Purification of Gypsum from the Phosphoric Acid Production by Recrystallization with Simultaneous Extraction

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Proefschrift

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Cover: Part of the phosphoric acid production plant of Kemira Agro Pernis.
Photograph by Cloosterman Communicatie.
Zuivering van Gips tijdens de Productie van Fosforzuur door Omkristallisatie met gelijktijdige Extractie

Samenvatting

In de 'natte' productieprocessen voor fosforzuur, wordt uit fosfaaterts en zwavelzuur ook een grote hoeveelheid gips gevormd, 2,3 ton per ton fosforzuur oplopend tot 100 miljard kilo wereldwijd. Tot de recentelijke ontwikkeling van het ProGips-proces was dit gips een afvalproduct, omdat verontreinigingen uit het erts daarin ingebouwd worden. Dit proefschrift beschrijft de mogelijkheid om met in-line extractietechnieken de verontreinigingen te verwijderen tijdens een bestaande omkristallisatiestap van calciumsulfaat hemihydraat naar dihydraat (gips). Deze technieken zouden aanvullend aan of als vervanging van het ProGips proces gebruikt kunnen worden om een schoner fosforzuur- en gipsproduct te verkrijgen met constante kwaliteit. Een ander voordeel van het gebruik van in-line extractietechnieken is dat het proces flexibeler wordt met betrekking tot de erts die gebruikt kunnen worden. De ontwikkelde technologie is overigens toepasbaar op tal van andere vloeistof-vast systemen.

De inbouw van verontreinigingen is afhankelijk van thermodynamische en kinetische parameters. Met computersimulaties van krachtvelden en quantummechanica kan een indicatie worden gevonden voor de thermodynamische parameters. Voor lanthaniden is gebleken dat zij bij grote voorkeur in het calciumsulfaatrooster inbouwen. Andere invloeden, zoals het vormen van een defect voor ladingscompensatie, lijken de neiging tot inbouw te verlagen.

Er zijn commerciële dragers en ionenwisselaars gevonden die in staat zijn de verontreinigingen te verwijderen uit het industriële fosforzuur. Deze dragers voldoen aan Pearsons regel over harde en zachte zuren en basen. Zo kunnen zacht lood, cadmium en kwik verwijderd worden door de zachte thiophosphinezuren, terwijl het harde calcium, dat in hoge concentraties aanwezig is, in oplossing blijft. Voor de lanthaniden geldt dat welke het meest wordt verwijderd afhankelijk is van de drager. Voor dragers met een hogere polariseerbaarheid dan water, zoals fosforzure dragers, neemt de verwijderingsgraad toe van lanthaan naar erbium, dus met toenemend atoomnummer. Voor dragers, welke minder polariseerbaar zijn dan water, zoals sulfonzure dragers, neemt de verwijderingsgraad af met toenemend atoomnummer. Dit is te verklaren uit het feit dat de sulfonzure groepen binden met het gehydrateerde ion, terwijl fosforzure groepen binden met het gedehydrateerde ion.

De extractie van de verontreinigingen resulteert ook in een significante verlaging van de concentratie van deze elementen in het gips bij behandeling tijdens de omkristallisatie van hemihydraat naar dihydraat.
De fosforzuurslurrie bevat ongeveer 40% gipsdeeltjes. Omdat bestaande extractietechnieken worden gebruikt voor heldere oplossingen, is nieuwe apparatuur ontwikkeld om de slurrie te kunnen behandelen. Er is onderzoek gedaan naar de toepasbaarheid van vloeibare membraanextractie in dwarsaangestroomde holle vezelmodules. De haalbaarheid hiervan is sterk afhankelijk van de grootte van de gipsdeeltjes die door de module gepompt worden. Bij te grote deeltjes moeten de afstanden tussen de vezels zo groot zijn dat er niet voldoende uitwisselend oppervlak overblijft om voldoende verontreinigingen te verwijderen. Een extra scheidingstap om de grove deeltjes te scheiden, voordat de slurrie in de module behandeld wordt, zou een mogelijkheid geven om de afstanden tussen de vezels te verkleinen en daarmee het contactoppervlak te vergroten.

Ionenwisseling is toegepast door ionenwisselaarsbolletjes toe te voegen aan de slurrie. Het is mogelijk om de ionenwisselaars terug te winnen uit de slurrie, te regenereren en her te gebruiken. De extractie-efficiëntie is veelbelovend, maar het regenereren van de ionenwisselaar blijkt moeilijk te zijn. Een economische evaluatie leert dat de regeneratie op dit moment nog de toepasbaarheid in de weg staat. Om duidelijkheid te krijgen in de effecten die de extractie beïnvloeden zijn simulaties van de omkristallisatie met gelijktijdige ionenwisseling gedaan. Hieruit is gebleken dat de extractie-efficiëntie zal stijgen als een grotere hoeveelheid ionenwisselaarsdeeltjes met een opener structuur wordt gebruikt, die kleiner zijn, een hogere affiniteit hebben voor de verontreiniging en als de groeisnelheid van het gips lager is. Daarnaast zal de extractie-efficiëntie hoger zijn geweest als deze was uitgevoerd in een minder zure omgeving dan het fosforzuur.

Daarnaast is een dwarsaangestroomde ionenwisselingsmodule ontwikkeld. Hiervoor zijn ionenwisselende staafjes gemaakt van met divinylbenzeen vertakte polystyreen. Dit materiaal is gefunctionaliseerd met sulfonzure groepen, zoals de gebruikte commerciële ionenwisselaarsbolletjes. Met de huidige methode wordt alleen het buitenste oppervlak van de staafjes gefunctionaliseerd. De module met 260 m²/m³ ionenwisselend oppervlak kan bedreven worden zonder de vorming van verstoppingen en resulteert in een significante verlaging van de lanthaanconcentratie in de fosforzuurslurrie.

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Summary

In the wet phosphoric acid production processes, not only phosphoric acid is formed from the reaction of phosphate ore with sulfuric acid, but also a large amount of gypsum amounting to 100 billion kg worldwide (2.3 kg per kg phosphoric acid). Until the development of the ProGips process in 1999, the gypsum had to be disposed of due to incorporated impurities. Simultaneous extraction during the recrystallization of calcium sulfate hemihydrate to dihydrate (gypsum), which is discussed in this thesis, is a technique, which can be implemented in the production process complementary to or instead of the ProGips process to produce a cleaner and sustainable phosphoric acid and gypsum product. A large advantage of the extraction process is that the production process will become more flexible with respect to the ores, which can be consumed. The developed in-line extraction techniques can also be used for other solid-liquid process streams.

The incorporation of impurities in the gypsum depends on thermodynamic and kinetic parameters. Force field and quantum mechanics calculations can give an insight in the thermodynamic parameters. From these calculations, it was found that the incorporation of lanthanides in the calcium sulfate lattice is quite favorable. Other factors, like the paired charge compensation defect, seem to reduce the incorporation tendency.

Commercial carriers and ion exchange resins have been found that can successfully remove impurities from clear industrial phosphoric acid. In agreement with Pearson's principle on hard and soft acids and bases, thiophosphinic acids were found to selectively remove the soft mercury, cadmium, and lead ions, and leave the hard calcium ions in solution. Phosphoric and sulfonic acids extract lanthanides. Which lanthanide is removed most depends on the carrier. Phosphoric acids have a higher polarizability than water and the degree of removal increases with increasing atomic number from lanthanum to erbium. Sulfonic acids have a lower polarizability than water and the degree of removal decreases with increasing atomic number. This effect can be explained from the fact that phosphoric acid carriers bind the dehydrated lanthanides, whereas the sulfonic acid carriers bind with the hydrated lanthanides.

The extraction of impurities also results in a lower impurity concentration in the gypsum when the phosphoric acid is treated during the recrystallization of hemihydrate to dihydrate.
The industrial phosphoric acid slurry contains 40wt.% of solids. The existing extraction techniques are developed for the treatment of clear process streams. So, new equipment has been developed to treat slurry streams. Transverse flow hollow fiber modules have been investigated as potential extraction equipment to treat the phosphoric acid slurry by liquid membrane extraction. The feasibility depends strongly on the size of the solid particles. If the particles are large, large pitches between the fibers are required to avoid clogging, resulting in a small contact area.

An extra separation step to remove the largest particles before treatment of the slurry in the module would make it possible to decrease the pitches between the fibers and increase the contact area.

Ion exchange extraction is performed by adding ion exchange resin beads to the crystallizer, in which the recrystallization is performed. The ion exchange resin can be recovered from the slurry, regenerated, and reused. The extraction efficiency is promising, but the regeneration of the resin is difficult. An economic evaluation shows that the regeneration makes this process economically not feasible yet. To gain an insight into the effects that influence the extraction efficiency most, simulations of the recrystallization with simultaneous ion exchange extraction were performed. They showed that the extraction efficiency increases when using more resin with a more open structure, with smaller beads, and a higher affinity for the impurities. Reducing the growth rate of gypsum would also result in higher extraction efficiencies. The extraction efficiency would also have been higher in a less acidic solution than the phosphoric acid.

As an alternative for the treatment with the resin beads, a transverse flow ion exchange module was developed. For this module, ion exchange bars of polystyrene crosslinked with divinylbenzene were manufactured. The bars are functionalized with sulfonic acid groups like the commercial resin beads used in this research. With the current functionalization procedure, only the surface of the bars is functionalized. The module with a contact area of 260 m²/m³ can be operated without clogging and treatment of the phosphoric acid slurry results in a significant decrease of the lanthanum concentration in the slurry.

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Chapter 1

Phosphoric Acid Production

Most phosphoric acid is produced in the wet processes, in which phosphate ore reacts with sulfuric acid. As a byproduct, calcium sulfate solids are formed. With the phosphate ore, also impurities enter the production processes. Some of these impurities end up in the calcium sulfate byproduct.

Due to continuous research and high investments, the Dutch phosphoric acid processes belonged to the most environmental friendly processes worldwide. By changing their process operation and using cleaner ores, they reduced their disposal of impurities significantly. In the recently developed ProGips® process, 90% of the former waste gypsum, the ProGips® product, can be separated from 10% of contaminated fines. The ProGips® product meets all requirements for usage as building material and is acknowledged by the Dutch and German government as a product.

This chapter describes the phosphoric acid production processes as they are operated in The Netherlands.
1.1 Introduction

At the Delft University of Technology, the phosphoric acid production process has been a subject of research for many years [1,2,3,4]. Purpose of this research was mainly to reduce the environmental impact of the phosphoric acid production. As a result of this research, modifications have been introduced to the sites in The Netherlands, resulting in two of the most environmentally friendly phosphoric acid production processes worldwide.

This chapter describes the phosphoric acid production processes, especially those that were operated in The Netherlands, their chemistry and their process improvements to gain higher efficiency, purer phosphoric acid, and a sustainable gypsum product.

Despite all the efforts resulting in the efficient production of pure phosphoric acid and gypsum products, both sites in The Netherlands have been closed in 1999/2000. The phosphoric acid will be produced in sites that are less concerned with the environment. This will result in less pure phosphoric acid and in an increase of the disposal of waste products with all kinds of impurities, worldwide. This is illustrated in figure 1.1 [5]. The figure shows that by importing phosphoric acid from Morocco the diffuse emission in Europe increases, whereas also the point emission in Morocco is much higher than that in The Netherlands before the phosphoric acid sites were closed.

**Figure 1.1.** The point emissions in The Netherlands and Morocco before the sites in The Netherlands were closed and the diffuse emissions in Western Europe when using either phosphoric acid from The Netherlands or from Morocco [5].
1.2 Phosphoric Acid Production

Phosphoric acid is produced either by the wet processes or by the electric furnace processes. About 10% of the phosphoric acid produced are manufactured in the latter processes. In these processes, first elemental phosphorus is produced from the phosphate ore (fluorapatite ore) using electrical energy. From the elemental phosphorus, a very pure phosphoric acid product is produced, almost exclusively for applications requiring high purity, like catalysts, foods, and drinks. The other 90% are produced by the wet processes, in which phosphate ore reacts with sulfuric acid to the phosphoric acid product and a solid calcium sulfate byproduct:

\[
\text{Ca}_{10}(\text{PO}_4)\text{F}_2 + 10\text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} 6\text{H}_3\text{PO}_4 + 10\text{CaSO}_4 \cdot x\text{H}_2\text{O} + 2\text{HF} \quad (1.1)
\]

Notice that for every ton of phosphoric acid also at least 2.3 tons of calcium sulfate byproduct is produced. Phosphoric acid from the wet processes is mainly used for the production of fertilizers.

In the wet processes, different process routes have been developed. Five different basic process routes can be distinguished [6]. First, the mostly used dihydrate processes, in which calcium sulfate dihydrate (DH, gypsum, \(x=2\) in equation 1.1) is formed as a byproduct. This process normally results in a relatively weak phosphoric acid product of 28-30% \(\text{P}_2\text{O}_5\). About 4-6% of the \(\text{P}_2\text{O}_5\) is lost due to its incorporation in the DH crystals.

With increasing energy prices, hemihydrate processes, in which calcium sulfate hemihydrate (HH, \(x=\frac{1}{2}\) in equation 1.1) is formed as a byproduct, became operational. These processes have the advantage of producing a stronger and purer phosphoric acid product of 38-42% \(\text{P}_2\text{O}_5\), therewith saving evaporation costs. The overall efficiency is lower than that of the DH processes, about 92%. The HH byproduct is contaminated with heavy metals, phosphate, and radioactive elements.

To increase the efficiencies of the production processes and to reduce the environmental impact of phosphoric acid production, the dihydrate and hemihydrate processes were extended. A recrystallization step of one form to the other was added to recover the phosphoric acid that was incorporated in the crystals formed during the reaction step.

In the dihydrate hemihydrate (DH/HH) processes, first DH is formed, which is filtered from the phosphoric acid product of 32-36% \(\text{P}_2\text{O}_5\). After filtration, the DH solids are recrystallized to a pure HH product, which can be used directly for the production of plasterboards. The process has an efficiency of 98.5%.
In the hemihydrate dihydrate recrystallization (HRC) processes, first HH is formed as a byproduct, which is recrystallized to DH:

\[
\text{Ca}_{10}(\text{PO}_4)_2\text{F}_2 + 10\text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} 6\text{H}_3\text{PO}_4 + 10\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 2\text{HF} \quad 1.2,
\]

\[
\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad 1.3.
\]

The produced acid has slightly higher strength than that of the DH processes, 30-32% P\textsubscript{2}O\textsubscript{5}. Advantages of these processes are the higher efficiency and the formation of a pure DH byproduct.

In the hemihydrate dihydrate (HDH) processes, first HH is formed, which is filtered from the strong and pure phosphoric acid product of 40-52% P\textsubscript{2}O\textsubscript{5}. After filtration, the HH is recrystallized to DH, which results in a very high efficiency of this process.

In The Netherlands, two different wet processes were operated, the one-filter HRC process (Kemira Agro Pernis) and the two-filter HDH process (Hydro Agri Rotterdam).

\subsection{1.3 Recrystallization}

Whether DH, HH, or calcium sulfate anhydrate (AH, x=0 in equation 1.1) is formed, depends on the process conditions, like the acid concentration and the temperature. The thermodynamic equilibrium lines of the system CaSO\textsubscript{4} – H\textsubscript{3}PO\textsubscript{4} – H\textsubscript{2}O, which are shown in figure 1.2, illustrate this [3,4].

The HRC and HDH processes have the recrystallization of HH to DH in common, although the recrystallization is effected differently. In figure 1.2, the conditions of these processes are indicated. In both processes HH and DH are formed in the area, in which AH is the most stable component. Due to kinetics, this thermodynamically stable AH is not formed, but the metastable HH and DH. This phenomenon is known as Ostwald's rule of stages [7]. In the HRC process, the recrystallization of HH to DH is effected by lowering the temperature of the phosphoric acid slurry, route A-B. In the HDH process, the HH crystals are filtered from the product acid before the recrystallization. The recrystallization is effected by both lowering the temperature and lowering the acid concentration, route C-D.

The recrystallization of HH to DH is a solvent mediated step. This means that HH crystals dissolve and DH crystals are formed simultaneous from ions in the solution. The solubility of both HH and DH strongly depend on the temperature and acid concentration, as is indicated by figure 1.3. In figure 1.3, the solubility product, K\textsubscript{SP} [mol/kg], defined as
\[ K_{SP} = \sqrt{[\text{Ca}^{2+}]_{\text{sat}} \cdot [\text{SO}_4^{2-}]_{\text{sat}}} \]

with the subscript sat indicating the concentration at saturation, for both HH and DH is plotted as a function of temperature for a constant acid concentration [4]. The dependence of the solubility on the crystal size is not taken into account here.

![Phase diagram](image.png)

**Figure 1.2.** The phase diagram of the system CaSO₄·H₂PO₄·H₂O with the indication of the process conditions in the HRC (A-B) and the HDH (C-D) processes.

At the temperature of point A, \( T_A \), the solubility of DH equals that of HH for this particular acid concentration. Below this temperature, the solubility of DH is smaller than that of HH. In this region, HH will recrystallize to DH. During the recrystallization, the product of the concentrations of calcium and sulfate will be in between the solubility products of HH and DH, resulting in an undersaturation for HH, which will therefore dissolve, and a supersaturation for DH, which will crystallize.

The rate determining step of the recrystallization is mostly the growth rate of DH [4], \( G_{DH} \) [m/s],

\[ G_{DH} = k_g \cdot \sigma_{DH}^2 \]

with \( k_g \) the growth rate constant [m/s]. The supersaturation, \( \sigma_{DH} \) [-], which is the driving force is defined as

\[ \sigma_{DH} = \sqrt{\frac{[\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}]}{K_{SP,DH}} - 1} \]

With increasing the temperature from \( T_1 \) to \( T_2 \), the supersaturation for DH decreases. Due to this, the recrystallization rate decreases with increasing temperature.
Figure 1.3. The solubility lines of HH and DH as a function of temperature for a constant acid concentration.

1.4 Impurities

In the phosphate ore, many impurities are present. The concentrations of these impurities depend strongly on the origin of the ore [6]. Table 1.1 shows the concentrations of some of the impurities in Russian (Kovdor), Moroccan (Bucraa), Florida and Jordan (El-Shidiya) ore.

The impurities end up either in the gaseous phase (silicon fluoride), in the phosphoric acid product (e.g. part of the cadmium, chromium, copper, arsenic), or in the gypsum byproduct (lanthanides, mercury, lead, radium).

Most heavy metals present in acid and gypsum are black or gray list components, indicating that they are harmful to the environment. Usage of ores with low concentrations of these elements, like Jordan ore, already results in sufficient low concentrations in the product acid. For other ores, additional treatment of the phosphoric acid is necessary. For instance, arsenic can be removed by sulfide precipitation and cadmium can be removed by extraction of cadmium chloride complexes after adding chloride ions [8].

Heavy metals that are present in the gypsum were disposed of directly with the gypsum until now. With the gypsum, also the incorporated lanthanides were disposed of. Although the disposal of lanthanides has not been proven harmful [9], an increase of the concentration of these foreign ions in the environment should be avoided. Besides heavy metals and lanthanides, also radioactive components, like
radium, end up in the gypsum. This limited the application of the gypsum from phosphoric acid production processes until now.

Table 1.1. Concentrations of some impurities in Russian (Kovdor), Moroccan, Florida and Jordan phosphate ore.

<table>
<thead>
<tr>
<th></th>
<th>Russian</th>
<th>Moroccan</th>
<th>Florida</th>
<th>Jordan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr [mmol/kg]</td>
<td>&lt;0.01</td>
<td>1.3</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>Ni [mmol/kg]</td>
<td>0.034</td>
<td>0.14</td>
<td>0.43</td>
<td>0.19</td>
</tr>
<tr>
<td>Cd [mmol/kg]</td>
<td>&lt;0.001</td>
<td>0.31</td>
<td>0.054</td>
<td>0.044</td>
</tr>
<tr>
<td>Hg [μmol/kg]</td>
<td>&lt;0.05</td>
<td>0.19</td>
<td>0.7</td>
<td>0.22</td>
</tr>
<tr>
<td>La [mmol/kg]</td>
<td>0.59</td>
<td>0.01</td>
<td>0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>Ce [mmol/kg]</td>
<td>3.9</td>
<td>&lt;0.07</td>
<td>1.0</td>
<td>0.16</td>
</tr>
<tr>
<td>Ra226 [Bq/kg]</td>
<td>52</td>
<td></td>
<td>638</td>
<td></td>
</tr>
<tr>
<td>U238 [Bq/kg]</td>
<td>45</td>
<td></td>
<td>662</td>
<td></td>
</tr>
</tbody>
</table>

*analysis by Kemira Agro

Some impurities do not only have a negative effect on the environment, but do also influence the production process itself. For example, the aluminum fluoride complexes, especially AlF<sub>5</sub><sup>-</sup>, retard the growth of HH and DH, resulting in an increase of the supersaturation [10,11]. The retardation of growth and the increase of superstauration have their effect on crystal shape, particle size distribution, and the uptake of other impurities.

Also lanthanides, which are mainly incorporated in the calcium sulfate phases, retard the crystallization of both HH and DH, and especially the recrystallization of HH to DH [12]. Due to this, the presence of lanthanides promotes the formation of small crystals, which form a poorly filterable cake. This will result in a lower production capacity.

1.5 Reduction of Emissions

Two phosphoric acid production plants were present in The Netherlands, both in the Rotterdam area. In the last few decades, large investments were made by the two companies to improve their production processes resulting in the HRC process operated by Kemira Agro Pernis and the HDH process operated by Hydro Agri Rotterdam.
The plant built in 1976 by Kemira Agro Pernis was built according to the best available technology, especially with respect to the co-production of a useful gypsum byproduct. To reduce the emissions, the plant was extended with a repulping section in 1994 (investment € 2.7 million). This resulted in a drastic decrease of the emission of phosphates with the gypsum, and thus in a higher efficiency of the phosphoric acid production.

In 1991, Hydro Agri Rotterdam extended its hemihydrate production process with a recrystallization section, resulting in the HDH process (investment € 16 million). By changing the HH process into an HDH process, the emissions of phosphate, cadmium and other heavy metals were reduced significantly. The efficiency of the production process increased to >99%.

Before 1990, both plants already managed to reduce their emissions significantly by improving their process operation and by changing from Moroccan and Florida ore to Jordan and Russian ore. In table 1.2, the summarized emissions of Hydro Agri Rotterdam and Kemira Agro Pernis in 1995 are compared to those in 1990 and 1985 [13].

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Gypsum (DH)</td>
<td>2.0·10^6</td>
<td>1.8·10^6</td>
<td>1.5·10^6</td>
</tr>
<tr>
<td>Phosphate (P)</td>
<td>1.2·10^4</td>
<td>8.6·10^3</td>
<td>2.3·10^3</td>
</tr>
<tr>
<td>Cadmium</td>
<td>13.4</td>
<td>3.2</td>
<td>0.39</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.7</td>
<td>0.28</td>
<td>0.16</td>
</tr>
<tr>
<td>Other heavy metals</td>
<td>79.1</td>
<td>46.4</td>
<td>11.8</td>
</tr>
<tr>
<td>(Σ Pb, Zn, Cr, Cu, Ni, As)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Although the emissions of heavy metals and phosphate were reduced considerably between 1985 and 1995, an agreement was made between the phosphoric acid producers and the Dutch government on reducing either the gypsum disposal with 90% in 2000, or the impurity disposal with 70-90%. To achieve this, Kemira Agro Pernis and Hydro Agri Rotterdam set up a cooperation and started a large-scale research project. This project was divided into two research routes, one with the aim of reducing the gypsum disposal and one to reduce the impurity disposal by reducing the impurity content in the gypsum.
1.5.1 Reduction of gypsum disposal

The most promising application of the gypsum is in the building industry. For this application the radium equivalence of the gypsum should not exceed 150 Bq/kg [5]. The radium equivalence, Ra-eq [Bq/kg], is calculated with

\[
Ra\text{-eq} = \frac{[^{226}\text{Ra}]}{1} + \frac{[^{40}\text{K}]}{13} + \frac{[^{232}\text{Th}]}{0.7}
\]

To achieve a radium equivalence of 150 Bq/kg, ores should be used with a low concentration of radioactive elements. There are two kinds of ores, igneous ores, like Kovdor (table 1.1), and sedimentary ores, like Jordan ore (table 1.1). Igneous ores have low concentrations of radioactive elements, but higher concentrations of lanthanides. Usage of igneous ores will therefore result in a calcium sulfate product with a low radioactivity. However, the lanthanides will hamper the DH growth resulting in filtration problems. Therefore, the igneous ore Kovdor is mixed with the sedimentary Jordan ore, which contains a higher concentration of radioactive elements, but a lower concentration of lanthanides. A mixture of 65% Kovdor ore and 35% Jordan ore resulted in a filterable gypsum product with 190 Bq/kg.

Moisset [14] reported that radium sulfate co-crystallizes with barium and strontium sulfate, which form very small crystals of 5-8 µm. It has been proven on pilot plant scale that by treatment of the gypsum slurry in a hydrocyclone, 90% of the gypsum (>15 µm), which meets all regulations for application as building material, can be recovered. The clean gypsum product has been named ProGips® to distinguish it from contaminated phosphogypsum. Figure 1.4 shows a schematic drawing of the HRC process extended with the so-called ProGips® process that was developed by the Dutch phosphoric acid industry.

The radium equivalence of ProGips® is 64 Bq/kg, which is far below the limit of 150 Bq/kg. In table 1.3, the radium equivalence of Progips® is compared to that of other building materials [15].

The radioactivity of ProGips® is higher than that of natural gypsum, but is comparable to that of other traditional building materials, like concrete. Tests on radiation, health, environmental, and technical aspects showed that ProGips® has all requirements for a useful application in the building industry. Therefore, the Dutch and German government regard ProGips® as a product. The ProGips® process is described further by Penders et al [16].

The 10% of fines with an increased concentration of radioactivity to a maximum of 5000 Bq/kg might be made into raise material for road construction and hydraulics by immobilization with flyash and cement.
Figure 1.4. Schematic drawing of the HRC process extended with a hydrocyclone to produce ProGips®, gypsum suitable for application in the building industry.

Table 1.3. Comparison of the radium equivalence of ProGips® from the phosphoric acid industry with that of other building materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>226Ra [Bq/kg]</th>
<th>40K [Bq/kg]</th>
<th>232Th [Bq/kg]</th>
<th>Ra-eq [Bq/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>50</td>
<td>150</td>
<td>50</td>
<td>133</td>
</tr>
<tr>
<td>Natural gypsum</td>
<td>10</td>
<td>70</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>Concrete</td>
<td>25</td>
<td>220</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>Sandlime brick</td>
<td>15</td>
<td>190</td>
<td>15</td>
<td>51</td>
</tr>
<tr>
<td>ProGips®</td>
<td>55</td>
<td>30</td>
<td>5</td>
<td>64</td>
</tr>
</tbody>
</table>

1.5.2 Reduction of the impurity content in gypsum

With the development of the ProGips® process, the goal of reducing the gypsum disposal with 90% was reached. Although, the in-line removal of impurities was no longer needed to reach the demands of the Dutch government, it could still be beneficial. During the recrystallization of HH to DH, lanthanides and other impurities can be removed by simultaneous ion exchange extraction or solvent extraction. The in-line removal of impurities results in a purer gypsum product, but also in a purer acid product, of constant quality and can give flexibility in the usage of different ores. Ores can be used with high concentrations of lanthanides, like
Kovdor ore, without causing filtration problems. The results that were gained on the in-line removal of impurities during phosphoric acid production are described in the following chapters of this thesis.

1.6 Conclusion

Due to continuous research and high investments, the Dutch phosphoric acid production processes belonged to the most environmentally friendly production sites worldwide. By changing their process operation and using cleaner ores, they reduced their disposal of impurities significantly. In the recently developed ProGips® process, 90% of the former waste gypsum, the ProGips® product, can be separated from 10% of contaminated fines. The ProGips® product meets all requirements for usage as building material and is acknowledged by the Dutch and German government as a product.

The remaining 10% of contaminated fines might be made into raise material for road construction and hydraulics by immobilization with flyash and cement.

The in-line removal of impurities by extraction during the recrystallization step, described in this thesis, can result in a more flexible production process with respect to ore usage and in purer phosphoric acid and gypsum products.

References


Chapter 2

The Scope of this Thesis
2.1 Introduction

As mentioned in chapter 1, most phosphoric acid is produced by the so-called wet processes, in which phosphate ore reacts with sulfuric acid to form a phosphoric acid product and calcium sulfate byproduct, mostly gypsum. With the phosphate ore, impurities, like heavy metals and lanthanides, also enter the phosphoric acid production processes. The impurities end up in either the gaseous phase (fluoride), the phosphoric acid product (cadmium, zinc, chromium), or the gypsum (lanthanides, radium).

Before the development of the ProGips process, which was described in chapter 1, about one year ago, the gypsum byproduct had to be disposed of, mainly because of the presence of radioactive elements. With the gypsum, also the incorporated heavy metals and lanthanides were disposed of. Most heavy metals are potentially harmful to the environment and their disposal should be avoided. And although the disposal of lanthanides has not been proven harmful [1], an increase of the concentration of these foreign ions in the environment should also be avoided.

