absence of lattice strain induced by the phosphate ions. A different solubility means that under given conditions the supersaturation imposed on the crystals in the solution, is also different, resulting into another growth rate of the crystals and another degree of incorporation of foreign ions. For this reason the AH seed crystals were prepared under conditions prevailing during the batch experiments. In order to check whether these seed crystals match with the experimental conditions, the conversion procedure was repeated once for one experiment, using the newly formed AH as seed crystals for the second recrystallization. No difference in growth kinetics or in uptake of Cd or  $P_2O_5$  was found between the first and second conversion, so probably the used seed crystals match with the experimental conditions. Therefore, for the HH into AH recrystallizations the conversion was performed only once.

Secondly the influence of the amount of seed crystals on the conversion rate was studied by performing experiments under the standard conditions of 40 w%  $P_2O_5$ , 10 w%  $H_2SO_4$  and 90°C with 2 w% HH source material, but with 0, 1, 2, 5 and 10 w% AH seed crystals (exp. 1 to 5). In figure 6.7 the percentage conversion is plotted versus the reaction time for two of the experiments with 0 and 10 w% AH. Even without seed addition, the conversion proceeds fast directly from the start. This

means that under given conditions, nucleation of AH apparantly the begins immediately.

on

the



The addition of seed crystals gives rise to a higher conversion rate, as follows from the steeper slope of the curve. The conversion rate thus seems to be more governed by the precipitation rate of the AH than by the dissolution rate of the HH crystals. The role of the amount of seed crystals is even more obvious, if the conversion rate instead of the percentage conversion is taken. The conversion rate is expressed as the inverse of time needed to reach a certain percentage of conversion. In figure 6.8 the so defined conversion rate is plotted versus the of AH seeds. For each percentage conversion the obtained percentage curve is almost a straight line, which means that the conversion rate is directly proportional to the amount of AH seed crystals. This indicates that the growth of the AH rules the process. Since the shape of the conversion curve for  $\alpha$  HH into AH rather resembles a conversion curve of a process dominated by the dissolution of the source material than one dominated by the growth of the newly formed phase, the shape of a conversion curve alone is not conclusive except perhaps for the two extreme cases (see section 4.1.1.). The conversion rate is not zero when no seed crystals are added, but a value of the intercept of -2 w% AH is found in figure 6.8. Heterogeneous nucleation of AH upon the HH crystals may explain this phenomenon. The high temperature and acid concentration needed for



AH growth might promote heterogeneous nucleation of AH, since under more moderate conditions AH nucleates slowly.

6.4.1.3. Influence of the  $H_2SO_4$  content.

The influence of the  $H_2SO_4$  content of the solution was studied by performing experiments with different H<sub>2</sub>SO<sub>4</sub> concentrations under further identical conditions of 40 w%  $P_2O_5$ , 90°C, 2 w%  $\alpha$  HH and 1 w% AH (exp. 2,6 6). In figure 6.9 the Cd and Ca concentration are plotted as a function of time, for 5 and 10 w%  $H_2SO_4$  in the solution respectively. For 5 w %  $H_2SO_4$ , total conversion was achieved in about 30 minutes, while for 10 % a reaction time of 20 minutes was required. Sulfate ions thus stimulate the conversion. For a 5 % H<sub>2</sub>SO<sub>4</sub> solution the Ca concentration remains much higher than for 10 % (about 400 and 150 ppm respectively). The Ca concentration is directly related to the sulfate content via a solubility product of CaSO4. It can also be seen in the figure that for 10 %  $H_2SO_4$  the Cd concentration remaining in the solution is lower (30 % of the original content vs. 70 % for 5 %  $H_2SO_4$ ), and thus the Cd uptake in the formed AH higher. The K(Cd) can be calculated to be about 18 for 5 %  $H_2SO_4$  in the solution, while for 10 %  $H_2SO_4$  a value of 60 is obtained. The corresponding D-values are  $3\cdot 10^{-2}$ and 4.10-2.

The influence of the sulfate concentration on the Cd uptake by the AH crystals is elucidated by plotting K(Cd) versus the sulfate concentration (figure 6.10). It can be seen that K(Cd) increases from about 2 at 2 w%  $H_2SO_4$  to about 50 at 10 %. The spread in data at 10 %, K(Cd) ranges from 40 to 65, in dependence on the amount of seed material used is significant. This spread is probably caused by the lower supersaturation when larger amounts of seed crystals are used. The DH into AH recrystallization experiments showed about equal K(Cd) values during conversion as for the HH into AH conversions at corresponding  $H_2SO_4$  concentrations. Comparison of a K(Cd) value of about 40, and a D 1.8\*10-<sup>2</sup>, (MSMPR) crystallization of obtained from continuous experiments of AH with these data shows a good agreement (exp. 11). When in these continuous crystallization experiment so called 'black acid' is used (exp. 12), K(Cd) is 65 (D =  $3.8*10^{-2}$ ). This higher uptake with respect to the experiment in chemically pure acid is caused by the

Figure 6.10.



impurities in the solution. An explanation for this phenomenon has yet to be found.

From the D(Cd) values for AH, as summarised in tabel 1, it follows that the value of D(Cd) is lying between 2 and 4  $\cdot$  10-2. Other experiments, not presented here, show that this D-value is constant for up to 20% replacement of  $Ca^{2+}$  ions in the AH structure by  $Cd^{2+}$  ions. Variations in D(Cd) can, as mentioned, be related to differences in growth rate. The lowest D value can be expected at equilibrium conditions, where the growth rate is zero. During growth the Cd<sup>2+</sup> ions at the crystal surface can be entrapped by propagating growth layers. At higher growth rates, i.e. at higher supersaturations, the uptake will thus increase. A constant D value at a given growth rate implies that the Cd uptake is directly proportional to the ratio of the Cd and Ca concentrations in the solution. This means that the Cd uptake is determined by a competition between the Cd and Ca ions in solution and thus by their relative rate of impingement upon the crystal surface. If the Ca concentration decreases, K(Cd) is favoured in the competition and the uptake, reflected by K(Cd), will increase. This can be achieved by e.g. a higher sulfate concentration in the solution or by a decrease in CaSO₄ solubility.

-107-



Figure 6.11. Conversion of  $\beta$ HH and DH into AH at various temperatures.

6.4.1.4. Influence of the temperature.

To study the influence of the temperature upon the HH into AH conversion, additional experiments were performed at 80 and 100°C in 40 w%  $P_2O_5$ , 5%  $H_2SO_4$  with 5 w%  $\beta$  HH and 1 w% AH seed crystals (exp. 7 to 9). The calculated percentage conversion was plotted as a function of time in figure 6.11. In particular the hollow shape curve below 50% conversion points at a growth dominated conversion process, as follows from comparison with curve 2 in figure 6.2a. The last parts of the conversion curves, obtained when the conversion is almost completed, indicate a dissolution controlled process as can be expected. The conversion rate, given by the shape of the curve demonstrates a higher conversion rate at increasing temperature. Comparison of the  $\beta$  HH into AH with the DH into AH conversion curve (exp. 10), both at 100°C, show that the latter proceeds more than two times slower. Surprisingly no lower D(Cd) value was found. More evidence is needed here. The D(Cd) values for the  $\beta$  HH conversion are increasing with temperature, which can be related to the higher growth rates at elevated temperatures. In experiments, described by [Witkamp et al., 1986] the  $P_2O_5$  uptake in AH, formed in 40 w%  $P_2O_5$  and 12 %  $H_2SO_4$  is low and decreases from 0.25 % at

 $70^{\circ}$ C to 0.14 % at  $90^{\circ}$ C. This decrease at higher growth rate must be resulting from another effect, which compensates for the higher uptake expected at higher growth rates.

# 6.4.1.5. Influence of the $P_2O_5$ concentration

To explore the influence of the  $P_2O_5$  concentration upon the Cd uptake a few additional experiments were done on the  $\alpha$  HH into AH conversion in a 35 and 45 w%  $P_2O_5$ , 10 %  $H_2SO_4$  solution at 90°C with 5 w% HH and 5 w% AH. The K(Cd) values given in tabel 1 (exp 13,14) reveal a strong increase in uptake at higher  $P_2O_5$  concentrations. This increase is probably caused by a decrease in CaSO<sub>4</sub> solubility, but for these experiments not enough data of the Ca concentration were available to calculate D.

# 6.4.2. Recrystallization of hemihydrate into dihydrate.

# 6.4.2.1. Influence of the seeds

The conditions where HH transforms into DH follow from the region of the phase diagram, where HH is unstable and DH stable or metastable. The conversions were carried out in solutions with 15-25 w%  $P_2O_5$ , 0-12 w%  $H_2SO_4$ , 10-16 w%  $\alpha$  HH and 5-8 w% DH. The influences of the amount of seeds, the  $H_2SO_4$  and  $P_2O_5$  concentrations of the solution as well as the temperature upon the conversion rate have not been studied systematically, since these effects are already extensively described. [Taperova (1950), Slack (1968) and Becker (1983)]. Only a few selected experiments were performed.

Contrary to the HH into AH recrystallization it appeared to be necessary to perform each conversion a second time, using the obtained DH from the first conversion as seed material for a second. This second conversion always proceeds at least 10 % slower. Performing the conversion a third time hardly has any influence on the conversion rate. A very small effect of repeated conversions can be expected, because the crystals become slightly larger after each conversion. The specific surface area of the DH thus decreases, giving rise to a lower conversion if the reaction is growth rate controlled, because the amount of rate, added seed crystals is constant. The necessity of a second conversion can be owed to the use of p.a. gypsum (Merck) as seed material for the first conversion, while for the AH experiments the seeds were prepared in phosphoric acid and resembled therefore more those formed at the selected recrystallization conditions. All results given in table 6.2 refer to the second conversion.  $\tau(50\%)$  denotes the time required for 50 2 conversion. In the table also the results of continuous crystallization experiments at 20 and 60 minutes residence time are given ( $\tau$ 20 and  $\tau$ 60). Apart from the influence of the type of seed crystals on the conversion rate, also the effect of the amount of seeds was tested. In figure 6.12 the percentage conversion is plotted versus the reaction time for an experiment with no seeds added and for an experiment with 5 w% DH seeds under further identical conditions (exp. 15, 16). The shape of the curve obtained with seeding resembles the  $\alpha$  HH into AH conversion curve given in figure 6.7. This conversion is thus at least to some extent controlled by the dissolution of  $\alpha$  HH. When no seeds are added an induction period of about 30 minutes preceeds the development of DH. At the given relatively mild conditions needed for DH growth the  $\alpha$  HH crystals do not seem to act as heterogeneous nuclei for DH.

For these experiments the Ca and Cd concentrations were not determined as a function of time during conversion, but only at the start and at the end. The mean Ca concentrations of the two samples table 6.2 are taken as representative for presented in the Ca concentration during the conversion. Since the Cd uptake by DH appeared to be much lower than for AH, the decrease in Cd concentration in the solution could neither be used for the calculation of K(Cd) nor for the determination of the degree of conversion. For this reason the K(Cd) was directly derived from the analyzed Cd incorporation in the DH crystals. The degree of conversion could accurately be deduced from the crystal water content of the sample.

-110-

Table 6.2. HH into DH recrystallization

solution						crystals							
exț nr	o. con- . versio	۳ <sub>2</sub> ۳۶	05 %H25	ppm C 304 %	a see	%soure	ce T( <sup>0</sup>	%P <sub>2</sub> O <sub>5</sub> C)	K(Cd)	D(Cd) (10- <sup>3</sup> )	τ(50%) (min)	)	
15	αНН→DH	25	6		0	10	65				50		
16	αHH→DH	25	6		5	10	65				7		
17	αHH→DH	>15	0.6	2600	5	10	40	1.4	0.20	2.2			
18	αHH→DH	15	2	1500	5	10	40	1.0	0.20	1.3			
19	αHH→DH	15	5	900	5	10	40	0.7	0.25	1.0			
20	αHH→DH	15	10	600	5	10	40	0.7	0.31	0.8			
21	αHH→DH	15	0.7	3000	5	10	60	1.1	0.20	2.5			
22	αHH→DH	15	2	1600	5	10	60	0.9	0.27	1.9			
23	αHH→DH	15	5	1100	5	10	60	0.6	0.31	1.5			
24	αHH→DH	15	10	900	5	10	60	0.4	0.43	1.6			
25	DH	25	1	3000	10	)	60	1.6	0.14	2.0	(cont	cryst.	τ20)
26	DH	25	6	730	10	)	60	0.65	0.43	1.5	(cont	cryst.	τ20)
27	DH	25	11	470	10	)	60	0.47	0.85	1.7	(cont.	cryst.	τ20)
28	DH	25	5	900	10	)	60	0.35	0.28	1.1	(cont	cryst.	τ60)
29	αHH→DH	25	6		9	16	50	0.44	0.42		10		
30	αHH→DH	25	6		9	16	60	0.32	0.43		16		
31	αHH→DH	25	6		9	16	70	0.25	0.37		60		
32	αHH→DH	15	6		9	16	60	0.37	0.37		7.5		
33	αHH→DH	20	6		9	16	60	0.38	0.38		5		
34	αHH→DH	25	6		9	16	60	0.42	0.43		60		
35	αHH→DH	15	10		9	16	70	0.30	0.60		8		
36	αHH→DH	15	10		9	16	70	0.32	0.60		27 (	(black a	icid)
37	αHH→DH	25	6		5	10	70				35		
38	αHH→DH	25	6		5	10	70				60 (	(0.8 %Al	F3)
39	αHH→DH	15	10		9	16	70	0.39	0.48		9 (	(10 ppm	Ce <sup>3</sup> +)
40	αHH→DH	15	10		9	16	70	0.33	0.65		17 (	(20 ppm	Ce <sup>3</sup> +)
41	αHH→DH	15	10		9	16	70	0.38	0.49		68 (1	100 ppm	Ce <sup>3</sup> +)
42	αHH→DH	15	10		9	16	70	0.39	0.59		140 (2	250 ppm	Ce <sup>3</sup> +)



6.4.2.2. Influence of the  $H_2SO_4$  concentration

The influence of the  $H_2SO_4$  concentration in the solution was tested by recrystallizing 9 w% HH with 6 w% DH seeds in 15 w%  $P_2O_5$  at 40 and 60 °C (exp. 17 to 24). The lowest  $H_2SO_4$  concentration was calculated from the stoichiometric calcium concentration, because no H₂SO₄ was added. When the  $H_2SO_4$  concentration increases from 0.6 % to 10 %, K(Cd) increases slightly from 0.20 to 0.31 at 40 °C, and from 0.20 to 0.43 at 60 °C. This minor increase is in contrast with the increase in K(Cd) for AH from about 5 to 50 in this range. The increase is very small since the Ca concentration decreases far less at higher H<sub>2</sub>SO₄ concentrations here than for the HH into AH conversion. At the relatively low  $P_2O_5$  concentration used here for the HH into DH conversion, the solubility of calcium sulfate is enhanced by an increase in  $H_2SO_4$  concentration, as can be seen from the  $[Ca]*[H_2SO_4]$  product which can be calculated from table 6.2. This higher solubility compensates for the decrease in calcium concentration at higher  $H_2SO_4$ concentrations due to the constancy of the solubility product. Since variations in the Ca concentration are taken into account in the calculation of D(Cd), its value should be constant. Table 6.2, however, shows that D(Cd) is not constant but decreases at both 40 and 60  $^{\circ}C$  with higher H<sub>2</sub>SO<sub>4</sub> concentrations. These decreases in D(Cd) may be caused by the use of an average of two values of the calcium concentration instead of the measured actual Ca concentrations, and have to be verified by measuring the actual Ca concentration during the conversion as has been done for the conversions into AH. The D-value of 1.7\*10-3 at 60 ٥C corresponds with D values obtained for continuous crystallization experiments of DH in 25 %  $P_2O_5$  at 60  $^{\circ}C$ , at  $H_2SO_4$  concentrations between 1 and 10 % (exp. 25 to 27). The residence time in these experiments was 20 minutes. When instead of 20 minutes 60 minutes was taken, the D-value  $1.1*10^{-3}$ 28). This diminished to (exp. indicates that the supersaturation and thus the growth rate, being higher for a shorter residence time, plays a role in the uptake. The observed D(Cd) value for DH of about 1 to  $2*10^{-3}$  is remarkably lower than for AH. The difference by a factor of about 20 can not be caused only by a difference in growth rate or by the different process conditions, but is probably inherent to the different calcium sulfate phases.

The  $P_2O_5$  uptake by the DH phase during recrystallization decreases with the  $H_2SO_4$  content of the solution, as shown in table 6.2. In analogy with the Cd/Ca competition in solution determining the Cd uptake, the phosphate over sulfate ratio is expected to dominate the phosphate uptake. This has formerly been proved to be true for the phosphate uptake by HH in 40 w%  $P_2O_5$  [Sluis et al. , 1986). For these HH into DH recrystallization experiments, however, such a competition model apparently does not describe the yielded  $P_2O_5$  values in DH, presented in table 6.2. An explanation for this discrepancy might be a change in the 15 to 25 %  $P_2O_5$  concentration constituents of the solution in the range. According to Elmore (1965) the composition of the solution changes in this range from mainly  $H_2PO_4$  - and  $H_3PO_4$  constituents into  $H_5P_2O_8$ - ions. In our case, in a 15 w%  $P_2O_5$  solution the effect of an increasing amount of  $H_2SO_4$  could be comparable with that of  $P_2O_5$ . This change in composition of the solution might affect the phosphate uptake by the crystals.

#### 6.4.2.3. Influence of the temperature

Comparison of the Cd and  $P_2O_{\kappa}$  uptake results obtained for experiments performed at 40 and at 60 °C, shows an increase in K(Cd) and D(Cd), and a decrease in the  $P_2O_5$  uptake at increasing temperature. Additional experiments, however, performed at 50, 60 and 70 °C in a 25 w%  $P_2O_5$  and 6 w%  $H_2SO_4$  containing solution (exp.29 to 31), gave rise to about equal K(Cd) values, which are also about equal to those obtained for the former experiments with 5 to 10 % H<sub>2</sub>SO<sub>4</sub>. No final conclusions can therefore so far be drawn about the influence of the temperature on the Cd uptake, only that this effect will be small. The decreasing  $P_2O_5$ uptake at higher temperatures is more obvious. This tendency is consistent with the results found for AH. To quantify the conversion rate at the various temperatures only the times required to achieve a 50 % conversion are presented. These times increase from 10 minutes at 50 °C through 16 minutes at 60 °C to 60 minutes at 70 °C. This tendency can be ascribed to the smaller difference in solubility between the HH and DH phases at higher temperatures, causing a lower driving force for the conversion.

### 6.4.2.4. Influence of the $P_2O_5$ concentration

The influence of the  $P_2O_5$  concentration on the Cd and  $P_2O_5$  uptake in DH was studied by performing experiments at 60 ° in solutions containing 15, 20 and 25 w%  $P_2O_5$  and 6 w%  $H_2SO_4$ . The effect of the variations in  $P_2O_5$  concentrations upon the Cd and  $P_2O_5$  uptake is only minor, as can be seen in table 6.2, exp 32 to 34. The time, needed to reach 50 % conversion , however, increases noticeably from about 6 minutes at 15 and 20 w%  $P_2O_5$  to 16 minutes at 25 w%  $P_2O_5$ . This can be explained by a smaller difference in solubility between HH and DH at the higher  $P_2O_5$  concentration.



6.4.2.5. Influence of impurities

Next to the already mentioned parameters, the conversion rate strongly depends on the presence of a number of impurities in the solution. One of the impurities, of which the strong impact is well known, is aluminum fluoride. The influence of 0.8 % AlF<sub>3</sub> on the conversion is shown in figure 6.13, where the conversion is plotted versus the time, with and without AlF<sub>3</sub> in a solution of 25 w%  $P_2O_5$ , 6 w%  $H_2SO_4$  at 70 °C, and where 10 w% HH and 5 w% DH were added (exp. 37, 38). The conversion rate, given by the slope of the curve, is evidently lower, i.e. about 30 %, in the presence of AlF<sub>3</sub>.

Other impurities are the lanthanides, which can be present in the phosphate ore in concentrations up to 1 %  $Ln_2O_3$  [Kijkowska, 1983]. The most predominant ion of these is  $Ce^{3+}$ . The influence of  $Ce^{3+}$  on the conversion rate is even greater. Therefore similar experiments were performed for various  $Ce^{3+}$  concentrations. (exp. 39 to 42). The results are presented in figure 6.14. Here the conversion rate is plotted against the  $Ce^{3+}$  concentration up to 250 ppm of  $Ce^{3+}$ . The conversion rate is expressed as the inverse of the time to achieve 25, 50 and 75 % conversion. Already at 20 ppm  $Ce^{3+}$  an effect is visible, and at 250 ppm  $Ce^{3+}$  the conversion rate is decreased by about a factor ten. The



Figure 6.14.

Rate of conversion of HH into DH as a function of the cerium concentration in the solution.

concentrations used are much lower than those of  $AlF_3$ , and it can be concluded that  $Ce^{3+}$  is a much stronger conversion inhibitor. Experiments under carefully controlled conditions, where in a 0.1 M NaClO<sub>4</sub> solution DH seed crystals were allowed to grow at a constant supersaturation indicate that the  $Ce^{3+}$  ions affect the growth rate of the DH.

When instead of chemically pure phosphoric acid, acid from a Nissan H proces was used, only the conversion rate was affected. In 15 w%  $P_2O_5$ , 10 w%  $H_2SO_4$  at 70 °C the K(Cd) equals in both cases 0.60, and the  $P_2O_5$  uptake is about 0.31 %. (exp. 35, 36). The required time for 50 % conversion increases from 8 minutes in chemically pure acid to 27 minutes in product acid. This decrease in conversion rate is probably imposed by impurities present in the black acid. The concentrations of only the Ce<sup>3+</sup> and AlF<sub>3</sub> ions in the solution are, however, not high enough to be responsible for this decrease in conversion rate. The Ce<sup>3+</sup> concentration was estimated to be 10 ppm, while the AlF<sub>3</sub> concentration was a few tenth %.

#### 6.5. Conclusions

From the results the following conclusions can be drawn:

- The recrystallization of HH or DH into AH in batchexperiments can easily be followed by recording the Cd content of the solution, because the uptake of Cd in AH is very high. The rate of conversion is determined by the growth of AH, but can also to some extend be affected by the dissolution of the source material.
- Under the given conditions, where conversion of HH into AH is completed within an hour, no induction period is observed. The addition of seed crystals, however, strongly promotes the conversion.
- 3. Under conditions where the recrystallization of HH into DH is completed within half an hour, an induction period of half an hour preceeds the conversion when no seeds are added. The conversion rate depends on by the type of seed crystals used.
- 4. Conversion into AH proceeds faster at higher  $H_2SO_4$  and  $P_2O_5$  concentrations. The Cd uptake by AH is also higher under these conditions.
- 5. The Cd uptake in AH and DH can be described by a competition between Cd and Ca ions, and will thus be low at high Ca concentration in the solution.
- 6. The  $P_2O_5$  uptake in DH and AH on the contrary, is lower at higher  $H_2SO_4$  concentrations and temperatures. The  $P_2O_5$  concentration in the solution plays a less important role.
- 7. The uptake of Cd in DH and AH can be expressed by a partition coefficient D, which equals 2 to 4\*10-<sup>2</sup> for AH and 1 to 2\*10-<sup>3</sup> for DH. The obtained D-value depends slightly on the supersaturation, through the growth rate of the crystals.
- 8. The conversion of HH into DH is stimulated by low temperatures and low  $P_2O_5$  concentrations. Literature data have shown that the  $H_2SO_4$ concentration causes an optimum in the conversion rate. The Cd uptake increases slightly with increasing  $H_2SO_4$  concentrations, and

with increasing temperatures. The  $\mathrm{P_2O_5}$  concentration has no visible effect.

9. Impurities can have strong influence on the conversion rate as has been shown for the HH into DH transformation. AlF<sub>3</sub> retards the conversion, and Ce<sup>3+</sup> has this effect even more. Conversion in black acid, containing a number of impurities, proceeds considerably slower than in chemically pure acid. The presence of these impurities promotes the Cd uptake during continuous crystallization of AH.