Some impurities do not only have their impact on the environment, but also effect the production process itself. For example, lanthanides retard the crystallization of calcium sulfate hemihydrate (HH) and gypsum, and especially the recrystallization of HH to gypsum [2]. This can lead to the formation of small crystals, which form a poorly filterable cake, resulting in a low production capacity.

2.2 The Objective of the Research

After significant reductions in the impurity content in the gypsum by improving the process operations and changing from Moroccan and Florida ore to Jordan and Russian ore, the Dutch phosphoric acid industry agreed with the Dutch government to further reduce either the gypsum disposal with 90% or the impurity disposal with 70-90%. To achieve this, the Dutch phosphoric acid industry started a large-scale research project. The development of the ProGips process, described in chapter 1, was one part of this project. The research described in this thesis was the other part of this project and had the objective of developing a process to remove impurities in-line from the production process to avoid their incorporation in the gypsum crystals.
2.3 In-line Separation of Impurities to gain purer Gypsum

2.3.1 General

Due to the fact that gypsum is only slightly soluble, it is economically and practically not feasible to dissolve the gypsum and, subsequently, remove the impurities from the solution. Therefore possibilities for in-line removal were investigated.

During the phosphoric acid production process, some impurities are incorporated in solids most of the time. First in the phosphate ore, then in the HH, and finally in the DH. To be able to successfully remove these impurities in-line, they should be free in solution. In the production process, this is the case during the reaction of the ore with sulfuric acid and during the solvent mediated recrystallization. During both these processes, the solids, in which the impurities are incorporated, are temporarily dissolved. This results in a, at least partial, release of the impurities in the acid before they are incorporated again in the newly formed solids. For this research, the recrystallization step was chosen for the removal of the impurities, because of its relatively mild process conditions compared to the reaction step (see chapter 1).

During the recrystallization step, the impurities are released from the HH crystals and will be present in the phosphoric acid in their ionic form until they are incorporated again in the DH. Not only impurities are present in the phosphoric acid, also calcium ions are present in the acid. A potential separation technique should therefore be able to selectively remove impurity ions in the presence of high concentrations of other ions. Solvent extraction, liquid membrane extraction, and ion exchange are known techniques for the selective removal of ions. The extraction of lanthanides during the recrystallization by ion exchange extraction is schematically illustrated in figure 2.1. The potential separation techniques are discussed in detail in the next paragraph. However, a prior condition is that carriers and ion exchange resins, which are able to selectively remove the impurities of interest from the phosphoric acid, should be available to be successful.

The techniques of solvent extraction, liquid membrane extraction, and ion exchange are conventionally used for the treatment of clear solutions. To be able to treat slurry streams, like the phosphoric acid slurry during the recrystallization step, the choice of an apparatus, in which the slurry is treated, should gain extra attention. Especially, clogging is an important issue. This is further discussed in §2.3.3.
Figure 2.1. Schematic representation of ion exchange extraction of lanthanides during the recrystallization of HH to gypsum.

2.3.2 Potential separation techniques

Liquid membrane extraction

A liquid membrane is an organic solution, which acts as a selective barrier between two inorganic solutions, a feed solution and a strip solution. The organic liquid membrane phase mostly consists of a solvent, like kerosene, and a carrier. This carrier selectively binds some ions from the feed solution and releases these ions again to the strip solution. This is schematically illustrated in figure 2.2.

Figure 2.2. Schematic illustration of liquid membrane extraction.

Different types of carriers are available, like those that bind cations, those that bind anions, or carriers that form complexes with neutral species. In this research, heavy metals and lanthanides are the species to be removed. These elements are known to be cationic species, although they may also form neutral and anionic complexes with anions present in the acid, like complexes of mercury and chloride. The transport of
cations through a liquid membrane can be performed co-currently or counter-currently. In the first case, the carrier not only transports the cation from the feed to the strip, but also an anion to maintain electroneutrality. Both cation and anion are transported in the same direction, explaining the term co-currently. With counter-current transport, the carrier not only transports the impurity cations from feed to strip, but also cations from strip to feed in order to maintain electroneutrality. The cations that are transported counter-currently to the impurity ions are in most cases protons. The advantage of counter-current transport is that the chemical potential difference, $\Delta \mu = \mu_{\text{feed}} - \mu_{\text{strip}}$, may be smaller than 0 due to the high proton activity in the strip. This will result in a transport of impurities from feed to strip, although the concentration of impurities in the strip may be higher than that in the feed. The counter-current cation extraction is illustrated in figure 2.3.

\[ \text{Driving force} \quad \Delta C \]

**Figure 2.3.** Counter-current cation extraction by a liquid membrane.

For extraction of anions and neutral complexes, the transport mechanisms are comparable to those of cation extraction.

Liquid membrane extraction can be performed in 3 different operations, bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM) [3]. BLM's are only used for laboratory experiments. Figure 2.4 shows a schematic drawing of a BLM set-up. BLM's are economically not applicable in industry due to the large amount of expensive liquid membrane phase necessary for operation.

For extraction with ELM's, first the inorganic strip solution is emulsified in the organic liquid membrane phase. The liquid membrane containing small droplets of strip solution is dispersed into the inorganic feed solution. Figure 2.5 shows an ELM. ELM extraction is a very fast process, because of the very thin membrane and large area per unit of feed volume, typical 3000 m²/m³. It is difficult to operate a stable ELM extraction. For the treatment of the feed stream with ELM's, a stable emulsion of liquid membrane phase and strip droplets is required to avoid breaking

17
down of the emulsion. However, the strip solution has to be recovered from the liquid membrane phase when completely loaded. To accomplish this, the emulsion has to be broken down easily. Due to these contradicting requirements, it is difficult to find optimum process conditions for ELM operation.

Figure 2.4. Schematic draw of a set-up for bulk liquid membrane extraction.

![Diagram of bulk liquid membrane extraction](image)

Figure 2.5. An emulsion liquid membrane.

In SLM’s, the liquid membrane is immobilized in a macroporous polymer support, either flat sheets or hollow fibers. Figure 2.6 shows a schematic drawing of a SLM. The liquid membrane is immobilized in the polymeric support by capillary forces, which makes the membrane more predictable in its stability behavior than ELM’s. Other advantages are that the feed and strip phases are easy recoverable and only a small amount of liquid membrane phase is necessary. Disadvantages are that very hydrophobic organic solvents are required to maintain a stable liquid membrane and the membrane area is much smaller than in ELM operation, typical 1000 m²/m³ in case of hollow fibers. Further, the thickness of the layer, through which the ion-carrier complex has to diffuse, is much thicker reducing the extraction rate. The layer is as thick as the wall thickness of the hollow fiber, in which the membrane phase is immobilized.

For this research, SLM’s were thought to be suitable for the extraction of impurities during the recrystallization of HH to gypsum. Due to the immobilization of the organic phase, it is not emulsified in the feed solution avoiding possible
contamination of the phosphoric acid product and gypsum byproduct. Another advantage of SLM extraction compared to solvent extraction is that extraction and stripping is combined in one apparatus, saving two organic/inorganic separation steps. SLM extractions are mostly performed in flat sheet set-ups or in hollow fiber membrane modules. Only the latter are interesting for industrial applications, because of their relatively high contact area per volume. The treatment of slurries, like the phosphoric acid slurry, in hollow fiber modules requires additional attention and will be discussed further in §2.3.3. ELM's were not chosen, because of expected stability problems of the emulsion in the phosphoric acid slurry.

![Diagram](image)

**Figure 2.6. Schematic draw of a supported liquid membrane.**

**Ion exchange extraction**

Ion exchange extraction is comparable to liquid membrane extraction. During both extraction processes, impurity ions are selectively extracted by reaction with functional groups. However, in liquid membrane extraction, the carrier with its functional groups is dissolved in an organic solvent, whereas in ion exchange the functional groups are bonded to a solid matrix. In ion exchange extraction, stability is therefore no longer an issue. This is an important advantage with respect to liquid membranes.

A disadvantage of ion exchange extraction is that it is, as solvent extraction, a semi-continuous process. The resin has to be separated from the feed solution before contacting it with a strip solution to reuse it. So, two extra separation steps are required compared to a liquid membrane process.

Most ion exchange resins are made of polymeric material, mostly polystyrene (PS) crosslinked with divinylbenzene (DVB) [4]. This material is chemically and thermally very resistant. The amount of DVB influences the swelling behavior of the resin and therewith the extraction behavior. With high amounts of DVB, the resin swells only a little resulting in the uptake of only small ions, whereas with low amounts of DVB also larger ions can be taken up by the resin. Although the selectivity of the resins is influenced by the amount of DVB, it is mainly determined
by the functional groups that are bonded to the resin. The PS-DVB resins can be functionalized with different groups, like sulfonic acids, phosphoric acids, carboxylic acids, etc, which are bonded to the resin matrix by chemical reaction. Each functional group has its own specific affinity.

2.3.3 Set-ups for the Treatment of Slurries

Supported liquid membrane extraction

Supported liquid membrane extraction is industrially operated in either spiral wound modules, which consist of numerous flat sheet support layers, and hollow fiber modules. A spiral wound module is not appropriate for the treatment of slurry streams, because contamination appears fast and cleaning is very difficult. With an appropriate design of a hollow fiber module, clogging can be prevented. If the module is contaminated, it can easily be cleaned by taking out the fiber packing.

To avoid clogging of the hollow fiber module, we have chosen for transverse flow hollow fiber modules instead of the more common parallel flow modules. The transverse flow operation has an advantage with respect to parallel flow for the treatment of slurries. In a parallel flow module, the feed enters the module with an angle of 90° and also leaves the module again with the same angle, as is schematically shown in figure 2.7. Due to this, settling of the solids at the bottom of the module will occur, which will eventually result in clogging of the module.

*Figure 2.7. A parallel flow hollow fiber module (left) and a transverse flow hollow fiber module (right).*

With transverse flow, the feed solution flows straight down from the top to the bottom of the module. When applying a top angle with a maximum of 8° and a bottom angle with a maximum of 25-30°, the solution flowing around the fibers will
follow the module wall preventing the formation of dead areas [5], in which settling of solids can occur. This will prevent clogging of the module. Another advantage of the transverse flow module may be the extra turbulence on the shell side of the fibers compared to parallel flow. This will result in a thinner laminar film, through which the ions have to diffuse. However, this is only an advantage if the diffusion through this film layer influences the extraction rate.

*Ion exchange extraction*

Ion exchange extraction is mostly performed in fixed and moving packed columns, resulting in an intense contact between resin and process stream. For the treatment of slurry streams, these columns cannot be used, because the solids would clog the columns. Several techniques have been developed to overcome this problem, like fluid bed ion exchange and resin-in-pulp contactors [6]. Fluid bed ion exchange can be used for the treatment of process streams with approximately 10 per cent of solids, but practical considerations have limited its use up to approximately 0.5 per cent of solids. Another limitation of the fluid bed ion exchange is that the fluidization properties of the solids should differ from those of the ion exchange resin. Preferably, the settling velocity of the resin should be higher than that of the solid particles.

Resin-in-pulp contactors, jigged bed contactors and stirred vessel contactors, can treat process streams with high amounts of solids, in case of jigged bed contactors up to 40 per cent solids. Jigged bed contactors are semifluidized beds in which the resin transfer is aided by the jigging action, preventing clogging of the resin. However, the requirement on the settling velocity for fluidization remains, the settling velocity of the resin should be higher than that of the solids. Another disadvantage is the high rates of mechanical wear by the jigging action of the bed. The application of stirred vessels minimizes the physical problems, but a disadvantage is the requirement of an external separation of ion exchange resin from the solids, like for example by means of vibrating screens.

For the treatment of the phosphoric acid slurry, extraction was performed by adding ion exchange resin to the stirred vessels, in which the recrystallization is performed. Since the commercial recrystallization process is also performed in stirred vessels, the results will give a good indication of the possibilities of ion exchange extraction in the commercial process.

To avoid the separation between the phosphoric acid slurry and the ion exchange resin beads, also the possibility of treating the slurry in transverse flow ion exchange modules was investigated. However, for this application ion exchange fibers or bars had to be developed, because they were not commercially available.
2.4 Outline of this Thesis

The thesis starts in chapter 1 with a short introduction on phosphoric acid production and the process improvements that were already introduced.

The degree of incorporation of impurities like the lanthanides is determined by kinetic and thermodynamic effects. In chapter 3, an insight is given into the influence of the thermodynamic effects by simulating the incorporation of lanthanides in gypsum with computer modeling techniques.

To be able to extract impurities, suitable carriers and ion exchange resins have to be found. Chapter 4 describes the results of a search for appropriate carriers and ion exchange resins. Chapter 5 discusses the extraction ability of some of these carriers during the recrystallization of HH to gypsum by direct contact of the carriers with the phosphoric acid slurry. Chapter 6 describes the applicability of transverse flow hollow fiber membrane modules for the removal of impurities from clear phosphoric acid solutions by impregnation of the carriers in the porous hollow fibers, and it discusses the applicability of these modules for the treatment of the phosphoric acid slurry during recrystallization. Mechanisms, which may result in additional instability due to transverse flow, are also discussed in this chapter.

The last chapters are on ion exchange extraction. Chapter 7 describes some factors influencing the extraction efficiency of ion exchange by analyzing results of batch recrystallizations with simultaneous ion exchange. In chapter 8 recrystallization with simultaneous ion exchange extraction is performed in continuous operation, as recrystallization is performed in the industrial production process. Because the product shape is an important process parameter influencing the efficiency and throughput of the process, the influence of extraction on this product shape is also subject of this chapter. To get a better understanding of parameters influencing the extraction efficiency during recrystallization, simulations of the recrystallization with simultaneous ion exchange extraction are performed with a dynamic simulation program, Crystals, and described in chapter 9. In chapter 10 an economic evaluation is made on ion exchange extraction during the continuously operated recrystallization in the phosphoric acid production process.

Chapters 7 to 10 describe the results obtained by adding commercial ion exchange beads to the crystallizers. To avoid the separation of ion exchange resin beads from the slurry and possible contamination of the gypsum product with ion exchange resin, a transverse flow ion exchange module is developed. The development of ion exchange bars for such a module is described in Chapter 11. Chapter 12 describes the experimental results gained with the transverse flow module during treatment of the recrystallizing slurry.
References


Chapter 3

Lanthanide Defects in Gypsum: the Embedded Cluster Model

During the production of phosphoric acid in the wet processes, many of the lanthanides from the phosphate ore are incorporated in the calcium sulfate byproducts. The uptake of the lanthanides depends on both kinetic and thermodynamic parameters. To give an insight into the influence of thermodynamic factors on the incorporation of lanthanides in calcium sulfate, the formation of lanthanide defects were simulated with computer modeling techniques. Without some form of charge compensation, the calculated defect energies for the lanthanides were uniformly negative. This suggests that the incorporation of lanthanides is actually quite favorable in gypsum. Other factors, in particular the paired charge compensation defect and solubility, seem to be responsible for the low incorporation levels.

Paper submitted by S. Fleming, C. Koopman, G.J. Witkamp to 13th International Conference on Crystal Growth.
3.1 Introduction

During the production of phosphoric acid in the so-called wet processes, calcium sulfate byproducts are also formed. With the phosphate ore, many impurities, such as heavy metals and lanthanides, enter the production process. Some of these impurities end up mostly in the phosphoric acid product, like cadmium and iron. Others mostly end up in the calcium sulfate byproducts, like lanthanides, lead and mercury. Some impurities not only influence the calcium sulfate or phosphoric acid product quality, but can also influence the production process itself. Aluminum fluoride and lanthanides are known to retard the calcium sulfate growth [1,2], having a strong influence on process efficiency and throughput.

It was found that 3-10⁻⁴ M of an individual lanthanide retarded the calcium sulfate growth by a factor of 2 to 10. The degree of retardation seems to depend on the ionic radius of the lanthanide ion. Lanthanides with a comparable ionic radius to calcium (126 pm [3]), like lanthanum (130 pm) and cerium (128 pm), retard calcium sulfate growth the most, whereas lanthanides with a substantially different ionic radius, like erbium (114 pm), do not effect the growth rate. This is also reflected in the degree of incorporation. Lanthanides with a comparable ionic radius to calcium are incorporated more in the calcium sulfate than lanthanides with a different ionic radius. This is illustrated in figure 3.1 by the partition coefficients, D [-], which are defined as

\[
D = \frac{[\text{Ln}^{3+}_{\text{crystal}}]}{[\text{Ca}^{2+}_{\text{crystal}}]} \frac{[\text{Ln}^{3+}_{\text{solution}}]}{[\text{Ca}^{2+}_{\text{solution}}]} \tag{3.1}
\]

with \([\text{Ln}^{3+}_{\text{crystal}}]\) and \([\text{Ca}^{2+}_{\text{crystal}}]\) the concentration of the defect lanthanide ion and the calcium ion in the crystal [mol/L], while \([\text{Ln}^{3+}_{\text{solution}}]\) and \([\text{Ca}^{2+}_{\text{solution}}]\) represent the concentrations in the solution [mol/L].

Figure 3.1 shows the partition coefficients for two different phosphoric acid production processes, the two-filter HemiDiHydrate process (HDH) and the one-filter HemiRecrystallization process (HRC). Both processes contain a reaction step and a recrystallization step. In the first step, phosphate ore reacts with sulfuric acid to produce phosphoric acid and calcium sulfate hemihydrate (HH). In the second step, HH is recrystallized to calcium sulfate dihydrate (DH, gypsum) to regain the incorporated phosphoric acid and increase the process efficiency. The phosphoric acid production process is described in more detail in chapter 1. The partition coefficients were calculated for the second step, the recrystallization. In the HDH
process, the HH crystals are separated from the product phosphoric acid before they are recrystallized to DH. The recrystallization is effected by both lowering the acid concentration and the temperature. In the HRC process, the HH crystals are recrystallized in the strong product acid by just lowering the temperature. The difference in partition coefficients between these two processes shows the influence of the process conditions on the incorporation. However, it also shows that the decreasing behavior of the partition coefficient as a function of the increasing deviation of the lanthanide radius from the calcium radius remains, despite the different process conditions.

![Graph showing partition coefficients as a function of lanthanide ionic radius.](image)

**Figure 3.1.** The partition coefficients, $D$ [-], in DH formed during recrystallization of HH as a function of the lanthanide ionic radius [3].

The uptake of impurity ions depends on both kinetic as well as on thermodynamic parameters. This chapter gives an insight into the influence of thermodynamic factors on the incorporation of lanthanides in calcium sulfate by simulating lanthanide defects in the calcium sulfate structure with computer modeling techniques.

### 3.2 Background

Molecular Modeling provides a useful tool in examining defects in ionic crystals. One common approach involves creating a defect inside a piece of material, which is then used as a basis in order to build the full crystal. Commonly, the Ewald summation method is used to evaluate the slowly (and conditionally) convergent coulomb interactions. Clearly, selection of the repeat unit size is important, as interaction between the defect's periodic images should be minimized, or at least
properly accounted for. There is an additional difficulty with this scheme when charged defects are examined, as the method must be adapted to include some form of compensation mechanism. This may be accomplished with the use of a uniform background charge [4,5], or the utilization of counter-ions and energy correction terms [6,7].

An alternative approach is to embed the defect in a finite cluster of suitable size. The termination at the cluster boundary means that care must be taken with defect energy convergence, particularly with the long-range coulombic terms. It is also important to consider lattice relaxation since, particularly for charged defects, significant displacement in the positions of the ions adjacent to the defect site may occur [8,9]. Furthermore, it is often desirable to combine a quantum cluster calculation of the defect and its immediate surroundings, and embed this in a larger cluster (governed by classical interaction terms) to account for the effect of longer range forces on the defect. The use of quantum mechanics, although computationally expensive, is required when electronic processes such as the breaking of orbital degeneracy, charge transfer, or excited state transition are to be modeled.

In this work, charged defects with very low incorporation levels are considered. Thus, the embedded quantum cluster model approach was taken. This avoids any form of defect interaction, and allows explicit modeling of the electronic processes immediately surrounding the defect.

### 3.2.1 Defect formation

Thermodynamically, the expected number of defect ions found in a crystal, \( n_{M^{\ast\ast}_{\text{crystal}}} \), where there are \( N \) available sites may be written as,

\[
n_{M^{\ast\ast}_{\text{crystal}}} = N \cdot \exp \left( \frac{-E_{\text{defe}}}{kT} \right) \tag{3.2}\]

where \( E_{\text{defe}} \) is the energy of formation of the defect [J], \( k \) is the Boltzmann constant [J/K], and \( T \) is the temperature [K]. In this work, the static lattice approximation was used, so that the change in vibrational entropy of the lattice due to the defect is not included. The defect energy is calculated as,

\[
E_{\text{defe}} = (C_{M^{\ast\ast}} - C_{Ca^{2\ast}}) - (L_{M^{\ast\ast}} - L_{Ca^{2\ast}}) \tag{3.3}\]

where \( C \) refers to the total cluster energy [J] and \( L \) indicates the lone ion energies [J]. Thus, equation 3.2 expresses the competition between \( M^{\ast\ast} \) and \( Ca^{2\ast} \) ions for lattice sites.
For the case when \( n_{M_{\text{crystal}}}^+ \ll n_{Ca_{\text{crystal}}}^{2+} \), it follows that \( N = n_{Ca_{\text{crystal}}}^{2+} \). In addition, in real systems, it may not be possible to ignore the effects of the solution. To include the effect of solubility [10], expression 3.2 may be modified as follows,

\[
\frac{[M_{\text{crystal}}^{x+}]}{[Ca_{\text{crystal}}^{2+}]} \approx \frac{[M_{\text{solution}}^{x+}]}{[Ca_{\text{solution}}^{2+}]} \cdot S_{CaSO_4} \cdot \exp \left( -\frac{E_{\text{defe}}}{kT} \right)
\]

with \( S \) the solubility product [mol/kg]. Note that the first 2 terms of this equation form the expression for the partition coefficient.

This work is concerned with the inclusion of the lanthanides in gypsum. However, isomorphic substitution of the divalent Ca ion by a trivalent lanthanide results in an excess of charge. It has been postulated [2,10] that this charge surplus is stabilized by either the incorporation of a monovalent ion (by replacing a Ca\(^{2+}\)), or by the inclusion of vacancies (also at Ca\(^{2+}\) sites). Both possibilities were considered in this work.

### 3.2.2 Defect modeling

The interaction of the defect species with the local crystal structure was accomplished with the aid of quantum cluster calculations performed at the ab initio Hartree-Fock level. However, the highly ionic character of the bonding in gypsum means that long-range effects cannot be ignored. These may be accounted for with the use of atomic point charges and force field interaction terms. Thus, a combined force field and quantum treatment of the problem was employed. Firstly, the local defect structure was allowed to relax via the Mott-Littleton approach. The final structure of the converged defect calculation was then trimmed to obtain a small cluster of ions immediately adjacent to the defect. This was used as input to the quantum cluster computation.

The program employed in this work to model the relaxation of the crystal around the defect was the GULP code [11]. The Mott-Littleton method is implemented in the package as follows. A spherical piece of gypsum is constructed and partitioned into three regions that are concentric with the point defect. In the inner region (region 1), the ions are permitted to relax freely in order to minimize the net force acting upon them. In the second region (region 2a), a similar approach is taken, but only small displacements from the lattice positions of the ions are permitted. And finally, in the outer shell (region 2b), a method analogous to the Ewald summation technique is employed to compute the sub-lattice polarization that arises due to the excess charge of the defect. The size of the outermost region is automatically assigned a suitable value by the GULP code.
All Hartree-Fock calculations in this work were performed with the GAMESS code [12]. After the force-field relaxed defect structure was obtained, different size clusters were extracted and used as input. These clusters were made as spherical as possible by including only those ions within a defined radius of the defect center. However, no bonds were allowed to be broken in the final cluster. In such an approach, a number of serious approximations are made. Most significantly, after the initial cluster has been set up, electron transfer across the boundary of the cluster is not permitted. Thus, it is assumed that the localized eigenstates of the defect cluster are a suitable approximation to the eigenstates of the entire crystal. The justification of this approach lies in the fact that the bonding in gypsum is highly ionic.

3.3 Defect Energy Calculations

3.3.1 Force-field

The empirical force fields used for gypsum were derived by Wilson et al. [13] which were fitted to a number of sulfate compounds, including CaSO\(_4\), CaSO\(_4\cdot\frac{1}{2}\)H\(_2\)O and CaSO\(_4\cdot2\)H\(_2\)O. It is worth noting that the only non-coulombic interaction for Ca acts on O. In addition, two different potential sets describing the lanthanide-gypsum interactions were considered. The first of these was taken from the work of Lewis and Catlow [14], whilst the second was derived by Bush et al. [15]. The latter work also includes the polarizability of the cation, via the core-shell model [16]. In addition, the parameters for the charge compensating cation (sodium) were also taken from this potential set.

Both works employ fitting methodologies based on the structural parameters of the metal oxide materials, and emphasize the transferability of the model to other related systems. In this paper, the methodology of Lewis and Catlow will be referred to as model 1, and that of Bush et al. as model 2. Note that in the paper by Bush et al. there are typographical errors in the potential parameters. However, updated potential sets have been made available [17].

The classical defect energies for a representative group of lanthanides at three different cluster sizes were computed. The differences between the total (relaxed) energies are displayed in table 3.1. These calculations were performed utilizing the Bush et al. potential parameters and thus are an upper bound on the cluster truncation error (since the Lewis and Catlow parameters do not allow for a defect dipole moment). The convergence of the cluster energy for La is the slowest, which is a result of the higher polarizability assigned by the potential model. In subsequent
work, region sizes of 15Å and 25Å (size 2) were used, since the additional expense of larger region sizes does not yield any significant improvement in accuracy.

**Table 3.1. Convergence of the classical defect energy calculation.**

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\Delta E_{2,1}$ (eV)</th>
<th>$\Delta E_{3,2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>0.00647</td>
<td>0.0000307</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>0.00331</td>
<td>0.00000673</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>0.00445</td>
<td>0.00000710</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>0.00274</td>
<td>0.0000100</td>
</tr>
</tbody>
</table>

Calculation 1 has a region 1 size of 13Å and a region 2a size of 20Å. Calculation 2 has a region 1 size of 15Å and a region 2a size of 25Å. Calculation 3 has a region 1 size of 15Å and a region 2b size of 30Å. The differences between converged defect energy calculations are given, with the subscript indicating the calculations being compared.

### 3.3.2 Hartree-Fock

Lanthanide basis sets were derived by Cundari and Stevens [18]. The basis sets consist of relativistic effective core potentials (ECPs) replacing the innermost 46 electrons, and a valence basis set. Both the ECP and the valence basis set were especially optimized for the Ln$^{3+}$ ground state configuration. The valence basis is constructed with 6, 6, 3 and 7 Gaussian functions for the s, p, d and f shells, respectively. A quadruple zeta contraction scheme is employed for the s centered and p orbitals, whilst a double zeta scheme is utilized for the d and f. All other basis sets used (gypsum ions) were developed by Stevens et al. [19] and Stevens et al. [20]. These are also ECP sets, with a double zeta (3,1) contracted Gaussian valence basis set.

Relaxed structures computed from the force field calculations were trimmed and supplied as input to the quantum cluster calculations. Presented in figure 3.2 is the reference cluster (Ca centered) which is compared against all lanthanide calculations to obtain the cluster defect energy contribution. Overall, after force-field relaxation, distortions in the lattice were found to be quite similar for all lanthanides for both potential models mentioned in § 3.3.1. Displayed in figure 3.2 is a picture of the lanthanide cluster used in the Hartree-Fock cluster calculations. The displacement of the adjacent water molecules was a common feature for all the lanthanide calculations.

The ionic nature of the bonding, and the core potential model employed make it unlikely that electron correlation correction will substantially improve the quantum
calculations. The Hartree-Fock defect energy calculation is assumed to be accurate since it is the difference, and not the absolute value, between clusters with related electronic configurations that is desired [6].

Figure 3.2. Standard cluster sizes for a) calcium compared with b) the force field relaxed defect calculation for lanthanide.

3.3.3 Combined results

The difference in energy between a cluster containing a defect and the reference cluster (correcting for the difference in self energy between Ca and the defect ion) represents the contribution to the defect energy and is given in table 3.2. Removing all interactions that are duplicated by the Hartree-Fock calculation, the remaining contribution from the classical force field calculation constitutes the long-range interaction energy. This value, and the final combined defect energy ($E_{\text{defo}}$), is also presented in table 3.2. The quantum contributions to the lanthanide defect energy are almost monotonic, with a tendency of increased stabilization for the heavier ions. This is likely due to the decreasing ionic radius, resulting in stronger local ionic bonding.

3.4 Comparison with Experiment

To compare the simulation results with the experimental values, the partition coefficients were used to calculate an experimental defect energy. Calculation of a thermodynamic partition coefficient from the simulated defect energies would result in large errors due to the exponential factor in equation 3.3 ($\pm 0.1$ eV is a factor of 50 in D).

The solubilities of lanthanide sulfates used for the calculation of the experimental defect energy were taken from Spedding et al [21]. They are shown in table 3.3. The solubilities were measured in water at 25 °C. The anomalous behavior of the
solubility could not be explained, but was thought to be the result of changes in crystal structure with increasing atomic number, changes in hydration, and/or differences in the various rare earth complexes in the saturated solution. The solubility of calcium sulfate dihydrate in water is 0.026 mol/kg [22].

Table 3.2. Lanthanide defect energies.

<table>
<thead>
<tr>
<th>Defect</th>
<th>FF contribution [eV]</th>
<th>HF contribution [eV]</th>
<th>Total $E_{defe}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model 1</td>
<td>Model 2</td>
<td>Model 1</td>
</tr>
<tr>
<td>Vacancy</td>
<td>9.36</td>
<td>0.80</td>
<td>10.16</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>3.66</td>
<td>0.35</td>
<td>4.01</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>-2.73</td>
<td>-2.67</td>
<td>-3.05</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>-2.72</td>
<td>-0.31</td>
<td>-3.03</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>-2.84</td>
<td>-0.34</td>
<td>-3.18</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>-2.79</td>
<td>-2.81</td>
<td>-3.13</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>-2.85</td>
<td>-2.80</td>
<td></td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>-2.85</td>
<td>-2.83</td>
<td>-3.25</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>-2.69</td>
<td>-2.78</td>
<td>-3.10</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>-2.80</td>
<td>-2.49</td>
<td>-3.23</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>-2.77</td>
<td>-0.44</td>
<td>-3.21</td>
</tr>
</tbody>
</table>

The sodium defect energy calculation for potential model 1 was used for model 2. Gaps in the table are due to the lack of potential parameters for the corresponding cationic species.

The defect creation energies, which were calculated from the experimentally determined partition coefficient and solubilities, are presented in table 3.4. The values represent the expected defect energy when only the difference in solubility is taken into account. Kinetic effects are not accounted for. The decreasing partition coefficient with increasing deviation of the lanthanide radius from the calcium radius does not result in the same trend of the defect energy as function of the radius. Taking the solubilities into account results also in an anomalous behavior of the defect energy.

The experimentally determined values may be compared to the modeling results. For the case where the inclusion of a lanthanide is coupled with other defects in order to neutralize the net charge, it can be shown that the formation energy is effectively the
average of the constituent defect energies [23]. Thus, the defect energies in table 3.4 were employed to calculate an expected formation energy for defects coupled as 1:1 for lanthanides and Na, and 2:1 for lanthanide to vacancy. For all cases, the vacancy compensation mechanism gave final defect energies that were approximately 1eV higher than for sodium, as is shown in table 3.4. This suggests that sodium is a much more likely compensation mechanism than vacancies.

As the defect energies calculated from experimental partition coefficients, the defect energies determined by simulation do also not show a direct relation with the lanthanide radius.

**Table 3.3. The solubilities of lanthanide sulfates in water of 25 °C [21].**

<table>
<thead>
<tr>
<th>Salt</th>
<th>S [mol/kg]</th>
<th>Salt</th>
<th>S [mol/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$(SO$_4$)$_3$</td>
<td>0.15</td>
<td>Gd$_2$(SO$_4$)$_3$</td>
<td>0.21</td>
</tr>
<tr>
<td>Ce$_2$(SO$_4$)$_3$</td>
<td>0.36</td>
<td>Ho$_2$(SO$_4$)$_3$</td>
<td>0.41</td>
</tr>
<tr>
<td>Pr$_2$(SO$_4$)$_3$</td>
<td>0.77</td>
<td>Er$_2$(SO$_4$)$_3$</td>
<td>0.91</td>
</tr>
<tr>
<td>Nd$_2$(SO$_4$)$_3$</td>
<td>0.39</td>
<td>Yb$_2$(SO$_4$)$_3$</td>
<td>2.08</td>
</tr>
<tr>
<td>Sm$_2$(SO$_4$)$_3$</td>
<td>0.10</td>
<td>Y$_2$(SO$_4$)$_3$</td>
<td>1.09</td>
</tr>
</tbody>
</table>

**Table 3.4. The calculated defect formation energies are presented for the sodium compensation mechanism.**

<table>
<thead>
<tr>
<th>Defect</th>
<th>Calculated $E_{def}$ [eV]</th>
<th>Experimental $E_{def}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>Model 1</td>
<td>Model 2</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.48</td>
<td>0.50</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>0.44</td>
<td>0.43</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>0.38</td>
<td>0.39</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>0.40</td>
<td></td>
</tr>
</tbody>
</table>

$^*$No solubility data available, no correction for the solubility of eq. 3.3.
3.5 Conclusions

The data from force field and quantum mechanics calculations suggest that lanthanide incorporation is quite favorable in gypsum. Other factors, in particular the paired charge compensation defect and solubility, seem to be responsible for the low incorporation levels. The defect energies calculated from experimental partition coefficients lose the increasing/decreasing trend of the partition coefficients with the lanthanide ionic radius, due to the fact that the solubility of the lanthanide sulfates, which fluctuates with the ionic radius of the lanthanides, was taken into account.

References


17. http://www.ri.ac.uk/potentials


Chapter 4

Extractants for Heavy Metal and Lanthanide Removal from Industrial Phosphoric Acid

Various commercial carriers and two ion exchange resins were screened for their ability to extract lanthanides and/or heavy metals from industrial phosphoric acid, aiming at a future application for the removal of these impurities during the solvent mediated recrystallization of calcium sulfate hemihydrate to dihydrate. Nacure 1052 (sulfonic acid) extracts light and heavy lanthanides from the phosphoric acid, whereas D2EHPA (phosphoric acid) only extracts the heavy lanthanides. Because the light lanthanides lanthanum and cerium are present in relatively high concentrations compared to the heavy ones, Nacure 1052 will be more appropriate for the removal of lanthanides during the recrystallization step. Unfortunately, Nacure 1052 does also show some affinity for the abundantly present calcium ions. The heavy metal ions copper, lead, cadmium, and mercury are extracted by the cation exchangers Cyanex 301 and Cyanex 302 (thiophosphinic acids). Due to the presence of chloride ions in the phosphoric acid, mercury is also extracted as mercury chloride anionic complexes by Alamine 336 (amine) and Aliquat 336 (ammonium chloride). Both Dowex C-500 and Amberlite IR-120 ion exchange resin, which contain sulfonic acid functional groups, extract light and heavy lanthanides and heavy metals. The affinity of the ion exchange resins is comparable to that of Nacure 1052 due to the similar functional groups, which implicates that also the resins show affinity for calcium ions.

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4.1 Introduction

For the application of solvent extraction, liquid membrane extraction, and ion exchange, liquid carriers and ion exchange resins have to be found that are able to achieve the desired separation. For both liquid carriers and ion exchange resins, three main types of extractive groups can be distinguished: cationic groups, anionic groups, and neutral ones. Cationic extractants exchange their cationic groups, mostly sodium or protons, for cations or cationic complexes from the solution. Carboxylic, phosphoric and sulfonic acids are most commonly used. Anionic extractants exchange their anionic groups, mostly nitrate or hydroxide, for anions or anionic complexes. Primary, secondary, tertiary, and quaternary amines belong to this group. Neutral groups extract neutral complexes. Tributylphosphoric acid, crown ethers, and calixarenes are part of this group.

The extraction efficiency and selectivity are not only dependent on the properties of the extractant, but also on the chemical properties of the solution, from which the ions have to be extracted, like pH, the concentration of the impurity ion, and the presence of other ions [1,2]. Also the temperature of the solution can have a large influence on the extraction.

Extraction techniques only extract ions or complexes from a solution. So, to gain a concentration decrease of impurities in the gypsum, the aim of this research project, the impurities have to be removed from the phosphoric acid solution, in which the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) is performed. If the impurities are removed from the phosphoric acid solution, they cannot be incorporated anymore in the gypsum crystals. So, the chemical properties of the industrial phosphoric acid solution play an important role in the choice of a successful liquid carrier or ion exchange resin. Due to the high acidity of the phosphoric acid (see § 4.2.1), it will be difficult to find this successful extractant.

The affinity of an extractant for a certain impurity ion A is indicated by the distribution coefficient, $K_A [-]$,

$$K_A = \frac{[A]_{org}}{[A]_{acid}}$$ \hspace{1cm} (4.1),

with $[A]_{org}$ the concentration of A in the organic phase [mol/kg] and $[A]_{acid}$ that in the phosphoric acid solution [mol/kg], both at equilibrium. A high $K_A$ indicates a high uptake of component A by the extractant, and thus a high affinity.

For a successful extraction of impurity A from industrial phosphoric acid, the extractant should have a certain affinity for this ion, $K_A > 0$. Another important quality of a successful extractant is that its affinity for calcium ions, which are
present in high concentrations compared to the impurity ions, should be low, $K_{Ca} \rightarrow 0$.
To concentrate an impurity with respect to calcium, $K_A$ must be higher than $K_{Ca}$. The
relation between the affinity of the extractant for an impurity ion A and that for
calcium is defined by the selectivity of the extractant, $\alpha_{A/Ca}$ [-],

$$\alpha_{A/Ca} = \frac{K_A}{K_{Ca}}$$  \hspace{1cm} 4.2.

If the selectivity is high, the amount of extractant can be much lower when the
selectivity is low, because the extractant is not 'contaminated' with calcium. Further,
with a high selectivity the solution used for regeneration of the extractant is a
concentrated solution of only the impurity ions. In case of, for example, lanthanide
extraction, this regenerant solution is much more valuable when no other ions are
present.

**4.2 Experimental**

**4.2.1 Chemicals**

The industrial phosphoric acid was obtained either from a two-filter HDH process or
from a one-filter HRC process using mixtures of Kovdor and Jordan phosphate ores.
Phosphoric acid of the recrystallization section from the first process contains
approximately 0.8 mol/kg H$_3$PO$_4$ and 0.5 mol/kg H$_2$SO$_4$ and that from the second
process 3.9 mol/kg H$_3$PO$_4$ and 0.2 mol/kg H$_2$SO$_4$. The concentrations of other
components like lanthanides and heavy metals strongly depend on the phosphate ore.

To facilitate analysis, the concentrations of Hg, La, Ce, Eu, Dy, Er, or Cu were
increased to 50 mg/kg by adding their nitrate salts to the phosphoric acid.

The carriers and ion exchange resins used for the screening experiments are listed in
table 4.1. The carriers were diluted or dissolved in kerosene, except for Nacure
1052, which was diluted with heptane to obtain the extraction liquid.

**4.2.2 Analysis**

The concentrations of La, Ce, Eu, Dy, Er, Hg, Al, Fe, Cu, and Ca in the phosphoric
acid were determined by means of Inductively Coupled Plasma - Atomic Emission
Spectroscopy (ICP-AES). The concentrations in the samples were determined by
either the standard addition method or from a calibration line by using pure ionic
solutions of 1000 mg/kg. The concentrations of Pb and Cd ions were determined by
means of polarography.
Table 4.1. The carriers and ion exchange resins screened for the removal of heavy metal and lanthanide ions from industrial phosphoric acids.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Active group</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-(2-ethylhexyl)phosphoric acid</td>
<td>D2EHPA</td>
</tr>
<tr>
<td>bis(2,4,4-trimethylpentyl)dithiophosphinic acid</td>
<td>Cyanex 301</td>
</tr>
<tr>
<td>bis(2,4,4-trimethylpentyl)monothiophosphinic acid</td>
<td>Cyanex 302</td>
</tr>
<tr>
<td>didodecylnaphthalenesulfonic acid</td>
<td>Nacure 1052</td>
</tr>
<tr>
<td>tributylphosphate</td>
<td>TBP</td>
</tr>
<tr>
<td>dicyclohexano-18-crown-6</td>
<td>DC-18C6</td>
</tr>
<tr>
<td>2-hydroxy-5-nonylacetophenone oxime</td>
<td>LIX 84</td>
</tr>
<tr>
<td>tri(C₆H₁₆)amine</td>
<td>Alamine 336</td>
</tr>
<tr>
<td>tri(C₆H₁₆) monomethyl ammonium chloride</td>
<td>Aliquat 336</td>
</tr>
<tr>
<td>Amberlite IR-120 H⁺-form</td>
<td>Amberlite</td>
</tr>
<tr>
<td>Dowex monosphere C-500 H⁺-form</td>
<td>Dowex</td>
</tr>
</tbody>
</table>

4.2.3 Procedure

10 Grams of an organic solution or various amounts of ion exchange resin were contacted intensively with 10 grams of industrial phosphoric acid in a shaking apparatus with a shaking frequency of 200 times per minute at a temperature of approximately 70 °C for at least 18 hours. Subsequently, the acid was separated from the organic solution in a separation funnel or from the ion exchange resin by filtration. The concentrations of the cations in the phosphoric acid were determined before and after each shaking experiment, which enabled the calculation of the distribution coefficient:

\[ K_A = \frac{[A]_{\text{acid,initial}} - [A]_{\text{acid,eq}}}{[A]_{\text{acid,eq}}} \times \frac{m_{\text{acid}}}{m_{\text{organic, resin}}} \]

with \([A]_{\text{acid,initial}}\) the concentration in the acid before shaking [mg/kg], \([A]_{\text{acid,eq}}\) the concentration in the acid after equilibration with the organic phase [mg/kg] and \(m\) the mass two phases [kg].
4.3 Results and Discussion

4.3.1 Solvent extraction

Table 4.2 shows the results of some shaking experiments with organic solutions with different carriers and acid from the two-filter HDH process.

*Table 4.2. Distribution coefficients of various ions after contacting industrial phosphoric acid from the two-filter HDH process with kerosene solutions with various carriers at 70 °C.*

<table>
<thead>
<tr>
<th></th>
<th>Cyanex 301</th>
<th>Cyanex 302</th>
<th>D2EHPA</th>
<th>LIX84</th>
<th>DC-18C6</th>
<th>Aliquat 336</th>
<th>Alamine 336</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>0.06</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Cu</td>
<td>238</td>
<td>243</td>
<td>-</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>5.3</td>
<td>5.7</td>
<td>0.11</td>
<td>0.16</td>
<td>5.3</td>
<td>6.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Pb</td>
<td>&gt;2.1</td>
<td>?</td>
<td>0.15</td>
<td>?</td>
<td>0.13</td>
<td>?</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>&gt;4.0</td>
<td>?</td>
<td>0.04</td>
<td>?</td>
<td>-</td>
<td>?</td>
<td>0.08</td>
</tr>
</tbody>
</table>

>=larger than, ? = not analyzed, - = no decrease in concentration in phosphoric acid

The initial feed concentrations were approximately 50 mg/kg for Ce, Cu, Hg, 1500 mg/kg for Ca, 900 mg/kg for Fe, 0.6 mg/kg for Pb, and 4 mg/kg for Cd.

Table 4.2 shows that the heavy metal ions are extracted from the phosphoric acid into the organic solution with Cyanex 301 as a carrier. For example, the concentration of lead in the acid decreased from 0.61 mg/kg to a value below 0.2 mg/kg, a reduction of over 67%. In agreement with Pearson's hard and soft acids and bases principle [3], Cyanex 301 and 302, which contain soft base groups (table 4.1), bind with most soft and borderline Lewis acid cations such as mercury, copper, cadmium, and lead ions from acidic media [4,5], and as demonstrated here also from phosphoric acid. Also in agreement with Pearson's principle is the fact that the Cyanex carriers have little or no affinity for the hard iron and lanthanide ions. The carriers also show no affinity for the hard calcium ions, and are therefore very suitable for the selective removal of heavy metal ions from phosphoric acid that contains high concentrations of calcium and iron.
The removal of mercury by Cyanex 302 from phosphoric acid is very efficient. After contacting acid from the one-filter HRC process with only 0.01 wt% of Cyanex 302 in kerosene, the reduction in mercury concentration was >87%.

The results in table 4.2 further show that mercury can also be effectively extracted with anion carriers like Aliquat 336 and Alamine 336. This is due to the presence of chloride ions in industrial phosphoric acid (usually 50 to 100 mg/kg, but in some cases even higher depending on the ore [6]), which form stable complexes with mercury [7] resulting in neutral or negatively charged complexes that can be extracted by tertiary and quaternary amines [8].

The distribution coefficients of copper, mercury, lead, and cadmium for D2EHPA and LIX84 were equal to or lower than 0.15 (table 4.2). For example, the concentration of lead in the acid reduced from 0.61 mg/kg to 0.53 mg/kg if contacted with D2EHPA.

D2EHPA and alkylsulfonic acids like Nacure 1052 are carriers used for the extraction of lanthanide ions [9,10], and show affinity for the lanthanides from phosphoric acid as is shown in figure 4.1.

The commercially used carrier TBP [11] showed no affinity for the lanthanides from phosphoric acid and combinations of D2EHPA with TBP or DC-18C6 resulted in lower distribution coefficients than for D2EHPA alone, contrary to findings in literature for other solvents [12,13]. Figure 4.1 shows that the distribution coefficients of D2EHPA increase with the atomic number of the lanthanide ions from 0 for lanthanum and cerium to 4.9 for erbium. In contrast to D2EHPA, Nacure 1052 shows a decreasing affinity with the atomic number of the lanthanide ions from 1.3 for lanthanum to 0.5 for erbium. Further, D2EHPA shows affinity for iron(III) (K_{Fe}=2.4), whereas Nacure 1052 shows affinity for calcium (K_{Ca}=0.66).

The difference in affinity sequence between D2EHPA and Nacure 1052 can be explained from the polarizability of the functional groups compared to that of water. The affinity for the cations depends, among other things, on the polarizability of the negatively charged carrier molecules and the polarizing power of the cation. The polarizability sequence of the carrier molecules was found to be POO\textsuperscript{−}>H\textsubscript{2}O>SO\textsubscript{3}\textsuperscript{−} [14]. If the carrier molecule is more polarizable than water, like D2EHPA, the molecule will bind to the unhydrated cation. The polarizing power of the cations increases with decreasing size, in this case, with decreasing size of the unhydrated cations. With a decreasing ionic radius of 1.30 Å for lanthanum to 1.14 Å for erbium [3] (coordination number 8), the affinity of D2EHPA will increase from lanthanum to erbium. If the carrier molecule is less polarizable than water, like Nacure 1052, the cations with the most polarizing power will be hydrated most. This results in a reverse sequence of the ionic radii for the hydrated lanthanides compared to that of
the unhydrated lanthanides. In literature [15], radii of hydrated lanthanides were found to increase from 4.61 Å for lanthanum and cerium to 4.74 Å for dysprosium and erbium. Due to this, the polarizing ability of the hydrated cations will be reverse to that of the unhydrated cations, resulting in a decreasing affinity from lanthanum to erbium of Nacure 1052. The reverse sequence of affinity was already described by Bregman [16] for ion exchange resins with phosphate and sulfonic acid functional groups reacting with monovalent cations.

![Distribution coefficient diagram](image)

**Figure 4.1.** Distribution coefficients, $K_{Ln} [-]$, between phosphoric acid from the two-filter HDH process and 40 wt% of D2EHPA in kerosene or 40 wt% of Nacure 1052 in heptane at 70 °C.

Figure 4.1 shows that the increase of the affinity of D2EHPA is much stronger than the decrease of the affinity of Nacure 1052. This is in accordance with the fact that the difference in size of the unhydrated lanthanides is larger than that of the hydrated lanthanides resulting in a larger difference in polarizing power.

From the explanation above, one would expect that the bonding between the phosphate carrier D2EHPA and the cations is much stronger than the bonding between the sulfate carrier Nacure 1052 and the cations, resulting in a higher affinity of D2EHPA for the lanthanides. However, this does not appear to be the case according to the experimentally determined distribution coefficients presented in figure 4.1. Bregman [16] also gained no higher distribution coefficients for the phosphate carriers than for the sulfonic acid carriers. It seems not possible to compare the performance of the phosphoric and sulfonic acid functional groups in this way, due to differences in chemical properties resulting in differences in bonding properties.
The reaction equations for D2EHPA and Nacure 1052 are [17]:

\[
\text{D2EHPA: } M^{n+} + n(\overline{HR})_2 \leftrightarrow \overline{M(RHR)}_n + nH^+ \quad 4.4, \\
\text{Nacure 1052: } M^{n+} + n\overline{HR} \leftrightarrow \overline{MR}_n + nH^+ \quad 4.5,
\]

in which M and HR represent the metal ion and the carrier, respectively, n is the charge of the metal ion, and the overbar indicates the species in the organic phase. Taking these equations into account, it is calculated that only 3.4 mol% of D2EHPA is used for the binding of iron(III) and lanthanide ions, of which 3.2 mol% serves for binding of iron (III) ions. Only 4.8 mol% of the active component in Nacure 1052 is used for the binding of lanthanide and calcium ions, of which 4.2 mol% serves for binding of calcium ions.

Small distribution coefficients, as were found for the heavy metals in case of D2EHPA, and low degrees of occupation, as were found for D2EHPA and Nacure 1052, do not at all implicate that solvent extraction could not be feasible. In a continuous extraction-stripping system, the impurity can be removed from the mother liquor and concentrated in the stripping solution by small amounts of carrier with only low degrees of occupation. However, with a low K_A a larger apparatus or a large recycle loop is needed to achieve high extraction efficiency.

### 4.3.2 Ion exchange

Dowex C-500 and Amberlite IR-120 ion exchange resins extract heavy metal, lanthanide, and calcium ions from industrial phosphoric acid, as is shown in table 4.3.

The affinity sequence for lanthanide ions of the resins is comparable with that of the carrier Nacure 1052 (figure 4.1), which is the result of the sulfonic acid functional group in these chemicals (table 4.1).

Table 4.3 shows that the distribution coefficients are not constant for varying amounts of ion exchange resin. This could be due to the fact that different amounts of resin are contacted with equal amounts of phosphoric acid, thus causing competition effects between the cations. For small amounts of resin, only the most preferred cations will be taken up, while by adding larger amounts of resin, active sites remain available for less preferred cations. This apparently results in a decrease of the distribution coefficient for the most preferred cations with an increasing amount of resin, and an increasing one for the less preferred cations. In this way, the behavior of Amberlite IR-120, shown in figure 4.2, could be explained. The distribution coefficients of the most preferred cations calcium and lanthanum
decrease while the distribution coefficient of the less preferred cation europium increases.

**Table 4.3.** Distribution coefficients of some ions after contacting industrial phosphoric acid of the two-filter HDH process with Dowex or Amberlite resins at 70 °C.

<table>
<thead>
<tr>
<th></th>
<th>Dowex C-500</th>
<th></th>
<th>Amberlite IR-120</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.5 g/kg acid</td>
<td>136 g/kg acid</td>
<td>9.3 g/kg acid</td>
<td>133 g/kg acid</td>
</tr>
<tr>
<td>Ca</td>
<td>9.2</td>
<td>13</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Cd</td>
<td>8.0</td>
<td>8.0</td>
<td>9.9</td>
<td>8.1</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>20</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>0.46</td>
<td>-</td>
<td>0.74</td>
</tr>
<tr>
<td>La</td>
<td>23</td>
<td>38</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Ce</td>
<td>19</td>
<td>34</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>Eu</td>
<td>10</td>
<td>20</td>
<td>5.6</td>
<td>17</td>
</tr>
<tr>
<td>Dy</td>
<td>7.4</td>
<td>16</td>
<td>5.3</td>
<td>14</td>
</tr>
<tr>
<td>Er</td>
<td>7.4</td>
<td>15</td>
<td>5.0</td>
<td>14</td>
</tr>
</tbody>
</table>

- = no decrease in concentration in phosphoric acid

The initial feed concentrations were approximately 50 mg/kg for Ce, Cu, Hg, 1500 mg/kg for Ca, 900 mg/kg for Fe, 0.6 mg/kg for Pb, and 4 mg/kg for Cd.

![Graph](image)

**Figure 4.2.** Distribution coefficients of calcium, lanthanum, and europium after equilibrating phosphoric acid of the two-filter HDH process with AMBERLITE ion exchange resin at 70 °C.
Table 4.3 also shows that in case of Dowex C-500 all determined distribution coefficients increase with an increasing amount of resin. This could be explained if the protons were the most preferred cations. The distribution coefficient of the protons would decrease, while the distribution coefficients of all the cations considered in this work increase. Calculations of the ratio between the number of active sites used for the binding of calcium and lanthanides and the initial number of active sites on the resin, the degree of occupation (figure 4.3), \( e \ [-] \), support this hypothesis.

\[
  e = \frac{N_{Ca} + N_{La} + N_{Ce} + N_{Eu} + N_{Dy} + N_{Er} + N_{Re}}{N_{initial}} \times 100\% \quad 4.6
\]

with \( N_X \) the number of active sites occupied by component \( X \) [meq] and \( N_{initial} \) the initial number of active sites [meq]. The degree of occupation is small for Dowex C-500, indicating that most of the active sites are occupied by protons.

![Figure 4.3. Degree of occupation of DOWEX C-500 and AMBERLITE IR-120 after equilibration with phosphoric acid of the two-filter HDH process at 70°C.](image)

Another explanation could be found in the presence of other cations in the phosphoric acid that were not considered in this work, like barium or nickel. Some of these cations could be the most preferred cations, of which the distribution coefficients decrease with increasing amounts of resin.

The differences in distribution coefficients between the lanthanide and the calcium ions yield a more favorable selectivity for the Dowex C-500 resin compared to that of the Amberlite IR-120 resin for the extraction of lanthanides from phosphoric acid, as is shown in figure 4.4. For Dowex C-500, the concentration of lanthanides on the
resin raises up to 2 times that of calcium. Due to the much higher degree of occupation of Amberlite IR-120 compared to that of Dowex C-500 (figure 4.3), the total amount of lanthanide ions on the resin is almost equal for both resins.

![Graph showing selectivity between lanthanide and calcium ions of DOWEX C-500 and AMBERLITE IR-120 after equilibration with phosphoric acid of the two-filter HDH process at 70°C.]

**Figure 4.4.** Selectivity between lanthanide and calcium ions of DOWEX C-500 and AMBERLITE IR-120 after equilibration with phosphoric acid of the two-filter HDH process at 70°C.

### 4.4 Conclusions

Some commercial carriers and resins can be applied for the extraction of heavy metal and lanthanide ions from phosphoric acid.

The cation carriers Cyanex 301 and 302 show a selective affinity for heavy metal ions in phosphoric acid, and mercury can also be extracted from the acid by the anion carriers Alamine 336 and Aliquat 336.

D2EHPA has affinity for the heavy lanthanide ions, increasing with an increasing atomic number, whereas Nacure 1052 has affinity for all lanthanide ions, increasing with a decreasing atomic number. Disadvantage of D2EHPA is its affinity for iron ions, and that of Nacure 1052 its affinity for calcium ions, which are both present in the phosphoric acid at relatively high concentrations.

Both heavy metal and lanthanide ions were extracted from phosphoric acid to low concentrations by the ion exchange resins Dowex C-500 and Amberlite IR-120. The selectivity for lanthanides with respect to calcium of Dowex C-500 is more favorable for the extraction of lanthanides from industrial phosphoric acid than that of Amberlite IR-120. However, the amount of uptake of lanthanides is almost equal, because of the higher degree of occupation of Amberlite IR-120.
References


Chapter 5

Removal of Heavy Metals by Solvent Extraction during a Batch Recrystallization

Cadmium, lead, zinc and copper were extracted by the carrier Cyanex 302 (bis(2,4,4-trimethylpentyl)thiophosphinic acid) in kerosene during the recrystallization of calcium sulfate hemihydrate to calcium sulfate dihydrate, an existing step in the HemiDiHydrate phosphoric acid production processes. This extraction resulted in a detected decrease of the concentrations of cadmium and zinc in the calcium sulfate phase. The concentrations of copper and lead in the calcium sulfate were below detection limit.

The affinity of Cyanex 302 for cadmium and copper was too high to recover these ions with 500 g/L sulfuric acid from the organic phase after extraction. For a successful application of solvent or liquid membrane extraction, other stripping solutions should be tested, like strong acidic hydrochloric acid that might be more efficient.

5.1 Introduction

In chapter 4, it was described that the commercial carriers Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) and Cyanex 302 (bis(2,4,4-(trimethylpentyl)thiophosphinic acid) extract mercury, copper, cadmium, and lead from industrial phosphoric acid. An advantage of these carriers is that these heavy metals are extracted very selectively. They do not show any affinity for the calcium ions, which are abundantly present in the industrial phosphoric acid.

The availability of carriers for the removal of impurity ions from industrial phosphoric acid is a requirement to attain a decrease in the concentration of these impurities in the gypsum. During the recrystallization of calcium sulfate hemihydrate (HH), which was formed during the reaction of phosphate ore with sulfuric acid, to dihydrate (DH, gypsum), HH crystals dissolve. With the HH crystals, also the impurities dissolve. Simultaneously, DH crystals are formed from ions in the solution. Without extraction, some impurities in the solution are incorporated again into the newly formed DH crystals. By extracting impurity ions from the phosphoric acid, these ions can not become incorporated again in the newly formed crystals.