#### 6.6. References

- Becker, P. 1989, Phosphates and phosphoric acid. Fertilizer Science and Technology Series, Vol.6. Dekker, New York.
- Bevington, P.R. 1969. Data reduction and error analysis. McGraw-Hill, New York.
- Cardew, P.T. and R.J. Davey. 1985. The kinetics of solvent-mediated phase transformations. Proc. R. Soc. Lond. <u>398</u> 415-428
- Elmore, K.L. et al. 1965. J. Phys. Chem. <u>69</u> 3520.
- Glazyrina, L.N., et al. 1980. Solubility of calcium hemihydrate and dihydrate in phosphoric acid containing  $Al^3+$ , F- and  $SiF_6^2$  ions. Translated from Z. Prikladnoi Khimii, <u>53</u> 2524-2527.
- Huheey, J.E. 1975. Inorganic Chemistry. Harper and Row, New York.
- Kijkowska, R.. 1983. Recovering rare earth elements from Kola apatite and Moroccan phosphate rock. Phosphorus & Potassium <u>127</u> 24
- Kushnir, J. 1980. The coprecipitation of strontium, magnesium, sodium, potassium and chloride ions with gypsum. An experimental study. Geochim. et Cosmochim. Acta <u>44</u> 1471.
- Slack, V. 1968, Phosphoric Acid. Fertilizer Science and Technology Series, Vol.1. Dekker, New York.
- Sluis et al. 1986. Crystallization of calcium sulfate in concentrated phosphoric acid. J. Crystal Growth <u>79</u> (1986) 620-629
- Taperova, A.A. and M.N. Shulgina. 1950. The kinetics of the transformation of the crystal hydrates of calcium sulfate in the presence of phosphoric acidJ. Appl. Chem (USSR) <u>23</u> 27

Weterings, C.A.M, and J.A. Janssen. July 1986. Patent pending.

(nr. 8601846 Dutch Patent Office).

- Schuit and G.M. 1986. Witkamp, G.J., S.P.J. van Rosmalen. Recrystallization of calcium sulfate modifications in phosphoric acid. Condensed papers of the Second International Congres on phosphogypsum, Miami 1986. University of Miami.
- 6.7. Appendix: calculation of cadmium uptake and conversion

## 6.7.1. Distribution coefficient K(Cd)

The dimensionless distribution coefficient K(Cd) is defined as the ratio of the Cd concentration in the crystals and in the solution:

 $K(Cd) = [Cd^2+](crystals)/[Cd^2+](solution).$ 

For continuous crystallization experiments, where a steady state can be obtained, the steady state values of the concentrations were used to calculate K(Cd). For batch experiments, however, the Cd concentration in the solution is not constant, but decreases with time due to the uptake of cadmium by the newly formed calcium sulfate crystals. Under the assumption that K(Cd) is constant during the experiment, K(Cd) can be calculated by integration.

The Cd uptake in kg (d Cd) per kg formed CaSO<sub>4</sub> is given by:

d Cd / d CaSO<sub>4</sub> =  $[Cd^2+](solution)*K(Cd) \iff$ 

d Cd =  $[Cd^2+](solution)*K(Cd)*d CaSO_4$ 

 $[Cd^2+](end)$ 

Dividing both sides by the total amount of solution gives:

 $d[Cd^{2}+](solution) = - [Cd^{2}+](solution)*K(Cd)*d[CaSO_{4}]$ 

The minus sign develops because the amount of Cd taken up by the calcium sulfate has been replaced by the amount of being removed from the solution. Sorting out parameters and integration leads to:

:

end  

$$\int \frac{d[Cd^2+](solution)}{[Cd^2+](solution)} = - K(Cd) * \int d[CaSO_4] \iff begin$$

$$- \ln \frac{[Cd^2+](begin)}{[Cd^2+](cad)} = - K(Cd) * ([CaSO_4](end) - [CaSO_4](begin)) \iff$$

$$K(Cd) = \frac{1}{[CaSO_4](formed, end)} * \ln \frac{[Cd^2+](begin)}{[Cd^2+](end)}, [CaSO_4] \text{ in kg/kg} \quad (1)$$

#### 6.7.2. Partition coefficient D

For the  $Cd-CaSO_4$  system the partition coefficient D is defined as the molar ratio  $Cd^2+/Ca^2+$  in the formed crystals divided by the same ratio in the solution:

$$D = \frac{[Cd^{2}+]/[Ca^{2}+](crystals)}{[Cd^{2}+]/[Ca^{2}+](solution)}$$
(1)

In the following the charges of the ions will be omitted.

In the continuous crystallization experiments, D is obtained by inserting the steady state concentrations of Cd and Ca in Eq. 1. In batch experiments, however, the Cd and Ca concentrations are a function of the reaction time. Under the assumption that D is constant during the experiment, D can be calculated from the Cd and Ca concentrations in the solution as a function of time, and the total amounts of solution and formed crystals.

The reaction time is divided in fractions  $\Delta t$ , and starts at t = 0. During the interval  $\Delta t$  the Cd concentration in the solution changes:

 $\Delta[Cd](solution) = [Cd](t+\Delta t) - [Cd](t)$ 

The Ca concentration in this interval has the mean value [Ca](t). The Cd concentration in the CaSO<sub>4</sub> formed during the time interval  $\Delta t$ , denoted as  $\Delta CaSO_4$ , is given by:

$$[Cd](\Delta CaSO_4) = -\Delta[Cd](solution) * \frac{mass of the solution}{mass of formed CaSO_4}$$
(2)

From the definition of D (equation 1) and from the relation

[Ca](crystal) = 1/0.136 (mole/kg) for anhydrite it follows that:

$$[Cd](\Delta CaSO_4) = \frac{D*[Cd](solution)}{0.136*[Ca](solution)}$$
(3)

Combining equations 2 and 3 gives:

$$\Delta CaSO_4 = - \frac{\Delta [Cd](solution) * 0.136 * [Ca](solution) * mass of solution}{D * [Cd](solution)}$$
(4)

-120-

(4) can be summated to yield the total amount of formed CaSO4:

$$i=n$$

$$-\Sigma \frac{([Cd](i\tau/n) - [Cd]((i-1)\tau/n))*0.136*[Ca](i\tau/n)*mass of solution}{D * [Cd](i\tau/n)} (5)$$

i=1

CaSO, (totally formed) -

where all concentrations refer to concentrations in the solution. r denotes the total reaction time. The summation can be written as an integral for n approaching infinity:

$$\frac{\text{totally formed CaSO}_{4}}{\text{mass of solution}} = - \int \frac{(d[Cd](t)/dt) * 0.136 * [Ca](t)}{[Cd](t) * D} dt \quad (6)$$

Since D and the left hand side of (6) are constant in time, they may be exchanged without affecting the result of the integration:

$$t(end)$$

$$D = - \int \frac{(d[Cd](t)/dt) * 0.136 * [Ca](t)}{[Cd](t)* (totally formed CaSO_4/mass of solution)} dt (7)$$

$$0$$

(7) can be evaluated when the Cd and Ca concentrations are known as a function of time. In order to allow this calculation, both concentrations are fitted by a function

$$g(t) = a_1 + a_2 * / t + a_3 * t + a_4 * (t+1)^{1/4} + a_5 * (t+1)^{-1/2} + a_6 * \exp(t/10)$$
(8)

For each set of data  $a_1 - a_6$  are calculated, yielding a best fit. For the fitting procedure an algorithm of Marquard is used [Bevington,1965] in a Pascal program. This algorithm also allows optimization of functions not linear in its parameters. The program runs with Turbo Pascal (Borland Inc.) on a MS-DOS compatible personal computer. Concentrations are expressed in ppm and the reaction time in minutes. For instance, for the data of exp. 3, the following functions are obtained for t = 0 to t = 25 minutes:

$$[Cd](solution) = 250.059 + 46.3767*/t + 2.54038*t - 220.1932*(t+1)^{1/4} + 100.590*(t+1)^{-1/2} - 2.47568*exp(t/10); (9)$$

$$[Ca](solution) = 922.223 + 43.9845*/t + 12.5996*t - 556.221*(t+1)^{/4} - 109.487*(t+1)^{-1/2} - 6.63790*exp(t/10)$$
(10)

$$\frac{d[Cd](t)}{dt} = 23.188 \times t^{-1/2} + 2.54038 - 55.0483 \times (t+1)^{-3/4}$$

$$- 50.2952 \times (t+1)^{-3/2} - 0.247568 \times \exp(t/10)$$
(11)

From Eq. 7, 9, 10, 11 and the conversion

[Ca] (mole/kg) = [Ca] (ppm)\*2.5\*10<sup>-5</sup> an expression for D follows, after a new fitting procedure

$$t(end)$$

$$D = -\int_{0}^{1} (1.72977*10^{-2} - 2.042173*10^{-2}*/t + 1.102350*10^{-3}*t + 0$$

$$4.50295*10^{-2}*(t+1)^{+1/4} - 3.67131*10^{-2}*(t+1)^{-1/2} - 2.56303*10^{-4}*exp(t/10)) dt$$

$$(12)$$

$$, yielding D = 0.040 \text{ for this example.}$$

#### 6.7.3. The Conversion.

6.7.3.1. Calculation from the Cd concentration in the solution.

This method is only applicable to the conversion of HH or DH into AH. The conversion at time t is defined by:

$$Conversion(t) = \frac{\text{mass of formed } CaSO_4(t)}{\text{mass of formed } CaSO_4(end)}$$
(1)

Under the assumption that K(Cd) remains constant during the recrystallization, the degree of conversion at time t can be calculated from Eq. 1, section 6.7.1.

$$K(Cd) = \frac{1}{[CaSO_4](formed,t)} * \ln \frac{[Cd](begin)}{[Cd](t)}$$
(2)

from Eq. 1 and 2 follows that

conversion (t) = 
$$\frac{[CaSO_4](formed,t)}{[CaSO_4](formed,end)} = \frac{\ln([Cd](begin)/[Cd](t))}{\ln([Cd](begin)/[Cd](end))}$$
(3)

6.7.3.2. Calculation from the Cd and Ca concentration in the solution.

(Only for the HH or DH conversion into AH)

The conversion as defined as in section 6.7.3.1, Eq. 1, yields, combined with Eq. 6, section 6.7.2, on integration to t instead of to t(end):

conversion(t) = 
$$\frac{1}{[CaSO_4](end)} * = \int \frac{(d[Cd](t)/dt * 0.136 * [Ca](t))}{D * [Cd](t)} dt$$

6.7.3.3. Calculation of the conversion from the crystal water content.

.

This method is only worked out for the HH into DH conversion.

. .

Assume that at the start is present an amount of dihydrate DH(0) and hemihydrate HH(0). The masses at time t are denoted as DH(t) and HH(t). The solubility of calcium sulfate is neglected. The conversion is defined as :

$$conversion(t) = \frac{DH(t) - DH(0)}{DH(end)}$$
(1)

Pure dihydrate contains 20.9 w%  $H_2O$ , and hemihydrate contains 6.2 %. The crystal water content of the sample, taken at time t contains x %  $H_2O$ . The fraction of dihydrate in the sample is then give by Eq. 2:

fraction dihydrate(t) = 
$$\frac{x(t)-6.2}{14.7}$$
 (2)

Since the molar weight of dihydrate is 172, and of hemihydrate is 145 grams/mole, the total crystal mass increases during the conversion:

$$mass(t) = DH(t) + HH(t)$$
  
= DH(0) + conversion(t)\*HH(0)\* $\frac{172}{145}$  + (1-conversion(t))\*HH(0)  
= DH(0) + HH(0)\*( $\frac{27}{145}$ \*conversion(t)+1) (3)

The fraction dihydrate is also equal to DH(t)/mass(t). This gives, in combination with Eq. 2 and 3:

 $\frac{x(t)-6.2}{14.7} = \frac{DH(0) + conversion(t) * HH(0) * (172/145)}{DH(0) + HH(0) * (27/145 * conversion(t)+1)}$ (4)

yielding, after rearrangement of parameters:

conversion(t) =  $\frac{14.7 * DH(0) + (6.2 - x(t)) * (DH(0) + HH(0))}{HH(0) * (x(t) * 27/145 - 18.59)}$  (5)

#### CHAPTER 7

# BATCHWISE RECRYSTALLIZATION IN PHOSPHORIC ACID II: HEMIHYDRATE INTO DIHYDRATE CONVERSION DESCRIBED WITH A MODEL.

#### Abstract

A model is presented for the solvent mediated batchwise recrystallization of hemihydrate into dihydrate. The model takes into account the rates of dissolution of hemihydrate and of growth of gypsum. These rates result from the driving forces (under- and supersaturation) that are influenced by temperature and acid concentrations, and from the rate constants, which are mainly affected by impurities. Secondary nucleation can be neglected with respect to the observed recrystallization rates. The presented model can also be applied more generally.

## 7.1. Introduction

In many processes recrystallization is applied as an intermediate step to improve the filterability and the purity of a crystalline product. This only succeeds if the conversion is a solvent mediated process, comprising dissolution of the original material followed by nucleation and growth of the new phase. The encaptured impurities become redistributed between the solution and the newly formed crystals.

In order to implement a recrystallization step, knowledge about the kinetic parameters, which govern the overall conversion rate is needed. These parameters vary in general with a change in process conditions such as the temperature and composition of the solution and the presence of impurities. For an optimal conversion rate, i.e. fast enough to meet the economic requirements but slow enough to prevent unacceptable impurity uptake, appropriate conditions must be selected. In this paper a model is given to calculate kinetic parameters from simple batchwise recrystallization experiments.

It has been worked out for the batchwise recrystallization of calcium sulfate hemihydrate into dihydrate from phosphoric acid

-125-

solutions at various operating conditions, but the model can also be applied to any other conversion system.

In part II of this paper the model will be extended to continuous recrystallization systems. The applicability of the kinetic parameters obtained from batch experiments, in the modelling of a continuous recrystallization process will be demonstrated.

The effect of impurities upon the kinetics will be presented in a forthcoming paper.

# 7.2. Recrystallization of calcium sulfate

During phosphoric acid production, calcium sulfate hemihydrate (HH) is precipitated by reaction of the ore with sulfuric acid. This HH is transformed into dihydrate by diluting the phosphoric acid from about 5.5 to 3.5 mol  $H_3PO_4$ , as well as by decreasing the temperature from about 90 to 60-75°C under simultaneous addition of sulfuric acid. These conditions follow from the phase diagram, where 1 w% excess sulfuric acid is equivalent to 1.5 w%  $H_3PO_4$  [1, 2, 3, 4]. More detailed information can be found in literature [1-8].

The conversion rate is dictated by the dissolution rate of the HH crystals as well as by the growth rate of the DH crystals. These rates depend on the respective rate constants and on the under- and supersaturation with respect to the solubilities of both phases [9]. A large difference in solubilities, as occurs far from the equilibrium line between the two phases, stimulates a fast conversion. The rate constants are influenced by process conditions such as the temperature and the acid concentrations as well as by impurities [10].

In batch experiments the calcium sulfate concentration changes with time. In the absence of DH seeds the initial CaSO<sub>4</sub> concentrations equal the HH solubility values. During growth of the DH crystals the concentration drops, the solution becomes undersaturated with respect to HH, and the HH phase continues to dissolve. After dissolution of all HH, the concentration decreases till the DH solubility is reached.

-126-

The conversion process can be followed in time by registering the  $CaSO_4$  concentration in the solution together with the degree of conversion of the solid, expressed by [11]

$$\alpha(t) \simeq \frac{[DH(t)] - [DH(0)]}{[HH(0)]}$$
(1)

## 7.3. The batch recrystallization model

The linear dissolution and growth rates are defined as:

$$D = k_{D} \sigma_{HH}^{n}$$
(2)  
and  
$$G = k_{G} \sigma_{DH}^{m}$$
(3)

where  $k_{D}$  and  $k_{G}$  are rate constants and where the under/supersaturation in solution  $\sigma$  is based on the total actual concentrations of the ions in solution and the solubility products,  $SP_{i}$ :

$$\sigma_{i} = \left| \sqrt{\frac{[Ca][SO_{4}]}{SP_{i}}} - 1 \right| \quad \text{with } SP_{DH} \leq [Ca] \cdot [SO_{4}] \leq SP_{HH} \quad (4)$$

For clarity the charges of the ions are left out. For the HH into DH conversion it is reasonable to take n = 1 and m = 2. Secondary nucleation in these seeded batch experiments can be neglected as will be discussed below.

The mass balance of the conversion expressed in moles per kg slurry is given by:

$$\frac{d[CaSO_4, l!}{dt} + \left(\frac{\rho}{M}\frac{dV}{dt}\right)_{HH} + \left(\frac{\rho}{M}\frac{dV}{dt}\right)_{DH} = 0 \quad (5)$$

The time derivatives of the total HH and DH volumes in eq. (7) follow from the moments of their CSD's:

dissolution and death of HHgrowth of DH $\frac{dN}{dt} = -D^0$ (6) $\frac{dN}{dt} = 0$  (10) $\frac{dL}{dt} = -ND$ (7) $\frac{dL}{dt} = N G$  (11) $\frac{dA}{dt} = -2 k_A L D$ (8) $\frac{dA}{dt} = 2 k_A L G$  (12) $\frac{dV}{dt} = -3 \frac{k_V}{k_A} A D$ (9) $\frac{dV}{dt} = 3 \frac{k_V}{k_A} A G$  (13)

The shape factors for HH and for DH are defined in such a way that  $a = k_A l^2$  and  $v = k_V l^3$ , where l represents the length of a crystal. The shape factors are assumed to remain constant during conversion. The change in total number of crystals is given for HH by its death rate  $D^0$ .

Since the HH comes from a continuous mixed suspension mixed product reactor (CMSMPR), their initial CSD's are adequately described by [12]:

$$n(l,0) = n(0,0) \exp(-l/G_c \tau_c)$$
 (14)

where n(l,0) is population density of crystals with length l at t = 0and  $G_c$  and  $r_c$  are the growth rate and the residence time of the HH crystals in the CMSMPR. At time t of the conversion the disappearance of HH crystals follows from:

$$\frac{dN}{dt} = -D^{0} = -D \cdot n(0,t) = \frac{1}{2}$$

$$= -D \cdot n(0,0) \exp(-\int_{0}^{t} Ddt / G_{c} r_{c}) (15)$$

In all experiments DH seed crystals obtained from a CMSMPR reactor were used and eq. (14) is used to describe their CSD with the proper  $G_c \tau_c$  value. Both for HH and DH n(0,0) was obtained from the added mass per unit of reactor volume, M, of source and seeds through

$$n(0,0) = \frac{M}{6 k_v \rho} \frac{(G_c \tau_c)^4}{(G_c \tau_c)^4}$$
(16)

Rate constants  $k_D$ ,  $k_G$  and equilibrium concentrations of calcium were determined by a best fit of the conversion and [Ca] curves through numerical solution of eqs. (1) to (15).

#### 7.4. Experimental

Chemically pure 85 w%  $H_3PO_4$ , 96 w%  $H_2SO_4$  and  $CaSO_4 \cdot 2H_2O$  were used. HH was obtained by continuous crystallization [13] from a 25 w% H<sub>3</sub>PO<sub>4</sub>, 2 w%  $H_2SO_4$  solution at 100°C with a residence time of 20 min. The DH seed crystals were produced by continuous crystallization from a 35 w%  $H_3PO_4$ , 5 w%  $H_2SO_4$  solution at  $75^{\circ}C$  with a mean residence time of 15 min. The influence of process parameters was determined with regard to standard conditions. This standard is described by: HH source; DH seeds; HH:DH = 8:1 (by mole); 75°C; 35% H<sub>3</sub>PO<sub>4</sub>; 5% H<sub>2</sub>SO<sub>4</sub>; 6% solids. The conversions of HH into DH were performed in a thermostated 1 liter round bottom vessel. The rotational speed of the PVDF coated propellor stirrer was between 400 and 600 rpm. The experiment was initiated by the addition of HH (unseeded) or by the either simultaneous or subsequent addition of HH and DH to the solution. During conversion samples were taken and filtered over Millipore prefilters (type AP 20). The filtrate was diluted, the crystals were carefully washed, first three times with saturated gypsum solutions to remove the acid, then three times with acetone to remove the water. All Ca, SO<sub>4</sub> and  $H_3PO_4$ concentrations were analysed by ICP spectroscopy. The H<sub>2</sub>O content of the crystals was determined by drying at 30°C for 24 hrs, weighing, followed by calcining at 800°C. The phases were checked by XRD. Specific surface areas of DH and HH crystals were estimated from SEM views and determined by BET.

#### 7.5. Results and discussion

## 7.5.1 General approach.

The results of the experiments are discussed in relation to the effects of (i) slurry density, (ii)  $H_2SO_4$ -concentration, (iii)  $H_3PO_4$ -concentration, (iv) temperature, (v) stirring, (vi) impurities and (vii) type of source and seed material.

These effects can be caused either by a change in kinetic constants (due to impurities,  $H_2SO_4$ -concentrations etc.) or in equilibrium concentrations of HH and DH (due to  $H_3PO_4$ -concentration, temperature etc.). Rate constants are determined for growth in the longitudinal direction and an averaged  $\ell/d$  ratio of 30 was observed and used for the computer simulations. The neglection of secondary nucleation in these seeded batch experiments will be discussed in more detail.

In the cases of low conversion rates the decoupling of the driving forces and the rate constants (see eqs. 2 and 3) cannot be achieved accurately from the calcium and conversion curves. Extra information on the equilibrium concentrations is used from solubility figures 7.1 and 7.2. It should be noted that experimental time cannot be extended too long, because of formation of calcium sulfate anhydrite, AH. Normally AH, the most stable sulfate under these conditions, is hardly formed here because of kinetical reasons. For these reasons we have chosen to limit the recrystallization times to 3 hrs.

# 7.5.2 The slurry density.

The slurry density is fixed by the amount of HH and DH added to the reactor. Figure 7.3 shows that below a slurry density of 18% the conversion rates are virtually constant as might be expected in the absence of secondary nucleation. This is also reflected in the rate constants and equilibrium calcium concentrations in table 7.1. The final calcium concentration of 23 mM obtained from figure 7.3 at 25%



Table 7.1 The influence of slurry density

Figure 7.1. Solubility of the calcium sulfate phases as a function of the temperature in 42% H<sub>3</sub>PO<sub>4</sub>.

solids should be regarded with caution. Because of the coupling effect a more likely value of e.g. 27 mM would result in higher  $k_{G}^{c}$  en  $k_{D}^{c}$  values.

#### 7.5.3 The H<sub>2</sub>SO<sub>4</sub>-concentration.

Addition of  $H_2SO_4$  to the solutions has two effects. It alters the solubility products analogously to  $H_3PO_4$  and it changes the calcium





Figure 7.2. Solubility of the calcium sulfate phases as a function of  $H_3PO_4$  concentration at 75 °C.



Figure 7.3 and 7.4. Conversion and calcium concentration during recrystallization at different solid contents and  $H_2SO_4$  concentrations.

over sulfate ratio according to the solubility product. The first effect is probably the reason for the decreasing conversion rate (figure 7.4) with higher sulfate concentrations. This can be seen from the smaller relative difference in DH and HH solubilities, making the driving force for conversion smaller at the high sulfate concentrations. It should be noted, however, that an optimum  $H_2SO_4$  concentration exists with respect to the recrystallization rate [2, 3, 11].

The rate constants at 8% H<sub>2</sub>SO<sub>4</sub> are inaccurate because of the low conversion at the end of the experiment of only 30%.

[H <sub>2</sub> SO <sub>4</sub> ] w%	k <sub>G</sub> µm∕s	k <sub>D</sub> µm∕s	Ca eq, HH mmol/kg solution	Ca eq, DH mmol/kg solution	
3.0	2.5	4	46	33	
5.0	7	7.5	34	28	
8.0	1-10	1-10	24	22±2	

Table 7.2 The influence of  $H_2SO_4$ -concentration

## 7.5.4 The H<sub>2</sub>PO<sub>4</sub>-concentration.

Figure 7.5 demonstrates that the conversion proceeds faster at lower  $[H_3PO_4]$ . According to table 7.3 this is caused by the large difference in solubilities of HH and DH at 30 and 35%  $H_3PO_4$ . At 40%  $H_3PO_4$  the conversion is too slow to determine the rate constants accurately. They were assumed to be equal to 7  $\mu$ m/s in order to find the calcium concentration in equilibrium with DH (see table 7.3).