The impurity concentration in the gypsum depends on the specific affinity of the gypsum for a certain impurity (physical properties, like ionic radius), as well as on the concentration in the acid. For impurity A, this is described by the distribution coefficient, $K_{A, DH} [-]$,

$$K_{A, DH} = \frac{[A]_{DH}}{[A]_{acid}}$$  \hspace{1cm} (5.1),

with $[A]_{DH}$ indicating the concentration of an ion A in the gypsum [mg/kg], and $[A]_{acid}$ indicating the concentration of this ion in the phosphoric acid [mg/kg]. At equilibrium, $K_{DH}$ is only determined by the intrinsic properties of the impurity ion, the acid, and the solid phase, like the chemical nature of the ions, ionic radii, the crystal structure, the hydration free energies, activities, etc. However, a crystallization reaction can never be performed at equilibrium. So, kinetics will also have their effect on the concentration in the gypsum. In general, a higher growth rate results in more incorporation of impurities. If it is assumed that the kinetics do not change during extraction, a decrease in the concentration of an ion in the acid during the recrystallization reaction will result in a proportional decrease of its concentration in the gypsum.

From the results described in chapter 4, it is expected that with the addition of either Cyanex 301 or Cyanex 302, heavy metal ions be extracted from the phosphoric acid, which will result in a decrease of their concentrations in the gypsum. To investigate this, solvent extraction was performed by adding an organic solution with Cyanex
302 to the recrystallizing phosphoric acid slurry. Although Cyanex 302 is a weaker carrier than Cyanex 301, Cyanex 302 was chosen, because in extraction processes also the recovery of the carrier by stripping is important. For the removal of cadmium from wet process phosphoric acid, it was found that Cyanex 302 was the preferred carrier based upon a compromise between extraction and stripping efficiency [1]. Zielinski et al. [2] already performed a similar extraction process for the extraction of lanthanides during the recrystallization of HH to DH successfully.

5.2 Equations

To indicate the efficiency of the solvent extraction process, the concentration of the impurities in the calcium sulfate after the reaction is related to that before the reaction with the ratio, \( R_{\text{CaSO}_4} [-] \), which is defined as

\[
R_{\text{CaSO}_4,A} = \frac{[A]_{\text{DH,after}}}{m_{\text{HH+DH}} \cdot [A]_{\text{HH, before}} + m_{\text{DH}} \cdot [A]_{\text{DH, before}}}
\]

with \( m \) the mass of the calcium sulfate phase [kg] (this mass increases during the recrystallization since DH (172 g/mol) has a higher molar mass than HH (145 g/mol)), subscripts \( \text{CaSO}_4 \) indicating the calcium sulfate phase, before the concentration before the reaction, and after the concentration after the reaction. For the extraction efficiency from the phosphoric acid solution, \( R_{\text{acid}} \), a similar equation can be drawn. So, an \( R \) smaller than 1 indicates a decrease in the concentration of \( A \) after the recrystallization, whereas an \( R \) larger than 1 indicates an increase.

Another indication on the extraction efficiency is the amount removed relative to the input amount, \( \eta [-] \),

\[
\eta = \frac{\text{mass } A \text{ extracted}}{\text{mass } A \text{ (input)}} = \frac{[A]_{\text{org}} \cdot m_{\text{org}} + [A]_{\text{strip}} \cdot m_{\text{strip}}}{[A]_{\text{HH, before}} \cdot m_{\text{HH}} + [A]_{\text{DH, before}} \cdot m_{\text{DH}} + [A]_{\text{acid, before}} \cdot m_{\text{acid}}}
\]

with subscript org. indicating the organic extraction phase, strip the solution used for the stripping of the extracting agent, and acid the phosphoric acid solution.

5.3 Experimental

5.3.1 Procedure

Analytically pure DH (1 g) and industrial HH (5.6 g) were added to industrial phosphoric acid (30 g). Experiments were performed without and with the addition of 7.2 g of 0.29 mol/kg Cyanex 302 in kerosene.
The solid and liquid phases are contacted intensively by stirring in an oven of 80 °C. After 5 hours, the organic extraction phase (3 g) was removed from the inorganic phase and contacted with a 500 g/L sulfuric acid stripping solution (10 g). The calcium sulfate particles were filtrated from the phosphoric acid, were washed twice with a hot saturated solution of analytically pure DH to wash away the acid and twice with acetone for drying.

The phosphoric acid solution (0.8 mol/kg H₂PO₄ and 0.5 mol/kg H₂SO₄) and HH were taken from the recrystallization section of a two-filter HDH production plant. The concentration of impurities in the acid and HH is strongly dependent on the phosphate ore used. In table 5.1, an indication of concentrations of impurities is given.

**Table 5.1.** An indication of concentrations of impurities in the industrial phosphoric acid solution and the HH before the recrystallization reaction.

<table>
<thead>
<tr>
<th>Phosphoric acid (mmol/kg)</th>
<th>HH (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.6</td>
</tr>
<tr>
<td>Mn</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.5</td>
</tr>
<tr>
<td>Co</td>
<td>0.007</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>0.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.04</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001</td>
</tr>
</tbody>
</table>

5.3.2 Analysis

Before analysis, the calcium sulfate and Cyanex 302 in kerosene were digested in a microwave oven. The phosphoric acid solution, the digested calcium sulfate, the digested organic extraction phase, and the sulfuric acid stripping solution were analyzed.

The concentrations of 35 elements were determined by High Resolution Inductively Coupled Plasma–Mass Spectroscopy (HR ICP-MS), which include the lanthanides, calcium, phosphate, and some heavy metals like copper, cadmium, and chromium.
5.4 Results and Discussion

Table 5.2 shows that after a conventional recrystallization reaction, the concentrations of cobalt, zinc, cadmium and titanium already have decreased in the calcium sulfate phase ($R_{CaSO_4} < 1$). The addition of Cyanex 302 resulted in a larger decrease of the concentration of cadmium, zinc, and titanium, indicating that these elements were extracted. However, titanium was not extracted as will be illustrated later in this chapter.

The results presented in table 5.2 are averages of the experiments. It has to be noted that the error in the value of the 4 experiments with Cyanex 302 is rather large (relative standard deviation of 20%), but the additional decreases were significant. The concentrations of lead, chromium, manganese, iron, nickel, copper, and mercury could not be determined in the calcium sulfate phase, because the concentrations were below detection limit.

<table>
<thead>
<tr>
<th>Element</th>
<th>$R_{CaSO_4}$ recrystallization</th>
<th>$R_{CaSO_4}$ recrystallization and extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>Zn</td>
<td>0.98</td>
<td>0.91</td>
</tr>
<tr>
<td>Cd</td>
<td>0.33</td>
<td>0.18</td>
</tr>
<tr>
<td>Ti</td>
<td>0.63</td>
<td>0.41</td>
</tr>
</tbody>
</table>

As expected, the concentrations of the hard Lewis acidic ions, like the lanthanides, yttrium, and aluminum were not further decreased in the calcium sulfate phase by the addition of Cyanex 302. This is in accordance with Pearson’s principle on hard and soft acids and bases [3], since the thiophosphinic groups of Cyanex 302 are soft bases. Only the concentration of the hard acidic titanium ion in the calcium sulfate is further decreased, but this ion is not extracted by the carrier. This is concluded from the extraction efficiency, $\eta$ (eq. 5.3), which was found to be only 2%. The additional decrease in the titanium concentration in the calcium sulfate is compensated by an additional increase of its concentration in the phosphoric acid solution, as is shown in table 5.3. So, due to the addition of the organic phase relatively less titanium is
incorporated into the gypsum crystals. It is not clear why the distribution of titanium changes in the presence of the organic phase.

As is shown in table 5.2 for some elements, a conventional recrystallization already results in a purified calcium sulfate byproduct. As a result, the concentration of most impurity ions increases in the phosphoric acid, as is shown in table 5.3. The addition of Cyanex 302 during the recrystallization resulted in a decrease of the concentration cadmium and copper in the acid, instead of the increase that was found without the addition.

**Table 5.3.** The ratio $R_{acid}$ of some heavy metals in the phosphoric acid solution after the recrystallization of HH to DH with and without the addition of 0.29 mol/kg Cyanex 302 in kerosene.

<table>
<thead>
<tr>
<th>Element</th>
<th>$R_{acid}$ recrystallization</th>
<th>$R_{acid}$ recrystallization and extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1.34</td>
<td>1.38</td>
</tr>
<tr>
<td>Ni</td>
<td>1.12</td>
<td>1.13</td>
</tr>
<tr>
<td>Cu</td>
<td>1.07</td>
<td>0.22</td>
</tr>
<tr>
<td>Zn</td>
<td>1.13</td>
<td>1.09</td>
</tr>
<tr>
<td>Cd</td>
<td>1.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>1.80</td>
<td>1.77</td>
</tr>
<tr>
<td>Cr</td>
<td>1.13</td>
<td>1.16</td>
</tr>
<tr>
<td>Mn</td>
<td>1.14</td>
<td>1.20</td>
</tr>
<tr>
<td>Fe</td>
<td>1.13</td>
<td>1.18</td>
</tr>
<tr>
<td>Ti</td>
<td>1.15</td>
<td>1.23</td>
</tr>
</tbody>
</table>

From table 5.2 and 5.3, it was concluded that Cyanex 302 showed a large affinity for copper and cadmium during the recrystallization reaction, which is in agreement with the results that were described in chapter 4 of this thesis. This conclusion is confirmed by the extraction efficiencies presented in table 5.4.

Cadmium and copper show extraction efficiencies larger than 1. Although this is not possible, it indicates a large affinity of Cyanex 302 for these ions. Table 5.4 also shows that lead has been extracted significantly from the slurry. Further, it shows that Cyanex 302 has absolutely no affinity for calcium, the lanthanides, cobalt, nickel, manganese, and chromium. This is also in accordance with Pearson's principle on the hard and soft acids and bases. Calcium, the lanthanides, cobalt,
manganese, and chromium are all hard Lewis acids [3]. Only nickel is indicated as a borderline acid, like copper and zinc, which are extracted by Cyanex 302. However, nickel is a harder acid than copper and zinc according to the theory, due to the fact that it has less d-electrons and is thus less polarizable. A high polarizability is an important property of a soft Lewis acid.

Table 5.4. Extraction efficiencies of some elements after the recrystallization reaction of HH to DH.

<table>
<thead>
<tr>
<th>Element</th>
<th>(\eta) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu</td>
<td>1.1</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
</tr>
<tr>
<td>Ca</td>
<td>0</td>
</tr>
<tr>
<td>La</td>
<td>0</td>
</tr>
<tr>
<td>Ce</td>
<td>0</td>
</tr>
</tbody>
</table>

For an economic feasible application of solvent or liquid membrane extraction, the impurity ions must be recovered from the carrier after extraction so that the carrier can be reused. For the recovery, a strong acidic stripping solution is required, like hydrochloric acid, nitric acid, or sulfuric acid. Because Cyanex 302 is very susceptible for oxidation, like all sulfur-containing dialkylphosphoric acid carriers, the oxidizing nitric acid causes rapid destruction of the carrier and is thus not suitable [4]. Sulfuric acid was chosen in this case, because this is also present in the treated phosphoric acid and would therefore cause no problems if some leakage would occur via the organic phase to the phosphoric acid feed during reuse of the organic phase during extraction. Due to the corrosive nature of hydrochloric acid, leakage of small amounts would already cause major problems in the phosphoric acid process.

So to recover the heavy metal ions, Cyanex 302 was contacted intensively with 500 g/L sulfuric acid. However, the analysis of the organic extraction phase and the 500
g/L sulfuric acid stripping solution showed that only lead was successfully recovered. The affinity of Cyanex 302 for cadmium and copper is too high and they remained in the organic extraction solution (0.21 mmol/kg cadmium and 0.15 mmol/kg copper).

For a successful application of solvent extraction or supported liquid membrane extraction, sulfuric acid is not suitable and another stripping solution should be tested, like 55 g/L HCl that might be more effective [1]. In that case, leakage of the stripping solution into the organic solution has to be prevented.

5.5 Conclusions

Cadmium, copper, zinc, and lead were extracted by Cyanex 302 during the recrystallization reaction, resulting in detected lower concentrations of cadmium and zinc in the gypsum. Unfortunately, lead, chromium, manganese, iron, nickel, copper, and mercury concentrations in the calcium sulfate phase were below detection limit.

Only lead was recovered from organic extraction solution by 500 g/L sulfuric acid. The affinity of Cyanex 302 for cadmium and copper was too high, and these elements remained in the organic solution. For a successful application of Cyanex 302 in solvent extraction or supported liquid membrane extraction, other stripping solutions should be tested, like 55 g/L hydrochloric acid that might be more efficient. In that case, leakage of the stripping solution via the organic phase to the phosphoric acid feed should be prevented, because of the corrosive nature of hydrochloric acid.

References

Chapter 6

Heavy Metal Extraction from Phosphoric Acid in a Transverse Flow Hollow Fiber Membrane Contactor

Mercury, copper, lead, and cadmium were extracted from an industrial phosphoric acid solution by Cyanex 302 (bis(2,4,4-trimethylpentyl)thiophosphinic acid) in kerosene in a transverse flow hollow fiber membrane contactor. The permeability was $3 \cdot 10^{-6}$ m/s.

With the same contactor, erbium and dysprosium were extracted also from the phosphoric acid solution by D2EHPA (di(2-ethylhexyl)phosphoric acid) in kerosene. The permeability was $2-6 \cdot 10^{-8}$ m/s.

Experiments had to be terminated, because of leakage of organic phase into the aqueous phase. Vibrations due to pulsation of the tube pumps are thought to be the main reason for instabilities during this research. Additional instability problems due to the formation of eddies could not be determined.

The feasibility of SLM extraction from slurries depends strongly on the particle size of the solids and the required pitches to avoid clogging.

6.1 Introduction

The results described in chapter 4 showed that commercial liquid carriers with affinity for either heavy metals or lanthanides from industrial phosphoric acid are available. In chapter 5, Cyanex 302 (bis(2,4,4-trimethylpentyl) thioposphinic acid) was used for the removal of heavy metals during the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) in phosphoric acid. This resulted in a detected decrease in the concentration of cadmium and zinc in the gypsum. This illustrates that it is possible to reduce the concentration of impurities in the gypsum by removing the impurities in-line during phosphoric acid production, which is the final aim of this work. The results of the extractions described in chapter 5 were obtained by contacting the organic extraction phase intensively with the recrystallizing slurry by stirring. Disadvantage of such a process is the emulsification of the organic phase in the phosphoric acid solution and its possible incorporation in the newly formed gypsum crystals.

To avoid this emulsification, supported liquid membrane (SLM) extraction is thought to be a potential separation as was discussed in chapter 2. For SLM extraction, the organic phase is immobilized in a porous polymeric support, like a polypropylene hollow fiber, preventing emulsification of the organic phase in the feed solution. The aim of this work is to investigate the application of a transverse flow hollow fiber contactor as a future apparatus for SLM extraction.

In a transverse flow contactors the feed slurry flows straight down from top to bottom of the module. When applying a top angle with a maximum of 8° and a bottom angle with a maximum of 25-30°, the solution follows the module wall [1] and no dead areas, in which settling of solids can develop, occur. In ordinary parallel flow contactors, the feed solution enters and leaves the module with an angle of 90°, resulting in dead areas. In these areas, settling of solids will occur resulting eventually in clogging. The flow in transverse and parallel flow modules is illustrated in figure 6.1. Another advantage of transverse flow compared to parallel flow may be the extra turbulence on the shell side of the fibers, which will result in a thinner diffusion layer.

Membrane contactors have also disadvantages. First, the contact area between the two phases is small and the layer, through which the ion-carrier complex has to diffuse, is thick. This layer is at least as thick as the wall thickness of the hollow fiber, in which the organic phase is immobilized. Another disadvantage is the instability, i.e. loss of organic phase from the pores of the fiber [2].

60
A disadvantage of a transverse flow contactor compared to a parallel flow contactor may be the extra instabilities due to the transverse flow. This will be discussed further in §6.2.2.

![Diagram of parallel flow hollow fiber module and transverse flow hollow fiber module](image.png)

**Figure 6.1.** A parallel flow hollow fiber module (left) and a transverse flow hollow fiber module (right).

This chapter describes results that were obtained by contacting clear industrial phosphoric acid with an organic phase in a transverse flow hollow fiber membrane contactor to remove impurity ions. In a membrane contactor, the organic phase is not only present in the pores of the hollow fibers, but also flows through the fibers. For the removal of heavy metals, Cyanex 302 in kerosene was used as the extractant phase and for the removal of heavy lanthanide ions D2EHPA (di(2-ethylhexyl)phosphoric acid) in kerosene was used. The phosphoric acid solution was pumped around the fibers, and the organic phase was pumped through the fibers. The extraction process is illustrated in figure 6.2.

![Diagram of extraction process using porous hollow fibers](image.png)

**Figure 6.2.** The extraction process using porous hollow fibers to separate the aqueous feed solution physically from the organic solution (white, gray, and black dots represent the impurity ion, the counter ion, and the carrier, respectively).
From the results gained with the membrane contactor after treatment of clear solutions, a feasibility study of the extraction with these kinds of modules during the recrystallization of HH to DH in the phosphoric acid process will be discussed at the end of this chapter.

6.2 Theory

6.2.1 Extraction in a membrane contactor

For solvent extraction, ions are taken up by the organic phase from the feed phase until thermodynamic equilibrium is reached. At equilibrium, the distribution coefficient, $K_A$ [-], is calculated with

$$K_A = \frac{[A]_{\text{org}}}{[A]_{\text{acid}}} \quad 6.1.$$

For a batch process (as is the case in the experiments described here), the flux of component A, $J_A$ [mol·m⁻²·s⁻¹], equals

$$J_A = -\frac{d[A]_{\text{acid}}}{dt} \cdot \frac{V}{A} \quad 6.2,$$

with $V$ the volume of the slurry [m³], $A$ the contact area [m²], and $t$ the time [s]. The flux can be corrected for the feed concentration, resulting in the permeability, $P$ [m/s], defined as

$$P = -\frac{1}{[A]_{\text{acid}}} \cdot \frac{d[A]_{\text{acid}}}{dt} \cdot \frac{V}{A} = \ln \frac{[A]_{\text{acid}, t=2}}{[A]_{\text{acid}, t=1}} \cdot \frac{V}{A} \cdot \frac{1}{t_2 - t_1} \quad 6.3.$$

6.2.2 Instability mechanisms

The instability of SLMs has been widely investigated. Kemperman et al. [2] made an extensive survey of instability mechanisms. The mechanisms that cause instability during SLM extraction do also occur in membrane contactors. It turned out that many factors influence the stability of the membranes. This chapter aims to give an insight in additional instability mechanisms in transverse flow modules compared to parallel flow modules. This will also give an insight into the most dominant instability mechanism in transverse flow hollow fiber membrane contactors.
Instability of SLMs may be the result of:

- pressure differences
- emulsification of the organic phase in the aqueous phase

**Pressure differences**

If the pressure difference between the shell and lumen side of the fiber, the transmembrane pressure, exceeds a critical pressure, the organic phase will be pushed out of the most susceptible pores of the support. The system is unstable and the aqueous feed solution will get contaminated with the organic phase. The critical pressure, $P_c$ [Pa] for cylindrical pores is given by the Laplace equation:

$$P_c = \frac{2 \gamma \cos \theta}{r}$$

with $\gamma$ the interfacial tension between the organic phase and the aqueous phase [N/m], $\theta$ the contact angle between the support pore wall and the organic phase [-], and $r$ the pore radius [m]. The dependence of the critical pressure on the interfacial tension and the contact angle indicate that the support material, the composition of the aqueous solution, the organic solvent and carrier influence the stability strongly.

In a transverse flow membrane contactor, pressure differences, which are absent in a parallel flow contactor, occur. These additional pressure differences may result in higher transmembrane pressures and thus promote instability of the system.

In a transverse flow membrane contactor, a pressure difference already occurs around the fibers. The transverse flow is illustrated in figure 6.3.

![Figure 6.3. A schematic representation of the transverse flow in the hollow fiber module.](image_url)

The pressure on the fiber is highest at point A. At this point, the feed velocity equals 0 and according to Bernoulli's equation, the pressure $P_A$ [Pa], becomes equal to

$$P_A = \sqrt{\frac{1}{2} \rho v_0^2} + P_{\infty}$$
with \( \rho \) the density of the feed solution [kg/m\(^3\)]. The pressure at point B is the lowest around the fiber. This pressure depends on the velocity between the fibers. The velocity between the fibers, \( v \) [m/s], is determined by

\[
v = v_\infty \cdot \frac{s/d}{\sqrt{d-1}}
\]

with \( s \) the longitudinal pitch [m], and \( d \) the fiber diameter [m]. The pressure is lowest when assuming no friction and equals

\[
P_B = -1 \frac{1}{2} \rho v^2 + P_\infty
\]

Due to the transverse flow, a pressure drop also occurs in the contactor due to drag forces. The pressure drop is a function of the geometry (transversal pitch, longitudinal pitch, fiber diameter), the number of fiber rows in the module, the feed velocity, and the physical properties of the feed.

It is assumed that the flow pattern around a fiber is not influenced by former rows of fibers, because the distance between the fibers is large in a contactor, in which a slurry stream is treated. For low Reynolds numbers when the flow field behind a cylinder is small, this will be a good assumption.

The pressure drop over 1 fiber, \( P_w \) [Pa], is calculated with

\[
P_w = C_w \cdot \left( \frac{1}{2} \rho v^2 \right)
\]

with \( C_w \) [-] the drag coefficient. The drag coefficient depends on the Reynolds number.

**Emulsification of the organic phase**

Emulsification is thought to be an important cause of SLM instability. Local deformations of the organic phase meniscus in the support pores combined with the Marangoni effect are probably the causes of the emulsification. These local deformations can have several origins, of which the most important are

- Kelvin-Helmholtz instabilities, two phases move with different velocities parallel to the interface creating waves,
- vibrations of the organic phase in the pores, small deformations on the organic phase meniscus due to pulsation of the aqueous phase resulting in the formation of ripples.

Once waves or ripples are formed on the organic phase meniscus, concentration differences can cause surface tension gradients on the organic/aqueous interface.
causing interfacial turbulence. This effect is called the Marangoni effect. The Marangoni effect is illustrated in figure 6.4. The interfacial turbulence may result in emulsification of the organic phase.

![Figure 6.4. The Marangoni effect.](image)

The presence of Kelvin-Helmholtz instabilities depends on the velocity difference between the two phases and on the density difference between these phases. The critical velocity difference, $\Delta v_c$, at which Kelvin-Helmholtz instabilities occur can be estimated with [3]

$$\Delta v_c = \left(\frac{2(\rho_1 + \rho_2)}{\rho_1 \rho_2}\right)^{0.5} (\Delta \rho g \gamma)^{0.25} \quad 6.9.$$ 

The effect of Kelvin-Helmholtz instabilities can be more severe for transverse flow than for parallel flow. In transverse flow, velocity gradients occur around the fiber, which is not the case in parallel flow. At point B of figure 6.3, the velocity along the fiber surface is higher than the superficial velocity. The critical velocity difference between the aqueous and organic phase is therefore reached at lower superficial velocities.

Especially the vibrations of the organic phase in the pores may be more severe in transverse flow than in parallel flow resulting in a less stable system. Due to transverse flow, eddy formation at the rear of the fibers may cause additional turbulence [1]. An increasing turbulence will result in more violent vibrations of the organic phase in the pores. The formation of eddies depends on the Reynolds number, $Re$ [-],

$$Re = \frac{\rho u d}{\eta} \quad 6.10,$$

with $\eta$ the viscosity [kg·m⁻¹·s⁻¹]. At laminar flow, $Re<1$, the stream lines follow the form of the fiber and no additional turbulence occur. Between $1<Re<70$, the flow at the rear becomes more turbulent and eddies are formed. At higher $Re$, $70<Re<150$, the eddies are dragged along with the flow and swirl away from the rear of the fiber. This is known as the Von Karman effect. At $150<Re<10^5$, the turbulence behind the
fiber increases further. The swirls become irregular and the turbulence area behind the fiber is large. Further increase of Re results in turbulence in the boundary layer of the fiber, whereas the turbulence area behind the fiber becomes smaller.

6.3 Experimental

6.3.1 Procedure and experimental set-up

The extraction of heavy metals with Cyanex 302 was performed with 175 g clear phosphoric acid from an industrial one-filter HemiRecrystallization (HRC) phosphoric acid process (3.8 mol H₃PO₄/kg, 0.2 mol H₂SO₄/kg) using 35% Jordan and 65% Kovdor ore. The density of the acid was determined to be 1280 kg/m³, and the viscosity 8.3·10⁻⁴ kg·m⁻¹·s⁻¹ [4]. The mercury concentration in the acid was increased to 0.25 mmol/kg by adding analytically pure mercury nitrate. The acid was pumped round the hollow fibers with a superficial velocity of 0.4 cm/s. The organic solution (130 g) of 1.18 mol/kg of Cyanex 302 in kerosene was pumped through the hydrophobic polypropylene fibers with a flow rate of 1.2 cm/s.

In the same module, the extraction of lanthanides with D2EHPA was performed with 175 g clear phosphoric acid from an industrial two-filter HemiDiHydrate (HDH) production process (0.8 mol H₃PO₄/kg, 0.5 mol H₂SO₄/kg) using 100% Jordan ore. The concentration of lanthanum, cerium, europium, dysprosium, and erbium was increased with 50 mg/kg by the addition of their nitrate salts. The density of this acid is 1120 kg/m³.

The transverse flow module (XTO, The Netherlands) has a compartment of 8 ml, which contains 4 rows with 31 fibers (Oxyphan 50/280) each. The outer diameter of the fibers is 0.38 mm, the inner diameter 0.28 mm, and they have a pore size of 0.2 µm. The fibers have a total contact area of 29.8 cm². The transversal pitch between the fiber rows is 4000 µm and the longitudinal pitch is 650 µm. This is schematically illustrated in figure 6.5.

Figure 6.5. Schematic illustration of the distances in the transverse flow hollow fiber module used.
6.3.2 Analyses

Copper, mercury and the lanthanides were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), whereas cadmium and lead were analyzed by polarography (stripping voltametry with hanging mercury drop electrode).

The sizes of the industrial calcium sulfate hemihydrate and calcium sulfate dihydrate particles were determined with a Malvern Mastersizer.

6.4 Results

6.4.1 Extraction

Contacting the industrial phosphoric acid feed solution with Cyanex 302 in kerosene in a transverse flow hollow fiber membrane contactor resulted in the extraction of mercury, lead, and cadmium, as is shown in figure 6.6.

![Figure 6.6](image)

**Figure 6.6. The concentration of lead, cadmium, and mercury during the treatment of industrial phosphoric acid with Cyanex 302 in a transverse flow hollow fiber membrane contactor.**

Only the concentration of mercury was determined as a function of time. After $25 \times 10^3$ s no more mercury was extracted. Apparently, thermodynamic equilibrium between the feed solution and the organic phase was reached with respect to mercury. Calculation of the distribution coefficient confirmed this. The calculated distribution coefficient was 5.1. This value is comparable to that determined after
shaking tests presented in chapter 4 of this thesis. At equilibrium, a distribution coefficient of 5.7 was found.

The average flux of mercury between 0 and $25\cdot10^3$ s was calculated to be $8\cdot10^{-7}$ mol·m$^{-2}$·s$^{-1}$ corresponding with a permeability of $3\cdot10^{-6}$ m/s. These fluxes and permeabilities have the same order of magnitude as those found in literature for SLM extraction [5,6].

Also copper was transported. The average copper flux was found to be $2\cdot10^{-7}$ mol·m$^{-2}$·s$^{-1}$, which corresponds with a permeability of $3\cdot10^{-6}$ m/s.

Similar extraction experiments were performed with the carrier D2EHPA in kerosene to remove lanthanides from the phosphoric acid. As expected from the results presented in chapter 4, the light lanthanides lanthanum, cerium, and europium were not extracted at all. The heavier lanthanides dysprosium and erbium were extracted, as is shown in figure 6.7.

![Graph](image)

*Figure 6.7. The concentration of lanthanum, dysprosium, and erbium in the acid during the treatment of industrial phosphoric acid with D2EHPA in kerosene in a transverse flow hollow fiber membrane contactor.*

The fluxes of the trivalent lanthanides were lower than those of the heavy metals during extraction with Cyanex 302. The average flux of erbium was $2\cdot10^{-8}$ mol·m$^{-2}$·s$^{-1}$, which results in a permeability of $6\cdot10^{-8}$ m/s. The permeability of dysprosium was lower. The average dysprosium flux was $6\cdot10^{-8}$ mol·m$^{-2}$·s$^{-1}$ and the permeability was $2\cdot10^{-8}$ m/s. The lower permeability is the result of the lower affinity of D2EHPA for this ion.
6.4.2 Instability

Experiments had to be terminated due to leakage of the organic phase, which flows through the hollow fiber, to the inorganic phosphoric acid phase, which flows around the fibers.

Pressure differences

For polypropylene fibers with a nominal pore diameter of 0.2 μm, the critical pressure difference increased with the wall thickness of the fiber. For fibers with wall thicknesses of 150 μm, 200 μm, and 500 μm, the critical membrane pressures were found to be $0.72 \cdot 10^5$ Pa, $1.13 \cdot 10^5$ Pa, and $1.36 \cdot 10^5$ Pa, respectively, for the system kerosene/water [7,8]. The fibers in the used membrane contactor have a wall thickness of only 50 μm. So, the critical pressure is thought to be lower than $0.72 \cdot 10^5$ Pa, but with the lack of a clear relation between the wall thickness and the critical pressure, it can not be estimated precisely.

Equation 6.4 shows that the critical pressure depends strongly on the interfacial tension. The above mentioned critical pressures were determined for a kerosene/water system. For extraction, a carrier is added to the kerosene phase. Generally, the addition of a carrier reduces the interfacial tension. This was illustrated for D2EHPA, which reduced the interfacial tension between water and n-dodecane from 52 mN/m to 14 mN/m, and LIX84 (2-hydroxy-5-nonylacetophenone oxime), which reduced the interfacial tension between water and kerosene from 42 mN/m to 20 mN/m [9]. Complexation of the carrier with an impurity ion may either decrease the interfacial tension further (nickel/D2EHPA) or may result in an increase of the interfacial tension (copper/LIX84) [10]. Equation 6.4 shows that the reduction in the interfacial tension results in a decrease of the critical pressure. If assuming the same effect of D2EHPA in kerosene as in n-dodecane, the interfacial tension becomes 12 mN/m instead of 42 mN/m. The critical pressure of $0.72 \cdot 10^5$ Pa of the kerosene/water system would become $0.21 \cdot 10^5$ Pa for D2EHPA/kerosene/water.

With equations 6.5, 6.6, and 6.7, it was calculated that with a superficial velocity of 0.4 cm/s of phosphoric acid, the maximum pressure difference around the fiber is only 0.2 Pa. Comparing this with the critical pressure, it is clear that this is no reason for an increase in instability compared to parallel flow. At a velocity of 1 m/s, the pressure difference around the fiber becomes $0.1 \cdot 10^5$ Pa. So, only at very high velocities around the fiber, the pressure difference will contribute to the instability of the system.

The Reynolds number during the experiments equals 5. At this low Reynolds number, the resistance coefficient used for the pressure drop of equation 6.8, is 4
The pressure drop becomes 0.2 Pa per fiber. With 4 rows of fibers, the total pressure drop in the contactor becomes 0.8 Pa. So, at these low velocities, the pressure drop will not cause significant additional stability problems. At a velocity of 1 m/s, Reynolds becomes 500 and the resistance coefficient then equals 1.2. Neglecting the influence of former rows of fibers on the flow pattern, the pressure drop becomes 675 Pa over a fiber. With this high velocity, the pressure drop equals $0.21 \cdot 10^5$ Pa after 31 rows of fibers. In that case, the extraction in the transverse flow membrane contactor can not be operated anymore without instability problems due to the pressure drop.

At the low velocities used during the experiments, additional pressure differences due to transverse flow are not significant enough to reduce the stability of the system. Only at higher velocities, the pressure differences will cause stability problems that do not occur in parallel flow contactors.

**Emulsification**

D2EHPA has a density of 974 kg/m$^3$. With the density of 790 kg/m$^3$ for kerosene, the density of the organic phase becomes 807 kg/m$^3$. With equation 6.9 and an interfacial tension that was estimated to be 12 mN/m for the D2EHPA/kerosene/water, it was calculated that the critical velocity difference for Kelvin-Helmholtz instabilities equals 16 cm/s. With an interfacial tension of 42 mN/m for the kerosene/water system, this critical velocity difference becomes 22 cm/s. With a velocity of 0 for the organic phase in the pores, the velocity of the aqueous phase may become as high as 16 cm/s before Kelvin-Helmholtz instabilities occur. During the experiments, the velocity around the fibers had a maximum velocity of 1 cm/s and Kelvin-Helmholtz instabilities are not expected to have played a role in the instability of the membrane.

The vibrations of the organic phase in the pores can not be quantified. However, it is expected that these vibrations are the cause of the instability problems. For pumping of the aqueous and organic phases tube pumps were used, which show pulsation during pumping. Although tube pumps were used with double tubing to reduce the pulsation, it is expected that the pulsation causes vibration of the organic phase and therewith instability. Additional instability problems due to the formation of eddies, which do already occur at a Reynolds of 5, can not be determined. More research should be performed to compare parallel and transverse flow operation to eliminate the effect of pumping pulsation.
Swelling

Swelling of the fibers may result in other stability problems, although these problems will also occur in parallel flow membrane contactors. Due to swelling, the fibers become longer and meander in the module. They will connect. In a membrane contactor, an organic film layer may be formed between the hydrophobic fibers. This organic layer on the surface of the fibers may be dragged along with the aqueous phase resulting in a continuous loss of organic phase to the aqueous phase.

6.5 Feasibility of SLM Extraction to Reduce the Impurity Content in Gypsum

The transverse flow hollow fiber membrane contactor used for the experiments described in this chapter is not suitable for the treatment of slurry streams, like the phosphoric acid slurry during the recrystallization of HH to DH. The longitudinal pitch of only 270 μm is too small to avoid clogging. However, increasing the pitches would make it possible to treat a slurry, but due to this increase the contact area per volume in the contactor will decrease.

This paragraph discusses the feasibility of the membrane contactor for the treatment of the recrystallizing calcium sulfate particles in phosphoric acid.

In the two-filter HDH process, the average particle size of the HH crystals is 50 μm with a maximum particle size of 260 μm. The DH particles are larger with an average size of 80 μm and a maximum of 530 μm. No design parameters were found in literature with respect to the size of the pitches needed to avoid clogging. For a first feasibility calculation, a distance between the fibers of 10 times the maximum particle size was chosen.

During recrystallization, the impurities in the phosphoric acid are redistributed between the acid and the newly formed crystals. This distribution is influenced by both thermodynamics and kinetics. To achieve a lower concentration in the gypsum, the concentration in the phosphoric acid should be reduced. To maintain a low concentration impurities in the acid, the ions that enter the recrystallization section with the phosphoric acid and those that are released from the HH crystals have to be extracted.

To illustrate the feasibility of the membrane contactor to remove impurities during the recrystallization, lead is taken as an example. The industrial recrystallization is performed in stirred vessels with a volume of 1000 m³ and a residence time of 210 minutes. So, the flow rate equals 0.08 m³/s. The relative amount of CaSO₄ solids in the input flow and in the recrystallizer equals about 40%. The concentration of lead in the acid is 0.54 mmol/m³, resulting in a supply of lead to the reactor with the acid
of $2.6 \times 10^{-5}$ mol/s. The conversion of HH to DH in the first recrystallizer is about 86%. With a concentration of lead in HH of 16 mmol/m$^3$, it can be calculated that 0.44 mmol Pb/s is released from HH into the acid. The total supply of lead becomes 0.47 mmol/s.

For a reduction of 70% of lead in the acid and in the gypsum, the concentration in the acid should become 0.16 mmol/m$^3$. Assuming a permeability coefficient of $3 \times 10^{-6}$ m/s (see §6.4.1), the flux through the membrane can be calculated with

$$J = \frac{P}{c_{\text{acid}}}$$

6.11,

with $c_{\text{acid}}$ the concentration of lead in the acid [mol/m$^3$]. The flux becomes $4.9 \times 10^{-10}$ mol·m$^{-2}$·s$^{-1}$. To remove 70% of the input amount of lead, 0.33 mmol/s, a contact area of $6.7 \times 10^5$ m$^2$ is required.

For a contactor with pitches of 5.38 mm (5 mm distance between the fibers, about 10 times the maximum particle size of the crystals) and fibers of 380 µm, the contact area per volume is 41 m$^2$/m$^3$. To gain the required contact area of $6.7 \times 10^5$ m$^2$, a contactor of $1.6 \times 10^4$ m$^3$ should be available. Taking into account that the recrystallizer has a volume of 1000 m$^3$, even a contactor, in which extraction and recrystallization are performed simultaneously, is not suitable to achieve the desired extraction efficiency. If the recrystallizer is used as a contactor, in which the recrystallization and the extraction are performed simultaneously, only 12% of the lead input can be removed with these pitches and fibers.

If smaller pitches could be applied, the contact area would increase significantly in the contactor. For a distance of 0.95 mm between the fibers (pitches of 1.33 mm), the contact area per volume of contactor increases to 675 m$^2$/m$^3$. With this contact area, 70% of the lead input can be extracted when using the 1000 m$^3$ recrystallizer as a contactor.

It is concluded that the feasibility of treating slurry streams in a membrane contactor depends strongly on the required pitches. It is important to search for the smallest pitches possible. More research should be performed on the clogging behavior of slurries passing beds of tubes.

### 6.6 Conclusions

Mercury, copper, lead, and cadmium were removed from clear industrial recrystallization acid in a transverse flow hollow fiber membrane contactor. The permeability of mercury and copper was $3 \times 10^{-6}$ m/s, which is comparable to that of SLM extraction.
With the same module, erbium was extracted also from the phosphoric acid solution by the extracting agent D2EHPA (di(2-ethylhexyl)phosphoric acid) in kerosene. The permeability of erbium was calculated to be $6 \cdot 10^{-8}$ m/s and that of dysprosium $2 \cdot 10^{-8}$ m/s.

Experiments had to be terminated, because of leakage of the organic phase into the feed solution. Transverse flow may result in additional instabilities compared to parallel flow. However, additional pressure differences and Kelvin-Helmholtz instabilities will only be significant at velocities higher than used in this research. Vibrations due to pulsation of the tube pumps are thought to be the main reason for instabilities during this research. Additional instability problems due to the formation of eddies could not be determined.

The feasibility of a membrane contactor to remove impurities from a slurry depends strongly on the particle size of the solids and the required pitches to avoid clogging.

**Acknowledgement**

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**References**


8. Results obtained by Berends A.M., Laboratory for Process Equipment, Delft University of Technology, The Netherlands.


Chapter 7

Ion Exchange Extraction with Sulfonic Acids during Batch Recrystallization

This chapter describes the results of batch recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) with simultaneous extraction of impurities. The extraction efficiency is influenced by the composition of the acid, the presence of other cations than impurity ions in the acid, kinetics and the uptake of the impurities by the newly formed gypsum.

The extraction of impurities, like the lanthanides, depends strongly on the acidity of the phosphoric acid. The extraction efficiency from process acid, which contains 3.1 M H₃PO₄ and 0.2 M H₂SO₄, is much lower than it is from process acid, which contains 0.8 M H₃PO₄ and 0.5 M H₂SO₄.

Although the ion exchange resin has a preference for lanthanides, it also has affinity for calcium, which is abundantly present in the process acid. To reach higher extraction efficiencies for the lanthanides with comparable amounts of ion exchange resin, a resin should be developed with more selectivity towards these ions and which is able to extract from very acidic media.

The extraction efficiency is also influenced by the affinity of gypsum for the impurities. For the two-filter HemiDiHydrate process, this is most obvious. Lanthanides that are taken up most readily by the gypsum are extracted least.

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7.1 Introduction

Chapter 6 describes the extraction of lanthanides and heavy metals in transverse flow hollow fiber membrane contactors from clear industrial phosphoric acid. Although liquid extractants were found with selective affinity for heavy metals and ones were found for the extraction of lanthanides, the stability of the membranes is a problem. The stability problems seem even more severe for transverse flow than for parallel flow. For the treatment of slurry streams, like the phosphoric acid slurry during the recrystallization, the transverse flow is required, as is explained in chapter 6.

As an alternative, ion exchange was investigated as a potential technique to remove impurities during the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) in phosphoric acid. Ion exchange resins contain functional groups, which are chemically bonded to a solid matrix. Stability problems, like those occurring in a membrane contactor, will not occur during ion exchange extraction.

Chapter 4 describes the extraction from clear phosphoric acid by ion exchange resins with sulfonic acid functional groups (-SO₃H). Although the ion exchange resins did not have the desired selectivity, further research was performed with these resins to investigate the ability of reducing the lanthanide concentration in the gypsum during the recrystallization of calcium sulfate hemihydrate (HH) to gypsum (calcium sulfate dihydrate, DH). More selective resins for extraction of impurities from the very acidic industrial phosphoric acid were not find yet.

To investigate several influences on the extraction efficiency and the feasibility of ion exchange extraction, recrystallizations with HH and phosphoric acid from both the one-filter Hemihydrate dihydrate ReCrystallization (HRC) process and the two-filter Hemihydrate DiHydrate (HDH) process were taken. The process conditions differ for these two production processes, as is explained in chapter 1. The first process uses mainly a mixture of 70% Kovdor and 30% Jordan ore as feed, whereas the latter process mainly uses 100% Jordan ore. During this research also HH and phosphoric acid from the HDH process were used from a production run with 50% Kovdor and 50% Jordan ore. The difference in feed will result in a difference in impurity concentration. The concentrations of some impurities in these 2 ores are presented in table 7.1. Due to these differences, the concentration of lanthanides will be higher in the one-filter process than in the two-filter process.

Another important difference is the acid, in which the recrystallization is performed. In the one-filter process, the recrystallization is performed in the phosphoric acid product, which contains 3.1 M H₃PO₄ and 0.2 M H₂SO₄. The recrystallization in the two-filter process is performed at higher temperatures, but in less acidic acid. The so-called recrystallization acid contains 0.8 M H₃PO₄ and 0.5 M H₂SO₄.
Table 7.1. Comparison of Jordan and Kovdor ore with respect to some impurities.

<table>
<thead>
<tr>
<th></th>
<th>Jordan ore [mg/kg]</th>
<th>Kovdor ore [mg/kg]</th>
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<tr>
<td>Cd</td>
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<td>0.25</td>
</tr>
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</tr>
<tr>
<td>Al</td>
<td>3000</td>
<td>400</td>
</tr>
<tr>
<td>Mg</td>
<td>1800</td>
<td>12000</td>
</tr>
<tr>
<td>La</td>
<td>0.05</td>
<td>0.59</td>
</tr>
<tr>
<td>Ce</td>
<td>0.16</td>
<td>3.9</td>
</tr>
<tr>
<td>Nd</td>
<td>0.07</td>
<td>0.69</td>
</tr>
<tr>
<td>Y</td>
<td>30</td>
<td>249</td>
</tr>
<tr>
<td>ΣREM</td>
<td>263</td>
<td>1378</td>
</tr>
</tbody>
</table>

ΣREM=∑ of all lanthanides

The aim of this chapter is to show the applicability of simultaneous ion exchange extraction during the recrystallization of HH to DH. Therefore, batch recrystallizations with simultaneous ion exchange extraction were performed. The ion exchange extraction efficiency is influenced by various factors during the recrystallization reaction. Four of these factors, which are thought to be the most important ones, will be discussed:

i). the pH of the phosphoric acid solution,

ii). the presence of other cations than the ones to be extracted,

iii). the affinity of the newly formed gypsum for the impurities.

iv). kinetics of gypsum growth and extraction reaction.
7.2 Theory

7.2.1 pH of the phosphoric acid solution

Resins with sulfonic acids as functional groups exchange their protons to extract cations from the solution

$$3\text{HSO}_3^- + \text{Ln}^{3+} \leftrightarrow 3\text{H}^+ + \text{Ln}({\text{SO}_3})_3^-$$

with Ln as a lanthanide ion, and R the polystyrene-divinylbenzene matrix of the ion exchange resin, to which the sulfonic group is bound. In case of cation exchange the functional group of the resin will only dissociate if the pH of the solution is higher than the pK of the resin. The sulfonic acid group is a strong acidic group with $pK < 1$. Normally, the sulfonic acid group is dissociated completely. However, the phosphoric acids have a very high acidity. Due to dimerization of the phosphoric acid, the pH will be lower than that based on dissociation of $\text{H}_3\text{PO}_4$. In these acids, the degree of ionization of the functional fixed groups may become lower and the exchange of protons by cations may become the limiting factor in ion exchange capacity. This will result in a lower effective capacity of the resin with decreasing pH of the acid.

7.2.2 Presence of other cations

The phosphoric acid solution does not only contain impurity ions, but also ions that need not be extracted, like the calcium ions. Resins with sulfonic acid functional groups have a preference for ions with a higher valence, or with a smaller solvated volume, or with a greater polarizability, or which participate least in complex formation with ionic species in the solution [1]. So, based on their increasing solvated volumes (461 pm for lanthanum to 474 pm for lutetium [2]), the affinity of the resin decreases from the light lanthanides to the heavy lanthanides, as was discussed in chapter 4. For the bivalent cations, the affinity sequence of these resins is in general [1]

$$\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}.$$ 

As is mentioned for the univalent and bivalent sequences, also the sequences for the trivalent and bivalent cations overlap, as is seen for Dowex C-500 for the extraction from industrial phosphoric acid of the two-filter process in chapter 4. The affinity sequence, which was found to be dependent on the amount of ion exchange resin per volume of acid in this multicomponent system, was for 11 g resin/kg acid

$$\text{La}^{3+} > \text{Ce}^{3+} = \text{Eu}^{3+} > \text{Pb}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Dy}^{3+} > \text{Er}^{3+} > \text{Fe}^{3+},$$

and for 150 g resin/kg acid
La$^{3+}$ > Ce$^{3+}$ > Eu$^{3+}$ = Pb$^{2+}$ > Dy$^{3+}$ > Er$^{3+}$ > Ca$^{2+}$ > Cd$^{2+}$ > Fe$^{3+}$.

The difference in affinity sequence with varying amounts of ion exchange resin is due to competition effects between cations for the available active sites of the resin, which is further explained in chapter 4. The experimentally found affinity sequence for bivalent cations equals the expected sequence mentioned above.

The sulfonic acid groups show also affinity for the calcium ions, which are abundantly present in the phosphoric acids.

From the affinity sequences of general ion exchange resins and Dowex C-500, it is expected that the presence of magnesium and iron only plays a minor role, although these ions are present in relatively high concentrations in the solution. It was already proven in chapter 4 that iron was not extracted significantly from industrial phosphoric acid by Dowex C-500 ion exchange resin. Barium and strontium sulfate particles, formed during leaching of the ore, are normally not dissolved during the recrystallization. However, ion exchange resin is known to be able to dissolve even sparingly soluble salts [1]. Due to the large affinity of a general ion exchange resin for these ions, their extraction may be significant.

The dissolution of the barium and strontium sulfate particles may also influence the lanthanide concentration in the solution (and thus their extraction efficiency), because these ions may also be present in the normally insoluble particles. In this way, it might be possible to extract ions, which are normally not accessible.

### 7.2.3 Affinity of the newly formed gypsum for the impurity ions

The concentration of an impurity ion in the gypsum depends on a specific affinity of the crystal for the impurity and the concentration in the acid. The specific affinity is described by the distribution coefficient $K_{DH}$ [-],

$$K_{DH,A} = \frac{[A]_{DH}}{[A]_{acid}} \quad \text{7.2.}$$

At equilibrium, $K_{DH}$ depends on the intrinsic properties of the acid solvent, the gypsum solid, and the impurity ion A, like the chemical nature of the ion, the ionic radius, the coordination with surrounding ions, the crystal structure, the hydration free energies, the complexing constants, etc. However, crystallization cannot be performed at equilibrium. So, kinetics also plays an important role on the concentration of impurity ions in the gypsum crystal. For example, a higher growth rate results in a higher uptake of impurities in the newly formed gypsum crystals [3,4]. It is also important to keep in mind that only the surface of the crystals is in contact with the acid. Impurities that are already overgrown by a new layer of
calcium sulfate ions are incorporated and cannot diffuse out of the crystal anymore. During an ordinary batch recrystallization, the concentration of impurities in the acid is not constant but increases due to dissolution of the impurities from the HH crystals. Every newly formed gypsum layer will have a higher concentration of impurities than the former layers and a concentration gradient will occur in the gypsum crystals.

The determination of $K_{DH}$ is therefore not very simple. Assuming that the amount of acid and the supersaturation are constant, the following relation was found

$$m_{DH,end} - m_{DH,start} = \frac{m_{acid}}{K_{DH,A}} \cdot \log \left[ \frac{172/145 [A]_{HH} - K_{DH,A} \cdot [A]_{acid,start}}{172/145 [A]_{HH} - K_{DH,A} \cdot [A]_{acid,end}} \right]$$  

7.3,

with $m_{DH}$ and $m_{acid}$ the amount of gypsum and acid [kg], $m_{DH,A}$ and $m_{acid,A}$ the amount of ion A in gypsum and acid, respectively, and start indicating before the recrystallization reaction and end after the recrystallization reaction. The derivation of this equation is shown in Appendix 7.1. For a first indication of the affinity of gypsum for a certain impurity ion, the $K^*_{DH}$ was calculated with

$$K^*_{DH,A} = \frac{[A]_{DH,end}}{[A]_{acid,end}}$$  

7.4.

In case of an increasing concentration in the acid and thus a concentration gradient in the gypsum crystals, this calculated $K^*_{DH}$ will be an underestimation of the real one. However, it shows the difference in the affinity of gypsum for several impurities. A higher calculated $K^*_{DH}$ indicates a higher real $K_{DH}$ and thus a higher uptake of this impurity compared to an impurity with a lower calculated $K^*_{DH}$.

The ion exchange extraction of the impurity ion A is determined by a specific affinity of the resin for this ion and its concentration in the acid. This is described by

$$K_{IR,A} = \frac{[A]_{IR}}{[A]_{acid}}$$  

7.5,

with $K_{IR,A}$ the distribution A between the ion exchange resin and the acid at equilibrium. $K_{IR}$ depends on the attraction between the functional groups of a resin and an ion. In case of the sulfonic acid functional groups, the affinity for the lanthanides decreases from lanthanum to lutetium, because of a decrease in the charge density of the solvated ions, as is described in chapter 4. Contrary to the gypsum crystals, impurities extracted by the resin can be exchanged again with ions in the acid to reach a new equilibrium. So, a changing concentration in the acid will result in a changing concentration in the whole resin phase. At the end of a batch
recrystallization, the concentration in the resin is at equilibrium with the final concentration in the acid.

The difference between $K_{DH}$ and $K_{IR}$ will strongly influence the distribution of the available impurity ions between the gypsum surface and the ion exchange resin. If $K_{DH}$ is much larger than $K_{IR}$, most impurities will be incorporated in the crystals. However, if $K_{IR}$ is much larger than $K_{DH}$, most impurities will end up in the ion exchange resin. By calculating $K_{DH}$ out of concentrations in phosphoric acid and gypsum from the continuously operated industrial production process, and $K_{IR}$ after equilibrating ion exchange resin with clear acid, a simple prediction can be made on the extraction efficiency of an ion from the gypsum after a recrystallization with simultaneous ion exchange extraction. Figure 7.1 shows the calculation.

![Diagram](image)

**Figure 7.1.** Calculation to predict the influence of the recrystallization reaction on the extraction efficiency for impurity ions during a recrystallization from experimentally determined distribution coefficients, $K_{DH}$ and $K_{IR}$.

### 7.2.4 Kinetics

During the recrystallization reaction, impurity ions are released from the HH crystals and taken up by DH continuously. Therefore, kinetics will have an important influence on the extraction efficiency. To reach high extraction efficiencies, the ion
exchange extraction needs to be as fast as or faster than the uptake by the gypsum crystals. Otherwise, the impurities will already be incorporated, before they are extracted.

The rate determining step of the extraction of electrolytes by common ion exchange resin is particle diffusion (diffusion through the pores of the resin) [1]. Only in a few cases the ion exchange reaction or the film diffusion are rate determining. The particle diffusion depends strongly on the amount of crosslinking agent in the polymer, on the capacity of the ion exchanger, and on the temperature (about 4 to 8 % per °C [1]).

The particle diffusion coefficient of bivalent cations is $\frac{1}{10}$ to $\frac{1}{100}$ of the diffusion coefficient in water, and that of trivalent cations $\frac{1}{100}$ to $\frac{1}{1000}$ [1]. The influence of the degree of crosslinking is indicated with diffusion coefficients for yttrium, which decrease from $9 \times 10^{-12}$ m$^2$/s for 5% divinylbenzene (DVB) to $7 \times 10^{-14}$ m$^2$/s for 16% DVB at 25 °C [5]. The diffusion coefficient of lanthanum in an ion exchanger with 16% DVB equals that of yttrium [5,6]. It is assumed that this is also the case for the diffusion coefficient in an ion exchanger with 8% DVB, which would result in a coefficient of approximately $10^{-12}$ m$^2$/s [4]. The rate constant, $k$ [m/s], depends on the penetration depth, $\delta$ [m],

$$k = \frac{D}{\delta}$$

with $D$ the diffusion coefficient [m$^2$/s]. The maximum penetration depth possible is the radius of the resin beads. The Dowex C-500 ion exchange resin that was used for the research has an average diameter of 500 μm. Using the maximum penetration depth, the rate constant becomes $4 \times 10^{-9}$ m/s. This is the worst case scenario, because the penetration depth is probably smaller and the rate constant thus higher. For a penetration depth of 100 μm, the rate constant becomes $10^{-8}$ m/s. The rate constant increases with increasing temperature. Assuming an increase of 4% per °C, the rate constant of $4 \times 10^{-9}$ m/s increases to $10^{-8}$ m/s for operating temperatures of 65°C and 80°C (the temperatures, at which the batch recrystallizations were performed). In case of a penetration depth of 100 μm, the rate constant would become $3 \times 10^{-8}$ m/s at the operating temperatures.

The rate determining step of the recrystallization reaction is the growth rate of gypsum [3]. At higher temperatures the difference between the solubility of HH and gypsum is smaller. This results in a smaller supersaturation for gypsum, thus in a smaller driving force, and smaller growth rate, as is shown in chapter 1. The growth rate is also smaller in the presence of growth retarding impurities, like aluminum fluoride and the lanthanides. Growth rates of approximately $10^{-7}$ m/s were found [3].
However, changes in feedstock or temperature have a large influence on the growth rate.

It seems that the growth rate of gypsum is larger than the rate constant of ion exchange extraction. This will result in lower extraction efficiencies during the recrystallization than expected from distribution coefficients at equilibrium.

7.3 Experimental

7.3.1 Chemicals

The industrial phosphoric acid and HH were obtained either from a two-filter HemiDiHydrate (HDH) process or from a one-filter HemiReCrystallization (HRC) process. The phosphoric acid of the HDH process contains approximately 0.8 mol/kg \( \text{H}_3\text{PO}_4 \) and 0.5 mol/kg \( \text{H}_2\text{SO}_4 \). The process mainly uses Jordan ore, but some experiments were performed with phosphoric acid and HH from a test run with 50% Kovdor and 50% Jordan ore. The usage of Kovdor ore results in higher concentrations of most lanthanides in the HH and the phosphoric acid. A comparison of the ores was presented in table 7.1. Actual values may vary in time due to differences within the phosphate mines.

The phosphoric acid of the HRC process contains approximately 3.1 mol/kg \( \text{H}_3\text{PO}_4 \) and 0.2 mol/kg \( \text{H}_2\text{SO}_4 \). The process uses 65% Kovdor and 35% Jordan ore, resulting in a relatively high concentration of lanthanides in HH and phosphoric acid. Chemically pure gypsum was used as seed.

The Dowex C-500 ion exchange resin is a polymeric resin of polystyrene crosslinked with divinylbenzene. The sulfonic acid functional groups are strongly acidic (pK<1). The theoretical capacity equals 4.9 meq/g or 1.9 meq/ml. The spherical wet beads have a size of 465-635 \( \mu \text{m} \).

7.3.2 Procedure

To investigate the influence of acid composition, clear industrial phosphoric acid of both the HDH and HRC process was equilibrated with 0.04 g Dowex C-500 resin per g of acid at 70 °C in a shaking bath. The determined \( K_{IR} \) were used for the prediction of the extraction efficiency.

For the determination of \( K_{DH} \) used for the prediction of the extraction efficiency, industrial phosphoric acid and industrial gypsum were taken directly from the production sites and were analyzed.

The batch recrystallization experiments were started by heating the phosphoric acid. After the phosphoric acid reached the reaction temperature, 80 °C for HH and acid
from the two-filter process and 65 °C for HH and acid from the one-filter process, first Dowex C-500 ion exchange resin was added and subsequently HH. For recrystallizations with acid and HH from the two-filter process, also analytical pure gypsum seeds were added.

During the recrystallization, samples of the slurry were taken regularly. The resin and calcium sulfate solids were separated from the phosphoric acid by filtration and were washed twice with a hot saturated solution of chemically pure gypsum to remove the acid and subsequently twice with acetone to facilitate drying of the crystals. The calcium sulfate particles are approximately 100 μm, and are separated easily from the dry resin beads by sieving with a 300 μm sieve.

After completion of the recrystallization, the ion exchange resin was recovered from the slurry by sieving. To separate the resin beads, tap water was used to wash away the wet calcium sulfate solids. The resin was regenerated by contacting it in a stirred vessel with 55 g/L hydrochloric acid. It was assumed that all ions present on the resin were taken up by the hydrochloric acid solution.

**7.3.3 Analyses**

To analyze the impurity content in the calcium sulfate crystals, they were dissolved in a solution of aqua regia using a microwave digestion system.

The concentrations of the lanthanides were either determined by High Resolution Inductively Coupled Plasma - Mass Spectrometry (HR ICP-MS) or by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). The concentrations of Ca, SO₄, and PO₄ were determined by ICP-AES.

From the determined concentrations in the HCl stripping solution and the input amounts in HH and acid, the extraction efficiency of ion A, \( \eta_A \) [%], was calculated with

\[
\eta_A = \frac{[A]_{\text{HCl}} \cdot m_{\text{HCl}}}{[A]_{\text{HH}} \cdot m_{\text{HH}} + [A]_{\text{acid}} \cdot m_{\text{acid}} + [A]_{\text{DH}} \cdot m_{\text{DH}}} \cdot 100\%
\]

7.7,

in which HCl indicates the hydrochloric solution after contact with the resin, HH, acid, and DH refer to the input concentrations and amounts in these phases. The extraction efficiency can also be calculated from the concentration differences in the calcium sulfate phase and in the phosphoric acid.