_ [H <sub>3</sub> PO <sub>4</sub> ] w%	k <sub>G</sub> µm∕s	k <sub>D</sub> µm/s	Ca eq, HH mmol/kg solution	Ca eq, DH mmol/kg solution
				· · ·
30	7	7	36	23
35	7	7.5	34	28
40	7	7	27	26

Table 7.3 The influence of H<sub>3</sub>PO<sub>4</sub>-concentration

## 7.5.5 Temperature.

Figure 7.6 shows a decreasing conversion rate with increasing temperature. The overall k value depends on temperature through the  $\exp(-E_A/RT)$  term, where the apparent activation energy  $E_A$  is estimated to be 50 kJ/mole [14, 15, 16, 17, 18]. This would mean a relative increase in overall k of 30% per 5°C temperature rise, which can not be observed within experimental errors. The difference in equilibrium levels of the calcium concentrations for HH and DH are rather sensitive to temperature and this completely overrules the effect of  $E_A$ . (Table 7.4).

The low conversion rate at 80°C introduces a relatively large uncertainty in both k and Ca-equilibrium values.

## 7.5.6 The stirring rate.

A decrease of stirring rate from 600 rpm to 400 rpm does not effect the conversion process (data are not shown). This observation is in agreement with the unimportance of secondary nucleation.

T °C	k <sub>G</sub> µm∕s	k <sub>D</sub> µm∕s	Ca eq, mmol/kg s	HH solution	Ca eq, DH mmol/kg solution	n
70 75 80	3 7 4	3 7.5 4	33 34 35		22 28 32	
(ca)e to <sup>1</sup> (ca)e	•••••	•	a [[a]+10 <sup>3</sup> (mol/kg solution) \$		° °	a
		0 30% H3P04 0 35% H3P04 0 40% H3P04	20- 	°	0 0 0 70°C 0 75°C 0 80°C	0 
0 0 7.5	5 5 time (10	-   <sup>3</sup> s}	0.	7.6	5 time (10 <sup>3</sup> s)	10

Table 7.4 The influence of temperature

Figure 7.5 and 7.6. Conversion and calcium concentration during recrystallization at different  $H_3PO_4$  concentrations and temperatures
### 7.5.7 Impurities.

Two systems have been used to study the effects of impurities. The results are shown in figure 7.7. The addition of 200 ppm  $Ce^{3+}$  slows down the recrystallization process by more than an order of magnitude through a small growth rate constant, whereas the dissolution rate constant, which is hard to determine, seems almost unaltered as might be expected. The black acid obtained from the Nissan-H process [19] hampers the recrystallization process, mainly through a slow dissolution rate of HH. A mechanism for such a phenomenon is not straightforward and further study is needed.

- Condition	k <sub>G</sub> μm/s	k <sub>D</sub> µm∕s	Ca eq, HH mmol/kg solution	Ca eq, DH mmol/kg solution
-				
standard	7	7.5	34	28
200 ppm Ce <sup>3+</sup>	0.1	>0.6	36.5	28*
black acid	1	0.25	26	20

Table 7.5 The in	fluence of	impurities
------------------	------------	------------

\* : concentration cannot be estimated from experiment

# 7.5.8 The type of source and seeds material.

As it was questionable whether the nature, viz. composition, CSD or specific surface area, of either HH source material or DH seeds would determine the process of recrystallization a series of tests have been performed [22], with DH from Merck (p.a.; platelets) and  $\alpha$ -HH prepared by heating of the forenamed DH during 5 hours at 150°C. It was concluded that the rate constants were not affected, only the conversion rate was increased due to a higher specific surface area of the  $\beta$ -HH [20, 21, 22].

## 7.5.9 Secondary nucleation.

Secondary nucleation is frequently described by the empirical relation:

$$B^{\circ} = k_{\rm R} N^{\rm a} \sigma^{\rm b} M^{\rm C}$$
 (17)

In these batch experiments secondary nucleation can be neglected since:(i) stirring rate does not affect the conversion rate,

(ii) slurry density has no influence on the recrystallization process(iii) photographs of the end product (not shown here) reveal the absence of small crystals.



Figure 7.7 and 7.8. Conversion and calcium concentration during recrystallization in black acid, with  $Ce^{3+}$ , and in absence of seeds.

Furthermore, heterogeneous formation of DH nuclei on HH crystals can be ignored as can be seen in figure 7.8, where it takes roughly 3000 s to start the recrystallization process in the absence of DH seeds.

7.6. Conclusions

- The rate constants for dissolution of HH in chemically pure solutions, assuming a first order process, are in the range 2-7  $\mu$ m/s.
- This rate constant for dissolution is lower in black acid (0.25  $\mu$ m/s) whereas the effect of 200 ppm Ce<sup>3+</sup> is uncertain.
- The rate constants for growth of DH in a second order process in c.p. solutions are also in the range 2-7  $\mu m/s$ .
- This rate constant is reduced to 0.1  $\mu\text{m/s}$  in the presence of 200  $\,\text{ppm}$  Ce  $^{3+}$  and to 1  $\mu\text{m/s}$  in black acid.
- The overall conversion rate can be controlled by affecting the equilibrium concentrations of both HH and DH through temperature,  $H_3PO_4$  and  $H_2SO_4$ -concentration.
- The type of seed DH and source HH materials have no effect upon the calculated kinetic parameters.
- Secondary nucleation can be neglected in these seeded batch experiments.

### 7.7. List of symbols and abbreviations.

Α	total surface area of a crystal population	(m <sup>2</sup> )
B <sup>0</sup>	nucleation rate	$(\#.s^{-1}.m^{-3})$
с	(index) HH crystallizer	
CSD	crystal size distribution	
Do	death rate	(∦.s- <sup>1</sup> .m- <sup>3</sup> )
D	dissolution rate	(m.s-1)
DH	calcium sulfate dihydrate	
G	growth rate	(m.s-1)
нн	calcium sulfate hemihydrate	

k <sub>A</sub>	shape factor for surface area	
k <sub>v</sub>	shape factor for volume of crystals	
k <sub>D</sub>	dissolution rate constant	(m.s-1)
k <sub>G</sub>	growth rate constant	(m.s-1)
l	crystal length	(m)
l	(as index): in the solution	
L	total length of a crystal population	(m.m- <sup>3</sup> )
М	molar mass	kg.mol-1
MSMPR	mixed suspension mixed product removal	
n( <i>l</i> ,t)	population density of crystals with	
	length $l$ at time t	(∦.m- <sup>1</sup> .m- <sup>3</sup> )
N	total number of crystals of a population	(#.m- <sup>3</sup> )
р	power input by stirring	$(J.s^{-1}.m^{-3})$
r <sub>1,2,3</sub>	(index) recrystallizers 1, 2 and 3	
t	reaction time	(s)
S <sub>HH DH</sub>	solubility of HH, DH	(kg.kg solution-1)
V	total volume of a crystal population	(m <sup>3</sup> .m- <sup>3</sup> )
V <sub>M</sub> HH, DH	molar volume of HH or DH	$(m^3.mol-1)$
α	degree of conversion	
αHH	HH modification obtained in solution	<b>`</b>
₿НН	HH obtained by calcination of DH	
σ <sub>DH</sub>	relative supersaturation of DH	
σ <sub>HH</sub>	relative undersaturation of HH	
τ	mean residence time in reactor	(s)

## 7.8. References

- [1] A.B. Zdanovskii and G.A. Vlasov, Zh. Prihl, Khim. 44(1) (1971) 15-20.
- [2] P. Becker, Fertilizer Science and Technology Series, Vol. 6, Dekker, New York (1989).
- [3] V. Slack, Fertilizer Science and Technology Series, Vol. 1, Dekker, New York (1968).
- [4] A.A. Taperova and M.N. Shulgina, J. App. Chem. (USSR) 23 (1950) 27
  [5] E.V. Khamshii, A.S. Bogamyvenko, S.Y. Lebedev, L.M. Lyamova and
- L.I. Marchenko, Zh. Prihl. Khim. 56(12) (1983) 2649-53.
- [6] E.V. Ivanov, E.V. Yavgel, B.D. Guller, R.Y. Zinyuk and M.E. Pozi Zh. Prikl Khim 56(10) (1983) 2161-65.

- [7] L.E. Marchenko and E.V. Khampshii, Ukr. Khim Zhurn. 52(11) (1986) 1131-33.
- [8] V.F. Karmyshov and N.G. Frolova, Zh. Prikl. Khim 49(12) (1976) 2626-9.
- [9] P.T. Cardew and R.J. Davey, Proc. R. Soc. Lond. A398 (1985)415
- [10] G.J. Witkamp, O.F. Abrahams, R.T. Blomsma and G.M. van Rosmalen, Proc. of BACG/IChE meeting, Ed. A.G. Jones, University College London (1988).
- [11] G.J. Witkamp and G.M. van Rosmalen, Proc. Sec. Int. Symp. on Phosphogypsum, Vol. 1, 377-405, Florida Institute of Phosphate Research, Bartow, U.S.A. (1988).
- [12] A.D. Randolph and M.A. Larson, Theory of Particulate Processes. 2nd edition. Academic Press Inc., New York (1988).
- [13] S. van der Sluis, G.J. Witkamp and G.M. van Rosmalen, J. Cryst. Growth 79 (1986) 620-29.
- [14] H.J. Kuzel, Neues Jahrbuch Miner. Abh. 156 (1987) 155-74.
- [15] J.D.C. McConnell, O.M. Astill and P.L. Hall, Mineralogical Magazine 51 (1987) 453-7.
- [16] A. Fowler, H.G. Howell and K.K. Schiller, J. Appl. Chem. 18 (1968) 366-72.
- [17] H.G. Wiedoman and M. Rössler, Thermochimica Acta 95 (1985) 145-53.
- [18] V. Vakhlu, P.S. Bassi, S.K. Mehta, Trans. Indian Ceramic Soc. 44 (1985) 29-32.
- [19] G.J. Witkamp and G.M. van Rosmalen in: Heavy metals in the hydrological cycle, Ed. M. Astruc, Selper Ltd., London 1988, 106.
- [20] B. Molony, J. Beretka, M.J. Ridge, Aust. J. Chem. 24 (1971) 449-56.
- [21] M.C. Ball and L.S. Norwood, J. Chem. Soc. Faraday Trans. I. 73 (1977) 932-41.
- [22] V.B. Okhotnikov, S.E. Petrov, B.I. Yakobson and N.Z. Lyahkov, Reactivity of solids 2 (1987) 359-372.

### CHAPTER 8

### CONTINUOUS RECRYSTALLIZATION IN PHOSPHORIC ACID

### Abstract

To allow prediction of continuous recrystallization behaviour from batch experiments, the model from chapter 7 has been extended to a three stage recrystallization system. The obtained equations describe the unsteady system. In addition equations for the steady state have been derived. A few continuous experiments have been performed to verify the model. The rate constants agree reasonably. The strong dependance of conversion rate on the solid content points at a dominating role of secondary nucleation.

## 8.1. Introduction

Recrystallization of calcium sulfate is sometimes performed batchwise e.g. in the building industry, but usually it is applied continuously. It is, however, less laborous to obtain data needed for a description of the conversion from batch experiments than from continuous operation. Also the effect of impurities present in a particular ore upon the conversion can be more easily tested in batch experiments. For a proper prediction of continuous recrystallization behaviour it is then necessary to be able to translate the batchwise obtained results to continuous operation. This applies to filterability, impurity uptake and conversion rate, but in this work the emphasis only lies on the conversion kinetics. The few literature data on continuous recrystallization [1,2] of other compounds also concern conversion kinetics only.

In this chapter the model for batch recrystallization presented in the previous chapter has been extended to a steady state as well as to an unsteady continuous system. In this model kinetic data obtained from batch experiments are used to describe continuous operation. The validity of the model for a steady state situation has been checked by comparing predicted with experimental results. For this purpose a few HH into DH conversion experiments have been performed in a three stage recrystallizer, placed in series with a continuous crystallizer which produces HH.

## 8.2. THEORY

### 8.2.1. Driving force

As mentioned in the previous chapter, the driving force for conversion is the difference in solubilities of HH and DH. From literature data [3,4] the diagram in figure 8.1 can be drawn, representing curves of equal solubility as a function of phosphate concentration and temperature. The points indicate equilibrium conditions of HH and DH. From fig. 8.1 it follows that the driving force is higher at low acid concentrations and temperatures. The data themselves are merely indications and can only be used qualitatively.

### 8.2.2. Unsteady continuous systems

The following assumptions have been made:

- The (re)crystallizers are operated as MSMPR systems, i.e. the slurry continuously withdrawn from the reactors has the same composition as the reactor content.
- The shape of the crystals does not alter during growth or dissolution.
- The recrystallization is solvent mediated.
- The balance of calcium sulfate does not affect the mass balances of  $H_2O$  and  $H_3PO_4$ .
- The growth or dissolution rate is equal for each crystal of DH or HH respectively in a given reactor. In other words, there is no growth or dissolution dispersion.

- Growth of DH takes place according to a second order in relative supersaturation.
- Dissolution of HH is a first order process.



Figure 8.1. Solubility of HH and DH as function of acid concentration and temperature

Analogously to the batch recrystallization, the conversion process can be written in differential form using the zeroth to third momentum of the CSD's. The advantage of this method is that these differential equations can easily be solved numerically, and that it gives information on the development in time of the conversion process. These equations are:

The mass balance:

$$\frac{1}{v_{\rm HH}^{\rm HH}} \frac{dv_{\rm HH}}{dt} + \frac{1}{v_{\rm M}^{\rm DH}} \frac{dv_{\rm DH}}{dt} + \frac{d \, CaSO_4, \ell}{dt} = 0 \tag{1}$$

:  $G = k_G \cdot \sigma_{DH}^2$  (m.s<sup>-1</sup>) (2) growth rate

(3)

dissolution rate:  $D = k_D \cdot \sigma_{HH} (m.s^{-1})$ nucleation rate :  $B^0 = k_B P^i V^j \sigma^k (\#.s^{-1})$ (4) in (4) i, j and k are exponents to be determined empirically. death rate :  $D^0 = -n(\ell = 0) \cdot D$  (5)

These equations have to be combined for each reactor with the moment equations of table 1. They are similar to those for the batch system (chapter 7) and contain in addition terms for influx and outflux. For the meaning of the symbols see chapter 7.

	crystal- lizer c	lst recrystalli	zer r <sub>1</sub>	2nd recrystalli	zer r <sub>2</sub>
	нн	нн	DH	нн	DH
dN	N	N <sub>c</sub> -N	N	N <sub>r</sub> -N r <sub>1</sub>	N - N r <sub>1</sub>
dt	$B^{0} - \frac{-}{\tau}$	$-D^{0}+\frac{\tau}{\tau}$	$B^{0} - \frac{-}{\tau}$	$-D^{0}+\frac{\tau}{\tau}$	$B^{0} + \frac{\tau}{\tau}$
dL	L	L <sub>c</sub> -L	L	L <sub>r</sub> -L	$L_{r_1} - L$
dt	$N.G-\frac{1}{\tau}$	$-N.D+\frac{1}{r}$	$N.G-\frac{-}{\tau}$	$-N.D+\frac{\tau}{\tau}$	$N.G+\frac{1}{\tau}$
dA	А	A <sub>c</sub> -A	А	A <sub>r</sub> -A	A <sub>r</sub> -A
dt	$2k_{A}.G.L-\tau$	$-2k_{A}$ . D. L $+\frac{\tau}{\tau}$	$2k_{A} \cdot G - \frac{1}{\tau}$	$-2k_{A} \cdot D \cdot L + \frac{\tau}{\tau}$	$2k_A \cdot L \cdot G + \frac{\tau}{\tau}$
dV	k <sub>v</sub> V	k <sub>V</sub> V <sub>c</sub> -V	k <sub>v</sub> V	$k_{V} V_{r_{1}} - V$	$k_{V} = V_{r_{1}} V$
dt	$3\frac{1}{k_A}$ .G.A- $\frac{1}{\tau}$	$-3\frac{1}{k_A}$ . D.A. $+\frac{1}{\tau}$	$3\frac{1}{k_A}$ .G.A- $\tau$	$-3\frac{1}{k_A}$ . D. A+ $\frac{1}{r}$	$3\frac{1}{k_A}$ . A. G+ $\tau$

Table 8.1. Compilation of the moment equations of DH and HH in the reactors

The parameters in table 1 are valid only for the specific column. For sake of clarity the indices are left out except those that are different from the others in the same column. Equations for the third recrystallizer are similar to those for the second. The total number of differential equations including the mass balances for the set of four reactors is 32.

-144-

From eqs. 1-5 and those in table 1 the recrystallization process following input of initial conditions can be approached by e.g. the Euler or Runge-Kutta method, analogously to the simulation of the batchwise recrystallization in the previous chapter. By minimizing the difference between the observed and calculated conversion and calcium sulfate concentrations in the solutions as a function of reaction time, the parameters ruling the conversion process and occuring in eqs. 1-5 can be derived. This has not been done here, because the few preliminary experiments do not allow accurate determination of so many parameters. In general, growth and dissolution kinetics can most easily be obtained from batch experiments, while nucleation data should be measured in a continuous system.

# 8.2.3. Steady state continuous system

In the following an expression for the steady state conversion in the first recrystallizer will be derived. For the MSMPR crystallizer of HH the well-known equation applies:

$$n_{c}(l) = n(o) \exp(-l/G_{c}\tau_{c}) \quad (HH)$$
(6)

The growing DH crystals in the first recrystallizer, denoted as r, can be described similarly, assuming that th HH crystals do not contribute to the breeding of DH crystals:

$$n_r(\ell) = n_r(o) \exp(-\ell/G_r r_r) \quad (DH)$$
(7)

For the dissolving HH it can be derived that:

$$n_{r}(l) = \frac{n_{c}(l)}{1 + \frac{D_{r}r}{G_{c}r_{c}}}$$
(8)

For the other recrystallizers similar equations can be written. Under the same assumptions as mentioned under 2.2 all moments (N, L, A and V) are proportional, for instance

$$\frac{N_{r}}{N_{c}} = \frac{V_{r}}{V_{c}} \quad (HH)$$
(9)

Since N is proportional to n(o), it follows from (6), (7) and (8) that

$$\frac{V_r}{V_c} = \frac{1}{1 + \frac{D_r \tau_r}{G_c \tau_c}}$$
(for HH) (10)

which leads to the following expression for  $\alpha$ :

$$\alpha = \frac{\frac{D_r \tau_r / G_c \tau_c}{1 + D_r \tau_r / G_c \tau_c}}{(11)}$$

N.B.  $\alpha$  can be based on either the amount of DH formed or on the amount of HH dissolved. This does not make any difference, because the amount of dissolved calcium sulfate is negligible compared to the amount in either the HH or DH phase. Eq. (11) allows the dissolution rate D to be calculated from the observed  $\alpha$ -value and the growth rate of HH in the crystallizer.

8.3. Experimental

### 8.3.1 Chemicals and equipment

Chemically pure  $H_3PO_4$  (85%),  $H_2SO_4$  (96%),  $Ca(OH)_2$ ,  $CaCO_3$ ,  $CaSO_4 \cdot 2H_2O$  (gypsum from Merck) were used. As black acid, product from a Nissan H plant was taken (before the evaporation step) which processed a Khouribga/Zin mixture. To all phosphoric acid solutions 100 ppm  $Cd^{2+}$  was added.



Fig. 8.2. Scheme of the continuous crystallizer/recrystallizer system

The equipment is given schematically in fig. 8.2. All double walled vessels were made of hard boron-silicate glass. By using three different crystallizer vessels, each with three outlets at different heights, the effective volume of the crystallizer could be varied between 0.25 and 2 liters. The three recrystallizers were all 2.5 liters. The crystallizer was thermostated by pumping oil through the double wall, while for the recrystallizers water was used. The sensors (either thermocouples or teflon covered mercury temperature contact thermometers) were submerged in the slurries to ensure an accuracy of  $1^{\circ}C$ . Agitation was performed by an oblique (45°) bladed stainless steel stirrer, coated with PVDF (polyvinylidenefluoride) to prevent corrosion. The power input was about  $0.4 \text{ J} \cdot \text{s}^{-1}$  per kg slurry at an impeller rate of 600 rpm. In the reactors 4-6 glass rods were suspended from the lid to serve as baffles to promote turbulent mixing.

The transport of the crystal suspension took place by overflow through glass tubes mounted under an angle of  $45^{\circ}$  downwards.

The feed streams were regulated by a computer (Olivetti M21) via galvanically isolated D/A converters, controlling Watson & Marlow peristaltic pumps with adapted rate control potentiometers. The stock vessels were placed on scales (Mettler PM30, TE/J30 or PM6), which send one by one several times per second the actual weight to the RS232 interface of the computer. Depending on the difference between these weights and the weights calculated from the feed rates and the reaction time, the pump rates were adjusted. The program controlling the experiments was written in Pascal.

### 8.3.2 Operation of the apparatus.

There are two modes of operation, depending on the phosphoric acid feed.

The first is applied when chemically pure phosphoric acid is used as medium. The stock solutions for the crystallizer are 96%  $H_2SO_4$  and a solution of a few %  $\rm Ca^{2+}$  in 25%  $\rm H_3PO_4$  . The temperature of the calcium phosphate stock solution is about 50°C, because only then the maximum solubility of 4% Ca<sup>2+</sup> can be applied, yielding up to 14% solids in the crystallizer which is operated at  $100^{\circ}$ C. A H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O mixture is fed together with the HH slurry from the recrystallizer into the first recrystallizer to obtain the appropriate acid concentrations and solid state content. This procedure was followed to ensure production of HH under always the same conditions  $(H_2SO_4 \text{ and } H_3PO_4 \text{ concentration},$ temperature, residence time, slurry density) while maintaining a great flexibility in conditions of recrystallization. The residence time of the crystallizer could be kept constant at different flow rates by adjustment of the crystallizer volume. The maximum attainable slurry density in the recrystallizer is limited to that of the crystallizer, viz. 14%.

The second mode is used when black acid is used. Since this acid contains a few % H<sub>2</sub>SO<sub>4</sub>, it can not be used for preparation of a calcium phosphate solution because of calcium sulfate precipitation. Instead a H<sub>2</sub>SO<sub>4</sub>/black acid mixture is added simultaneously with a

 $Ca(OH)_2$  slurry (20 w%) to the crystallizer. The disadvantage of this method is that a steady, homogeneous stream of calcium hydroxide could only be obtained at rather high flow rates (about 1 gram per second), which restricts its operation range. The stream into the first recrystallizer consists of a black  $acid/H_2SO_4/H_2O$  mixture, analogously to the first mode. In some experiments none of these modes were used, but only the recrystallizers were operated, using dry HH, prefabricated similar to the HH used in the other experiments, or  $\beta$ HH (exp. 1).

The starting procedure was as follows.

All reactors were filled with the appropriate solutions. An amount of HH seeds from a former experiment was added to the crystallizer. The recrystallizers were prefilled with DH from a former experiment or from Merck in a quantity corresponding with half the amount of HH plus DH expected during the experiment. The crystallizer was run free for a few residence times, which is enough to reach steady state because of the HH seed crystals. Then the outlet of the crystallizer was connected to the first recrystallizer, and the third feed stream was started. During each experiment the stock vessels had to be filled a few times because of the limited volume of the thermostated stock vessels.

Each two residence times samples were taken and treated in the same way as described for the batch experiments.