The error in the extraction efficiency is calculated from the error in the amount of input, which is determined by standard deviation

\[
S_{\eta,A}^2 = \frac{n \sum (m_{\text{input},A} - \langle m_{\text{input},A} \rangle)^2}{n(n-1)}
\]

7.8,
with $m_{input,A}$ indicating the amount of ion A in the input, $s$ the error [kg], and n the number of analyses of the input amount [-]. The error in the amount in the stripping phase was also calculated with eq. 7.8. This resulted in the error of the extraction efficiency

$$\text{%error}_A = \frac{\text{error}_A}{\eta_A} \cdot 100\% = \sqrt{\left( \frac{s_{input,A}}{m_{input,A}} \right)^2 + \left( \frac{s_{HCLA}}{m_{HCLA}} \right)^2}$$ 7.9.

The degree of conversion during the recrystallization was determined by measuring the percentage of crystal water in the calcium sulfate phase. Calcium sulfate was heated in an oven at 400 °C to remove the water in the crystal. The fraction of gypsum was calculated from the weight difference by

$$\text{%DH} = \frac{(m_{before\ heating} - m_{after\ heating}) - 6.2}{20.9 - 6.2}$$ 7.10,

in which $m$ is the mass of the sample [kg], 6.2 the water content in pure HH (6.2 wt%), and 20.9 the water content of pure gypsum (20.9 wt%).

### 7.4 Results and Discussion

#### 7.4.1 Extraction efficiency

Figure 7.2 shows the maximally obtained extraction efficiencies by adding 200 g resin/kg total slurry for both the HRC process and the HDH process. The extraction efficiencies for the lanthanides are plotted against their ionic radii (coordination number 8) [7].

The results of europium, gadolinium, thulium, and lutetium were removed from the graph, because the error in extraction efficiency was larger than 15%, which is shown in table 7.5. The extraction efficiencies are higher for the HDH process for all lanthanides. The figure also shows different sequences of the extraction efficiency as a function of the ionic radius for the two production processes. This will be discussed further in paragraph 7.4.4.

#### 7.4.2 Influence of the composition of the phosphoric acid

The influence of the acidity on the extraction efficiency is illustrated by comparing the results of equilibrating industrial phosphoric acid from the two-filter process (0.8 M $H_3PO_4$ and 0.5 M $H_2SO_4$) with those of acid from the one-filter process (3.1 M $H_3PO_4$ and 0.2 M $H_2SO_4$) with the same amount of ion exchange resin. Figure 7.2 shows the extraction efficiencies at equilibrium.
Figure 7.2. The extraction efficiency for lanthanides from the slurry after a recrystallization with 200 g resin/kg slurry (HH and acid from the two-filter process from 100% Jordan ore) as a function of their ionic radii.

Figure 7.3. The extraction efficiency after equilibration of 40-50 g resin/kg acid in clear industrial phosphoric acid.

Although also other properties of the acids differ, it is thought that the lower extraction efficiency for the acid of the one-filter process is caused by the stronger acidity. During contact with acid from the one-filter process, the sulfonic acid functional groups will dissociate less due to the high acid concentration, 3.3 M. The dissociation will be higher when the resin is in contact with acid of the two-filter process, which has a acid concentration of 'only' 1.3 M. This is illustrated by the degree of occupation of the theoretically available active sites,
occupation degree = \frac{2 \cdot \text{mmoles of Ca extracted} + 3 \cdot \Sigma \text{mmoles of Ln extracted}}{4.9 \cdot m_{\text{IR}}}

7.11.

with Ln representing a specific lanthanide, 4.9 the theoretical concentration of active sites [meq/g], and \( m_{\text{resin}} \) the amount of resin added to the acid [g]. The mmoles of calcium are multiplied by 2, because 1 mmole of calcium equals 2 milli-equivalents. Only calcium and the lanthanides were taken into account for this calculation. The occupation degree of the resin is only 1.3% after contact with one-filter process acid, whereas it is 6.5% after contact with two-filter process acid. The degree of occupation is for both low, because of the excess amount of resin. However, it is still clear that the occupation degree is lower for acid of the one-filter process. This lower degree cannot be explained from lower concentrations of lanthanides and calcium in the acid, because these are comparable to those in the two-filter process acid.

A low extraction efficiency can be translated to a low \( K_{\text{IR}} \). Thus, \( K_{\text{IR}} \) is much lower for one-filter process acid than it is for two-filter process acid, as is shown in table 7.2 for some lanthanides.

\textbf{Table 7.2. The calculated distribution coefficients, } K_{\text{IR}} [-], \text{ after equilibration of 80-90 g resin/kg clear phosphoric acid.}

<table>
<thead>
<tr>
<th></th>
<th>two-filter process</th>
<th>one-filter process</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>41</td>
<td>7</td>
</tr>
<tr>
<td>Ce</td>
<td>33</td>
<td>5</td>
</tr>
<tr>
<td>Eu</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Dy</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>Er</td>
<td>13</td>
<td>2</td>
</tr>
</tbody>
</table>

A lower \( K_{\text{IR}} \) for clear phosphoric acid will, of course, also result in a lower extraction efficiency from the recrystallizing slurry. So, a lower extraction efficiency during recrystallization from both acid and calcium sulfate is expected for the one-filter process compared to the two-filter process. As figure 7.2 shows, this is also found experimentally.

It is concluded that due to the lower pH of the phosphoric acid of the one-filter process, the extraction efficiency is lower for this process than for the two-filter process.
7.4.3 Influence of the presence of other cations

Calcium ions, which are abundantly present in the phosphoric acid, are also extracted by sulfonic acid resins, as was already shown in chapter 4. The extraction efficiency of calcium during a recrystallization with simultaneous ion exchange extraction is compared with the extraction efficiencies of some lanthanides in table 7.3.

Table 7.3. Extraction efficiencies, $\eta$ [%], from the slurry after a recrystallization with 50 g resin/kg slurry (acid and HH from the two-filter process from 50% Jordan and 50% Kovdor ore).

<table>
<thead>
<tr>
<th></th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>14</td>
</tr>
<tr>
<td>Ce</td>
<td>10</td>
</tr>
<tr>
<td>Eu</td>
<td>16</td>
</tr>
<tr>
<td>Dy</td>
<td>21</td>
</tr>
<tr>
<td>Ca</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 7.3 shows that calcium ions are extracted significantly, but less than the lanthanides. Despite this, the extraction of calcium is thought to have a large influence on the extraction of other ions, like the lanthanides. Although only 3.2% of the input amount of calcium was extracted, 35% of the available active sites were occupied by calcium. Active sites that are occupied by calcium ions cannot be used for the extraction of impurity ions.

Table 7.4 shows the extraction efficiencies for several ions other than lanthanides after a recrystallization with simultaneous extraction for the one-filter process with 115 g resin/kg total slurry. Also the input amounts are presented, which indicate the amount of a specific ion on the resin when multiplied with the extraction efficiency. Table 7.5 shows the results for the lanthanides of the same experiment.
Table 7.4. The input amount, extraction efficiency, \( \eta \) [%], and error in extraction efficiency, error [%], for several ions after a recrystallization with 115 g resin/kg slurry (HH and acid from one-filter process).

<table>
<thead>
<tr>
<th></th>
<th>input amount [mg]</th>
<th>( \eta ) [%]</th>
<th>error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>643</td>
<td>3.7</td>
<td>9</td>
</tr>
<tr>
<td>Mg</td>
<td>4052</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>Al</td>
<td>233</td>
<td>1.6</td>
<td>12</td>
</tr>
<tr>
<td>Sc</td>
<td>2.04</td>
<td>2.0</td>
<td>7</td>
</tr>
<tr>
<td>Mn</td>
<td>123</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Co</td>
<td>1.19</td>
<td>19</td>
<td>9</td>
</tr>
<tr>
<td>Ni</td>
<td>4.86</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td>Cu</td>
<td>6.23</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>Zn</td>
<td>13.0</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Y</td>
<td>6.32</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>Cd</td>
<td>0.59</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Ba</td>
<td>7.79</td>
<td>4.5</td>
<td>4</td>
</tr>
<tr>
<td>Hg</td>
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<td>13</td>
<td>4</td>
</tr>
<tr>
<td>V</td>
<td>10.5</td>
<td>1.8</td>
<td>3</td>
</tr>
<tr>
<td>Cr</td>
<td>5.59</td>
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<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>571</td>
<td>0.7</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 7.4 shows that sodium, aluminum, scandium, barium, vanadium, chromium, and iron are not extracted significantly. The low extraction efficiencies for these ions have different causes. All ions except barium show a low affinity for the gypsum lattice, and remain mostly in the phosphoric acid. They are in principle easy accessible for the ion exchange resin. Still, they are not extracted. The low extraction of sodium is due to its univalent charge, resulting in a very low charge density of 0.86 \( e^2/\text{Å} \) for the non-solvated cation [7]. The charge densities of aluminum, scandium, vanadium, chromium, and iron are high, from 13.3 \( e^2/\text{Å} \) for aluminum to 10.2 \( e^2/\text{Å} \) for scandium (for comparison, the charge densities of the non-solvated lanthanides increase from 7.68 \( e^2/\text{Å} \) for lanthanum to 8.99 \( e^2/\text{Å} \) for lutetium). Due to the high charge density, the acidity of these ions is very high. Due to the high charge density, one may expect a very strong attraction between the ion exchange resin and the cations. However, according to Pearson's principle on hard and soft acids and bases, the hard cations prefer to form complexes with hard bases. Hard bases, like
fluoride and phosphate, are present in high concentrations in the industrial phosphoric acid and they will form strong complexes with the hard acids. The complexes between the hard acids and hard bases will be stronger than the complexes between the hard acids and the dissociated sulfonic acid groups of the resin, which are indicated as borderline bases by Pearson. The sulfonic acids will therefore not be able to replace the fluorides and phosphates and the hard cations will remain in solution as complexes with fluoride and phosphate. The formation of aluminum fluoride and phosphate complexes in industrial phosphoric acid is well known [3].

Table 7.5. The input amounts, extraction efficiency, η [%], and error in extraction efficiency, error [%], for the lanthanides after a recrystallization with 115 g resin/kg slurry (HH and acid from one-filter process).

<table>
<thead>
<tr>
<th>Input amount [mg]</th>
<th>η [%]</th>
<th>Error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>23.3</td>
<td>22</td>
</tr>
<tr>
<td>Ce</td>
<td>50.5</td>
<td>19</td>
</tr>
<tr>
<td>Pr</td>
<td>5.87</td>
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</tr>
<tr>
<td>Nd</td>
<td>22.1</td>
<td>19</td>
</tr>
<tr>
<td>Sm</td>
<td>3.34</td>
<td>17</td>
</tr>
<tr>
<td>Eu</td>
<td>1.03</td>
<td>16</td>
</tr>
<tr>
<td>Gd</td>
<td>13.0</td>
<td>28</td>
</tr>
<tr>
<td>Tb</td>
<td>0.45</td>
<td>18</td>
</tr>
<tr>
<td>Dy</td>
<td>1.91</td>
<td>17</td>
</tr>
<tr>
<td>Ho</td>
<td>0.27</td>
<td>16</td>
</tr>
<tr>
<td>Er</td>
<td>0.73</td>
<td>17</td>
</tr>
<tr>
<td>Tm</td>
<td>0.13</td>
<td>14</td>
</tr>
<tr>
<td>Yb</td>
<td>0.47</td>
<td>13</td>
</tr>
<tr>
<td>Lu</td>
<td>0.11</td>
<td>12</td>
</tr>
</tbody>
</table>

The charge densities of the lanthanides are lower than for the hard cations already discussed. So, complexes formed with hard bases, like fluorides and phosphates, will be less stable. From table 7.5, it becomes clear that the complexes in solution are not stable enough to avoid reaction with the sulfonic acid groups of the extractants. The charge density of the lanthanides also explains the extraction efficiency sequence of table 7.5. The charge densities of the lanthanides increase from lanthanum to
lutetium, resulting in an increase of stability of the lanthanide complexes with fluoride and phosphates in the solution. A stable complex makes bonding with the sulfonic acid functional groups of the resin difficult. So, the extraction efficiency increases with a decreasing stability of the complexes in solution and thus increases from lutetium to lanthanum.

The low extraction efficiency for barium, for which the ion exchange resin shows a high affinity if in solution, is probably caused by the fact that the barium sulfate present in the HH crystals does not dissolve. Hardly any barium is present in solution due to the low solubility and it can therefore not be extracted. Impurities that may be present in these barium sulfate particles, like radium, will also not dissolve in the acid during recrystallization and can also not be extracted.

The extraction efficiency for magnesium and the heavy metals manganese, cobalt, nickel, copper, zinc, mercury, and cadmium is comparable to that for the lanthanides. The sequence of extraction efficiency does not follow the sequence that was mentioned in § 7.2.2. This is due to the influence of the recrystallization reaction, especially the affinity of gypsum for the impurities, on the extraction efficiency. Also the strength of formed complexes in the solution will have its influence on the extraction efficiency. The influence of the uptake by gypsum will be illustrated in the next paragraph for the lanthanides.

So, elements like aluminum and iron, which are present in the acid in relatively high concentrations, do not influence the extraction of other impurities, because they are not extracted. Magnesium will have its influence, but this will be negligible compared to the influence of calcium. Although the extraction efficiency for calcium is lower than that for magnesium, its concentration in the acid is much higher and this results in a high degree of occupation of the resin by calcium. To gain higher extraction efficiencies for impurities like the lanthanides with the same amount of resin, a resin should be developed with a higher selectivity for the specific impurities with respect to calcium, but it should still be able to extract impurities at very low pH values.

7.4.4 Influence of the affinity of the newly formed gypsum

The affinity of gypsum for the lanthanides depends strongly on their ionic radii. This is illustrated in figure 7.4, in which the distribution coefficients, $K_{DH}$, are plotted as a function of the ionic radii of the lanthanides.
Praseodymium and neodymium are incorporated most in the gypsum, because their ionic radii approach that of calcium. The affinity of the gypsum decreases with an increasing deviation of the lanthanide ionic radius from that of calcium. Due to differences in process conditions, the incorporation of lanthanides in gypsum is lower for the HRC process than for the HDH process. This does not mean that the concentration of lanthanides in gypsum of the HRC process is lower. The HRC process uses more Kovdor ore and the concentration of lanthanides in the production process is therefore higher, resulting also in a higher concentration in the gypsum.

With $K_{DH}$ from figure 7.4 and $K_{IR}$ from table 7.6, a prediction of the total extraction efficiencies for the lanthanides during a recrystallization was made by the calculation presented in figure 7.1. The results for both the HRC and HDH process are presented in figure 7.5.

Table 7.6. The distribution coefficients, $K_{IR}$, after equilibrating clear phosphoric acid with 100 g resin/kg acid.

<table>
<thead>
<tr>
<th></th>
<th>one-filter process</th>
<th>two-filter process</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>8.5</td>
<td>38</td>
</tr>
<tr>
<td>Ce</td>
<td>6.4</td>
<td>34</td>
</tr>
<tr>
<td>Eu</td>
<td>1.5</td>
<td>20</td>
</tr>
<tr>
<td>Dy</td>
<td>1.6</td>
<td>17</td>
</tr>
<tr>
<td>Er</td>
<td>1.2</td>
<td>15</td>
</tr>
</tbody>
</table>
The predicted extraction efficiencies for all lanthanides are significantly lower for the one-filter process than they are for the two-filter process. This is due to the lower $K_{IR}$ values. Further, the predicted extraction efficiencies show a different sequence as a function of the ionic radii for the one-filter process than they do for the two-filter process. For the one-filter process, the predicted extraction efficiency sequence equals that from clear phosphoric acid, whereas the sequence for the two-filter process shows a dip for the extraction efficiency for lanthanides that are incorporated most readily in the gypsum crystals, as was shown in figure 7.4. The difference in the sequences between the one-filter and two-filter process is due to the lower $K_{DH}$ values.

So, from the prediction it is expected that the extraction sequence is not influenced by the recrystallization reaction for the one-filter process, whereas it is influenced strongly by the recrystallization for the two-filter process.

Figure 7.2 showed the experimental extraction efficiencies from the total slurry of recrystallizations from the one-filter and two-filter process with 200 g resin/kg total slurry. Comparison of figure 7.2 with figure 7.5 shows that the experimental behavior is similar to the predicted one. The overall extraction efficiency of all lanthanides is higher for the two-filter process than for the one-filter process, although the difference is not as large as predicted. The extraction efficiency for the one-filter process is much higher for the heavier lanthanides than predicted, whereas the extraction efficiency for cerium and europium for the two-filter process is lower than predicted.
7.4.5 Influence of kinetics

One of the kinetic effects is the increasing incorporation of impurities in gypsum with increasing supersaturation and thus increasing growth rate. The larger uptake of cerium by gypsum at higher supersaturations was described by De Vreugd et al [4]. The growth rate of gypsum increases with the addition of ion exchange resin. This is illustrated in figure 7.6 by plotting the gypsum content in the calcium sulfate phase as a function of the reaction time. A faster conversion indicates a higher gypsum growth rate, because this is the rate determining step during the recrystallization [3,4]. The figure shows that after 300 minutes only 70% of the calcium sulfate is DH without ion exchange extraction. With the addition of 50 g resin/kg slurry, already after 160 minutes 96% of the calcium sulfate was DH.

![Graph showing gypsum content as a function of reaction time with and without resin](image)

**Figure 7.6. The amount of gypsum in the calcium sulfate phase as a function of reaction time for a recrystallization without and with 50g ion exchange resin/kg slurry (HH and acid from the one-filter process).**

The increasing growth rate by adding ion exchange resin is due to the extraction of growth retarding elements, like the lanthanides, from the acid by the ion exchange resin. Due to the higher growth rate, it is expected that the uptake of impurities in the gypsum is higher during a recrystallization with simultaneous ion exchange extraction. This is also experimentally found, as is shown in figure 7.7.

The higher $K_{DH}$ for a recrystallization with ion exchange extraction indicates that the reduction in the lanthanide concentration is higher in the acid than it is in the gypsum crystals. Figure 7.8 shows the reduction of lanthanides in the acid and gypsum separately, which were already summarized in figure 7.2.
The increased $K_{DH}$ also results in a lower extraction efficiency than predicted from $K_{DH}$ determined from an ordinary recrystallization.

![Graph showing distribution coefficients, $K_{DH}$, after a recrystallization with and without 200 g resin/kg slurry (HH and acid from the two-filter process from 100% Jordan ore).](image)

**Figure 7.7:** The distribution coefficients, $K_{DH}$, after a recrystallization with and without 200 g resin/kg slurry (HH and acid from the two-filter process from 100% Jordan ore).

![Graph showing extraction efficiency in the acid and gypsum after a recrystallization with 200 g resin/kg slurry (HH and acid from the two-filter process from 100% Jordan ore).](image)

**Figure 7.8:** The reduction in the lanthanide concentration in the acid and gypsum after a recrystallization with 200 g resin/kg slurry (HH and acid from the two-filter process from 100% Jordan ore).

It is concluded that a high affinity of gypsum for an impurity ion, thus a high $K_{DH}$, results in a low extraction efficiency. In the experimentally determined $K_{DH}$ not only thermodynamics are included, but also kinetics. Due to the extraction of growth retarding elements, like the lanthanides, the growth rate increases for a
recrystallization with simultaneous extraction and therefore $K_{DH}$ increases. This results in a lower extraction efficiency from the gypsum than expected from predictions. For a high extraction efficiency of impurities that are readily taken up by the gypsum, it is important to keep the growth rate low.

7.5 Conclusions

The extraction efficiency for impurities, like the lanthanides, during the recrystallization of HH to gypsum with simultaneous ion exchange extraction is lower for the one-filter process than for the two-filter process. This is due to the higher acidity of the one-filter process acid.

Although, the ion exchange resin has a preference for lanthanides, it also has affinity for calcium ions, which are abundantly present in the phosphoric acid. To reach higher extraction efficiencies for the lanthanides with comparable amounts of ion exchange resin, a resin should be developed that is more selective for these ions and is still able to extract from very acidic media.

The ion exchange resin has to compete with the gypsum crystal with respect to the uptake of the impurity ions. Lanthanides that are taken up most readily by the gypsum are extracted least.

The extraction of lanthanides results in a decrease in the concentration of these gypsum growth retarding elements in the acid, and the recrystallization reaction becomes faster. Due to this, the incorporation of impurities, like lanthanides, increases. This results in a lower reduction in the lanthanide concentration in the gypsum than expected. For a high extraction efficiency of impurities that are readily taken up by the gypsum, it is important to keep the growth rate low.

References


Appendix 7.1

Determination of $K_{DH}$ after a Batch Recrystallization

As mentioned in paragraph 7.2.3, the concentration in the newly formed gypsum layer is determined by an affinity coefficient, the distribution coefficient $K_{DH}$, and the concentration in the acid.

$$[A]_{DH} = K_{DH,A} \cdot [A]_{acid} = K_{DH,A} \cdot \frac{m_{acid,A}}{m_{acid}} \quad A7.1.$$  

For component A, a mass balance can be written. The increase or decrease in the amount of A in the acid, $dm_{acid,A} \ [mg]$, is determined by the amount of release of A from HH and the amount of uptake by the gypsum. This is described by equation A7.2

$$d \ m_{acid,A} = [A]_{HH} \cdot d \ m_{HH} - K_{DH,A} \frac{m_{acid,A}}{m_{acid}} \cdot d \ m_{DH} \quad A7.2.$$  

It is assumed that the supersaturation remains constant during recrystallization. This is also the case until the end of the recrystallization. At the end, the supersaturation will decrease from the solubility of HH to that of gypsum. At constant supersaturation

$$d \ m_{HH} = \frac{172}{145} \ d \ m_{DH} \quad A7.3,$$

with 172 the molar mass of DH \ ([g/mol]) and 145 the molar mass of HH \ ([g/mol]). Substitution of A7.3 in A7.2 gives the following relation

$$d \ m_{acid,A} = \left(\frac{172}{145} [A]_{HH} - K_{DH,A} \frac{m_{acid,A}}{m_{acid}}\right) d \ m_{DH} \quad A7.4.$$  

It is assumed that the amount of acid remains constant, which is not really the case because the formation of gypsum requires some water from the acid. However, during recrystallization of 0.2 kg HH/kg acid the amount of acid only decreases with 3.5%.

Substitution of the constants

$$C = \frac{172}{145} [A]_{HH} \quad A7.5,$$

98
\[ D = -\frac{K_{DH,A}}{m_{acid}} \] \hfill A7.6,

Gives the following relation, which is easy to solve

\[ \frac{d m_{acid,A}}{C + D \cdot m_{acid,A}} = d m_{DH} \] \hfill A7.7.

The solution of this equation is

\[ m_{DH,end} - m_{DH,start} = m_{acid} \cdot \frac{\log \left[ \frac{172/145 [A]_{HH} - \left( \frac{K_{DH,A}}{m_{acid}} \right) \cdot m_{acid,A,start}}{172/145 [A]_{HH} - \left( \frac{K_{DH,A}}{m_{acid}} \right) \cdot m_{acid,A,end}} \right]}{K_{DH,A}} \] \hfill A7.8.
Chapter 8

Continuous Recrystallization with Simultaneous Extraction by Sulfonic Acids

For the two-filter HemiDiHydrate (HDH) phosphoric acid production process, extraction by 250 g ion exchange resin/kg phosphoric acid slurry during the continuously operated recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) resulted in a decrease of the lanthanide concentration from 44% for lanthanum via 28% for neodymium to 54% for ytterbium in DH. Due to ion exchange extraction of growth retarding elements, the growth rate increases significantly. During industrial recrystallization, large agglomerates of DH are formed due to slightly higher supersaturation caused by the growth retarding influence of aluminum fluoride. It seems that the extraction of aluminum reduces the supersaturation and prevents agglomeration of DH.

Using phosphoric acid and HH from the one-filter HemiReCrystallization (HRC) process, addition of the same amount of resin resulted in an extraction efficiency of 39% for lanthanum to 6.5% for lutetium. The needle shape of the crystals is not influenced by the extraction.
8.1 Introduction

In the industrial phosphoric acid production processes, the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) is performed continuously (see chapter 1), in contrast to the batch-wise recrystallizations that were described in chapter 7. This chapter describes the results obtained during recrystallization with simultaneous ion exchange extraction in continuous operation to investigate the extraction efficiencies that may be obtained in the industrial processes. Although the experimental set-up is much smaller than the industrial process, which contains 3 crystallizers of 1000 m³ each, the results from the experimental set-up are a good prediction of possible results in the industrial process. Recrystallization processes can be scaled up very well, because of the lack on requirements on mixing and heat transport, and the fact that the under- and supersaturations are relatively low.

Recrystallizations were performed with industrial HH and acid, from i) the one-filter HemiRecrystallization (HRC) process and from ii) the two-filter HemiDiHydrate (HDH) process. These processes were described in chapter 1. In these processes, the HH crystals formed during reaction of ore with sulfuric acid are recrystallized into DH to increase the efficiency of the production process by lowering the phosphate content of the crystals. In the one-filter process, the recrystallization is performed in the product acid, which contains 3.1 M H₃PO₄ and 0.2 M H₂SO₄, by solely lowering the temperature of the phosphoric acid slurry. In the two-filter process, HH is recrystallized in 'recrystallization acid', which contains 0.8 M H₃PO₄ and 0.5 M H₂SO₄. The difference in acid concentration results in difference in operating conditions, like the recrystallization temperature.

The particle shape is an important process parameter. It determines together with the particle size distribution the filterability or permeability and washability of the filter cake. In general, the filtration rate increases with increasing particle size and increasing regularity of the crystals [1] resulting in a high process efficiency.

In addition to the process conditions, various impurities in the solution can also have a large impact on particle shape. An example is aluminum fluoride, which adsorbs on to the \{011\} and \{1\,1\,1\} DH crystal faces blocking their growth [2,3,4]. This results in the formation of small agglomerated block shaped crystals. Another example is the lanthanides, which retard the growth of all crystal faces except the \{1\,1\,1\} face.

The impurities, like aluminum fluoride and the lanthanides, enter the production process with the feed stock. The two-filter process mainly uses 100% Jordan ore, whereas the one-filter process mainly uses a mixture of 65% Kovdor and 35%
Jordan ore. Table 8.1 shows the differences for some impurities between Jordan and Kovdor ore. Both processes have been optimized based on these ore compositions, which have their influence on impurity content and process operation, like the filtration of the filter cake.

Table 8.1. Comparison of Jordan and Kovdor ore with respect to some impurities.

<table>
<thead>
<tr>
<th></th>
<th>Jordan ore [mg/kg]</th>
<th>Kovdor ore [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>Hg</td>
<td>0.03</td>
<td>0.002</td>
</tr>
<tr>
<td>As</td>
<td>6</td>
<td>1.5</td>
</tr>
<tr>
<td>Co</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Mn</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>250</td>
<td>400</td>
</tr>
<tr>
<td>Al</td>
<td>3000</td>
<td>400</td>
</tr>
<tr>
<td>Mg</td>
<td>1800</td>
<td>12000</td>
</tr>
<tr>
<td>La</td>
<td>0.05</td>
<td>0.6</td>
</tr>
<tr>
<td>Ce</td>
<td>0.15</td>
<td>4</td>
</tr>
<tr>
<td>Nd</td>
<td>0.07</td>
<td>0.7</td>
</tr>
<tr>
<td>Y</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>ΣLn</td>
<td>260</td>
<td>1400</td>
</tr>
</tbody>
</table>

ΣLn=sum of all lanthanides

The differences between the two processes result in different particle shapes of DH. Figure 8.1 shows the agglomerated block shaped crystals formed in the two-filter process and figure 8.2 shows the needle shaped crystals that are formed in the one-filter process.

Chapter 7 showed that addition of ion exchange resin results in the removal of various impurities, like the lanthanides. These impurities have their influence on the growth rate, and also have an influence on the particle shape. Extraction of these impurities can therefore lead to changes in crystal shape and agglomeration behavior.

In addition to the gained extraction efficiencies during recrystallization with simultaneous ion exchange, this chapter will focus on the influence of extraction on the DH particle shape.
8.2 Particle Shape

Aluminum fluoride [2,3,4] and lanthanides [4,5] have a strong retarding effect on the growth of DH, which leads to changes in DH growth kinetics and therewith to changes in impurity uptake, crystal shape and agglomeration behavior.

8.2.1 Aluminum fluoride [2,3,4]

Phosphate ore, which consists mostly of fluoroapatite, always contains aluminum as impurity [6], but the content of commercial ore can vary widely, usually from 0.2 to 3% as Al₂O₃. During the reaction of phosphate ore with sulfuric acid, aluminum ions form strong complexes with the fluoride ions released from the ore:

\[ \text{Al}^{3+} \leftrightarrow \text{AlF}^2+ \leftrightarrow \text{AlF}_2^+ \leftrightarrow \text{AlF}_3 \leftrightarrow \text{AlF}_4^- \leftrightarrow \text{AlF}_5^{2-} \leftrightarrow \text{AlF}_6^{3-} \]

Which complex is present predominantly depends on the aluminum/fluoride ratio, the absolute concentrations of aluminum and fluoride, the solvent, and the presence of other ions, like silicium, which forms stronger complexes with fluoride than aluminum. By determining aluminum and fluoride concentrations in the DH crystals [4], it was found that AlF₅²⁻ is the most influential complex regarding DH growth.
The AlF$_5^{2-}$ ions retard the growth by substituting SO$_4^{2-}$ ions at the DH crystal surfaces. The AlF$_5^{2-}$ complexes adsorb mainly on the {011} and {111} DH crystal faces. Due to the selective retardation of these two faces, the length/width ratio of the crystal will decrease in the presence of aluminum fluoride. This is illustrated in figure 8.3.

Due to the growth retarding effect of aluminum fluoride, crystals with smaller average size are formed and supersaturation becomes higher. In a more supersaturated solution agglomerates are formed more easily by bridge formation between crystals if they collide [1].

So, the presence of aluminum fluoride promotes the formation of small agglomerated crystals, which have a hexagonal type shape (small length/width ratio), instead of large non-agglomerated needle shaped crystals, which are formed in the absence of aluminum fluoride.

In recrystallization processes, the supersaturation for the stable component is limited by the solubility of the less stable component, in this case the HH solubility.

![Figure 8.3. The dependence of the DH morphology on the amount of aluminum fluoride in the acid [4].](image)

### 8.2.2 Lanthanides [4,5]

The influence of lanthanides on the growth rate depends on the supersaturation. At high supersaturation, none of the lanthanides is able to hinder the growth significantly. At these high supersaturations, the growth proceeds so fast that
overgrowth of adsorbed impurity ions occurs more easily. This is confirmed by the increased uptake of impurities with increasing supersaturation.

The retardation of the lanthanides depends on the nature of the individual lanthanide ion. It was found that the retardation effect decreased in the order Ce$^{3+}$ = La$^{3+}$ = Eu$^{3+}$ > Er$^{3+}$. By 3-10$^{-4}$ M of the individual lanthanide ion, the growth was retarded with a factor 2 to 10 in a 0.1 M NaNO$_3$ solution.

The degree of retardation of the lanthanides depends on their ionic radius. Lanthanides with comparable ionic radii as the calcium ion (126 pm [7]), like cerium (128 pm), retard the DH growth most, whereas lanthanides with different ionic radii, like erbium (114 pm) have less effect.

The presence of lanthanides does not promote the formation of smaller and agglomerated crystals. This indicates that the retarding effect of the lanthanides is less than that of aluminum fluoride.

The presence of lanthanides itself, as was shown for cerium, does not have a large influence on the crystal morphology. At low supersaturation, the crystals seem to get more needlelike in the presence of cerium ions, and the $\{011\}$ faces seem to be more preferentially formed. So, the lanthanides retard the growth of all faces, except the $\{111\}$ face.

8.2.3 Particle shape differences

The differences in particle shape of the DH product between the two-filter and one-filter process, shown in figures 8.1 and 8.2, are related to differences in aluminum content in the feed ore. The two-filter process consuming Jordan ore with a high amount of aluminum (3000 mg/kg) gives small, block shaped agglomerated crystals. In the one-filter process consuming a mixture of 35% Jordan and 65% Kovdor ore (400 mg/kg Al), far less aluminum enters the process resulting in non-agglomerated needle shaped crystals.

In the one-filter process using Kovdor ore, the crystal growth may be influenced by the relatively high amount of lanthanides.

During batch recrystallization with simultaneous ion exchange extraction, lanthanides were extracted significantly, whereas aluminum was not extracted. Based on this, it is expected that addition of ion exchange resin will not prevent the formation of small agglomerated crystals in case of the two-filter process and large non-agglomerated needle shaped crystals in case of the one-filter process.
8.3 Experimental

8.3.1 Chemicals

For the experiments, phosphoric acid and HH were obtained from the one-filter HRC and the two-filter HDH processes. The acid from the one-filter process contains 3.1 mol/kg H₃PO₄ and 0.2 mol/kg H₂SO₄ and was obtained from a production run with 65% Kovdor ore and 35% Jordan ore. The acid from the two-filter process contains 0.8 mol/kg H₃PO₄ and 0.5 mol/kg H₂SO₄ and was obtained from a production run with 100% Jordan ore. A comparison of Kovdor and Jordan ore was shown in table 8.1. Table 8.2 shows the concentrations of some lanthanides in the acid and HH for both the one-filter and the two-filter process, as were measured before the performance of the continuous experiments.

*Table 8.2. The concentrations of some lanthanides in the acid and HH that were used for the continuous experiments.*

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Acid [mg/kg]</th>
<th>HH [mg/kg]</th>
<th>Acid [mg/kg]</th>
<th>HH [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>29</td>
<td>131</td>
<td>1.9</td>
<td>15</td>
</tr>
<tr>
<td>Ce</td>
<td>75</td>
<td>405</td>
<td>1.6</td>
<td>17</td>
</tr>
<tr>
<td>Pr</td>
<td>7.6</td>
<td>43</td>
<td>0.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Eu</td>
<td>1.8</td>
<td>8.8</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
<td>Dy</td>
<td>3.2</td>
<td>14</td>
<td>0.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Er</td>
<td>1.4</td>
<td>5.4</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Lu</td>
<td>0.2</td>
<td>0.5</td>
<td>0.09</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The ion exchange resin used for the experiments was Dowex C-500, which was also used during batch recrystallizations described in chapter 7. Dowex C-500 ion exchange resin is functionalized with 4.9 meq/g or 1.9 meq/ml sulfonic acid functional groups. The beads are perfectly spherical with sizes between 465-635 μm.

8.3.2 Experimental set-up

The experimental set-up contains 2 recrystallizers of 4.7 L each. The experimental set-up is schematically shown in figure 8.4.
The recrystallizers have a double wall, through which hot oil from thermostats is pumped. The temperature of the slurry in the recrystallizers is controlled by thermocouples that are connected to the thermostats. Due to this, constant temperature was obtained during the experiments, 78°C during experiments with acid and HH from the two-filter process and 45°C during experiments with acid and HH from the one-filter process.

In the recrystallizers, a draft tube baffle system is present. By using a draft tube in combination with a marine type propeller, classification in the recrystallizers is prevented.

Figure 8.4. A schematic representation of the experimental set-up for the performance of continuous recrystallization with simultaneous ion exchange extraction.

Before entering the first recrystallizer, the acid is preheated in a vessel that is also connected to a thermostat. The recrystallization rate increases with decreasing temperature, as was shown in chapter 1. Preheating of the acid avoids the rapid recrystallization of HH and also helps to keep the temperature in the first vessel constant.

The set-up contains 2 solid feeders to feed the HH and ion exchange resin to the first vessel. The slurry leaves the vessel by overflow. A chord baffle placed in front of the overflow prevents direct bypassing from the feed to the outlet.

8.3.3 Procedure

The residence time of the continuous recrystallization is determined from the conversion rate during batch recrystallization. To be able to extract as many lanthanides as possible, complete conversion is required to get access to all lanthanides. The extraction efficiency is also influenced by the conversion rate,
which should be low to extract as many lanthanides as possible before they are incorporated into the DH crystals. Low conversion rates are obtained by recrystallizing at high temperatures. The low conversion rate results in high residence times.

Taking the same operating conditions, the conversion rate during batch recrystallization increases when adding ion exchange resin, as was proven in chapter 7. Smaller residence times are needed to gain the same degree of conversion. Table 8.3 shows the feed rates and residence time during the experiments.

**Table 8.3. Feed rates during continuous recrystallization with and without simultaneous extraction.**

<table>
<thead>
<tr>
<th></th>
<th>With resin</th>
<th>Without resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time [h]</td>
<td>3.15</td>
<td>6.06</td>
</tr>
<tr>
<td>Feed rates [kg/h]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>2.08</td>
<td>1.31</td>
</tr>
<tr>
<td>HH</td>
<td>0.6</td>
<td>0.33</td>
</tr>
<tr>
<td>Resin</td>
<td>0.69</td>
<td>-</td>
</tr>
</tbody>
</table>

Before feeding is started, the vessels are filled with phosphoric acid and HH, which is converted to DH in one residence time. In this way, the experiment is started with compositions representative to the expected steady state situation.

During the experiments, samples are taken regularly. The acid is filtered from the solids by vacuum filtration. Subsequently, the solids are washed twice with a saturated solution of analytically pure DH in ultrapure water to remove phosphoric acid and additionally twice with acetone to facilitate drying and prevent further recrystallization. If ion exchange resin is present in the solid sample, it is separated from the calcium sulfate sample by sieving.

### 8.3.4 Analyses

**Crystal shape**

With Scanning Electron Microscopy (SEM), pictures of the HH feed and the calcium sulfate product are made.

**Degree of conversion**

The degree of conversion is determined by measuring the amount of crystal water in the dried calcium sulfate samples. This is done by first weighing a sample, after
which it is calcined at least 12 hours. With the weight difference before and after calcining, which represents the amount of crystal water, the degree of conversion can be indicated by the relative amount of DH in the sample,

\[
\%DH = \frac{(m_{\text{before}} - m_{\text{after}}) \cdot 100\%}{m_{\text{before}} - 20.9 - 6.2} \cdot 100\%
\]  \hspace{1cm} 8.1,

with \( m \) the mass of the calcium sulfate sample before and after calcining, 6.2 the water content of pure HH, and 20.9 the water content of pure DH.

**Impurity content and extraction efficiency determination**

The concentrations of impurities in acid and calcium sulfate are determined by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS). Before ICP-MS analysis, the calcium sulfate samples are digested in aqua regia by microwave digestion. From the feed flow of impurity A, \( \varphi_{\text{feed},A} \) [mg/h], and product flow of A, \( \varphi_{\text{product},A} \) [mg/h], an extraction efficiency, \( \eta_A \) [\%], can be calculated with

\[
\eta_A = \frac{\varphi_{\text{feed},A} - \varphi_{\text{product},A}}{\varphi_{\text{feed},A}} \cdot 100\%
\]  \hspace{1cm} 8.2.

Feed and product flow of A [mg/h] are calculated with

\[
\varphi_{\text{feed},A} = \varphi_{M,HH} \cdot [A]_{HH} + \varphi_{M,\text{feedacid}} \cdot [A]_{\text{feedacid}}
\]  \hspace{1cm} 8.3,

\[
\varphi_{\text{product},A} = \varphi_{M,\text{CaSO}_4} \cdot [A]_{\text{CaSO}_4} + \varphi_{M,\text{productacid}} \cdot [A]_{\text{productacid}}
\]  \hspace{1cm} 8.4,

with \( \varphi_M \) the mass flow [kg/h] (see table 8.3 for the mass flow of HH and feed acid), [A] the concentration of A [mg/kg], feedacid indicating the acid entering the vessels, and productacid the acid from the outlet of the second vessel, and CaSO4 indicating the calcium sulfate from the outlet.

**8.4 Results and Discussion**

In this paper, the terms "incorporation" and "uptake" are solely used for the uptake of impurities by the DH crystals, whereas "extraction" is used for the extraction by the ion exchange resin.

**8.4.1 The two-filter HDH process**

HH was successfully recrystallized to DH. About 95-98% of the calcium sulfate leaving the recrystallizers was DH.
Figure 8.5 shows the extraction efficiency for some lanthanides after recrystallization with simultaneous ion exchange extraction with 250 g resin/kg phosphoric acid slurry. The extraction efficiency decreases from lanthanum to neodymium and then increases again. The same behavior of the extraction efficiency was found during batch recrystallizations described in chapter 7 and is the result of competition between the DH crystals and the ion exchange resin. Lanthanides with a comparable ionic radius to calcium (126 pm [7]), like neodymium (125 pm [7]), are taken up most readily by DH and are therefore extracted least. The affinity of DH to take up the lanthanides decreases with an increasing deviation of their ionic radius from that of calcium. With a large deviation from the calcium radius, lanthanides possess lower incorporation ability making them more available for extraction. This is described more extensively in chapter 7.

![Graph showing extraction efficiency across lanthanide elements](image)

**Figure 8.5.** *Extraction efficiencies during continuous recrystallization (two-filter process) with 250 g ion exchange resin/kg phosphoric acid slurry after 2 residence times.*

Figure 8.6 shows the concentration of lanthanum in the acid and the DH at the outlet of the second vessel after the recrystallization with and without extraction as a function of the run time. The other lanthanides show similar behavior. The concentration of lanthanum decreases sharply in both the acid and the calcium sulfate phase when adding ion exchange resin, which is the result of the extraction of lanthanum by the resin. Without ion exchange resin, the concentration lanthanum in the acid first decreases a little, but this is the result from a redistribution of lanthanum, because the concentration in the calcium sulfate first increases. Although steady state was not reached for the recrystallization without ion exchange resin, which is indicated by the still changing concentrations of lanthanum in acid and
calcium sulfate, the results give a good indication of the effect of the addition of ion exchange resin on the lanthanum concentration.

![Graph](image)

**Figure 8.6.** The concentration of lanthanum in calcium sulfate and acid as a function of the runtime of continuous recrystallization (two-filter process) with and without 250 g ion exchange resin/kg phosphoric acid slurry.

Figure 8.7 shows the crystals after recrystallization with ion exchange extraction and figure 8.8 shows the product without ion exchange extraction. The sample of figure 8.7 was taken after 3 residence times, whereas the sample of figure 8.8 was taken after 2 residence times.

The crystals formed with ion exchange extraction (figure 8.7) are larger than those formed without ion exchange extraction (figure 8.8). Furthermore, crystals formed in the presence of ion exchange resin show less tendency to agglomerate than crystals in the absence of ion exchange resin.

The crystals formed with ion exchange resin are larger despite the shorter residence time, which indicates that the growth rate increased significantly. This results from a decreasing growth retardation, due to the extraction of retarding ions, like the lanthanides, aluminum fluoride, or both.

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Figure 8.7. DH crystals formed during continuous recrystallization with 250 g resin/kg phosphoric acid slurry after 3 residence times (two-filter process).

Figure 8.8. DH crystals from continuous recrystallization (two-filter process) without the addition of resin after 2 residence times.

The absence of agglomerates after recrystallization with ion exchange extraction implicates that the supersaturation is lower than that during industrial recrystallization and than that during the recrystallization performed without resin. This implicates that aluminum is extracted. ICP-MS analysis of aluminum shows that this is actually the case. Without resin, the aluminum concentration increases from 5 g/kg to 7 g/kg in the solution, whereas with resin the concentration aluminum in the solution slightly decreases to 4 g/kg. In both cases, the aluminum content of the crystals decreases from 3 g/kg to 0.3 g/kg. And although it is difficult to determine from these pictures, it seems that the length/width ratio is larger for the crystals of figure 8.7, also indicating a lower aluminum fluoride concentration in the acid.

So, in contrast with the results of batch recrystallizations with simultaneous ion exchange, some aluminum seems to be extracted during continuous operation. It is not clear yet, why aluminum is extracted. Aluminum forms strong complexes with fluoride ions, because of its high charge density, as was mentioned in chapter 7. The stronger interaction between aluminum and fluoride than that between aluminum and the functional groups of the ion exchange resin was thought to be the reason for
the fact that aluminum was not extracted. However, now it seems possible to extract either aluminum or positive aluminum fluoride complexes, influencing also the concentration of $\text{AlF}_3^{2-}$.

8.4.2 The one-filter HRC process

The conversion of HH to DH was successful for the one-filter process. The product contained 90-93% DH after recrystallization without resin and 93-98% DH after recrystallization with ion exchange resin.

By adding 250 g resin/kg phosphoric acid slurry, lanthanides were extracted. This is illustrated in figure 8.9, in which the extraction efficiencies for the lanthanides are plotted as a function of their ionic radius [7]. In the one-filter process, the extraction efficiency decreases from lanthanum to lutetium, whereas it shows a minimum for neodymium in the two-filter process. This difference in extraction efficiency sequence between the one-filter and two-filter process was also found for batch recrystallization, as was described in chapter 7. From distribution coefficients of lanthanides between DH and phosphoric acid, it was found that the interaction between lanthanides and DH is not as strong in the one-filter process as it is in the two-filter process. The distribution coefficients were presented in chapter 7. Therefore, the ion exchange resin has to compete less with the DH to extract the lanthanides and the efficiency is no longer influenced by the uptake by DH in the one-filter process. The extraction sequence equals that from clear phosphoric acid, which decreases from lanthanum to lutetium due to a decreasing charge density of the hydrated ions. This was discussed in chapter 7.

Comparison of figure 8.9 with figure 8.8 shows that the extraction efficiencies are all lower in the one-filter process than in the two-filter process. As was already discussed in chapter 7 for the extraction from clear phosphoric acid, this is due to the higher acid concentration in the one-filter process than in the two-filter process. Due to this, the resin is dissociated less in the one-filter process, and does not extract as many impurities as in the two-filter process.

Figure 8.10 shows the extraction efficiency of lanthanum as a function of the runtime of the continuous recrystallization. During the first 2 residence times, the extraction efficiency is still decreasing, indicating that steady state has not been reached. Probably, the extraction efficiency remains slightly under 40%.
Using phosphoric acid and HH from the one-filter HRC process, addition of the same amount of resin resulted in an extraction efficiency of 39% for lanthanum to 6.5% for lutetium. The needle shape of the crystals is not influenced by the extraction.

Acknowledgement

Ninke Hiemstra and Sahar Mhiyo are acknowledged for their work on continuous recrystallization. Joop ter Horst is acknowledged for the discussions on the experimental results.

References


Chapter 9

Simulation of the Recrystallization and Impurity Uptake with Simultaneous Extraction

For the simulation of the recrystallization the computer program Crystals was used. This program is developed to simulate (re)crystallization processes dynamically, like the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) in the phosphoric acid process. Equations describing the distribution of impurities between solution and crystals, and equations describing extraction were included in the program. This makes it possible to simulate (re)crystallization with simultaneously removal of impurities by ion exchange extraction or solvent extraction.

A semi-quantitative simulation of the recrystallization indicates that the conversion of HH to DH is more efficient in 3 smaller tanks with a recycle loop from the 3rd to the 1st tank than in 1 tank with a large residence time. The introduction of the recycle loop also increases the stability of the recrystallization process. Simulations of the recrystallization with simultaneous ion exchange extraction indicate that the extraction efficiency of impurity ions increases with increasing amount of resin, decreasing growth rate of DH, a more open structure of the resin (higher rate constants), higher affinity for the impurity ion, and smaller resin beads. The extraction efficiency would also be higher when applied in a less acidic solution than the industrial phosphoric acid.
9.1 Introduction

This chapter describes the dynamic simulation of the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum) in the HemiDiHydrate (HDH) phosphoric acid production processes with and without simultaneous ion exchange extraction of lanthanum. The recrystallization step is described in detail in chapter 1. During the recrystallization, HH crystals dissolve and simultaneously DH crystals are formed and grow. Impurities enter the recrystallization section with the phosphoric acid and the HH solids. These impurities are redistributed between the acid and the newly formed DH crystals according to a distribution coefficient, which is determined by thermodynamics and kinetics. By introducing an ion exchange resin during the recrystallization, impurities may be taken up by the resin, preventing the uptake of these impurities in the newly formed DH crystals. The extraction also depends on thermodynamics and kinetics, which can be described by an affinity coefficient (thermodynamics) and a rate constant (kinetics).

For the simulation of the recrystallization and the distribution of the impurities, a computer program, Crystals [1], was used. This program is developed to dynamically simulate (re)crysstallization processes, like the recrystallization step in the phosphoric acid process, the crystallization of sodium chloride, the (re)crysstallization of calcium phosphate, etc. By combining mass balances and kinetic parameters, like nucleation, growth, and dissolution, with population balance equations, time dependent processes like the start-up of continuous processes and batch processes can be simulated. Also the optimum response to disturbances can be simulated to improve the process control.

In chapters 7 and 8, it was shown that impurity ions, like the lanthanides, could be extracted from the phosphoric acid by commercial ion exchange resin resulting in lower impurity concentrations in the acid product and DH by-product. A reduction of, for example, 48% of the concentration lanthanum in the slurry was gained due to the addition of 0.1 kg resin/kg slurry during batch recrystallization. To get a better insight in the parameters influencing the extraction efficiency, equations describing the extraction process are included in the Crystals program. By simulating the recrystallization with simultaneous extraction, the properties influencing the extraction most can be tracked down. Improvement of these properties may in future result in higher extraction efficiencies during a recrystallization step.

9.2 Simulation by Crystal

Crystals can simulate crystallization and recrystallization processes. The aim of Crystals is not to give a state of the art description of crystallization processes, but a
simple model, which describes the (re)crystallization. Equations can be adjusted when more specific knowledge of a crystallization process is available, like a description of attrition, which is not included here. The relations used for the simulation of the recrystallization of HH to DH in phosphoric acid are described here.

9.2.1 Recrystallization

The recrystallization is described by mass balances, kinetic parameters (nucleation, growth, dissolution), and population balances.

Mass balances

The mass balance for calcium is:

\[
\frac{d \text{Ca}_1}{dt} + \frac{d \text{Ca}_3}{dt} \cdot \varphi_{\text{in}} + \varphi_{\text{out}} = 0 \tag{9.1}
\]

with \( \text{Ca}_1 \) the amount of calcium in the solvent [mol/m\(^3\)], \( \text{Ca}_3 \) the amount of calcium in the solid phase per volume of solvent [mol/m\(^3\)], \( \varphi_{\text{in}} \) the flux of calcium into the crystallizer [mol·m\(^{-3}\)·s\(^{-1}\)], and \( \varphi_{\text{out}} \) the flux of calcium leaving the crystallizer [mol·m\(^{-3}\)·s\(^{-1}\)].

For sulfate a similar mass balance can be set up.

For batch recrystallization, the fluxes into and out of the crystallizer equal 0.

Kinetics

The rate of recrystallization depends on the dissolution rate of HH or growth rate of DH as well as on the total surface area of the HH or DH crystals. The dissolution rate of HH, \( D \) [m/s], and growth rate of DH, \( G \) [m/s], are described by the semi-empirical expressions

\[
D = -k_D \cdot \sigma_{\text{HH}}^d \tag{9.2}
\]

\[
G = k_G \cdot \sigma_{\text{DH}}^g \tag{9.3}
\]

with \( \sigma \) the underor supersaturation [-], \( k_D \) the dissolution rate constant [m/s] and \( k_G \) the growth rate constant [m/s]. The power \( d \) is usually 1 and \( g \) lies in general between 1 and 2 [2,3,4]. Since supersaturation is mostly low during recrystallization, it seems justified to take a value of 2 for \( g \) (spiral growth) [2,3,4].
The undersaturation or supersaturation represent the driving force of the crystallization reaction. Thermodynamically, the driving force, i.e., the difference in chemical potential $\Delta \mu$, is given by

$$\Delta \mu = \mu_1 - \mu_s = RT \ln \left( \frac{a}{a_{eq}} \right) = RT \ln \left( \frac{\gamma^+ \gamma^-}{(\gamma^+ \gamma^-)_{eq}} \cdot \frac{[\text{Ca}][\text{SO}_4^2^-]}{([\text{Ca}][\text{SO}_4^2^-])_{eq}} \right)^{\frac{1}{2}}$$

9.4,

with $a$ the activity [mol/L], $\gamma$ the activity coefficient [-], $c$ the concentration [mol/L], $T$ the temperature [K], and $R$ the gas constant [J·mol⁻¹·K⁻¹], $s$ referring to the solid phase, $l$ to the liquid, and $eq$ to the equilibrium condition. For relative low supersaturation (or undersaturation), like during recrystallization, $\Delta \mu$ can be simplified to

$$\Delta \mu = RT \ln \left( \frac{[\text{Ca}][\text{SO}_4^2^-]}{([\text{Ca}][\text{SO}_4^2^-])_{eq}} \right)^{\frac{1}{2}} = RT \ln \left( \frac{[\text{Ca}][\text{SO}_4^2^-]}{([\text{Ca}][\text{SO}_4^2^-])_{eq}} - 1 \right) = RT \sigma$$

9.5.

where the undersaturation of HH, $\sigma_{HH}$ [-], and the supersaturation for DH, $\sigma_{DH}$ [-], is given by

$$\sigma_{HH} = \sqrt{\frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{([\text{Ca}^{2+}][\text{SO}_4^{2-}])_{eq,HH}}} - 1$$

9.6,

$$\sigma_{DH} = \sqrt{\frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{([\text{Ca}^{2+}][\text{SO}_4^{2-}])_{eq,DH}}} - 1$$

9.7.

in which $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ are the concentrations of calcium and sulfate in the phosphoric acid [mol/m³].

For a seeded batch recrystallization, the development of new crystals will merely occur by secondary nucleation rather than by primary nucleation. The secondary nucleation, $B$ [#·m⁻³·s⁻¹], is approximated by a power law

$$B = k_B \cdot \sigma_{DH}^k \cdot M$$

9.8,

with $k_B$ the secondary nucleation rate constant [#·m⁻³·s⁻¹], $M$ the total mass of crystals per m³ solvent [kg/m³]. The power $k$ usually has a value between 0 and 3. In the simulations $k$ was taken 3.

Heterogeneous primary nucleation, $J$ [#·m⁻³·s⁻¹], may also occur, although the supersaturation during recrystallization is low. Primary nucleation can be described with
with \( k_1 \) the primary nucleation rate constant [\( \# \cdot m^{-3} \cdot s^{-1} \)]. The power \( k \) is usually assumed to be 3 or higher. For the simulations, heterogeneous primary nucleation was ignored.

Agglomeration, which may occur dependent on the phosphoric acid production process (see chapter 8), has not been taken into account in the model.

**Population balances**

The crystalline product can be described by the shape factors and the CSD. To characterize the form of the product, two form factors, \( k_v \) and \( k_a \) [-], are defined

\[
V = k_v \cdot L^3 \quad 9.10,
\]

\[
A = k_a \cdot L^2 \quad 9.11,
\]

with \( V \) the volume of the crystal [\( m^3 \)], \( A \) the area [\( m^2 \)], and \( L \) the characteristic length [\( m \)]. For example, for cubic and spherical crystals \( k_v \) equals 1 and \( k_a \) is 6. These values were also used for the simulations of the recrystallization.

The CSD is described by a population density function, \( n(L) \) [\( \#/m^4 \)]. For the simulation, the total size range is divided into a number of size intervals, \( i \), with a size \( \Delta L \) [\( m \)]. During the simulation, the number of crystals, \( N(i) \) [\( \# \)], in the size interval \( i \) changes in a simulated time interval, \( \Delta t \) [\( s \)], with

\[
\Delta N(i) = g(i-1) - g(i) + \varphi_{in}(i) - \varphi_{out}(i) \quad 9.12,
\]

in which \( g(i-1) \) is the number of crystals that enter interval \( i \) from interval \( i-1 \) due to growth, \( g(i) \) the number of crystals that leave interval \( i \) due to growth, \( \varphi_{in}(i) \) the number of crystals in interval \( i \) that enter the crystallizer with the feed, and \( \varphi_{out}(i) \) the number of crystals in interval \( i \) that leave the crystallizer. For the interval \( i=0 \), the term \( g(i-1) \) is replaced by the secondary nucleation term \( B \). The \( g \) and \( \varphi \) terms are calculated with

\[
g(i-1) = N(i-1) \cdot G \cdot \frac{\Delta t}{\Delta L} \quad 9.13,
\]

\[
g(i) = N(i) \cdot G \cdot \frac{\Delta t}{\Delta L} \quad 9.14,
\]

\[
\varphi_{out}(i) = N(i) \cdot \frac{\Delta t}{\tau} \quad 9.15,
\]
with $\tau$ the residence time of the continuously operated crystallizer [s]. The flux into the crystallizer, $\varphi_{\text{in}}(t)$, depends on the feed composition, flow and CSD. The simulation time interval, $\Delta t$, should be chosen such that

$$G \cdot \Delta t << \Delta L$$

9.16.

9.2.2 Uptake of impurities in the crystals

The differential uptake of the impurity by the newly formed DH crystals is determined by the concentration of the impurity in the solvent and by a distribution coefficient $K_{\text{DH}}$ [-],

$$\frac{\Delta I_{\text{DH}}}{\Delta D} = K_{\text{DH,}\text{I}} \cdot [I]_I$$

9.17,

with $\Delta I_{\text{DH}}$ the amount of impurity ion I [mol] taken up by a newly formed DH layer, $\Delta D$ the amount of DH [m$^3$] formed in the simulation time $\Delta t$, and $[I]_I$ the concentration of I in the solvent [mol/m$^3$]. The distribution coefficient is assumed to be constant. Both kinetic and thermodynamic effects on the uptake should be included in the distribution coefficient.

The change in the concentration of impurity ion I in the solvent is determined by the concentration in HH, the dissolution rate of HH, the incorporation in the newly formed DH, and the flux into and out of the crystallizer

$$\frac{\Delta [I]_I}{\Delta t} = \varphi_{\text{I,in}} - \varphi_{\text{I,out}} + \frac{D}{[I]_{HH}} \cdot A_{\text{HH}} - K_{\text{DH,}\text{I}} \cdot [I]_I \cdot G \cdot A_{\text{DH}}$$

9.18,

in which $\varphi_{\text{I,in}}$ represents the amount of I entering the crystallizer with the solvent [mol/m$^3$].