## 8.4. Results and discussion

## 8.4.1. General

First it was verified repeatedly by particle size analysis (Malvern) that no classification occurs using the overflow system described in the experimental part. This was shown by comparing the samples taken from several places in the vessels with the slurry from the overflow. In table 8.2 an overview of the experimental conditions and results is given.

exp. solution		composition	res.time	temp.	solids	% conversion		
nr.	% H₃PO₄	% H <sub>2</sub> SO <sub>4</sub>	10 <sup>3</sup> s	٥C	X	r <sub>1</sub>	r <sub>.2</sub>	r <sub>3</sub>
1β	35	5.8	2.7	60	11.8	100	100	100
2	36 BA	2.9	2.7	70	11.6	30	45	70
3	33	5.8	2.7	60	11.6	100	100	100
4	35	6.0	2.7	70	11.6	99	100	100
5	35 BA	2.0	1.8	70	10.0	80	100	100
6	35 BA	10.5	1.8	70	10.0	30	30	50
7	35	5.5	1.8	75	2.5	5	47	95
8	35	5.5	1.8	75	4.0	10	30	80
9	33	5.5	1.8	75	5.5	55	98	98
10	35	5.6	1.8	75	7.5	50	93	98
11	35	5.5	1.8	75	7.5	55	90	97
12	33	5.3	1.8	75	11.3	85	96	97
13	33	5.5	1.8	75	13.5	75	94	95

Table 8.2. Recrystallization conditions and steady state conversions

 $\beta$  = with  $\beta$ HH

BA = black acid

Variables in recrystallization conditions are the type of HH ( $\alpha$  or  $\beta$ , see previous chapter), the sulfate concentration, the percentage of solids and the use of either chemically pure or black acid. There is also another difference: in exps. 1-4 the HH was not crystallized simultaneously, but was prepared separately and added in dry form. This seems to be of no influence.

The HH crystals are needles up to more than 500  $\mu$ m long (fig. 8.3). The width is about 20-30 times smaller. By handcounting the CSD was measured (fig. 8.4). From the reasonably straight line of the ln n( $\ell$ )



Figure 8.3. Typical HH product from crystallizer.



Figure 8.4. Crystal size distribution of HH.

versus  $\ell$  plot it can be seen that the crystallizer acts as an MSMPR, as expected. The growth rate of HH in the length direction is  $1.2 \cdot 10^{-7}$ meter per second. Unfortunately the supersaturation cannot be measured reliably so calculation of reaction parameters is not possible. The same problem was encountered for the DH formation. From the analyses of the calcium concentration it was not possible to see differences in supersaturation. The absolute value of about  $3 \cdot 10^{-2}$  M Ca<sup>2+</sup> for exp. 5 corresponds, according to solubility data from the previous chapter, with a supersaturation around 10%. The growth rate of DH, found for batch experiments at  $\sigma=0.1$  with  $k_{\rm G}=5\cdot 10^{-6}$  ms<sup>-1</sup> is approximately  $5\cdot 10^{-8}$  ms<sup>-1</sup>, which is in reasonable agreement with the growth rate for the gypsum needles (fig. 8.5), determined by the CSD (fig. 8.6). The undersaturation, being around 10% as well, corresponds with a dissolution rate of  $3\cdot 10^{-7}$  ms<sup>-1</sup> according to batch experiments. This value cannot be verified through the size distribution, but from eq. 11, and the observed conversion of 0.8, a dissolution rate of  $10^{-7}$  ms<sup>-1</sup> is calculated, which is three times lower.

Apparently the model needs refining, such as taking into account that the shape factors for HH crystals can vary during dissolution. Another improvement would be a better determination of the calcium concentration in the solution. By lack of these data, only qualitative conclusions can be drawn.

To illustrate the development of the resulting conversion in time, the  $\alpha$ -values of experiment 12 are plotted versus the reaction time in fig. 8.7. The conversion in the first recrystallizer drops below 50% in 4 residence times and then rises to more than 90% at 10  $\tau$ .

After 18 residence times the system was still changing, although only a little. The steady state conversion is estimated at 75%. In the second and third recrystallizer the conversion approaches 100%. From this experiment it follows that the number of residence times needed to reach a proper steady state is at least 15. Most experiments, however, had only been run for 12 residence times. This means that the results may contain some additional error. It would be interesting to see whether such "oscillations" are also found in simulations using the unsteady model.

# 8.4.2. Influence of (re)crystallization conditions.

In exps. 5 and 6 with 2.0 and 10.5  $\%~{\rm H_2SO_4}$  respectively it was found



Figure 8.5. Typical DH product from third recrystallizer.



Figure 8.6. Crystal size distribution of obtained DH.

that the conversion is higher at the low sulfate concentration. Such behaviour was also found for batchwise recrystallizations, and can be attributed the smaller difference in HH and DH solubility at higher acid concentrations in this region of the phase diagram. At lower phosphate concentration and/or lower temperature an optimal sulfate concentration has been found [3] with a maximal conversion rate. In exps. 7-13 the slurry density was varied from 2.5 to 13.5 % solid material. The resulting conversion in the first reactor increases from 5% to 85% with increasing solid content. Also in the second reactor an increase is observed (fig. 8.8). This strong dependance on solid state



Figure 8.7. Conversion vs. reaction time for exp. 12.  $\tau = 3.30$  min.

content seems in contrast with the observation in batch experiments (preceding chapter), but it must be realized that in batchwise conversion nucleation does not necessarily play a role, while for continuous operation all crystals are formed by nucleation. By proper measurement of the CSD the constants in the nucleation formula (4) could be determined, but this has not been done here. For doing so, first a separation of the formed DH and undissolved HH has to be performed, for instance by bringing the crystals in a  $CH_2Br_2/acetone$  mixture with a density between that of DH (2300 kg m-<sup>3</sup>) and HH (2600 kg m-<sup>3</sup>). After separation the CSD can be determined by handcounting. Lacking these data, it is still possible to give a rough estimate of the effect of slurry density on the nucleation rate. Assuming an



Figure 8.8. Conversion in reactor 1 and 2 vs. solid content. (exp.7-13)

equal supersaturation for all these experiments, a preliminary calculation based on eq. (4) yields that the nucleation rate is proportional to the mass of DH to the power 1 to 1.5.

The influence of the temperature cannot be seen from exps. 3 and 4 at 60 and 70 °C respectively because of the 100% conversion in both cases. In exp. 12 at 75°C the conversion in the first recrystallizer is 85%, which lower value is partly due to the shorter residence time (1.8 vs.  $2.7 \cdot 10^3$  s), but probably also to the higher temperature. This effect can be explained, analogously to the batchwise obtained results, by a lower driving force.

The effect of the impurities from the black acid can be estimated from exps. 2 (BA) and 4 (chemically pure acid). Despite the lower sulfate concentration in exp. 2, which is, under these conditions expected to enhance the conversion rate, the conversion proceeds much slower in exp. 2 ( 30% vs. 100% in exp. 4). Such retarding effect is caused by impurities in black acid, which hamper the growth of DH by their adsorption.

Finally, in exp. 1  $\beta$ HH is used with a much larger surface area (10 m<sup>2</sup> per gram vs. 0.5 for  $\alpha$ HH). Since in both exp. 1 and exp. 3 ( $\alpha$ HH) the

conversion is completed in the first reactor, a possibly faster conversion with  $\beta$ HH is not visible.

8.5. Conclusions

- The crystal size distribution of continuously produced HH is representative for a MSMPR distribution without growth dispersion.

- The growth rate of gypsum determined from the CSD of one experiment corresponds roughly with that obtained in the batch experiments. The dissolution rate of HH, estimated from the conversion in steady state, is 3 times higher than for the batch experiments.

-A steady state in the three stage recrystallizer is obtained after at least 15 residence times.

- Near the DH-HH phase equilibrium, the conversion rate decreases with increasing sulfate concentration. Also a higher temperature has a retarding effect.

- A fast conversion is promoted by a high solids content of the slurry. For a prediction of continuous recrystallization nucleation behaviour should be investigated.

8.6. References.

- J. Garside, "Hydrate transformation in continuous crystallization process", North West. Branch Papers <u>2</u> (1982), Inst. Chem. Eng., UK
- [2] W.J. Moody and Bennett (Monsanto Res. Comp.), 9 March 1984, Report for the US Energy Dept., Mound, Miamisburg, Ohio.
- [3] P. Becker, Fertilizer Science and Technology Series, Vol. 6, Dekker, New York (1989).
- [4] V. Slack, Fertilizer Science and Technology Series, Vol. 1, Dekker, New York (1968).

-156-

## CHAPTER 9

## REDUCTION OF CADMIUM UPTAKE BY COMPLEXING AGENTS

### Abstract

The reduction in cadmium uptake in presence of complexing agents such as halides and thiosulfate has been investigated. The effectivity of halides decreases in the order I > Br > Cl, while in aqueous solutions  $S_20_3^2$  was found to be more effective than the halides. The effectiveness is higher in stronger acid or electrolyte solutions and at lower temperatures. There is no synergistic effect. Halides are not incorporated.

# 9.1. Introduction

The uptake of cadmium during crystallization can be reduced by addition of compounds that keep cadmium in solution by complexation, provided the complex cannot be incorporated in the calcium sulfate crystals. Uptake of Cd<sup>2+</sup> cannot take place without exchange of ligands. If this exchange were a slow process, the growth kinetics would play an important role with respect to the degree of uptake. At high exchange rates as for cadmium halides [1], the reduction in uptake only results from the increase in energy required for Cd<sup>2+</sup> to desolvate and become incorporated. This increase is related to the desolvation energy. In both cases the amount of cadmium taken up by the crystals has a relation with the degree of complexation. In order to achieve a reduction in cadmium uptake in calcium sulfate crystallized from phosphoric acid solutions, additives have to be used that are specific to  $Cd^{2+}$  and are stable under the severe conditions of the process. Application of halides can be considered, as described in literature [2,3,4]. Cl is the cheapest, but leads to corrosion problems. Br is more effective, but also more

expensive. Most effective is I, but this is easily oxidized to volatile  $I_2$  by air in an acidic medium. The remaining Cd-I complexes can be removed from the solution by ion exchange [5]. In this chapter the cadmium uptake in DH recrystallized from phosphoric acid or formed in 0.1 M NaClO<sub>4</sub> solution is described for some halide concentrations. In phosphoric acid the effect of halides on Cd uptake in HH during continuous crystallization has been studied. Finally, the reduction in uptake in the presence of thiosulfates in aqueous solution has been investigated. For aqueous solutions it has been attempted to relate the experimental Cd incorporation with the degree of complexation, calculated from literature data.

9.2. Theory.

The complexation of  $Cd^{2+}$  by for instance I is represented by the following equations:

 $\begin{array}{c} Cd^{2+} + I & \stackrel{K_{1}}{K} CdI^{+} & (1a) \\ CdI^{+} + I & \stackrel{K_{2}}{K} CdI_{2} & (1b) \\ CdI_{2} + I & \stackrel{K_{3}}{K} CdI_{3}^{-} & (1c) \\ CdI_{3} + I & \stackrel{K_{4}}{K} CdI_{4}^{2}^{-} & (1d) \end{array}$ 

where 
$$K_n = \frac{[CdI_n^{2-n}]}{[CdI_{n-1}^{3-n}] \cdot [I^-]}$$

. .,

Often the overall complexation constants  $\beta_n$  are listed, defined by  $\beta_n = \frac{[CdI_n^{2-n}]}{[Cd^{2+}][I_n]^n} = \frac{i\overline{I}_n^n}{i\overline{I}_n^n} K_i \qquad (3)$ With excess I present in the solution, the fraction of free Cd<sup>2+</sup> is given by:  $\frac{[Cd^{2+}]}{[Cd^{2+}]} = \frac{1}{[Cd^{2+}]} K_i \qquad (4)$ 

$$\frac{[Cd^{2+}]}{[Cd]}_{total} = \frac{1}{1+\beta_1[1]+\beta_2[1]^2+\beta_3[1]^3+\beta_4[1]^4}$$
(4)

The fraction free  $Cd^{2+}$  is then independent of the total concentration of  $Cd^{2+}$ .

The shape of the free  $Cd^{2+}$  concentration vs. [I] curve, as presented in the results, can qualitatively be understood from eq. 4. The concentrations of all species involved could be calculated from the total concentrations and the  $\beta$ -values by an iterative procedure with a computer program.

Some  $\beta$ -values for complexation of halides with  $Cd^{2+}$  from literature are:

	$\beta_1$	$\beta_2$	$\beta_3$	β
F	2.9	3.4		
c1	35	159	195	
Br <sup>-</sup>	45	250	1900	
1	120	708	105	3.106
_				

In 3 M NaClO₄ at 25°C: [6]

In pure water at 25°C: [6]

$$S_2 O_3^2 - : \beta_1 = 8.3.10^3, \beta_2 = 2.8.10^6$$

In  $H_3PO_4$  for I [4]:

		$\log \beta_1$	$\log \beta_2$	log $\beta_3$
55% H3PO4	55°C	2.5	6.4	9.5
	74°C	2.4	6.0	9.0
65% H₃PO₄	55°C	3.5	7.5	10.7
	72°C	3.3	7.1	10.3

The complexation in phosphoric acid is apparently somewhat stronger than in perchlorate. The  $\beta$ -values are the highest at low temperatures and high acid concentrations. The influence of the phosphoric acid concentration on the complexation is, however, dominant. Accordingly, the highest reduction in uptake is expected in systems with the highest electrolyte concentrations.

9.3.Experimental.

Recrystallizations into DH are performed as described in chapter 5. [6]. About 13 w% HH was brought in a solution containing 7w% Merck DH seed crystals. The solution consisted of 28 w%  $H_3PO_4$ , 4 %  $H_2SO_4$ , 0.01 % Cd<sup>2+</sup> and varying amounts and combinations of KI, KBr or KCl. The course of the recrystallization was followed by analysing samples of the crystals taken during conversion. These samples were obtained by filtration of slurry followed by three times washing with hot saturated gypsum solution in water to remove the adhering acid and subsequently three times with acetone to remove the water and drying at 40°C. If the washing step with gypsum solution were not applied, the crystals have a twice as high apparent Cd content. After the conversion had been completed, the recrystallization was repeated once more with fresh HH, using the formed DH as seeds for the next conversion.

Continuous crystallizations of HH were performed in a solution containing 55 w%  $H_3PO_4$  at 90°C according to the procedure described in chapter [3]. A  $H_2SO_4$  solution and a solution of 3.5 w% Ca in phosphoric acid containing 0.01 %Cd<sup>2+</sup> and various concentrations of halides were continuously fed into a 1 liter crystallizer, while unclassified withdrawal of the HH suspension occurred simultaneously. Residence times of 20 to 60 minutes were maintained, and the suspension contained 10 w% HH. The  $H_2SO_4$  concentration was kept constant at a fixed value lying between 0.25 and 4 w%. Sample treatment was similar to that of the recrystallization experiments. In constant composition suspension growth experiments ( described in chapter 2) well defined, aged seed crystals were allowed to grow till 200% of their original mass at constant supersaturation. The solution contained 0.1 M NaClO<sub>4</sub>, 0.5-1.10-<sup>4</sup> M Cd<sup>2+</sup> and up to 2.5.10-<sup>2</sup> M halides as salts. The temperature was  $25^{\circ}$ C and the crystals occupy less than 1% of the total volume. After outgrowth the gypsum crystals were washed three times with saturated gypsum solution and dried at  $40^{\circ}$ C. The supersaturation was 0.10 to 0.15. Since the solubility and the growth kinetics depend on the electrolyte concentration, the addition of halide was compensated by reduction in the amount of NaClO<sub>4</sub>, keeping the total ionic strength constant. The difference in solubility caused by the substitution of ClO<sub>4</sub> by I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> was found to be almost negligible from separate solubility measurements.

## 9.4.Results

### 9.4.1 Recrystallization of HH into DH.

The presence of cadmium and/or halogenides do not influence the recrystallization kinetics. This makes an effect upon the cadmium uptake through the growth kinetics unlikely. For data on conversion rates see chapter 5. In fig. 9.1 the normalized cadmium uptake, equal to the ratio of the actual uptake and the uptake in the absence of additive, has been plotted versus the halide concentration  $[X^{-}]$ . Obviously I<sup>-</sup> is most effective, followed by Br<sup>-</sup> and Cl<sup>-</sup>. For a 50% reduction in Cd-uptake respectively 2·10-<sup>2</sup>, 4·10-<sup>2</sup> or 8·10-<sup>2</sup> M X<sup>-</sup> is required, corresponding to a 1:2:4 ratio.

For a smaller reduction the difference in effects between I, Br and Cl becomes smaller. This means that the choice of additive depends on the desired reduction in uptake.

Assuming that only the fraction free  $Cd^{2+}$  contributes to the uptake, the following  $\beta$ -values are obtained:

 $\beta_1$  (I) = 40,  $\beta_2$  (I) = 1000,  $\beta_1$  (Br) = 29,  $\beta_1$  (Cl) = 14. In these  $\beta_1$  values the contribution of the higher terms  $\beta_{2,3,4}$  are included, because the accuracy of the measurements does not allow determination of so many independent parameters from one curve. The values for I are much lower than those in 55% H<sub>3</sub>PO<sub>4</sub> at 55 °C. ( $\beta_1$  = 300,  $\beta_2$  = 2.5·10<sup>6</sup>,  $\beta_3$  not included). This is probably due to the higher electrolyte concentration in the latter case, because in 65% H<sub>3</sub>PO<sub>4</sub> at

 $55^{\circ}C$   $\beta_1$  equals  $3 \cdot 10^3$  and  $\beta_2$   $3 \cdot 10^7$  which is much higher than in 55%  $H_3PO_4$ . The assumption that the fraction free  $Cd^{2+}$  determines the uptake can not be verified. To determine a possible synergistic effect, i.e. if certain combinations of additives yield a higher reduction in uptake than the sum of their individual contributions, mixtures given in table 9.1 were applied. The resulting uptake has also been listed.



Figure 9.1. Cadmium uptake in the presence of halides during recrystallization of HH into DH.

Table 9.1. Effects of halide mixtures								
10 <sup>3</sup> x [I <sup>-</sup> ] (M)	10 <sup>3</sup> x [Br <sup>-</sup> ] (M)	10 <sup>3</sup> x [C1 <sup>-</sup> ] (M	) normalized uptake					
*			´					
10	0	40	0.6					
10	20	0	0.6					
10	0	40	0.6					
0	20	40	0.6					
10	20	40	0.6					
0	20	40	0.6					

For a proper explanation of these values of the obtained reduction in uptake they should be compared with the reductions in uptake that can be calculated from the contributions of the individual halides. This has not been done here, but a preliminary calculation, together with the observation that the decrease in uptake seems not exceptional for these mixtures makes a synergistic effect unlikely.

### 9.4.2 Continuous crystallization of HH.

The crystals formed in the presence of halides do not differ in size and shape from those obtained from a clean acid environment, i.e. needle shaped (see chapter 4) with a length up to 1 mm. An effect on growth kinetics is therefore probably absent.

The influence on Cd-uptake is clearly visible in fig. 9.2, where the normalized uptake is plotted versus halide concentration. Each point corresponds with a separate experiment. The concentrations required for 50% reduction are 3.10-3 M I, 7.10-3 M Br or 2.10-2 M Cl. Note these values are several times lower than for the that recrystallization experiments described 9.4.1. in The higher effectiveness under these conditions is probably due to the higher acid concentration and occurs despite the higher temperature. At higher acid concentration the complexation constants becomes higher, and this effect is apparently stronger than the reduction in complexation due to the higher temperature.

#### 9.4.3 Constant composition growth experiments.

The growth rate is not affected by halides or thiosulfate as followed from comparison with the blanc experiments of chapter 2. Therefore data on growth rate values are not given here. In the halide experiments  $\text{ClO}_4^-$  was chosen as background electrolyte because of its indifferentness towards most cations. The experiments in thiosulfate needed no background electrolyte because the low concentrations of thiosulfate did not have an effect on the ionic strength.

In fig. 9.3 and 9.4 two quantities are plotted versus the halide or thiosulfate concentration: the relative Cd uptake (points), and the relative concentrations of free  $Cd^{2+}$  and Cd complexes in solution as calculated from the complexation constants taken from [6] (lines). The reduction in uptake is about equal for Cl and Br , approximately 50% at  $2 \cdot 10^{-2}$  M, while for I 70% is obtained. Thiosulfate, being a strong complexant, is much more effective:  $5 \cdot 10^{-4}$  M in pure water yields more than 50% reduction.

In aueous solutions at moderate temperature  $(25^{\circ}C)$  it is possible to estimate the concentration of free  $Cd^{2+}$  from the literature data on complexation constants but for halides, however, only data for 3 M solutions are available. The lines drawn in fig. 9.3 for NaCl0, halides therefore do not represent not the species in 0.1 M NaClO, but in stronger electrolyte solutions. In 0.1 M solution complexation will be less, yielding a higher actual free Cd<sup>2+</sup> solution. Given the fact that the uptake is somewhat higher than the calculated free  $Cd^{2+}$ concentration, this leads to the conclusion that single complexated Cd is already excluded from incorporation, and that it is not necessary to have e.g. two- or threefold complexes to prevent uptake. A suggestion to unravel the parameters behind the reduction in Cd uptake by complexing agents is to determine the complexes by polarography or to measure the  $Cd^{2+}$  activity with a  $Cd^{2+}$  selective electrode.



Figure 9.2. Cadmium uptake in presence of halides during continuous crystallization of HH



Figure 9.3. i) cadmium uptake in gypsum during constant composition growth as function of halide concentration (symbols) and ii) calculated concentrations of cadmium complexes (lines)



Figure 9.4. Uptake of cadmium and complex formation in thiosulfate solutions

## 9.4.4 Incorporation of halides.

In addition to the cadmium uptake, it has also been verified whether any halide uptake occurs. In table 9.2 the uptake figures of  $Cd^{2+}$  and halides for some experiments are given.

experiment		solution				crystal			
		[Cd <sup>2-</sup>	<sup>+</sup> ]x10 <sup>3</sup>	'(M)	[X-]x1	0 <sup>3</sup> (M)	[Cd2+	]x10 <sup>3</sup>	[X <sup>-</sup> ]x10 <sup>3</sup>
						mole	. kg - 1	mole.	kg-1
Cont. c	rystallization	(HH)	0.3	2.	4 I <sup>-</sup>	0.	06	0.002-	0.004
n	"		0.3	13	Br	0.	06	< 0.	01
11	"		0.3	13	C1 <sup>-</sup>	0.	06	< 0.	02
constan	t composition (	(DH)	0.4	22	Br <sup>-</sup>	0.	015	< 0.	02

Table 9.2. Incorporation of cadmium and halides

From the low uptake of halides with respect to the  $Cd^{2+}$  uptake it was concluded that  $Cd^{2+}$  is not incorporated as a complex and that separate uptake of halides does hardly occur.

9.5. Conclusions.

- The effectivity of halides as Cd uptake reducing agents decreases in the sequence  $I_{1} > Br > C1$ .
- In aqueous solutions thiosulfate is more effective than I.
- No synergistic effect of a mixture of halides is observed.
- The achieved reduction in Cd uptake at a given halide concentration decreases in the sequence: 55% H<sub>3</sub>PO<sub>4</sub>,  $90^{\circ}$ C > 28% H<sub>3</sub>PO<sub>4</sub>,  $60^{\circ}$ C > 0.1 M NaClO<sub>4</sub>,  $25^{\circ}$ C.

- Halides are incorporated in DH and HH only to a very limited extent.

- Halides do not have an effect on calcium sulfate growth kinetics.

- 9.6. References.
- [1] H.G. Hertz, Z. Elektrochemie 65 (1961) 36-50.
- [2] T.T. Tjioe, H. van der Woude, J. verbiest, F.P.M. Durville and G.M. van Rosmalen, Cryst. Res. Tech. <u>21</u> (1986) 1287-97.
- [3] S. van der Sluis, G.J. Witkamp and G.M. van Rosmalen J. Crystal Growth <u>79</u> (1986) 620-629.
- [4] Environmental Technology, Eds. K.J.A. de Waal, W.J. van den Brink. Martinus Nijhoff publishers, Dordrecht, The Netherlands (1987). p. 148-150 and p. 334-336.
- [5] T.T. Tjioe, P. Weij, J.A. Wesselingh and G.M. van Rosmalen, Solvent Extraction and Ion Exchange <u>6</u> (1988) 335-60.
- [6] I.M. Kolthoff and P.J. Elving, Treatise on analytical Chemistry, Vol 3, part 2. Interscience, New York (1961).
- [7] Proceedings Sec. Int. Symp. on Phosphogypsum, Vol. 1. Florida Inst. Phosph. Res. (Jan. 1988) p. 377-405.

## CHAPTER 10

#### UPTAKE OF IMPURITIES

#### Abstract

During the precipitation of calcium sulfate from phosphoric acid processes, all kinds of impurities are distributed between the solution and the crystals. The uptake of foreign ions by the crystals can occur interstitial Ъv incorporation, isomorphous substitution or coprecipitation. Isomorphous substitution is quantified bv a thermodynamic partition coefficient, which depends on the ionic radius and the solubility of the impurity as well as on the formed calcium sulfate phase. The uptake has no direct correlation with the dehydation energy, the charge or the dehydration frequency of the foreign cation.

# 10.1. Introduction

In industrial processes where crystallization or precipitation is applied as a separation technique, incorporation of impurities from the solution into the growing crystals is a widely studied topic. During the precipitation of mineral salts as byproducts from the processing of ores, for instance, uptake of impurities in the minerals often occurs. Such impurities either prevent the disposal of the minerals owing to the toxic character of the impurities or hamper the development of useful products from the contaminated minerals. Notorious examples are the huge amounts of calcium sulfates and jarosites from processes such as wet phosphoric acid production, flue gas desulfurization as well as hydrometallurgical zinc and copper production and biological coal The impurities present in the solution during the desulfurization. formation of the mineral, and originating from the ores, are released into the solution by the digestion or leaching of the ore. The tendency of mineral salts to incorporate foreign ions is even used as a commor

technique to remove impurities and in particular residual heavy metal ions from waste streams. In a neutral or basic solution calcium carbonate is mostly precipitated for this purpose, while in acid solutions calcium sulfate is formed. There is, however, a rising awareness for the environmental implications of the disposal or even further use in new products of minerals contaminated with toxic ions. In this sense special attention has been paid to the uptake of ions as cadmium, chromium, mercury, lead and phosphate. Increasing effort is therefore put into the development of methods to prevent or minimize the uptake of unwanted foreign ions by the given minerals.

In order to find methods to reduce the uptake of foreign ions of different nature, proper understanding of the various mechanisms by which their uptake proceeds is needed. In this study attempts have been made to identify the modes in which various foreign ions are incorporated in a substrate, here chosen to be the three calcium sulfate modifications. These modes of incorporation determine the parameters which govern the distribution coefficients of the impurities between the solid phase and the solution. Since some of these parameters are related to the precipitation conditions, optimization of the uptake can be pursued by a proper choice of these conditions.

Calcium sulfate precipitated from phosphoric acid has been selected as the system to be studied because phosphate ores contain many impurities, which end up in the products in varying concentrations [1]. Calcium sulfate is precipitated from phosphoric acid solutions according to the reaction

$$Ca_{10}(PO_4)_6F_2 + 10 H_2SO_4 + 10 H_2O \rightarrow 10 CaSO_4 \cdot n H_2O_4 + 6H_3PO_4 + 2HF^{\dagger}$$

Which one of the three modifications is formed depends on the phosphoric acid and the sulfuric acid concentrations in the solution as well as on the temperature [2]. Normally either hemihydrate ( $CaSO_4 \cdot \frac{1}{2}H_2O$ , HH) or dihydrate ( $CaSO_4 \cdot 2H_2O$ , DH or gypsum) is formed. Subsequent transformation of one modification into another can be achieved by changing the composition and the temperature of the

solution [3]. Recrystallization of the hemihydrate phase into the dihydrate phase is applied in the so-called hemi-dihydrate phosphoric acid processes to reduce the phosphate uptake by the calcium sulfate, thereby improving the economics of the process. By an adequately performed recrystallization also the cadmium uptake by the mineral can be lowered. No commercial phosphoric acid processes are known where anhydrite ( $CaSO_4$ ,AH) is formed. The precipitation of only a few percent of the total amount of calcium sulfate as anhydrite has, however, been patented as a method for cadmium removal from the phosphoric acid stream. Because of the high Cd uptake in anhydrite, the subsequently precipitated hemihydrate has a relatively low cadmium content [4].

10.2. Modes of foreign ion incorporation

## 10.2.1. Interstitial incorporation

Three major ways can be identified by which foreign ions can become incorporated into the precipitated substrate. The first way is interstitial incorporation, where the foreign ions are accomodated at lattice positions between the host lattice ions. interstitial Interstitial incorporation in gypsum preferably occurs by the uptake of hydrophylic ions in the crystal water layers (fig. 10.1). In the available openings of 200 pm diameter in these layers ions like Na<sup>+</sup> or  $Mg^{2+}$  [5] with ionic radii of 116 and 90 pm respectively in an 8-fold coordination [6] can easily be incorporated. Stabilization of these ions in the water layers can occur, since a higher negative charge of the water oxygens was measured in comparison with the charge of the sulfate oxygens. The H<sup>+</sup> ions on the other hand should hamper this type of incorporation for positive ions.

The hemihydrate modification is very suitable for interstitial accomodation of foreign ions because of the presence of 300 pm wide chanels in its lattice, through which water molecules and foreign ions can move freely. The uptake of Na<sup>+</sup> and Mg<sup>2+</sup> ions in hemihydrate formed

in sea water is more than twenty times higher than in gypsum or in anhydrite [7]. The tight anhydrite structure hardly allows interstitial incorporation and defects have to be introduced in the anhydrite lattice to make this kind of uptake possible.

The differences in Na<sup>+</sup> uptake by the three calcium sulfate modifications can thus be explained from their crystal structures and from an interstitial incorporation mechanism.

Since interstitial uptake is strongly dominated by the available interionic or interatomic space in the crystal structure, the influence of precipitation conditions such as temperature, solution composition and stoichiometry in the solution is hardly predictable.



Fig. 10.1. Stereoscopic view of the gypsum structure

#### 10.2.2. Coprecipitation

Another uptake mode results from coprecipitation of the foreign ion with a counter ion present in the solution. If the foreign ion forms a more sparingly soluble salt with e.g. the common counter ion, coprecipitation of a second salt as a separate phase can happen when its solubility product is exceeded. Examples are the formation of  $RaSO_4$ ,  $BaSO_4$  and  $SrSO_4$  next to the  $CaSO_4$  modifications [8]. Especially at high sulfate concentrations the development of these minerals is stimulated. Also the uptake of  $CaF_2$  in the  $CaSO_4$  modifications occurs by coprecipitation. The crystals or conglomerated particles of such
foreign phases are smaller than those of the major component. They can remain totally apart from the host crystals, become adsorbed upon the crystal surface of the major component, or even become intergrown with the host crystals. The last situation will occur if the host lattice serves as a suitable substrate for the heterogeneous nucleation and subsequent growth of the coprecipitating phase. Particles of radium sulfate in combination with Ba, Sr and Ca sulfate tend to become intergrown with the calcium sulfate crystals [8,9]. In some cases it is even hard to distinguish between coprecipitation and another way of incorporation.

If, however, coprecipitation dominates, the totally formed weight of the foreign phase should depend only on the composition of the solution and e.g. not on the amount of precipitated host mineral. The response of the uptake of the foreign phase to changes in precipitation conditions can reveal the ruling mechanism. If for instance the curve of the relationship between the  $H_2SO_4$  concentration in a phosphoric acid solution and the Ra uptake in the solid phase were of a shape, with no uptake below a certain  $H_2SO_4$  content followed by a steep rise up to an asymptotic value, coprecipitation is a likely mechanism.

#### 10.2.3. Isomorphous substitution

The third mode of foreign ion uptake is by isomorphous replacement of the host lattice ions. In such a solid solution a redistribution of competing ions takes place. This means that the ratio of the corresponding foreign and lattice ions differs from their ratio in the solution. A measurable parameter which is indicative for the extent of redistribution in the solid can be defined. This parameter, named the partition coefficient D is given by [10]:

$$D = \frac{[M]/[H] \text{ (solid)}}{[M]/[H] \text{ (liquid)}}$$
(1)

where [M] is the concentration of the foreign ions in the solid phase, c.q. the crystals, and in the solution or liquid respectively, and [H] is the concentration of the host ions. In case of the three  $CaSO_4$ modifications either the  $Ca^{2+}$  or the  $SO_4^{2-}$  ions can be substituted. The uptake of  $Cd^{2+}$ ,  $Ce^{3+}$ ,  $Sr^{2+}$ ,  $HPO_4^{2-}$  and  $AlF_5^{2-}$  ions in the  $CaSO_4$ lattices can be recognized as examples of isomorphous substitution.

This type of incorporation can be distinguished from the other two mechanisms by the constancy of the D value over a wide range of M and H concentrations in solution, provided that the composition of the solution is not largely altered. The value of D for a given impurity and a host mineral depends on thermodynamic parameters [11]. The relationship between D and the thermodynamics of the system is given by (see appendix):

 $D = \frac{\gamma(HX)s}{\gamma(HX)s} \cdot \frac{\gamma(MX)\ell}{\gamma(HX)\ell} \cdot \frac{Ksp(HX)}{Ksp(MX)} \cdot exp(-\epsilon_{el}/RT) \cdot exp(-\Delta\mu(MX \rightarrow HX)/RT) (2)$ 

where X refers to the common ion, which can be either the  $Ca^{2+}$  or  $SO_4^2$ ions in case of  $CaSO_4 \cdot nH_2O$ .

- M and H are the foreign ion and the host ion respectively
- the subscripts s and  $\ell$  refer to the crystals and the solution repectively
- Ksp is the thermodynamic solubility product of the solid phases.
- $\Delta\mu$ (MX→HX) is the free energy required to transform the MX lattice into a lattice isomorphous with the HX lattice.
- $\gamma$  stands for the activity coefficient in either the solution or the solid phase of the mixed lattice.
- $\epsilon_{a1}$  is the elastic deformation energy.

The activity coefficients represent deviations from ideality and are related to the excess Gibbs energies according to :  $\Delta\gamma(\text{excess}) = - \text{ RTln}\gamma$ . The term  $\gamma(\text{HX})s/\gamma(\text{MX})s$  in eq. (2), which describes the deviations in the solid state, thus equals  $\exp((\Delta\mu(\text{MX})\exp s - \Delta\mu(\text{HX})\exp(RT))$  and is derived from the energy difference in bonds between the M and H ions in their corresponding identical MX and HX lattices.

The energy of the elastic deformation of the HX lattice induced by the substitution of H ions by M ions in the case that the ionic radii of H and M are not equal, is taken into account in the term  $\exp(-\epsilon_{el}/RT)$ . The strong influence of the ionic radius of M compared to the one of H is demonstrated by Chernov [12], who quoted the D values of the lanthanides in CaMoO<sub>4</sub> as a function of their ionic radii.

The last term in eq.(2),  $\exp(-\Delta\mu(MX\rightarrow HX)/RT)$  is also related to the solid state, and will be more important when the MX and HX lattices are less alike in structure. A large deviation in structure and in particular in the coordination number of the corresponding ions will lead to a lower partition coefficient [13]. Also the sensitivity of an ion for the directions of its bonds can have an effect on the uptake. For hydrated transition metal sulfates Balarew has determined phase transition energies [14,15].

A variation in one parameter can have its effect upon D through more than one term. A change in radius for example can also influence the bond energies. Various terms are thus in fact interlinked, and their splitting up in separate terms is rather artificial. These terms can only be approximated in a quantitative way for exceptional cases, such as for hydrates [14,15].

An example, where the differences in D values cannot be assigned to changes in ionic radii is found when the uptake of cadmium ions in the three calcium sulfate phases is compared. In the anhydrite phase the D value for  $Cd^{2+}$  uptake is about  $10^{-2}$ , while for hemihydrate or dihydrate D values of about  $10^{-3}$  are obtained. The differences between these values can be attributed to disparities in the comparable Cd an Ca sulfate structures particularly concerning the coordination numbers, and in a minor degree also to inequalities between the  $Cd^{2+}$ and  $Ca^{2+}$  bonds with the oxygen ions of the sulfate groups and the crystal water molecules.

So far only terms in eq.(2) for D have been discussed, which are correlated with the solid state. The thermodynamic solubility

products of the comparable phases of the two compounds is partly determined by their respective crystal structures and partly by the interaction of their ions with the pure solvent. The solubility products only depend on the temperature.

The ions in the aqueous solutions are hydrated and also form complexes with or are solvated by the ions present in the solution. Phosphate or sulfate ions for example can replace water molecules as ligands. The activity coefficients of the ions in the solution are therefore most susceptible to changes in the composition of the solution and to the temperature. Since D reflects the ratio of the activity coefficients of M and H, methods for their calculation or measurement in solutions of various composition are essential. For concentrated aqueous solutions Pitzer [16] developed an ion-interaction model for the calculation of  $\gamma$ , where the interactions between ions, pairs of ions and water are taken into account. For phosphoric acid Louis and Bessieres [17,18] used measured solutions in water solubilities and normal potentials to calculate the activity coefficients of many ions at various phosphoric acid concentrations. The log  $\gamma$  for Cd<sup>2+</sup> at 25% for instance increases from 3.4 in 2 M H<sub>3</sub>PO<sub>4</sub> at  $25^{\circ}$  up to 9.3 in 8 M acid.

It is clear from the discussion above that the temperature not only affects the partition coefficient through its influence upon the exponential terms, but also through its effect upon other terms.

From all the parameters determining D in eq.(2), the  $\Delta\mu(MX \rightarrow HX)$  term is the most difficult to quantify. Its value is mostly small, but small errors in it can lead to large differences in the predicted D values.

10.3. Kinetical influence on incorporation

In the discussion above on the mechanisms of incorporation the thermodynamics of the uptake and parameters following from these thermodynamics have been emphasized. Thermodynamic conditions, however, only exist at equilibrium. Since uptake of foreign ions occurs during growth and since growth never proceeds at equilibrium, kinetical parameters have to be defined, which are representative for the kinetical impact upon the degree of incorporation.

In case of isomorphous substitution the partition coefficient D tends to go to a value of one with increasing overall growth rate of the crystals. If the affinity of the foreign ions towards the crystal surface and in particular towards the counter ions in the surface is rather weak. the D values are lower than one. In these cases a higher growth rate, which results from a higher supersaturation, will lead to a higher D value. The foreign ions at the crystal surface will become more easily entrapped by the propagating growth layers. If, on the contrary, the foreign ions are strongly attracted by the structural surface, the D values can be higher than one. At higher growth rates less time will be available for their adsorption at the surface and lower D values will be attained. An example of the first case is the incorporation of  $Cd^{2+}$  in  $CaSO_4 \cdot 2H_2O$ , where the D value of  $5 \cdot 10^4$ - at low supersaturations and thus at low growth rates increases up to  $5\cdot 10^{-3}$  at 100% relative supersaturation  $\sigma$  (see fig. 10.2) [19]. For the Cd<sup>2+</sup> uptake in CaCO<sub>3</sub>, however, the D value decreases from 70 at low growth rates to 10 at a  $2.10^3$  times higher overall growth rate [20]. The thermodynamic D value can thus in principle be obtained by extrapolation of the D versus R or  $\sigma$  curve to a R or  $\sigma$  value of zero.

In order to derive parameters which are relevant as yardsticks for the kinetical influence upon D, the separate steps in the growth process have to be closely considered. During growth a competition takes place between the foreign and the host ions, here the  $Cd^{2+}$  and  $Ca^{2+}$  ions. The various stages in the growth process are:

- diffusion from the bulk solution towards the crystal surface
- adsorption at the surface
- surface diffusion towards the steps upon the surface
- incorporation in the kink positions of the steps

During the last three stages gradual dehydration or desolvation of the ions takes place. For many salts and also for sulfate salts the cations

-176-



fig. 10.2 Uptake of Cd in  $CaCO_3$  and  $CaSO_4 \cdot 2H_2O$  as a function of growth rate. Data for  $CaCO_3$  from Lorens [20]

are more strongly hydrated than the anions. Nielsen [21] has proven that the dehydration frequency of the cations strongly dominates the growth rate together with the number of growth units impacting upon the crystal surface. This number is represented by the concentration of ions in solutions. The dehydration frequency of  $Cd^{2+}$  compared to this frequency for  $Ca^{2+}$  is therefore an important kinetic parameter. Melikhov studied the kinetic entrapment of some foreign ions in ionic compounds [22].

### 10.4. Thermodynamic and kinetic parameters

To explain measured values of partition coefficients or ultimately to predict their order of magnitude, the potentially ruling parameters should be identified. These parameters are summarized below. Their discussion has been focussed on the studied system of the incorporation of foreign ions in the three calcium sulfate modifications. The character of the parameters can be of a more intrinsic nature or reflect in overall terms the interaction of the foreign ion with its surrounding:

- the ionic radius

In the first columns of tables 10.3 to 10.7 the ionic radii of the foreign ions are given. The radius of an ion depends not only upon its electron shells, but also on its coordination number, its valence and sometimes on its electron configuration in relation to the crystal field stabilization energy.

In a high spin configuration the spins of the d-electrons are parallel, each in a different orbital and thus occupying more space than paired electrons in the same orbital. This applies to ions like  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$ .

- the coordination number

The number is 8 in the three calcium sulfate modifications [23,24,25], although Abriel [26] reports a value of 9 for  $CaSO_4 \cdot 0.8$  H<sub>2</sub>O. Because not all the radii of the foreign ions are known in an 8 coordination, the radii of these ions are given for their 6 coordination mode in table 10.3 to 10.7, rather than making an extrapolation of their radii to the 8 coordination values. Because the coordination of an ion in its own lattice with a similar chemical composition as the host lattice represents its most favoured environment, the similarity of both lattices, c.q. both crystal structures, is an important measure for the tendency towards incorporation of the foreign ion.

- the valence

The valence of the ions not only influences their radii but also has its impact upon the bonds with the counter ions in the solid and upon the interaction with other ions in solution. In some cases the correct valency of the ions in solution has to be derived from their redox potentials and from the measured redox potential in the phosphoric acid solution.

- chemical nature

Depending on the chemical nature of the foreign ions, their bonding with the counter ions in the lattice and also their incorporation can either be stimulated or hampered. The mutual attractiveness of ions is influenced by their so called hardness or softness, a measure for the polarizability of their bonding orbitals. Soft ions like Cd and Hg ions for instance preferably form slightly covalent bonds, while hard ions like Ca, Al, Ba, and Sr ions as well as the lanthanides tend to form more ionic bonds [6]. Since sulfate ions are also hard, their bonding with hard cations is favoured.

- the dehydration free energy

The dehydration free energy, which on its turn is related to the radius and the charge of the ion, not only affects the solubility product of its compound MX in eq.(2), but also has an effect upon the associates formed in solution and thus influences its activity coefficient in solution. By lack of sufficient comparable data of the Gibbs energies, the available corresponding enthalpy data are given in tables 10.3 to 10.7 [27]. It was, however, verified that the sequence of the free energies is hardly affected by the use of the enthalpies.

- the dehydration frequency

The effect of this parameter is only noticeable in the kinetical influence upon the partition coefficient as mentioned in section 3.

- the activity coefficient

The activity coefficient of the foreign ion in solution in relation to the coefficient for the host ion serves in eq.(2) as a sort of overall parameter which covers all interactions between the ions in solution. In the calculation of the activity coefficient no differentiation is made between the various types of complexing species. For physical properties such as the solubility, the osmotic pressure or the vapour pressure this is of no importance. For the degree of incorporation, however, it is relevant whether the foreign ion is strongly associated with a counter ion, which keeps it in solution, or with e.g. an ion of the growing crystal. In the last case its uptake is stimulated. The activity coefficients therefore have to be valued together with the type of associates and their strengths, given by the association constants. Since obviously several of the above mentioned parameters are interrelated, any observed correlation between partition coefficients and a parameter does not have to be directly causal.

### 10.5. Experimental

Chemically pure  $H_3PO_4$ ,  $H_2SO_4$ ,  $H_2SiF_6$ ,  $Ca(OH)_2$ ,  $CaCO_3$ ,  $CdCO_3$ ,  $ZnCO_3$ ,  $Hg(NO_3)_2$  and  $SrCO_3$  were used. Most reagents were purchased from Merck or Baker. The lanthanide nitrates of minimal 99% purity were obtained from Aldrich and Johnson Matthey. The black phosphoric acid with 40 to 80w%  $H_3PO_4$  came from a Nissan H plant, which processes Khouribga ore.

The batch recrystallization experiments are detailed in ref.[3]. The DH seed crystals were either chemically pure or obtained from a former recrystallization experiment. Simultaneously 5w% DH seeds and 10w% HH source material, obtained by continuous crystallization as described below, were added to 1 kg solution with a concentration and temperature appropriate to induce a HH into DH conversion. After conversion the crystals were washed three times with hot saturated gypsum solutions and three times with acetone, and subsequently dried at  $30^{\circ}$ C. The filtrate was diluted with water or a 0.1 N HCl solution in a one over one ratio to prevent precipitation during cooling. Apart from the element analyses of the filtrate and the crystals, the water content of the crystals was determined as well as their phase by X-ray diffraction.

Continuous crystallization experiments were performed as described elsewhere [2]. In the first type of experiments a chemically pure solution of 4w% Ca<sup>2+</sup> in phosphoric acid was added continuously to a 1 l crystallizer simultaneously with concentrated sulfuric acid. In the second type of experiments a slurry of 20w% Ca(OH)<sub>2</sub> in water was added simultaneouly with a H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> mixture prepared from black acid. The level in the crystallizer was kept constant by continuous withdrawal of the formed calcium sulfate slurry. After about six residence times a steady state was reached. The crystals and the filtrate were treated as described above.

-180-

The continuous recrystallization experiments consisted of a crystallization unit as described above in combination with three recrystallization vessels in series connected by overflow tubes. The HH slurry coming from the crystallizer, is gradually converted into a DH suspension due to the lower temperature in the recrystallizers. In the third recrystallization vessel the conversion was between 70 and 100% depending on the conditions. Crystals and filtrate were again treated as given above.

The element analysis of the crystals and the filtrate happened by means of inductively coupled plasma emission spectroscopy (ICP), atomic absorption spectroscopy (AAS) and by instrumental neutron activation analysis (INAA) at the Interfacultair Reactor Instituut in Delft (IRI).

## 10.6. Results and discussion

The conditions, prevailing during the continuous crystallization and recystallization experiments, such as the  $H_3PO_4$ ,  $Ca^{2+}$ ,  $H_2SO_4$  and foreign ion concentrations and the temperature, are given in table 10.1. as well as the calcium sulfate modification of the developed crystals. The supersaturation during the recrystallization experiments was always rather low, because it is limited by the solubility of the dissolving phase. A few earlier semi-batch crystallization and batch recrystallization experiments are also added to this table. The partition coefficients are measured for foreign ions in pure phosphoric acid and in so-called black acid, obtained from a Nissan H plant, where Khouribga phosphate is processed with a composition given in table 10.2. This black acid already contains a large variety of foreign ions, and no additions were needed. The dosed concentrations of the foreign ions in the experiments with chemically pure acid were sometimes higher than in black acid to increase the accuracy of their analysis. For Cd<sup>2+</sup> and  $Hg^{2+}$  for instance a starting concentration of 100 ppm in solution was chosen. The foreign ions were added to the pure acid separately or

Table	10.2.	Composition	of	the	ore	(partly	from	[30])

<u>compound</u>	7.	compound	ppm <sup>.</sup>	compouna	ppm
P0₄ <sup>3</sup> -	43	Zn	200	A1	3000
Ca <sup>2+</sup>	37	Ni	50	Fe	1300
S0₄²-	2	Cu	40	v	200
F-	4.2	Cd	20	U	150
Si02	2.2	Mn	15	As	15
Na <sup>+</sup>	0.7	Нg	0.01-0.05	Sb	3
		Pb	3		
		Ra	40pCi/gram		

Table 10.3. Conditions of the experiments and Cd uptake

CC - continuous crystallization CR - continuous recrystallization always 10% solids BR = batch recrystallization

BA = black acid τ = res. time

exp nr	. type	additive	τ (min)	[H <sub>3</sub> PO <sub>4</sub> ] (%)	[H <sub>2</sub> SO <sub>4</sub> ] (%)	[Ca <sup>2</sup> +] (ppm)	Т (°С)	phase	D(Cd) (10- <sup>3</sup> )	D(Cd) (10- <sup>3</sup> ) <sup>eq</sup>
1	сс	BA	40	55	10	170	95	AH	38	<8
2	CC	100 ppmLn <sup>3</sup> +	60	55	7	350	95	AH	30	<8
3	CC	0.8%A1F3	40	55	12	170	95	AH	39	<8
4	CC	100 ppm Hg <sup>2</sup> .	+ 40	55	10		95	AH		<8
5	CC	BA	40	55	8		95	нн		<0.8
6	CC	0.8%A1F <sub>8</sub>	20	55	3	1900	90	нн	7	<0.8
7	CC	2%H_SiF	40	55	3		90	нн	2	<0.8
8	CC	100 ppm Hg <sup>2</sup> -	⊦ 20	55	10		70	HH		<0.8
9	CC	100 ppm Hg <sup>2</sup> -	⊦ 20	55	10		40	нн		<0.8
10	CR	BA	3x30	40	3	1800	75	DH	0.3	3 < 0.8
11	BR	BA		40	3	1700	75	DH	0.6	5 <0.8
12	CC	0.8%A1F,	20	40	5	1100	60	DH	3.6	5 <0.8
13	from [	30] BA		65	2		90	нн	2(est	tim)
14	from Ni	ssan H plant		40	3		70	DH		-

Table 10.3. Partition coefficients of 2+ metals

Metal	r(6)	r(8)	D(AH)	D(HH)	D(DH)	exp	-∆Hdeh	∠deh
	pm	pm				nrs.	kJ/mole	Hz.
Mn²+	67/82	93	2.10-4		5.10-4	1,10	1874	107
$Ni^2+$	70	1			2.10-4	·	2119	5.104
Cu <sup>2</sup> +	73			5.10-4	10- <sup>3</sup>		2123	109
Zu²+	75		6.10-5	2.10-5	10-4		2070	3.107
Cd <sup>2</sup> +	95	107	10-2	10- <sup>3</sup>	10- <sup>3</sup>		1833	5.10 <sup>8</sup>
Ca <sup>2</sup> +	100	112	1	1	1		1602	5.10 <sup>8</sup>
Hg²+	102	114	10-5	5.10-4	10-²		1853	10 <b>9</b>

All dehydration frequencies are from ref. [75],[76] or [77]. The dehydration enthalpies are from ref. [27].

as a blend with a few exceptions. Separate experiments were performed with lanthanides in concentration of 100 ppm. At these concentrations which are much higher than the concentrations of

a few ppm in black acid (except about 10 ppm Ge), the lanthanides influence the crystallization kinetics, and can thus indirectly affect the uptake of other foreign ions. Such high concentrations are, however, not unrealistic if Kola apatite ore is processed, which contains lanthanides in amounts up to 1% [28]. Also  $AlF_3$  and  $H_2SiF_6$ , which are present in concentrations up to at most 0,3% in the used black acid, are studied separately because of their influence upon the kinetics.

Since all D values given in the tables '10.3 to 10.7 are measured for growing crystals, extrapolation to a growth rate zero is in principle needed to obtain the thermodynamic D values. This has been done for Cd, which is an important polutant owing to its toxity combined with its relatively high concentration in the phosphate ore [1,29,30]. To study the effect of the kinetics upon the D(Cd) value, continuous crystallization experiments were performed with various residence times, i.e. with various supersaturations or growth rates. thermodynamic D(Cd) values in the three phases obtained by The D(Cd) extrapolation to infinite residence time and denoted by are also given in table 10.1 together with the actual D(Cd) values. It can concluded that the difference between the actual and be the thermodynamic values is only a factor of about two to maximal four for the experiments in chemically pure acid. Because the D value for Cd is rather low and thus sensitive to kinetic influences, it can be assumed that also the D values of the other elements are relatively close to their thermodynamic values and can be mutually compared.

As mentioned in section 2, the use of partition coefficients D is restricted to isomorphous substitution, because only then D is a true constant. For most cations and for  $HPO_4^2$ - this is the case, but not for all ions. For comparison, however, the uptake of all cations and  $HPO_4^2$ - is expressed as a D value, while for the complex ions like  $AlF_5^2$ - and  $UO_4^2$ - a distribution coefficient K, defined as the ratio of

their concentrations in the crystals and in the solution, is given. This has been done, because the complex ions incorporated in the lattice often do not even exist in solution or because it is unknown whether its incorporation is a replacement of the crystal cations or instead of the anions.

The elements are divided in five groups based on their charge to facilitate the comparison of their partition or distribution coefficients. These groups are :

1. Cd<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>

2. Ra<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>

- 3.  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ , and the lanthanides ( $Ln^{3+}$ )
- HPO<sub>4</sub><sup>2</sup>-, AlF<sub>5</sub><sup>2</sup>-, SiF<sub>6</sub><sup>2</sup>-, complexes with Sb, As and U, and metallic Au.
- 5. Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>.

#### <u>Group 1</u>

In table 10.3 the partition coefficients of metal ions of group 1 with a valence 2+ are presented together with some of their physical and chemical parameters as discussed in section 4. The uptake of these elements shows a relationship with the radii of the ions. The elements with a ionic radius up to about 90 pm except  $Cu^2$ + have partition coefficients below about 5·10-<sup>4</sup> for all three phases while  $Cd^{2+}$  with a radius of 107 pm has D values of about 10-<sup>3</sup> for DH and HH and 10-<sup>2</sup> for AH.

Next to its ionic radius the preferential coordination of the foreign cation can be an important parameter. This is clearly the case for  $Cd^{2+}$ , since the D values are not the same for the three calcium sulfate phases. To explain these differences the coordinations of the Cd and Ca ions in the crystal structures of their sulfate salts are compared. The Cd coordination in  $CdSO_4$  is eightfold (see fig. 10.3) and the  $CdSO_4$  and  $CaSO_4(AH)$  crystal structures are almost identical [31,25]. This explains the higher D value for Cd in AH. The lower D values for Cd in HH and DH are consistent with the non-

existence of hydrated cadmium sulfates with an identical amount of



Fig. 10.3. Coordination of Cd in CdSO<sub>4</sub>

crystal water and a similar crystal structure. Under conditions where HH or DH is formed, apparently the most favourable coordination of Cd in the best corresponding lattices  $CdSO_4 \cdot H_2O$  [32] and  $3CdSO_4 \cdot 8H_2O$  is sixfold [33]. For DH and  $3CdSO_4 \cdot 8H_2O$  the coordinations of the cations are shown in figure 10.4.

In spite of the similarity in ionic radii of  $Cd^{2+}$  and  $Ca^{2+}$ , the D(Cd) values are rather low. This follows from the fact that the dehydration energy [27] for  $Ca(H_2O)_9^{2+}$  [34,35] is lower than for Cd  $(H_2O)_6^{2+}$ , and that the solubility product Ksp is higher for the cadmium than for the calcium sulfates. The association constants of Cd and Ca ions with  $SO_4^{2-}$  ions are about equal [36,37,38].

Also  $Hg^{2+}$  has an ionic radius close to  $Ca^{2+}$  and forms a  $HgSO_4$  crystal structure, which is isomorphous with  $CdSO_4$  and  $CaSO_4$ . A high D value for the Hg uptake in AH was thus expected instead of  $10^{-5}$ . An explanation for this anomalous behaviour of Hg is the formation of  $Hg_2^{2+}$ , which reduces the incorporation process. An estimation of the redox potentials of this formation in combination with the redox potentials of all ions governing the phosphoric acid system, as described by Louis and Bessieres [17,18] makes the formation of the  $Hg_2^{2+}$  double ions likely. Only experiments performed under strongly

oxydizing conditions would provide insight in the incorporation of  $\mathrm{Hg}^{2+}$  ions.

The D values for Hg of  $5 \cdot 10^{-4}$  in HH and  $10^{-2}$  in DH are surprisingly high compared to the uptake in AH. This could result from the fact that these lattices are more flexible owing to the crystal water. The presence of either the channels in HH or the water layers in DH might allow the uptake of Hg<sub>2</sub><sup>2+</sup> by a combination of isomorphous substitution and interstitial incorporation. It has also to be noticed, that the AH and HH phases were obtained from chemically pure phosphoric acid, while DH was obtained from a Nissan H plant. It can therefore not be excluded that oxydizing components from the black acid kept more Hg ions in the Hg<sup>2+</sup> form, thus stimulating their uptake in the DH lattice. The Hg<sub>2</sub><sup>2+</sup> pairs will probably not split up in the host lattices, since they even remain paired in the Hg<sub>2</sub>SO<sub>4</sub> lattice with only one additional bond with a SO<sub>4</sub><sup>2-</sup> ion [39].

The Cu and Zn ions have about the same radius, but the D(Zn) is about ten times lower than D(Cu) for HH and DH. Also their dehydration enthalpies are almost equal. For most first row transition metals also their complexation constants with  $SO_4^2$  in water are almost equal [40,41,42]. The coordination of Cu<sup>2+</sup> in its anhydrous sulfate lattice is a bit less symmetrical than that of  $Zn^{2+}$ , which slightly lengthens some of the  $Cu^{2+}-SO_4^{2-}$  bonds [43]. Such minor differences can, however, not explain a tenfold higher D(Cu) value. The solubility of  $ZnSO_4$  in water is much higher than that of  $CuSO_4$ . This implies, that through the thermodynamical solubility products in eq.2 the D(Zn) should be lower, which agrees with the result. The activity coefficients, which also affect the D values, are estimated to be  $\log\gamma(2n^{2+})=7.9$  and  $\log_{\gamma}(Cu^{2+})=4.5$  for 55%% phosphoric at 25°C [17,18]. According to eq.2 this would lead to a  $5 \cdot 10^3$  times higher D value for  $Zn^{2+}$  than for  $Cu^{2+}$ , which is very unrealistic. Similar discrepancies are found between measured and calculated D values, if the activity coefficients from refs [17] and [18] are used for the calculations. For this reason these activity coefficients are left out of the tabels. Also the softness or hardness of the ions seems to have no correlation with the D values and



Coordinations of Ca in  $CaSO_4$   $2H_2O$  (up) and of Cd in  $3CdSO_4$   $.8H_2O$  (down)



Fig. 10.4

their values are not given in the tables.

The partition coefficient increases, as said before, with increasing radius up to r(Ca), and therefore also approximately rises with decreasing dehydration enthalpy. That no direct relationship excists between the partition coefficients and the dehydration enthalpies, but only through the radius, follows from the D values of trivalent ions and from a comparison between the two groups of ions. <u>Group 2</u> The divalent metal ions, which form sparingly soluble sulfates have been treated as a separate group 2. Reliable D values could so far not be obtained, because incorporations up to almost 100% were measured, except for Sr<sup>2+</sup>. Beside substitution, coprecipitation as a separate sulfate takes place, especially for the most sparingly soluble Ba and Ra sulfates. The sulfates can be formed as separate phases upon the growing CaSO<sub>4</sub> crystal surfaces ending up in the crystals or as individual particles in solution. Formation of small Ra containing calcium sulfate particles have been observed in the solution and embedded in the DH crystals [8]. Recrystallization of Ra contaminated HH crystals into large Ra free gypsum crystals, which could easily be separated from the mother liquor, has been patented as a method for Ra removal [9]. Moisset [8] has studied the composition of such small Ra containing particles and in solution, showed the presence of Ba and Sr next to calcium sulfate. It was also found that the D values for Ra in sulfates are quite high and decrease in the order the other  $D(Ra)(BaSO_4) > D(Ra)(SrSO_4) > D(Ra)(CaSO_4)$  [44].

Metal	r(6)_	r(8)	D(AH)	D(HH)	D(DH)	exp	-∆Hdeh	vdeh_
	pm	pm				nrs.	kJ/mole	Hz
Sr <sup>2+</sup>	116	125	0.6		0.05	1,10	1470	10 <sup>9</sup>
Pb <sup>2+</sup>	118	131					1572	
Ba <sup>2+</sup> Ra <sup>2+</sup>	136	142					1332	

Table 10.4 Faitlion coefficients of 2+ metal	Fable ]	L0.4	Partition	coefficients	of	2+	meta]
--	---------	------	-----------	--------------	----	----	-------

The modes of incorporation in these sulfates are different. Isomorphous substitution occurs for the uptake of Ra by  $BaSO_4$  [44], while metastable mixed crystals have been reported for  $Ca-BaSO_4$  [45],  $Ca-SrSO_4$  [46] and  $Sr-BaSO_4$  [47]. In our experiments we probably have an isomorphous substitution mechanism in case of  $Sr^{2+}$ , as suggested by the low D value of about 0.2 in AH and 0.05 in DH. The reason for this way of uptake is the relatively high solubility of  $SrSO_4$  in phosphoric acid with respect to  $BaSO_4$  and  $RaSO_4$ .

Contrary to our findings with phosphoric acid solutions, Kushnir [5] observed for crystallization of calcium sulfates from seawater, that the uptake of  $Sr^{2+}$  hardly depends on the phase. This indicates a coprecipitation mechanism, just as for Ba and Ra. The solubility of  $SrSO_4$  in seawater is lower than in phosphoric acid.

If an isomorphous uptake were measurable apart from the coprecipitation, higher D values for the earth alkaline metal ions were expected in AH than in HH and DH, since no hydrated earth alkaline sulfates exist.

## Group 3

The third group of elements is characterized by the valence 3+ of the ions. They are listed in table 10.5 together with their partition coefficients. Their uptake does not seem to be significantly hampered by the charge mismatch with  $Ca^{2+}$ , since the D values are of the same order of magnitude as for the divalent ions. Apparently charge compensation is easily achieved by the formation of vacancies or by the simultaneous uptake of e.g. Na<sup>+</sup> ions [48] or even by uptake of PO<sub>4</sub><sup>3</sup>-ions on sulfate lattice sites. The uptake of the Al, Fe, Cr, V and Sc ions is low, probably due to their small radius compared to the ionic radius of Ca. Besides, in its own anhydrous sulfate lattice Al<sup>3+</sup> has a six coordination [49], while also the other transition ions have a preference for a six coordination, which does not fit with the 8 coordination in the three CaSO<sub>4</sub> lattices.

The uptake of  $Al^{3+}$  in the three phases is the lowest with a D value of  $10-^{5}$ , followed by  $Fe^{3+}$  and  $Cr^{3+}$  with D values of  $10-^{4}$ . The reason for this increase by a factor of ten is unknown. It can hardly result from the minor differences in radii of the ions, nor from specific differences in their chemical interactions. Complex formations of all three ions have been reported with sulfate ions as well as phosphate ions [40,50,51,52,53]. The bonding directions are just as unfavourable for  $Fe^{3+}$  as for  $Cr^{3+}$ . The  $Al^{3+}$  ions are like the  $Ca^{2+}$  ions rather symmetrical, with their number of nearest bonds only determined by sterical factors, c.q. by the available space. The  $Fe^{3+}$  and  $Cr^{3+}$  ions have preferential bonding directions and can less easily

adapt to a different surrounding. There is also no correlation with the dehydration energy. The solubility of  $Fe_2(SO_4)_3$  in water is a few tenth mole per kg, while the solubilities of the  $Al^{3+}$  and  $Cr^{3+}$  sulfates are about one mole per kg. This means, assuming a relationship between the thermodynamic solubility products and the solubilities, that the uptake should be higher for  $Fe^{3+}$  than for  $Al^{3+}$  and  $Cr^{3+}$ . This is not the case. The complexation with phosphate ions could be different for the three ions, which should be reflected by their  $\gamma(\ell)$  values. These values as estimated from refs. [17] and [18], however, did not lead to realistic differences in D values, just as for  $Zn^{2+}$  and  $Cu^{2+}$ .

For the higher dehydration enthalphy of the trivalent metal ions and from their charge mismatch with  $Ca^{2+}$ , a much lower uptake had been expected than for the divalent ions. This excludes the dehydration enthalpy as a predominant parameter, and stresses the direct influence of the radius upon the uptake.

<u>Metal</u>	r(6)	r(8)	D(AH)	D(HH)	D(DH)	exp	-∆Hdeh	vdeh
	pm	pm			•	nrs.	kJ/mole	Hz
			_	_				
A13+	53		10-5	10-5		from[3]	4715	1.3
Fe <sup>3+</sup>	55/65		10-4	10-4		1.5	4462	$1.6.10^{2}$
Cr <sup>3+</sup>	62		10-4	4.10-4	10-4	1,5,10,11	4670	2.4.10-6
vs+	64						4450	5.10- <sup>2</sup>
Sc <sup>3+</sup>	75		2.104	ł		13	3967	
Lu <sup>3+</sup>	85	95	1.5.10-	3	2.3.10-3	2,10,11	3695	
¥Ъ³+		98	2.7.10-	3	$4.6.10^{-3}$	เท่	3742	0.4.108
Tm <sup>3+</sup>		99				н	3695	0.8.108
Er <sup>3+</sup>		100	10- <sup>2</sup>			11	3674	1.2.108
γ3+		102	9 10 - 3			11	3594	
- Ho <sup>8+</sup>		102				"	3639	1 9 108
Dv3+		103	2 9 10-	2			3604	3 9 108
~у тъ\$+		104	2 0 10-	2	1 5 10-2		3580	5 108
C43+		104	3 2 10-	2	1.5.10		3549	109
F1184		107	3 8 10-	2	3 8 10-2	: "	3535	10
Sm3+		109	4 5 10-	2	6 1 10-2		3492	
NAS+		112	7 1 10-	2	0,1.10	*1	3447	
Dr8+		114	11 10	2		11	3411	
Co8+		114	4 5 10	2			3367	
1_9+		110	4.3.10-	- 2	0 10 3		2210	
La <sup>*</sup>		118	0.3.10-	-	0.10-0		2212	

Table 10.5 Partition coefficients of 3+ metals

The equality of the incorporation of each of the above trivalent ions in all three phases points again at the primary role of the radius (see fig. 10.5). Owing to the large difference between their size and the  $Ca^{2+}$  radius, the chemical and structural differences in the surroundings of these cations in the three phases apparently become less dominant, leading to a similar uptake.

The dehydration frequency of the transition metal ions is very low and particularly the Al and Cr ions dehydrate extremely slowly. It is therefore surprising that these ions do become incorporated at all in the calcium sulfate crystals, because growth proceeds much faster. It is not unthinkable that phosphate or other ions in the solution catalyze the dehydration, as happens for  $Cr^{3+}$  by the presence of  $Cr^{2+}$ ions [51]. In a chemically pure 1 M NaNO<sub>3</sub> solution, however, comparable D values have been found for  $Cr^{3+}$  in DH. This also proves that  $Cr^{3+}$  is not incorporated as a phosphate complex. Besides, if dehydration were a rate determining step for the  $Cr^{3+}$  uptake, a higher D value would be expected in DH than in AH, since for uptake in DH no complete dehydration is required.

For the trivalent lanthanides, which are close in chemical properties, the uptake increases almost continuously with their ionic radius. Maximal substitution of the Ca ions was found for the lanthanides with a radius close to 112 pm. Even  $Y^{3+}$ , which is not a real lanthanide fits into this schedule, which is imposed only by the radii. Only Ce<sup>3+</sup> seems to form an exception for so far unknown reasons. The phenomenon of a maximum uptake of the lanthanides with a radius around that of Ca<sup>2+</sup> was also observed for DH developed in a 1 M NaNO<sub>3</sub> solution [19]. Surprisingly a reverse trend was reported for Yb, L, Tb, Ce and La in HH with a maximum uptake for Yb [30]. Also for their uptake in CaMoO<sub>4</sub> a maximum was found, but here around Gd, which was ascribed to a minimum lattice strain for compatible radii [12].

For the total range of lanthanides the dehydration energy decreases continuously. This indicates that the incorporation is directly determined by their radii and not through the dehydration energy, since in that case no maximum would exist.



Fig. 10.5a Partition coefficients of metal ions in AH.



Fig. 10.5b. Partition coefficients of metal ions in DH.

The lanthanides are symmetrical ions and the larger ions can accomodate more bonds. This leads to a coordination number of nine for the larger lanthanides [54,55] which matches better with a number of 8 for  $Ca^{2+}$  than the 6 coordination of most transition metals.

All the trivalent ions given here are able to form complexes with the sulfate ions [51,56,57]. Since, however, phosphate ions act as competing ligands, the stability constants of the various sulfate complexes are unknown and thus their potential influence upon the uptake.

## Group 4

This group consists of complex ions, but each such ion has its individual behaviour and thus its own way of incorporation. For some of the complexes, however, replacement of the  $SO_4^2$ - ions in the  $CaSO_4$  crystals is likely. Because of the strong variations in uptake mechanisms, distribution coefficients K have been used instead of partition coefficients D.

compound	incorporated species	radius	K(AH)	K(HH)	K(DH)	exp. nrs.
AlF <sub>3</sub>	AlF <sub>5</sub> <sup>2</sup> -		0.3	0.3	0.5	3,6,12
υŪ	$UO_{2}^{2+}/UO_{4}^{2}-/U$	4 +	1	15	0.2-1.5	1,5,10,11
H <sub>2</sub> SiF <sub>6</sub>	SiF <sub>6</sub> <sup>2</sup> -			0.05		7
As	HAsO₄²-	248	0.07	<0.01	0.1-1	1,5,10,11
SЪ	(HSb0 <sub>4</sub> 2-)	260	0.7	0.1-1	0.02	1,5,10,11
Au	Au			1		11
H <sub>3</sub> PO4	HP0₄²-	238	0.03	0.01	0.01	11
H₂SO₄	504 <sup>2</sup> -	230				

Tabl	Le	10.	6	Distri	bution	coefficier	nts of	several	compounds
------	----	-----	---	--------	--------	------------	--------	---------	-----------

AlF<sub>3</sub> is incorporated in a comparable degree in the three  $CaSO_4$ phases with a distribution coefficient K = [AlF<sub>3</sub>] crystals/[AlF<sub>3</sub>]solution, of 0.3 to 0.5. The uptake is much higher than for Al<sup>3+</sup> (D=10<sup>-5</sup>, corresponding with K=10<sup>-3</sup>), which indicates that AlF<sub>3</sub> goes into the lattice and not Al<sup>3+</sup> on its own. The fluoride content of the HH crystals is about seven times higher on a molar base than the Al<sup>3+</sup> concentration. This implies that AlF<sub>3</sub> is most likely incorporated as a complex ion together with some  $CaF_2$ . In the literature [58] the uptake of  $AlF_3$  in DH has been reported to occur by replacing SO<sub>4</sub> ions by  $AlF_5^2$ - ions. This finding is consistent with the equally high uptake in all three phases.

That the uptake of foreign ions indeed proceeds via an adsorption step at the crystal surface, is clearly shown in figure 10.6. The  $AlF_5^2$ - ions are preferentially adsorbed on the top faces of the AH crystals and strongly retard the growth process. This effect is only noticeable at  $AlF_3$  concentrations above 0.5 w% in solution, which is close to the solubility of  $AlF_3$  in phosphoric acid. This solubility is rather high, probably due to the coordination of these ions by the phosphoric acid [59].



Fig. 10.6 CaSO<sub>4</sub> crystals grown from concentrated phosphoric acid at  $95^{\circ}C$ , in clean acid (left) and in presence of 0.8 w% AlF<sub>3</sub> (right)

A side effect of the growth retardation by  $AlF_3$  is, that in a continuous crystallization system the supersaturation of the calcium sulfate phase increases. Owing to this higher supersaturation, the growth rate of the unaffected crystal faces is probably enhanced, since an increase in Cd uptake was observed for phosphoric acid solutions with a relatively high  $AlF_3$  content [60].

The uptake of uranium varies from K=1 in AH and DH to 15 in HH. A similar high K value in HH has also been observed earlier [61]. This high uptake might be related to interstitial accommodation of uranium ions in the 300 pm wide channels in the HH lattice. What kind of incorporation occurs, depends on the form in which the uranium is present in solution. The ionic species can be  $U^{4+}$ ,  $UO_2^2$ + or  $UO_4^2$ -. present in amounts depending on the redox potential of the whole solution system [17,18]. Incorporation of U<sup>4+</sup> can take place by substitution of  $Ca^{2+}$  or interstitially. Its radius of 108 pm allows both mechanisms.  $UO_2^2$  + is too large for substitution of  $Ca^{2+}$ , but the existence of a rhombohedral CaUO<sub>4</sub> salt [62] suggests that  $UO_4^2$ - ions can replace  $SO_4^2$ - ions in the lattice. If that were the case the higher uptake in HH is not understandable. Besides, preferential uptake of  $U^{4+}$  has been proven, since an enhanced uptake of uranium by previous reduction is used as a method for its concentration from black acid [61].

Phosphate ore normally contains  $SiO_2$  as sand particles, which become dispersed in the phosphoric acid and finally end up in the crystals. Therefore crystallization experiments were performed in chemically pure phosphoric acid, where  $H_2SiF_6$  was added. A low distribution coefficent of 0.05 in HH was found, bases on Si. The  $H_2SiF_6$  is a strong acid, which forms  $SiF_6^2$ - ions in solution, but is also in equilibrium with the HF and  $SiF_4$  in the gas phase [63]. Since the existence of  $CaSiF_6$  in phosphoric acid solutions is reported [64], incorporation of  $SiF_6^2$ - most likely occurs by replacing the  $SO_4^2$ - ions in the lattice. Because of the low uptake the F- content of the HH could not be analysed.

The incorporation of phosphate ions can in a wide range of precipitation conditions be described by the following equation [2]:

$$\frac{[\text{HPO}_4^2 - ]\text{crystal}}{[\text{SO}_4^2 - ]\text{crystal}} = D * \frac{[\text{H}_3\text{PO}_4]\text{solution}}{[\text{H}_2\text{SO}_4]\text{solution}}$$

with  $D = 1.4 \cdot 10^{-4}$  for DH and HH and  $D \approx 10^{-3}$  for AH. This corresponds with K values of around 0.1. The concentrations in solution are total

concentrations, irrespective of the state in which the acids are present. The uptake of phosphate ions proceeds through isomorphous replacement of  $SO_4^2$ - by HPO\_4^2- ions, since both ions have an almost equal size of 230 and 238 pm respectively and at first sight also similar chemical properties. This is reflected by the existence of two isomorphous CaSO<sub>4</sub>•2H<sub>2</sub>O and CaHPO<sub>4</sub>.•H<sub>2</sub>O salts, which form mixed crystals [65]. The CaSO<sub>4</sub> phase has its equivalent in CaHPO<sub>4</sub> [66]. For such a similarity higher partition coefficients than those given above were expected. An explanation for the low uptake is that the dominating ions in the phosphoric acid solutions are  $H_5 P_2 O_8$ - ions and  $HSO_4$  - ions rather than the incorporated  $HPO_4^2$  - and  $SO_4^2$  - ions [67,68]. The incorporation process thus has to include a step where phosphate bonds are broken and protons eliminated. In additon, a dehydration has to take place [69,70,71]. The energies required for these steps is reflected by the lower D value.

The concentrations of gold in the solution as well as in the crystals are about 30 ppb. Given the redox potential of the solution, gold is presumably present in a metallic form. Its uptake depends on how finely divided the Au particles are dispersed in solution and on their physical adsorption onto the crystals. Their behaviour has some similarity with the  $RaSO_4$  incorporation, although  $RaSO_4$  forms particles together Sr, Ba,  $CaSO_4$  which are more embedded in than adsorbed on the host crystals.

Arsene is slightly incorporated in all three calcium sulfate phases with K values between 0.01 and 1. Uptake can occur as  $HAsO_4^2$ , replacing  $SO_4^2$ - in analogy with the incorporation of  $HPO_4^2$ - where at the same  $H_2SO_4$  concentration the K value equals 0.01. The lattice strain induced by this substitution is small, because the radius of  $AsO_4^3$ - (248 pm) resembles that of  $SO_4^2$ - (230 pm). The similarity of arsenate and phosphate is emphasized by the existence of two isomorphous  $H_3AsO_4.0.5H_2O$  and  $H_3PO_4.0.5H_2O$  lattices, and almost identical pK values of  $H_3AsO_4$  and  $H_3PO_4$  [51]. Since formation of  $H_5As_2O_8$ - ions are therefore likely to exist as well in solution. This comparison with phosphate is, however, only correct if the arsenate is present in solution as  $As^{5+}$  and not as  $As^{3+}$ . Whether this is the case depends on the redox potential of the phosphoric acid system.

The incorporation of Sb in AH and HH is about ten times higher than for the chemically related As, while the uptake in DH is lower. If uptake would happen as  $HSbO_4^2$ - (260 pm) its K value would be below K(As) because of its larger radius. It is also less equal to P with its preference for a 6 coordination in contrast to the 4 coordination of P. Since only a little is known about the Sb complexes in solution, no conclusions can so far be drawn.

### <u>Group 5</u>

Only for partition coefficients of the univalent ions in calcium sulfate as given in literature and only a few D values of Na<sup>+</sup>, K<sup>+</sup> and Ag<sup>+</sup> are measured here. The D value of Na<sup>+</sup> in AH is much lower than in HH. This tendency has also been reported for AH formed by recrytallization of DH from seawater [7].

If isomorphous replacement of  $Ca^{2+}$  were the mechanism through which K<sup>+</sup> and Na<sup>+</sup> were incorporated, a higher uptake of Na<sup>+</sup> were expected. Its radius of 116 pm is closer to that of  $Ca^{2+}$  (112 pm) than the radius of K<sup>+</sup> (151 pm). The difference in D by a factor of three is smaller than would follow from the large difference in ionic radii. Another explanation is then interstitial uptake, which is easier in the HH and DH phase than in AH, as emphasized in section 2.1. In that case the influence of the radius is hard to estimate.

Metal	r(6)	r(7)	D(AH)	D(HH) D(DH)	exp	-∆Hdeh	Vdeh
	pm	pm			_nrs,	kJ/mole	Hz
Na+	102	116	3.10-4	5.10-3	1,5	416	>109
Ag+	115	130	3.10-4		1	483	
K∓	138	151		2.10- <sup>3</sup>	13	33	>109
·							

Table 10.7 Partition coefficients of univalent metals

The D value of  $Ag^+$  in AH equals  $D(Na^+)$ . The chemical properties of  $Ag^+$  are different from those of  $Na^+$  and  $K^+$ , which makes their comparison difficult. The coordination of  $Ag^+$  in water is 4

[72], while the alkali metal ions have an instable water shield with a very high dehydration frequency and coordination numbers up to 6 [73]. From the low solubility of  $Ag_2SO_4$  in water with respect to  $Na_2SO_4$  and  $K_2SO_4$  [74], a higher uptake had been expected for  $Ag^+$  in AH.

## 10.7. Conclusions

In the three calcium sulfate modifications uptake of foreign ions occurs by isomorphous substitution of either the  $Ca^{2+}$  or the  $SO_4^2$ - ions, by coprecipitation of a separate phase or by interstitial incorporation.

In case of isomorphous substitution by divalent and trivalent ions such as  $Cd^{2+}$ ,  $Ca^{2+}$  or  $La^{3+}$ , the uptake can be quantified by a thermodynamic partition coefficient. This coefficient is defined as the molar ratio of the foreign ion concentration and the substituted host ion in the crystals, divided by the same ratio in the solution. Relevant parameters with a strong influence on the D-value are:

i) the ionic radius of the foreign ion, which is demonstrated for e.g. the lanthanides, ii) the formed calcium sulfate phase, as follows from differences in uptake of especially  $Cd^{2+}$  in the three phases, and iii) the solubility of the impurity.

The uptake neither has a direct correlation with the dehydration energy, nor with the charge and the softness or hardness of the ions which properties are related to the chemical nature of the ions. The interaction of the ions with the solution, reflected by the available calculated activity coefficients in phosphoric acid also does not seem to be a parameter which affects the distribution coefficient. This is not even the case if the association constants are thereby taken into account. Extremely low dehydration frequencies as for  $Cr^{3+}$  are apparently no real barrier for the incorporation of these ions.

Since the solubility product of  $BaSO_4$ ,  $PbSO_4$  and  $RaSO_4$  are exceeded, their uptake is almost complete due to coprecipitation, while  $SrSO_4$  can also be incorporated by isomorphous substitution.

#### 10.8. Appendix

## Derivation of the thermodynamical distribution coefficient

In the case that two identical lattices are mixed together, the molar free energy of the new mixed solid is represented by

$$G_{is} = G + \Delta G_{mix}$$
(1)  

$$G = R (x\mu_{+} + (1-x) \mu_{n}^{*})$$
(2)

where  $\mu_A$  and  $\mu_B$  are the molecular chemical potentials of the two pure components and x the mole fraction of component A in the solid

$$\Delta G_{\text{mix}} = RT \left\{ \begin{array}{l} 2\Psi \\ \bar{R}\bar{T} \end{array} : x (1-x) + x \ln x + (1-x) \ln (1-x) \right\}$$
(3)

where the first term represents  $\Delta U_{mix}$  in a mean field approximation, the two other terms represent TAS and where PAV = 0  $\Phi = \Phi^{AB} - \frac{1}{2} (\Phi^{AA} + \Phi^{BB})$  is the normalised bond energy and Z the

 $\Phi = \Phi^{AB} - \frac{1}{2} (\Phi^{AA} + \Phi^{BB})$  is the normalised bond energy and Z the coordination number.

From the equation for G and from  $\mu_i = (\frac{\delta G}{\delta x_i}) P, T, x_j$  it can be deduced that

$$\mu_{A} = Z \Phi (1-x)^{2} + RT \ln x + \mu_{A}^{*}$$
(4)

$$\mu_{\rm B} = Z \Phi x^2 + RT \ln (1-x) + \mu_{\rm B}^{\star}$$
<sup>(5)</sup>

From the definitions:

$$\mu_{A} = \mu_{A}^{*} + RT \ln \gamma_{A} x \text{ and}$$
 (6)

$$\mu_{\rm B} = \mu_{\rm B}^{\star} + RT \ln \gamma_{\rm B} (1-x) \tag{7}$$

it follows that

$$\gamma_{\rm A} = \exp \frac{Z\Phi}{R\tilde{T}} \cdot (1-x)^2 \tag{8}$$

$$\gamma_{\rm B} = \exp \frac{Z\Phi}{\bar{R}\bar{T}} \cdot x^2 \tag{9}$$

The impurity MX is here denoted as component A and is normally present as phase I with its own crystalline structure at the given P and T values. The host compound HX is here denoted as component B and is present as phase II with its crystalline structure which can differ from the structure of phase I of component A.

In order to obtain the mixed solid, the following processes have to take place

component A (
$$\mu_{A}^{*}$$
, phase I)  
 $\Delta \mu_{I \rightarrow II^{1}}$   
 $\Delta \mu_{I \rightarrow II^{1}}$   
A (phase II<sup>1</sup>)  
 $\Delta \mu = \epsilon_{el}$   
A (phase II)  
 $\Delta \mu_{mix} = RT \ln \gamma_{A} x$   
mixing  
 $\alpha_{A}$  (phase II)  
 $\Delta \mu_{mix} = RT \ln \gamma_{A} x$   
 $\alpha_{A}$  (phase II)  
 $\Delta \mu_{mix} = RT \ln \gamma_{A} x$   
 $\alpha_{A}$  (phase II)  
 $\alpha_{A}$  (phase II)

component A in mixed crystal.

In the phase transformation  $I \rightarrow II$  it is merely assumed that the two lattices are isomorphous, which means that the surroundings of the ions are the same and thus their coordination numbers. To reach a situation where also all bond lengths are adapted in such a way that equation (1) can be applied, a lot of energy is needed. After mixing, however, the lattice tends to relax and during this relaxation process energy is gained. The summation of these energies involved in the adaption of the host lattice needed for the uptake of the foreign ions is given by the term  $\Delta \mu = \epsilon_{\mu 1}$ . This term equals:

$$\epsilon_{e1} = 8 \Pi G_{s} r_{H} (r_{M} - r_{H})^{2}$$
 (10)

with  $G_s$  - shear stress  $r_M$  - radius of the foreign ion  $r_H$  - radius of the replaced ion H of the host lattice

When a saturated mixed solution is in equilibrium with the mixed solid, this can only be that case if

$$\mu_{A,B} = \mu_{A,L}$$
 and  $\mu_{B,S} = \mu_{B,L}$ 

where S and L in the subscripts refer to the solid and to the solution respectively.

This leads to:  

$$\mu_{A}^{*} + RT \ln \gamma_{A,S} x_{A,S} + \epsilon_{el} + \Delta \mu_{I \rightarrow II^{1}} = \mu_{B}^{\Theta} + RT \ln \gamma_{A,L} x_{A,L} (11)$$

$$\mu_{B}^{*} + RT \ln \gamma_{B,S} x_{B,S} = \mu_{B}^{\Theta} + RT \ln \gamma_{B,L} x_{B,L} (12)$$
where  $x_{B,S} = (1 - x_{A,S})$  and  $x_{B,L} = (1 - x_{A,L})$ 

For saturated solutions of the pure component in equilibrium with the pure solid, it counts that

$$\mu_{\rm A}^{\star} = \mu_{\rm A}^{\Theta} + \text{RT ln} (\gamma_{\rm A,L} x_{\rm A,L}) \text{eq}$$
(13)

$$\mu_{\rm B}^{\star} = \mu_{\rm B}^{\Theta} + RT \ln (\gamma_{\rm B,L} x_{\rm B,L}) eq$$
(14)

Since the  $\mu^{\theta}$  values of eqs (13) end (14) are defined for the P and T conditions of the equilibrium conditions of the pure components these  $\mu^{\theta}$  values can differ from those given for the ruling P and T conditions in eqs (11) and (12). For solutions, however, the differences in P and T values are mostly negligible, contrary to the situations for growth from the melt, and the  $\mu^{\theta}$  values can be assumed equal. Therefore substitution of

$$\exp \left\{ \frac{\mu_{A}^{\Theta} - \mu_{A}^{*}}{RT} \right\} = \frac{1}{(\gamma_{A,L} x_{A,L})_{eq}} = \frac{1}{K_{SP}(A)}$$
(15)

exp { 
$$\frac{\mu_{B}^{\theta} - \mu_{B}^{*}}{RT}$$
 } =  $\frac{1}{(\gamma_{B,L} x_{B,L})_{eq}} = \frac{1}{K_{SP}(B)}$  (16)

into the next equation, obtained from eqs (11) and (12)

$$\frac{\gamma_{A,S} x_{A,S}}{\gamma_{B,S} x_{B,S}} \cdot \frac{\gamma_{B,L} x_{B,L}}{\gamma_{A,L} x_{A,L}} = \exp \left\{ \frac{(\mu_A^{\Theta} - \mu_A^{*} - \Delta \mu_{I \to II^1} - \epsilon_{e1}) - (\mu_B^{\Theta} - \mu_B^{*})}{RT} \right\}$$
(17)

leads to

$$\frac{x_{A,S} / x_{B,S}}{x_{A,L} / x_{B,L}} = \frac{\gamma_{B,S}}{\gamma_{A,S}} \cdot \frac{\gamma_{A,L}}{\gamma_{B,L}} \cdot \frac{K_{SP}(B)}{K_{SP}(A)} \cdot \exp\left(-\frac{\Delta \mu_{I \to II^{1}} + \epsilon_{el}}{RT}\right)$$
(18)

and this term equals D, because

$$D = \frac{{}^{m}_{A,S} / {}^{m}_{B,S}}{{}^{m}_{A,L} / {}^{m}_{B,L}} = \frac{{}^{x}_{A,S} / {}^{x}_{B,S}}{{}^{x}_{A,L} / {}^{x}_{B,L}}$$
(19)

10.9. References

- Becker, P., Phosphates and phosphoric acid. Fertilizer Science and Technology Series Vol. 6. Dekker, New York (1989).
- Van der Sluis, S., Witkamp, G.J. and van Rosmalen, G.M., J. Crystal Growth 79 (1986) 620
- Witkamp, G.J. and van Rosmalen, G.M., Proc. Sec. Int. Symp. on Phosphogypsum, Vol. 1, p. 377-405. Florida Institute of Phosphate Research, Jan. 1988.
- Weterings, C.A.M. and Janssen, J.A., July 1986.
   Patent pending. (nr. 8601846 Dutch Patent Office).
- 5. Kushnir, J., Geochim. Cosmochim. Acta 44 (1980) 1471-1482
- 6. Huheey, J.E., Inorganic Chemistry, Harper & Row, New York (1975)
- 7. Kushnir, J., Geochim. Cosmochim. Acta 46 (1982) 433.
- Moisset, J., Proceedings of the Second International Symposium on Phosphogypsum, Vol. 1, p. 303-317. Florida Institute of Phosphate Research, Jan. 1988.
- 9. Palmer, J. United States Patent 4388292 (1983), 4421731 and 4424196 (1984).

10.	McIntire, W.L. Geochim. Cosmochim. Acta 27 (1969) 1209-1264.
11.	Balarew, C., Proc. 13th gen. meeting Int. Mineral. Ass.,
	Varma (1982) Publ. House Bulg. Acad. Sci. p. 287-293.
12.	Chernov, A.A., Modern Crystallography III, Springer Verlag(1984)
13.	Stoilova, C.C., Balarew, C., Comp. Rend. de l'Acad. Bulg. d. Sci.
	Tome 34 no. 10 (1981) 1397-1400.
14.	Balarew, C. Z. Anorg. Allg. Chem. 422 (1976) 283-288
15.	Aslanian, S., Balarew, C., Proc. 13th gen. meeting Int. Mineral.
	Ass., Varma (1982) Publ. House Bulg. Acad. Sci. p. 811-819.
16.	Pitzer, K.S., J. Sol. Chem. 5(4) (1976) 269-278 and ref. therein.
17.	Louis, C., Bessiere, J., Canad. Journ. Chem. 64 (1986) 608-614.
18.	Louis, C., Bessiere, J., Talanta 34(9) (1986) 763-777.
19.	Rosmalen, G.M., Vreugd, C.H. de, and Witkamp, G.J., Tagungsband
	der Jahrestreffen 1988 der VDI, Hannover september 1988.Hannover
20.	Lorens, R.B., Geochim. Cosmochim. 45 (1981) 553-561.
21.	Nielsen, A.E. and Toft, J.M., J. Crystal Growth 67 (1984) 278-288
22.	Melikhov, I.V., Growth of Crystals, Vol. 11, ED. A.A. Chernov,
	Consult. Bur. NY p. 309-321 (1979).
23.	Pedersen, B.F., Acta Cryst. B38 (1982) 1074-1077.
24.	Florke, O.W., Neues Jahrb. Min. Abh. 4(2) (1952) 189–240.
25.	Kirfel, A., and Will, G., Acta Cryst. B36 (1980) 2881-90.
26.	Abriel, W., Acta Cryst. C39 (1983) 956-958.
27.	Marcus, Y., J. Chem. Soc., Faraday Trans. 1 83(2) (1987) 339-349.
28.	Kijkowska, R., Phosphorus & Potassium 127 (1983) p. 24.
29.	Hutton, M., Phosphorus&Potassium 123 (1983) 33
30.	Tjioe, T.T., Thesis, Delft Univ. Techn., The Netherlands (1987).
31.	Aurivillius, K. and Stalhandske, C., Z. fur Krist. 153 (1980) 121
32.	Bregeault, J.P., and Herpin, P., Bull. Soc. Fr. Mineral.
	Cristallogr. 93 (1970) 37-42.
33.	Caminiti, R., and Johansson, G., Acta Chem. Scand. A35 (1981) 451
34.	Novaro, O., Int. J. Quantum Chem. 23(4) (1983) 390-394.
35.	Hewisch, N.A., Neilson, G.W., and Enderby, J.E., Nature 297
	(1982) 138.
36.	Hellwege, H.E., and Schweitzer, G.K.J., J. Inorg. Nucl. Chem.
• -	27 (1965) 991.
37.	Leden, I. Acta Chem. Scand. 6 (1952) 971.
38.	Genin, C. Thesis, Inst. Nat. Polytechnique de Lorraine,
Fra	nce(1986)
39.	Dorm, E., Acta Chem. Scand. 23 (1969) 1607-1615.
40.	Kragten, J., Atlas of Metal-Ligand equilibria in aqueous solution
	Publ. Ellis Horwood Ltd, Chichester.
41.	Yatsimirski, K.B., and Vasilev, V.P., Instability Constants of
	Inorganic Compounds, Pergamon Press Oxford (1960).
42.	Radnai, T., Palinkas, G., and Caminiti, R., Z. Naturforsch.
	37A (1982) 1247-1252.
43.	Aslanian, S., and Balarew, C., Krist.u.Techn. 12(5) (1977) 435-46
44.	Langmuir, D., and Melchior, D., Geochim. Cosmochim. Acta
	49 (1985) 2423-2432.
45.	Vojtech, O., Moravec, J., and Krivy, I., J. Inorg. Nucl. Chem.
	34(11) (1972) 2245-3350.
46.	Vojtech, O., Moravec, J., and Krivy, I., J. Inorg. Nucl. Chem.
	Letters 9 (1973) 863-867.

- 47. Krivy, I., Moravec, J., and Vojtech, O., Collect. Czech. Chem. Comm. 39(12) (1974) 3603-3607. 48. Danby, R.J., Manson, N.B., J. Chem. Phys. 81(12) (1984) 5462.
- 49. Kato, E., and Diamon, K., Yogyo Kyokaishi 87 (1979) 590-595. 50. Kopylev, B.A., Lyubchenko, T.V., and Pozin, M.E., Z. Prikl. Khim. 42(11) (1969) 2429-2434.Fe-Po4 russen
- 51. Bailor, J.C. et al. Ed., Comprehensive Inorganic Chemistry, Pergamon Press, New York
- 52. Veintemillas Verdaguer, S., and Rodriguez Clemente, R, J. Crystal Growth 79(1986) 198-204.
- 53. Akitt, J.W., Farnsworth, J.A., and Letellier, P., J. Chem. Soc. Faraday Trans. I 81 (1985) 193-205.
- 54. Sirotinkin, S.P., Efremov, V.A., Kovba, L.M., and Pokrovskii, A.N., Kristallografiya 22(6) (1977) 1272-1273.
- 55. Sirotinkin, S.P., and Pokrovskii, A.N., Zh. Neorg. Khim. 27 (1982) 2142-2143.
- 56. Carvalho, R.G. de, and Choppin, G.R., J. Inorg. Nucl. Chem. 29 (1967) 725-735.
- 57. Bilal, B.A. and Koss, V., J. Inorg.Nucl.Chem. 42(7) (1980)1064
- 58. Kitchen, D., and Skinner, W.J., J. Appl. Chem. Biotechn. 21 (1971) 56.
- 59. Akitt, J.W., Greenwood, N.N., and Lester, G.D., J. Chem Soc. (A) (1971) 2450.
- 60. Witkamp, G.J., and van Rosmalen, G.M., Proc. 10th Symp. Ind. Cryst. in Press (Elsevier, Amsterdam)
- 61. Weterings, K., and Janssen, J., Hydrometallurgy 15 (1985) 173-90
- 62. Holc, J., Kolar, D., J. Solid State Chem. 47 (1983) 98-102.
- 63. Sluis, S. van der, Thesis. Delft Univ. Techn. The Netherlands (1987).
- 64. Dmitrevskii, B.A., Yarosh, E.B., Kopylev, B.A., and Akhmetov, A.S., Zh. Prikl. Khimii 56(2) (1983) 372-380.
- Eymery, J.P., Guilhot, B., et Soustelle, M., C.R. Acad. Sc. 65. Paris, 290 (1980) 125-128.
- 66. Dickens, B., Bowen, J.S., and Brown, W.E., Acta Cryst. B28 (1972) 797-806.
- 67. Elmore, K.L., Hatfield, J.D., Dunn, R.L., and Jones, A.D., J. Phys. Chem. 69 (1965) 3520.
- 68. Wertz, D.L., and Cook, G.A., J. SOl. CHem. 14(1) (1985) 41-48.
- 69. Caminiti, R,, Chem. Phys. Letters 96(3) (1983) 390-394.
- 70. Caminiti, R., Chem. Phys. Letters 88(1) (1982) 103-108.
- 71. Camiiti, R., Cucca, P., and Atzei, D., J. Phys. Chem. 89 (1984) 1457
- 72. Sandstrom, M., Neilson, G., Johansson, G., and Yamaguchi, T.Y., J. Phys. C:Solid State Phys. 18(36) L1115-L1121.
- 73. Maarel, J.R.C. van der, Lankhorst, D., Bleijser, J. de, and Leyte, J.C., J. Phys. Chem. <u>90</u> (1986) 1470
- 74. Linke, W.F., Solubilities, D. Van Nostrand, Princeton (1958).
- 75. Cossy, C. , Helm, L. and Merbach, A.E., Inorg. Chim. Acta 139 (1987) 147-149
- 76. Merbach, A.E. Pure & Appl. Chem. 59(2)(1987) 161-172
- 77. Friedman, H.L., Chemica Scripta 25 (1985) 42-48

### CHAPTER 11

### IMPURITY DISTRIBUTION IN A PHOSPHORIC ACID PROCESS

11.1. Objective

In this chapter the formerly determined distribution coefficients have been used to calculate the distribution of many impurities, originating from the ore, over the phosphoric acid and calcium sulfate modifications in a selected phosphoric acid process. In this process initially formed hemihydrate is filtered and recrystallized into dihydrate. In the phosphoric acid recycle stream a small portion of 5% of the total amount of calcium sulfate is formed. If suitable process conditions are chosen, this anhydrite captures a great deal of the cadmium ions from the stream, thus depleting the solution in the process with respect to cadmium. This calculation has only been made as an illustrative example.

### 11.2. Distribution coefficients

In table 11.1. the composition of a typical ore is given (Khouribga or Zin) together with the typical distribution coefficients, K, defined as:

$$K = \frac{[impurity]_{crystal}}{[impurity]_{solution}}$$
. These K-values are taken from chapter 10

## 11.3. Impurity distribution in a phosphoric acid process

Using these data, the concentrations of the impurities in the product acid as well as in the dihydrate, hemihydrate and the anhydrite formed in a phosphoric acid process were calculated. This was done by solving the mass balance equations of the impurities in the process depicted in figure 11.1 with the computer program "Eureka" from Borland. This process is an implementation of the patented Cd-removal method by AH precipitation. In the recrystallization section only a dilution of the

Compound	Content of ore 10 <sup>6</sup> x weight fraction	к <sub>DH</sub>	к <sub>нн</sub>	K <sub>AH</sub>
Ca	37000	-	-	-
PO	440000	0.01	0.01	0.01
F	40000	*	*	*
Na				
Fe	1500	< 0.1	0.2	0.2
Zn	400	0.01-0.1	0.03-0.06	0.06
Cr	200	0.02-0.4	0.3	0.2
U	150	0.01-1	15	1.1
Cu	50	0.1 -0.5		
Ni	50	0.04		
Ce, La	30			
Ca	20	0.1 -0.3	0.2-1.0	30
Mn	20	0.05-0.10		0.6
As	15	0.1 -1	0.05	0.07
Sb	3	0.02	· 1.2	0.7
Pb	2	0.6 -5		
Hg	0.02	1 - 2	0.3-3	0.04

Table 11.1. Distribution coefficients of compounds from ore.

\*: as AlF<sub>3</sub>

phosphoric acid with a factor of 3 has been chosen. A further dilution leads to a significant decrease in cadmium uptake in the dihydrate.

The resulting concentrations are listed in table 11.1.

The largest uncertainties are for U, As, Zn, Pb, Cr. These errors are not given in table 11.2, but can be deduced from table 11.1.

Especially U and As are hard to estimate because their chemical appearance is not exactly known (see chapter 10). Zn has a low distribution coefficient, but due to the high concentration in ore (400 ppm) its uptake is significant. Most Pb will end up in the gypsum or the anhydrite. Uptake of Cr needs further study. In the following the consequences of variation in Cd uptake is described.

# 11.4. Cd uptake

The cadmium concentration in the ore is one of the most important parameters, because the cadmium disposal will be limited in the future to a few tons per year. With a DH disposal of yearly 2.10<sup>6</sup> tons this

Compound	Content of ore 10 <sup>6</sup> x weight fraction (=ppm)	10 <sup>6</sup> x wei DH	ght frac HH	tion in: AH	product acid
F	40000	2000	2500	3500	8000
Na					
Fe	1500	125	470	230	1600
Zn	400	12	23	24	460
Cr	200	17	63	36	210
U	150	94	230	14	15
Cu	50	7	9	12	47
Ni	50	1	2	2	58
Ce, La	30				
Cd	20				
Mn	20				
As	15	2	0.2	1	15
Sb	3	0.1	1.5	2	3
Pb	2	1.7	2.3	1.8	0.5
Hg	0.02	0,008	0.01	0.0004	0.01

Table 11.2. Concentrations of impurities from table 11.1 in the process of figure 11.1.

means that the concentration in DH should be at most 0.5 ppm (weight fraction  $5 \cdot 10^{-7}$ ). For this reason in table 11.3 an estimation is given for the Cd concentration resulting from various K-values in DH, HH and AH lying in a reasonable range. Whether these K-values are achieved depends on the (re)crystallizing conditions (see chapter 6).

Table 11.3. Cd-concentration in product acid, dihydrate and anhydrite for some K-values in the process (fig. 1)  $[Cd^{2+}](ore) = 20.10^{-6} (w/w)$ .

к <sub>DH</sub>	к <sub>нн</sub>	KAH	10 <sup>6</sup> x weight fraction of Cd <sup>2+</sup> product acid DH A		
0.4	0.2	50	6.2	1.1	133
0.4	0.2	100	5.1	0.9	145
0.4	0.4	50	6.0	1.5	129
0.4	0.4	100	4.9	1.2	141
0.4	0.6	50	5.8	i.9	125
0.4	0.6	100	4.8	1.6	138
0.2	0.2	50	6.4	0.7	137
0.2	0.2	100	5.2	0.6	149
From table 11.3 it follows that the resulting  $Cd^{2+}$  concentration is a strong function of the K-values in HH and DH, but also depends on K(AH).

Whether a concentration of for example  $10-^6$  (w/w) or 1 ppm can be obtained depends on relatively small differences in distribution coefficients.

In addition, the AH needs to be recrystallized into DH, because on a production of  $2.10^6$  tons DH the amount of formed AH is still  $1\cdot4.10^5$  tons, which is too much for storage. The Cd<sup>2+</sup> uptake by the gypsum formed during such recrystallization adds up to the total cadmium disposal. It is suggested to remove Cd<sup>2+</sup> from this recrystallizing solution by for instance ion exchange.





The cadmium taken up by the gypsum is disposed of, as well as other impurities incorporated in the gypsum. To get an idea of the implications of this disposal with respect to the current situation, in table 11.4 the disposal figures in tons per year in The Netherlands are given. No accuracy is claimed, the table is only meant to show the order of disposal and which impurity may want further investigation.

new process, based on $2 \cdot 10^6$ ton gypsum/year.		ton gypsum/year.
Compound	Disposal 1986 tons/year	Disposal presented process tons/year
Fe		125
Zu	17	12
Cr	14	17
U		180
Cu	10	14
Ni	4	1
Cđ	15	1-3
As		4
РЪ	9	3
Hg	0.15	0.016

Table 11.4. Current disposal, and estimated figures for disposal with

Apparantly Zu, Cr, U, Cu, Cd and As need more study.

### SUMMARY

Crystallization is a widely encountered process, both in nature and industry. When applied as a separation method in industrial processes the purity is often an important parameter, either because of the product quality or for environmental reasons when the crystals are byproduct which is disposed.

The process of uptake of impurities resembles that of crystal growth: in both cases compounds from the solution are transported to the growing crystal surface and become part of the solid phase that is formed. The courses of these two process are determined by the driving force (thermodynamics) and by the rate at which the equilibrium state can be reached (kinetics).

This resemblance forms the basis of the description of the uptake of impurities during crystallization of calcium sulfate as a byproduct during production of phosphoric acid. This waste product is contaminated with impurities, originating from the phosphate ore, of which the most important is cadmium, which toxic effects are well known.

The aim of this investigation is to identify the kinetical and thermodynamical parameters ruling the uptake, and to determine the (re)crystallization kinetics of calcium sulfate without or in presence of impurities.

By the constant composition method it was found that the growth kinetics of gypsum follow a parabolic law in aqueous solutions, and are of an order of 1 to 4 in sodium nitrate solutions, depending on the supersaturation. Some crystal faces become roughened. In these experiments, but also in precipitation and continuous crystallization experiments it was found that the cadmium uptake, expressed by an partition coefficient D, is approximately  $3 \cdot 10^{-4}$  in aqueous solutions, and becomes higher at higher growth rate, temperature and electrolyte concentration. Adsorption of  $Cd^{2+}$  on the surface of gypsum crystals could not be detected.

-210-

The D-value of cadmium in the hemihydrate phase, formed in continuous crystallization in concentrated phosphoric acid is about  $10^{-3}$ . The D-value for phosphate uptake is  $1.4 \cdot 10^{-4}$ . The constancy of the D-value points at a competition between Cd and Ca, and between phosphate and sulfate, and imposes an increasing cadmium uptake and decreasing phosphate uptake at increasing sulfate concentrations.

Presence of 0.8% AlF<sub>3</sub> in the phosphoric acid leads to an enhanced Cd uptake in a continous crystallization of the dihydrate, the hemihydrate and the anhydrite phase. The crystal growth is strongly retarded at the top faces.

In batch experiments it has been shown that recrystallization of hemihydrate into anhydrite proceeds through the solution and is faster at higher temperature, phosphoric acid and sulfuric acid concentrations, and with addition of more seed crystals. In the absence of seed crystals no induction time preceeds the conversion. For anhydrite D(Cd) is 2 to  $4 \cdot 10^{-2}$ , which is more than ten times higher than for the other two phases.

batchwise conversion of hemihydrate into dihydrate has been The described by a model taking into account the rates of dissolution of hemihydrate and of growth of dihydrate, each determined by a rate constant and a driving force, which is related to a difference in solubilities of the phases. Also the crystal size distributions play a role in this model. The rate constant for gypsum growth is lower in the presence of  $AlF_3$  and  $Ce^{3+}$ . The driving force is smaller at higher temperature and acid concentrations. From the independance of conversion rate on the percentage of solids in the slurry it follows that secondary nucleation does not affect the rate of conversion in these batch systems.

To predict continuous behaviour using parameters derived for the description of batch experiments the model has been extended to describe a continuous three stage recrystallization system. Contrary to batchwise conversion, the recrystallization was experimentally found to proceed much faster at higher slurry densities, apparently due to secondary nucleation. The growth and dissolution rate constants agree reasonably with the values obtained from the batchwise operation.

Uptake of cadmium in hemihydrate and dihydrate was reduced by addition of halides. Their effectivity decreases in the sequence I > Br > Cl, and is higher in stronger acid solutions or at lower temperatures. In aqueous solutions it was found that thiosulfate is more effective than I. Uptake of halides does not occur.

By comparing the incorporation of all kinds of compounds with their specific properties, it was found that the charge of the foreign ion, the polarizability and the dehydration energy and frequency do not have a correlation with the partition coefficients in anhydrite and gypsum. Parameters that are important are the ionic radius and the solubility of the sulfate salts of the metal ions. The higher D-value of cadmium in anhydrite than in the other phases could be related to the existence of an isomorphous cadmium sulfate phase only for anhydrite.

The determined or estimated distribution coefficients of several compounds were used to calculate their distribution over the acid and the calcium sulfate phases that are formed in a phosphoric acid process containing a recrystallization step.

### SAMENVATTING

Kristallisatie is een veel voorkomend proces, zowel in de natuur als in de industrie. Indien het wordt toegepast als scheidingstechniek is de zuiverheid van de verkregen kristallen van belang vanwege de produktkwaliteit of vanwege de milieuvervuiling die kan optreden wanneer het als bijprodukt gevormd en vervolgens geloosd wordt.

In het proces van opname van zowel reguliere bouwstenen als van verontreinigingen in het kristal vindt transport plaats van materiaal vanuit de vloeistof naar het oppervlak waar het opgenomen wordt om deel uit te maken van de vaste fase.

Het verloop van deze twee processen wordt bepaald door de drijvende kracht (thermodynamica) en door de snelheid waarmee de evenwichtstoestand bereikt kan worden (kinetiek).

Deze overeenkomst tussen inbouw van bouwstenen en verontreinigingen is als uitgangspunt genomen voor de beschrijving van de inbouw van in calciumsulfaat bijprodukt dat verontreinigingen bij de wordt. Dit afvalprodukt fosforzuurproduktie gevormd bevat verontreinigingen afkomstig van het fosfaaterts. De belangrijkste hiervan is cadmium vanwege de concentratie in combinatie met de giftigheid.

Het doel van het onderzoek is de kinetische en thermodynamische parameters van inbouw te bepalen, en de kristallisatiekinetiek van calciumsulfaat te beschrijven in aan- en afwezigheid van verontreinigingen.

Met de "constante samenstelling" methode is gevonden dat de groeikinetiek van gips in waterige oplossing plaatsvindt volgens een 2e orde in de overzadiging, maar volgens een le tot 4e orde verloopt in natriumnitraat oplossingen, afhankelijk van de overzadiging. Bepaalde kristalvlakken worden verruwd. Uit deze experimenten, evenals uit spontane precipitatie en continue kristallisatieproeven, is gebleken dat de partitiecoeficient D van cadmium in gips gelijk is aan 3.10-4 in waterige oplossing bij 25 °C en bij lage groeisnelheid, maar hoger wordt bij toenemende groeisnelheid, temperatuur en electrolyt

concentratie. Adsorptie van  $Cd^{2+}$  op het kristaloppervlak is te gering om te kunnen worden aangetoond.

De D-waarde van cadmium in calciumsulfaat hemihydraat, gevormd tijdens continue kristallisatie in fosforzuur is ongeveer 10-<sup>3</sup>. De D voor fosfaatinbouw is 1.4.10-<sup>4</sup>. Het constant zijn van D wijst op een competitie tussen Cd en Ca, en tussen fosfaat en sulfaat, en resulteert in een toenemende cadmium inbouw en een afnemende fosfaatinbouw bij toenemend sulfaatgehalte.

Door toevoegen van 0.8% AlF<sub>3</sub> aan het fosforzuur wordt de cadmium inbouw verhoogd bij continue kristallisatie van alle drie calciumsulfaat fasen, terwijl de groei van de kopvlakken geremd wordt.

Batchexperimenten wijzen uit dat de omkristallisatie van hemihydraat naar anhydriet plaatsvindt door de vloeistof en sneller verloopt bij hogere temperaturen en zuurconcentraties, en bij toevoegen van meer entkristallen. Ook zonder enten vangt de conversie direct aan. D(Cd) in anhydriet is 2-4·10-<sup>2</sup>, hetgeen meer dan tien keer hoger is dan voor de andere fasen van calciumsulfaat.

De batchgewijze omzetting van hemihydraat naar dihydraat is beschreven met een model dat rekening houdt met oplossnelheden van hemihydraat en beide bestaande groeisnelheden dihydraat, uit van een snelheidsconstante en een drijvende kracht die gekoppeld is aan het oplosbaarheidsverschil beide fasen. 0ok de tussen kristalgrootteverdelingen zijn in het model betrokken. De groeisnelheidsconstante van gips is lager in aanwezigheid van  $AlF_3$  en  $Ce^{3+}$ . De drijvende kracht is kleiner bij hogere temperaturen en zuurconcentraties. De conversie snelheid hangt in dit batchsysteem niet af van het vaste stofgehalte, en wordt dus ook niet beinvloed door secundaire nucleatie.

Om het continue omkristallisatiegedrag te voorspellen aan de hand van batchexperimenten is het model uitgebreid naar een continue drietrapsomkristallisatie. In tegenstelling tot de batchomkristallisatie is voor een dergelijk systeem gevonden, dat de conversiesnelheid hoger is bij hogere slurrydichtheden, kennelijk als gevolg van secundaire nucleatie. De snelheidsconstanten komen wel overeen met de batchsituatie.

De inbouw van cadmium kan worden gereduceerd door toevoeging van halogeniden. De effectiviteit hiervan daalt in de volgorde  $I^>Br^>Cl^$ , en is groter in geconcentreerdere zuur oplossingen of bij lagere temperaturen. In waterige oplossing blijkt thiosulfaat effectiever dan jodide. Halogeniden worden zelf niet ingebouwd.

Door de mate van inbouw van allerlei verontreinigingen te correleren met hun eigenschappen is gevonden dat de ionlading. de polariseerbaarheid en de dehydratatieenergie en -frequentie geen verband met de inbouw houden, terwijl de straal en de oplosbaarheid van de sulfaatzouten van de metaalionen wel belangrijk zijn. De hoge D(Cd) voor anhydriet ten opzichte van de andere fasen is gerelateerd aan het alleen bij anhydriet voorkomen van een isomorfe cadmiumsulfaat fase.

Met geschatte distributiecoefficienten is de verdeling van een aantal verontreinigingen berekend over het zuur en de vaste fasen in een fosforzuurproces met een omkristallisatiestap.

### NAWOORD.

Deze studie is verricht met als uiteindelijke doelstelling een reductie van de hoeveelheid verontreinigingen die met afvalgips, gevormd bij de fosforzuurproduktie geloosd wordt. Ik hoop dat met dit werk de oplossing voor dit afvalprobleem een stap naderbij is gekomen, zodat een schoner milieu wat meer binnen bereik komt. Daarnaast is het wellicht mogelijk om op deze manier ook iets aan andere problemen met inbouw van verontreinigingen in kristallen te doen.

Uiteraard is het tot stand komen van dit proefschrift het werk van velen geweest, en ik wil op deze plaats mijn dank uitspreken aan hen die hun onmisbare bijdrage hebben geleverd. Wetende dat ik niet iedereen kan noemen, en met excuus aan diegenen die hier ten onrechte niet staan vermeld dank ik:

de afstudeerders en stagiairs Otto Abrahams, Ruud Blomsma, Rene van Bijnderen, Pete Coenders, Marcel van der Hart, Emile Naburgh, Frits Oukes, Jan Willem van der Poorten, Bas Schuit, Marcello Seckler, Jens Smeding, Henk Velthuis, Reinoud van Wolferen en alle studenten van het derdejaars practicum analytische chemie voor hun inzet en goede verslaggeving waardoor het schrijven van dit proefschrift zeer vergemakkelijkt is, en dr. Dolf Bruinsma, dr. Jan van der Eerden en prof. P. Bennema, mijn collega's dr. Sietse van der Sluis, dr. Tjien Tjioe en drs. Kees de Vreugd voor de prettige samenwerking en de stimulerende discussies.

Verder dank ik ir. Z. Kolar van het IRI voor het opzetten en doen uitvoeren van de adsorptieexperimenten met radioactief Cd<sup>2+</sup>, prof. Kroon en zijn afdeling voor uitleg over en het mogen gebruiken van de PS300 terminal voor de grafische representatie van verbindingen en kristalstructuren.

Gerard Mulder en Martin Nieuwkerk van de electronische dienst, de fotografen Fred Hammers en Piet Dullaart, de glasblazers van de afdeling van Piet Molenkamp, de tekenaars Ary Schriel, Bas Sodderland en Wim Hoogstadt, de instrumentmakers Theo Bosman en Karel Klok, de analytisch chemicus ing. Johan Tiggelman en de onderzoeksmedewerkers ing. Jan Verbiest en Rob Hoefnagel, en de secretaresses Ella van Hagen en Edith Uylen ben ik zeer erkentelijk voor de inzet, de nauwgezetheid en snelheid waarmee zij verzoeken om haastklussen honoreerden, en voor hun suggesties voor hoe het beter kon. Voor soortgelijke verdiensten en hulp dank ik hr. van Lent voor de vele Guinier-De Wolff opnamen, ing. Nico van der Pers voor aanwijzingen bij Rontgenscans, hr. ing. van Dam en Jan Toth voor de SEM opnamen, Astrid van der Meer, Anneke Ammerlaan en Lucie Westing van het IRI voor het vele werk aan de neutronenactiveringsanalyses.

Voor de financiering van en interesse voor dit onderzoek, zonder welke het nooit had hunnen plaatsvinden, dank ik DSM en de ministeries van VROM, Economische Zaken, Landbouw en Visserij en Verkeer en Waterstaat.

# CURRICULUM VITAE G.J. Witkamp

11 mei 1961	geboren te Kerkrade
1979	eindexamen VWO-B met achtste vak Latijn s.g. "De Ring van Putten", Spijkenisse
1982	kandidaatsexamen S3 (scheikunde en natuurkunde). Rijksuniversiteit Leiden.
1985	doctoraalexamen scheikunde met hoofdvak heterogene katalyse. Rijksuniversiteit Leiden.
1989	promotie aan de TU Delft op het onderwerp "Kristallisatie van calciumsulfaat en inbouw van verontreinigingen"
vanaf 1989	Universitair docent TU Delft, Faculteit der Scheikundige Technologie en der Materiaalkunde

### LIST OF PUBLICATIONS

Some of the chapters have been or will be published as follows:

- Chapter 2 has been submitted for presentation at ICCG-9, to be held in Sendai, Japan in August 1989, and will appear in the Journal of Crystal Growth.
- Chapter 4: Journal of Crystal Growth, Volume 79 (1986) p. 620-629.
- Chapter 5: Industrial Crystallization 87, Eds. J. Nyvlt and S. Zacek, Elsevier Amsterdam 1989, p.265-270.
- Chapter 6: Proceedings of the Second International Symposium on Phosphogypsum, Volume 1, Florida Institute of Phosphate Research, 1988, p.377-405.

Chapter 7: as chapter 2.

Chapter 10: Heavy Metals in the Hydrological Cycle, M. Astruc, ed. Selper Ltd., London 1988. p. 108.p.377-405.

## Stellingen

- De door Chernov gehanteerde definitie van de partitiecoefficient als de verhouding van de molfractie verontreiniging in de vaste stof en in de vloeistof is onpraktisch.
  A.A. Chernov, Modern Crystallography III, Springer Verlag (1984)
- De relatief hoge cadmium inbouw in calciumsulfaat hemihydraat bij lage sulfaatconcentaties wordt veroorzaakt door een kinetisch effect.
- Het effect van silica-additie bij de fosforzuurbereiding op de verkregen habitus van calciumsulfaatkristallen berust op een competitie tussen aluminium en silicium voor complexering met fluoride.
- 4. Voor het aanduiden van het sulfaatgehalte van fosforzuur is de totale concentratie beter geschikt dan het in de praktijk veel gebruikte vrij-zwavelzuurgehalte dat gebaseerd is op de molaire overmaat ten opzichte van calcium.
- 5. In geval van snel uitwisselende liganden verdient het wellicht de voorkeur om de effecten van complexering op de activiteiten van ionen te verdisconteren in de activiteitscoefficienten in plaats van in de concentratie vrije ionen.
- 6. Het bij voorbaat verwaarlozen van de weerstand voor het afvoeren van warmte van het kristaloppervlak naar de bulk van de vloeistof is zeker in het geval van meer geconcentreerde oplossingen niet altijd gerechtvaardigd.

R. de Goede, proefschrift, Delft (1988)

- 7. Het is de vraag of het milieu gebaat is bij een vervanging van de fosfaten in wasmiddelen door een combinatie van zware metaalionenafvangende zeolieten en biologisch slecht afbreekbare polymeren.
- 8. Bij de vaststelling van produktprijzen zou rekening gehouden moeten worden met de kosten van het verwerken van de afvalstoffen die tijdens de produktie en de uiteindelijke vernietiging gevormd worden.
- De gedachte dat het in Nederland werkzaam zijn van buitenlanders schadelijk is voor onze arbeidsmarkt getuigt niet van economisch inzicht.
- 10. De onmogelijkheid tot parkeren alsmede de onveiligheid bij vele treinstations nodigt niet uit tot gebruikmaking van het openbaar vervoer.
- Vaak lijkt wat aangekondigd wordt als een radioprogramma voor muziek meer op een telefoonquiz of op een praatprogramma.
- 12. Aan iedere instelling werken zowel inslapers als uitslapers.

Delft, 22 juni 1989

G.J. Witkamp

Stellingen behorende bij het proefschrift "Crystallization of calcium sulfate and uptake of impurities"