Only isomorphous substitution of cations or anions can be simulated with Crystals. Precipitation or crystallization of the impurity ion is not accounted for and also the formation of inclusions is not taken into account.

9.2.3 Ion exchange extraction

For recrystallization with simultaneous ion exchange extraction, the impurity ion is not only incorporated in the newly formed gypsum, but also extracted by the ion exchange resin. The amount of an impurity ion on the resin depends on various factors; a thermodynamic equilibrium constant (affinity coefficient), diffusion rates in the film layer or in the resin particle, the concentration in the solution, the concentration of other ions in the solution (also that of protons) and the maximum capacity of the ion exchange resin.
The resin strives for equilibrium with the surrounding solution at all times. At equilibrium, the concentration on the resin depends on the concentration in the solution and on an affinity coefficient, $K_{IR}$ [-],

$$[I]_{IR,eq} = K_{IR,I} \cdot [I]_{l,eq}$$  \hspace{1cm} \text{(9.19)}

During recrystallization, ions dissolve from the HH crystals and are also incorporated in the DH crystals. Due to this, the concentration in the solution changes constantly. Therefore, also the concentration on the resin changes constantly. To be able to simulate the formation of a new equilibrium, ions are released from the ion exchange resin first. The amount of ions leaving the ion exchange resin depends on the simulated time interval and the rate constant of the ion in the ion exchange resin beads, $k_{kin}$ [m/s],

$$\Delta l_{IR} = \Delta t \cdot k_{kin,I} \cdot [I]_{IR} \cdot IR \cdot \frac{A}{V}$$  \hspace{1cm} \text{(9.20)}

with $IR$ the amount of ion exchange resin [kg] and $A/V$ the surface area per volume of ion exchange resin. With a similar equation also an amount of protons leaving the ion exchange resin is calculated. Due to that, free capacity is created to take up ions from the solution again in a next step. Before simulating the uptake by the resin, an uptake factor, $F$ [-], is calculated

$$F = \frac{C_{\text{free}}}{\Delta t \cdot \frac{A}{V} \cdot \frac{1}{k_{kin,I} \cdot K_{IR,I} \cdot [I]_{l} \cdot n}}$$  \hspace{1cm} \text{(9.21)}

with $C_{\text{free}}$ the free capacity [eq/kg] and $n$ the charge of ion $I$ [-]. Due to the uptake factor, the maximum capacity of the resin can not be exceeded. With the uptake factor, the uptake of the ions by the free capacity can be calculated with

$$\Delta l_{IR,in} = F \cdot \Delta t \cdot \frac{A}{V} \cdot [I]_{l} \cdot IR \cdot k_{kin,I} \cdot K_{IR,I} \cdot M_{I}$$  \hspace{1cm} \text{(9.22)}

with $M_{I}$ the molar mass of ion $I$ [kg/mol].

### 9.4 Results and Discussion

Before simulating the recrystallization of HH to DH with simultaneous ion exchange extraction, simulations with Crystals of the recrystallization are presented in paragraph 9.4.1 for different kinetic parameters. In paragraph 9.4.2, an impurity ion is introduced. These paragraphs will give an insight in the behavior of recrystallization processes and the distribution of impurity ions.
In paragraph 9.4.3, an example is given on the applicability of Crystals on gaining a better understanding of the industrial recrystallization of HH to DH. The effect of the introduction of a growth retarder to an industrial recrystallization section with 3 crystallizers in series is shown.

In paragraph 9.4.4, batch recrystallization with simultaneous ion exchange extraction is simulated to give a better insight into the parameters that influence the extraction efficiency most.

In paragraph 9.4.5, a continuous recrystallization with simultaneous ion exchange extraction is simulated, as may be performed in the industrial production process.

### 9.4.1 Batch recrystallization

Table 9.1 shows the initial composition of the phosphoric acid. The values are based on the experiments performed on laboratory scale. The experimental results were described in chapter 7. The composition of the solution agrees with that of industrial acid in the recrystallization section. The initial CSD used for all simulations is shown in table 9.2. This CSD was not determined during the laboratory experiments, but the average of 100 μm agrees with the average size of the industrial HH crystals. Table 9.3 shows the values of parameters that were varied in the simulations. These values are based on values found in earlier research [2,3,4].

**Table 9.1. The initial composition of the phosphoric acid slurry in the batch crystallizer used in the simulations.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass fraction DH in reactor [-]</td>
<td>0.05</td>
</tr>
<tr>
<td>mass fraction HH in reactor [-]</td>
<td>0.15</td>
</tr>
<tr>
<td>mass fraction PO₄³⁻ in solution [-]</td>
<td>0.32</td>
</tr>
<tr>
<td>mass fraction SO₄²⁻ in solution [-]</td>
<td>0.05</td>
</tr>
<tr>
<td>mass fraction Ca²⁺ in solution [-]</td>
<td>0.0015</td>
</tr>
<tr>
<td>solubility DH [mol/L]</td>
<td>0.113</td>
</tr>
<tr>
<td>solubility HH [mol/L]</td>
<td>0.136</td>
</tr>
</tbody>
</table>
Table 9.2. The initial CSD used for all simulations.

<table>
<thead>
<tr>
<th>Length [µm]</th>
<th>Number fraction [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.05</td>
</tr>
<tr>
<td>90</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>0.8</td>
</tr>
<tr>
<td>110</td>
<td>0.05</td>
</tr>
<tr>
<td>120</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 9.3. Values of parameters that were varied for different simulations of the recrystallization of HH to DH.

<table>
<thead>
<tr>
<th></th>
<th>SIM1</th>
<th>SIM2</th>
<th>SIM3</th>
<th>SIM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_G [m/s]</td>
<td>10^{-6}</td>
<td>10^{-6}</td>
<td>10^{-7}</td>
<td>10^{-7}</td>
</tr>
<tr>
<td>k_D [m/s]</td>
<td>10^{-6}</td>
<td>10^{-7}</td>
<td>10^{-6}</td>
<td>10^{-6}</td>
</tr>
<tr>
<td>k_B [#/m^3-s^-1]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10^{6}</td>
</tr>
</tbody>
</table>

Figure 9.1 shows the simulated supersaturation for DH during seeded batch recrystallizations with different growth and dissolution rate constants. No secondary nucleation was considered.

Figure 9.1. Supersaturation for DH during 3 simulations of the recrystallization of HH to DH with SIM1 (k_G 10^{-6}, k_D 10^{-6}), SIM2 (k_G 10^{-6}, k_D 10^{-7}), SIM3 (k_G 10^{-7}, k_D 10^{-6}).

Lowering of either the growth constant or the dissolution constant results in a slower
recrystallization. For $k_G$ is $10^{-7}$ m/s and $k_D$ is $10^{-6}$ m/s (SIM3), the supersaturation for DH remains high for a long time. The concentration in the acid almost equals the solubility product of HH until it drops fast to the solubility of DH at the end of the reaction when all HH is dissolved. This behavior of the supersaturation illustrates that the growth of DH is the rate-determining step. For $k_G$ is $10^{-6}$ m/s and $k_D$ is $10^{-7}$ m/s (SIM2), the supersaturation decreases constantly during the recrystallization indicating a combined effect on the recrystallization rate of dissolution and growth.

For a dissolution rate determined recrystallization, the concentration in the acid would almost be equal to the solubility of DH. With $k_G$ is $10^{-6}$ m/s and $k_D$ is $10^{-6}$ m/s (SIM1), the recrystallization becomes very fast. The curve of the supersaturation has a form in between that of SIM2 and SIM3, as might be expected. The concentration in the acid remains first close to the solubility of HH, but decreases then gradually to the solubility of DH when more DH surface area is available to consume the supersaturation.

In SIM4, secondary nucleation is introduced. The $k_G$ and $k_D$ equal that of SIM3. The supersaturation during SIM4 is compared with that of SIM3 in figure 9.2.

![Graph](image)

**Figure 9.2.** Supersaturation for DH during recrystallization without secondary nucleation (SIM3) and with $k_B$ is $10^6$ #/m$^3$·s$^{-1}$ (SIM4).

Due to the introduction of secondary nucleation, the recrystallization becomes faster. As was mentioned before, the rate-determining step in the recrystallization of SIM3 is the DH growth. By the introduction of secondary nucleation, the DH crystals become smaller resulting in a larger crystal surface area and the supersaturation is consumed more quickly.
In figure 9.3, the CSD of SIM3 is compared with that of SIM4. In SIM3, the DH seeds just grow to larger crystals, whereas in SIM4 a large amount of small DH crystals are formed due to secondary nucleation.

![Graph showing CSD of DH after recrystallization without secondary nucleation (SIM3) and with \( k_g = 10^5 \text{#/m}^3\text{s}^{-1} \) (SIM4).]

**Figure 9.3.** CSD of DH after recrystallization without secondary nucleation (SIM3) and with \( k_g = 10^5 \text{#/m}^3\text{s}^{-1} \) (SIM4).

**9.4.2 Uptake of impurities**

For the simulation of the incorporation of impurities, lanthanum is introduced to the initial composition of the slurry presented in table 9.1 and 9.2. The concentration lanthanum in the acid solution is chosen to be \( 10^{-3} \text{ kg/kg} \) and the concentration in the HH crystals is taken \( 10^{-4} \text{ kg/kg} \). The latter agrees with the concentration of lanthanum in industrial HH. The lanthanum concentration in the acid is taken 10 times higher than that in the industrial acid so that the effect of changing parameters becomes more distinct. The kinetic parameters describing the recrystallization reaction were taken as those for SIM4, presented in table 9.3. Two different simulations were performed for the uptake of lanthanum in the newly formed DH, one with a distribution coefficient, \( K_{DH,La} \), of 10 (SIM5) and one with a \( K_{DH,La} \) of 100 (SIM6). The first \( K_{DH,La} \) is comparable to that found in the laboratory experiments, which showed an average \( K_{DH,La} \) of 8 (see chapter 7).

With \( K_{DH,La} \) 10 the concentration lanthanum in DH becomes \( 7.6 \times 10^{-5} \text{ kg/kg} \). In one of the experiments an amount of \( 8.6 \times 10^{-5} \text{ kg/kg} \) lanthanum in the calcium sulfate phase was found. It looks like the simulation gives comparable results as the experiments, but in the simulation the concentration lanthanum in the acid was taken a factor of 10 higher. Comparison of the simulated values with experimental ones is impossible, because of the presence of non reacted phosphate ore in the solids obtained from industry, which contain high concentrations of lanthanides.
In the model, the kinetic and thermodynamic effects are combined in one constant distribution coefficient. To account for different kinetic effects, like the increase of the uptake with increasing growth rate, as was found in the laboratory experiments, the distribution coefficient should be adjusted before simulation. This effect was not considered here.

Because the distribution coefficient is constant, the newly formed DH layer will always have a concentration of lanthanum of $K_{DH,La}$ times the concentration in the acid. This does not mean that the overall concentration of lanthanum in the crystals is constant. Due to a changing concentration in the acid, the concentration in a new layer will be different from that in the former formed crystal layers and a concentration gradient in the crystal will occur. This is illustrated clearly in figure 9.4, in which the overall concentration of lanthanum in the DH crystals is plotted against time for SIM5, $K_{DH,La}$ is 10, and SIM6, $K_{DH,La}$ is 100. In SIM5, the concentration lanthanum in the DH phase gradually increases with increasing reaction time, so increasing conversion. In SIM6, the concentration in the first formed layers of DH becomes very high. As a result, the concentration in the acid becomes very low, although lanthanum is constantly released from the HH crystals. At a certain time, the concentration in the acid times $K_{DH,La}$ is lower than the overall concentration in the DH crystals formed until then and a lower concentration in the new layers results. This will result in a decrease of the overall concentration in the DH crystals.

![Graph](image)

*Figure 9.4. The overall lanthanum concentration in DH during the recrystallization of HH to DH with $K_{DH,La}$ is 10 (SIM5) or 100 (SIM6).*
9.4.3 Simulation of a continuous recrystallization with introduction of a growth retarder

The simulated process is illustrated in figure 9.5 and is similar to the two-filter production process that was operated by Hydro Agri in Rotterdam.

![Diagram](image)

**Figure 9.5. The simulated two-filter process.**

The simulations describe the effect of changing the number of crystallizers on the conversion of HH to DH, the effect of introducing a growth retarder, like AlF$_3$, and the effect of inserting a recycle loop between the 3rd and 1st crystallizer in the recrystallization section. The simulated values will not equal the values in the industrial production process, but the effects of changes will show the same trends.

For the simulation, the rate constants were chosen in such a way that the conversions and CSD’s equal that of experiments in a chemically pure system [3]. The rate constants also equal those of SIM4, presented in table 9.3.

The degree of conversion depends on the residence time in the crystallizer. Figure 9.6 shows that complete conversion is still not reached with a residence time of 10,000 s for one crystallizer. However, with 3 crystallizers in series complete conversion is already reached when using a residence time of 2000 s for each crystallizer.

The average size of the crystals does not increase with the number of crystallizers in series. This is illustrated in figure 9.7. So, the filterability of the DH product does not increase by using more crystallizers. This is due to the fact that in all three crystallizers, nucleation as well as growth occurs.

Figure 9.8 shows the conversion in 3 crystallizers in series as a function of reaction time. Until $6 \times 10^4$ s, the conversion is constant and reaches 0.88 in the 3rd crystallizer. At $6 \times 10^4$ s, a growth retarder is added, AlF$_3$. The effect of the growth retarder is simulated by reducing $k_G$ in the simulation. Due to the growth retarder, the conversion in the 1st crystallizer decreases to 0 and becomes only 0.2 in the last crystallizer. The process adjusts very slowly to the new situation. Only after 80 residence times a new steady state is reached. This slow decrease of the conversion
due to growth retardation was also found in the industrial production process of Hydro Supra in Sweden.

**Figure 9.6.** The degree of conversion as a function of the number of crystallizers in series and the residence time in the crystallizer (● crystallizer 1, □ crystallizer 2, and ▲ crystallizer 3).

**Figure 9.7.** The CSD as a function of the number of crystallizers in series (● crystallizer 1, □ crystallizer 2, ▲ crystallizer 3).

The introduction of a recycle loop between the 3rd and 1st recrystallizer resulted in an increase of the conversion again. Due to DH from the 3rd crystallizer, more DH surface area is present in the 1st crystallizer. Within 10 residence times, the conversion in the last crystallizer increases from 0.2 to 0.6. So, a recycle loop increases the degree of conversion and the stability of the process.
9.4.4 Batch recrystallization with simultaneous ion exchange extraction

The initial parameters presented in tables 9.1 and 9.2 were also used for the simulations of batch recrystallizations with simultaneous ion exchange extraction. The properties chosen for the ion exchange resin are based on the resin used in the laboratory experiments described in chapter 7. This resin was a polystyrene polymer bead with 8% divinylbenzene (DVB) with 4.9 meq/g sulfonic acid functional groups and a diameter of 500 µm.

In the first simulations, the crystallization parameters were not varied and taken as those in SIM5 (kG 10^{-6}, kD 10^{-7}, kB 10^{-9}) including the distribution coefficient, K_{DH,La}, which was 10. Laboratory experiments showed that K_{DH,La} increases due to the addition of ion exchange resin (see chapter 7). This is not taken into account here, because the increasing K_{DH,La} is probably the result of a higher relative uptake of impurities due to an increasing growth rate, as is discussed in chapter 7. A correction of this phenomenon should therefore not be introduced by an increase of the distribution coefficient, but of an increase of the crystallization rate constants. The influence of the growth rate on the concentration lanthanum in DH will be discussed later in this paragraph.

The initial parameters of the ion exchange reaction that are varied during a first set of simulations are presented in table 9.4. The rate constants in the ion exchange resin are estimated from diffusion coefficients of Y^{3+}, Zn^{2+}, and Na\(^+\) in an ion exchange resin with 12% DVB [5]. The diffusion coefficient of yttrium in a resin with 12% DVB and a capacity of 4.9 meq/g was found to be 10^{-12} m^2/s. For a DVB-content of 8% the diffusion coefficient is higher, about a factor of 10. The diffusion coefficient of bivalent ions is about 10 times that of trivalent ions and that of monovalent ions about 100 times that of trivalent. The rate constant of an ion i, k_{i,n,i} [m/s], in the resin
can be calculated from the diffusion coefficient, D [m²/s], and the penetration depth, \( \delta [m] \), with

\[
k_{\text{kin},i} = \frac{D}{\delta}
\]

With an estimated penetration depth of 100 µm in the resin beads, the rate constants of lanthanum, calcium, and hydrogen are estimated to be \( 10^8 \) m/s, \( 10^7 \) m/s, and \( 10^6 \) m/s, respectively.

The uptake is not only determined by kinetics, but also by thermodynamics. The thermodynamic effects are taken into account by the affinity coefficient. The affinity coefficient will depend on, for example, the charge density of the ion. For a sulfonic acid resin, the affinity increases with increasing charge of the cation and decreasing ionic radius (increasing charge density). So, the affinity coefficient of lanthanum will be higher than that of calcium, which will be higher again than that of hydrogen. Affinity coefficients of 10 for lanthanum, 1 for calcium, and 0.1 for hydrogen were taken. Laboratory experiments showed an affinity coefficient for lanthanum of 31 (see chapter 4). However, an increase or decrease of the three affinity coefficients by the same factor does not change the extraction efficiencies found in the simulations.

**Table 9.4. Parameters that were varied for simulations of the recrystallization of HH to DH with simultaneous ion exchange extraction.**

<table>
<thead>
<tr>
<th></th>
<th>SIM7</th>
<th>SIM8</th>
<th>SIM9</th>
<th>SIM10</th>
<th>SIM11</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{kin},H} ) [m/s]</td>
<td>( 10^{-6} )</td>
<td>( 10^{-6} )</td>
<td>( 10^{-5} )</td>
<td>( 4 \times 10^{-6} )</td>
<td>( 10^{-6} )</td>
</tr>
<tr>
<td>( k_{\text{kin},Ca} ) [m/s]</td>
<td>( 10^{-7} )</td>
<td>( 10^{-7} )</td>
<td>( 10^{-6} )</td>
<td>( 4 \times 10^{-7} )</td>
<td>( 10^{-7} )</td>
</tr>
<tr>
<td>( k_{\text{kin},La} ) [m/s]</td>
<td>( 10^{-8} )</td>
<td>( 10^{-8} )</td>
<td>( 10^{-7} )</td>
<td>( 4 \times 10^{-8} )</td>
<td>( 10^{-8} )</td>
</tr>
<tr>
<td>( K_{IR,La} ) [-]</td>
<td>10</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( K_{IR,Ca} ) [-]</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( K_{IR,H} ) [-]</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>( A/V_{\text{resin}} ) [1/m]</td>
<td>6000</td>
<td>6000</td>
<td>6000</td>
<td>60000</td>
<td>6000</td>
</tr>
<tr>
<td>mass fraction</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>IR [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.9 shows the effect of the addition of ion exchange resin on the overall concentration of lanthanum in the DH. Due to the extraction of lanthanum by the resin, the concentration lanthanum in the solution decreases. Due to this, the concentration lanthanum in DH decreases. With an affinity coefficient \( K_{IR,La} \) of 10
(SIM7), the concentration of lanthanum in DH after recrystallization decreases from $7.5 \times 10^{-5}$ kg/kg without resin to $2.6 \times 10^{-6}$ kg/kg with 0.1 kg/kg resin, a reduction in lanthanum concentration in DH of 97%. With a higher $K_{R,\text{La}}$ 100 in SIM8, the overall concentration lanthanum in DH becomes even lower, $0.28 \times 10^{-6}$ kg/kg. The reductions in the simulations are much higher than those found in the laboratory experiments. A reduction of 39% in the lanthanum concentration of DH was found with 0.2 kg/kg resin. The lower experimentally found reduction in lanthanum concentration is due to the fact that also other lanthanides and cations are taken up by the ion exchange resin, as is shown in chapter 7, and occupy some of the limited available sites on the resin. This is not taken into account in the simulations.

![Graph showing concentration of lanthanum over reaction time for SIM5, SIM7, and SIM8](image)

**Figure 9.9.** The overall concentration of lanthanum in the DH crystals without (SIM5) and with ion exchange resin with different $K_{R,\text{La}}$ 10 (SIM7) and 100 (SIM8).

The rate constant of lanthanum in the resin is lower than the growth rate of DH, the rate-limiting step of the recrystallization, $10^{-8}$ m/s versus $10^{-7}$ m/s. Due to this, some ions will already be incorporated in the DH crystals before they can be extracted. Increasing the rate constant in the resin is therefore expected to result in a higher extraction efficiency and a lower lanthanum concentration in the DH crystals. To gain a higher rate constant, either the diffusion coefficient in the resin should be increased or the diameter of the beads should be decreased. With the latter, the penetration depth becomes smaller, resulting in a higher rate constant. The effect of decreasing the diameter of the resin beads with a factor of 10 (SIM10) and increasing the diffusion coefficients with a factor of 10 (SIM9) is illustrated in figure 9.10.
Figure 9.10. The overall concentration of lanthanum in the DH crystals with ion exchange resin with varying rate constants for the ions, $k_{\text{kin}}$ in SIM9 are 10 times $k_{\text{kin}}$ in SIM7, and varying bead size, A/V in SIM10 is 10 times A/V in SIM7 (see table 9.5). The latter adjustment results also in higher rate constants, $k_{\text{kin}}$ in SIM10 are 4 times $k_{\text{kin}}$ in SIM7.

The overall concentration of lanthanum in DH in SIM9 ($k_{\text{kin,H}} 10^{-5}$, $k_{\text{kin,Ca}} 10^{-6}$, $k_{\text{kin,La}} 10^{-7}$) becomes 98.7% lower than without the addition of ion exchange resin (SIM5), whereas the reduction in SIM7 ($k_{\text{kin,H}} 10^{-6}$, $k_{\text{kin,Ca}} 10^{-7}$, $k_{\text{kin,La}} 10^{-8}$) is 97%. So, increasing the diffusion coefficient and thus the rate constant of lanthanum in the ion exchange resin increases the extraction efficiency, indicating that in SIM7 the ion exchange extraction is limited by diffusion of the impurity ions into the beads. An increase of the diffusion coefficient in the ion exchange resin can practically be established by increasing the capacity, or by decreasing the DVB content, which results in a more open structure of the resin.

By using smaller resin beads in SIM10, 50 µm instead of 500 µm (SIM7), the rate constant will become higher and the factor A/V will increase. For beads with a diameter of 50 µm, the penetration depth becomes 25 µm. The rate constants become $4 \times 10^{-7}$ m/s for lanthanum, $4 \times 10^{-6}$ m/s for calcium, and $4 \times 10^{-5}$ m/s for hydrogen, 4 times those in SIM7. The factor A/V becomes 60000 l/m, instead of 6000 l/m in SIM7. Figure 9.10 shows that smaller resin beads result in a lower concentration of the impurity ion in DH.

The addition of more ion exchange resin to the slurry, for example 0.25 kg/kg instead of 0.1, will result in more theoretical extraction capacity in the system. Due to an increasing amount of resin also the surface area will increase. The effect of the increase of the amount of resin on the lanthanum concentration is shown in figure 9.11.
Another effect of adding more ion exchange resin is that the concentration on the resin will decrease, because the total amount of impurities in the system remains equal. This is shown in Table 9.5 for SIM7 and SIM11. This was also found in the laboratory experiments.

**Table 9.5. The charge density of hydrogen, and mass fractions of calcium and lanthanum on the ion exchange resin after the as a function of the amount of resin in the slurry (SIM7 0.1 kg/kg and SIM11 0.25 kg/kg).**

<table>
<thead>
<tr>
<th></th>
<th>SIM7</th>
<th>SIM11</th>
</tr>
</thead>
<tbody>
<tr>
<td>([H^+]_{IR}) [eq/eq]</td>
<td>0.67</td>
<td>0.73</td>
</tr>
<tr>
<td>([Ca^{2+}]_{IR}) [kg/kg]</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>([La^{3+}]_{IR}) [kg/kg]</td>
<td>2.0\times10^{-4}</td>
<td>7.9\times10^{-5}</td>
</tr>
</tbody>
</table>

In SIM11, the ion exchange resin is less dissociated than in SIM7 as is indicated by the higher proton concentration in the resin. This may be due to the fact that the lanthanum and calcium ions are no longer available. However, this is not the case, because calcium is abundantly present.

The dissociation may also be limited by the pH of the solution. The initial pH in the simulated system is very low, -1.29. With such low pH's, the concentration of protons in the solution is already high and may prevent further dissociation of the resin. This would imply that with a higher initial pH of the solution, the resin would dissociate more and take up more species other than hydrogen. This was tested in
SIM12. In SIM12, the mass fraction of \( \text{PO}_4^{2-} \) was taken 0.1 instead of 0.32 that was used in the earlier simulations (see Table 9.1). Due to this, the pH of the solution becomes -0.68, instead of -1.29.

It was found that the overall concentration of lanthanum in DH was lower for pH -0.68 (SIM12) than for pH -1.29 (SIM7), 1.6 \( \times \) \( 10^{-6} \) kg/kg versus 2.6 \( \times \) \( 10^{-6} \) kg/kg. The mass fraction protons on the resin was 0.67 kg/kg for SIM7, for SIM12 it was 0.41 kg protons/kg resin. So, a higher pH of the solution will result in a higher dissociation of the resin and therefore in a higher uptake of impurities. This was also indicated by laboratory experiments, in which the extraction efficiency from clear phosphoric acid from a two-filter process (0.8 mol/kg H\(_3\)PO\(_4\) and 0.5 mol/kg H\(_2\)SO\(_4\)) was compared with that from phosphoric acid from the one-filter process (3.2 mol/kg H\(_3\)PO\(_4\) and 0.2 mol/kg H\(_2\)SO\(_4\)) (Chapter 4). In the first case, 68% of lanthanum was removed with 0.05 kg resin/kg acid and in the latter, more acidic acid, only 22%.

The lanthanum ions have to compete with calcium and hydrogen ions for the available sites on the resin. For the phosphoric acid solution, most sites on the resin are occupied by hydrogen. A lower affinity for protons, i.e. a more acidic ion exchange resin, is expected to increase the dissociation of the resin and increase the uptake of other ions, like calcium and lanthanum. This effect is simulated in SIM13, for which the resin parameters are shown in Table 9.6.

**Table 9.6. The parameters used for simulations SIM13 and SIM14.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SIM13</th>
<th>SIM14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{kin,H}} ) [m/s]</td>
<td>( 10^{-6} )</td>
<td>( 10^{-6} )</td>
</tr>
<tr>
<td>( k_{\text{kin,Ca}} ) [m/s]</td>
<td>( 10^{-7} )</td>
<td>( 10^{-7} )</td>
</tr>
<tr>
<td>( k_{\text{kin,La}} ) [m/s]</td>
<td>( 10^{-8} )</td>
<td>( 10^{-8} )</td>
</tr>
<tr>
<td>( K_{IR,La} ) [-]</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( K_{IR,Ca} ) [-]</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>( K_{IR,H} ) [-]</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>( A/V_{\text{resin}} ) [l/m]</td>
<td>6000</td>
<td>6000</td>
</tr>
<tr>
<td>Mass fraction IR [-]</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In figure 9.12, the effect of a lower affinity coefficient for protons, \( K_{IR,H} \) is 0.05 (SIM13) instead of 0.1 (SIM7), is illustrated. Due to the lower affinity for protons, the concentration of calcium on the resin increases significantly, but the effect on the concentration of lanthanum on the resin is negligible.
**Figure 9.12. The concentration hydrogen, lanthanum, and calcium on resins with a different acidity, simulated by taking different $K_{IR,H}$, 0.1 (SIM7) and 0.05 (SIM13).**

In chapter 7, it was mentioned that a resin with a higher selectivity for the lanthanides with respect to calcium would result in higher extraction efficiencies for the lanthanides. This was simulated in SIM14, for which the resin parameters are given in table 9.6, by taking a lower affinity coefficient for calcium, $K_{IR,Ca}$ is 0.1 (SIM14) instead of 1 (SIM7). Due to the lower affinity for calcium, the calcium concentration on the resin decreases significantly, from 0.03 to 0.005 kg/kg. This results in an increase of the lanthanum concentration on the resin from $2.08 \times 10^{-4}$ kg/kg (SIM7) to $2.14 \times 10^{-4}$ kg/kg (SIM14). Contrarily of what was expected, the effect of a lower affinity for calcium is almost negligible on the lanthanum extraction efficiency. The concentration of protons on the resin increases significantly due to the lower affinity for calcium from 0.67 (SIM7) to 0.95 (SIM14).

Although the somewhat disappointing increase of the lanthanum concentration on the resin, the concentration decrease in DH is still significant due to the lower affinity of the resin for calcium, from $2.6 \times 10^{-6}$ kg/kg for $K_{IR,Ca}$ is 1 (SIM7) to $1.8 \times 10^{-6}$ kg/kg for $K_{IR,Ca}$ is 0.1 (SIM14), as is shown in figure 9.13.

As was discussed in chapter 7, the concentration lanthanum in DH is expected to depend on the DH growth rate. If the growth rate is much faster than the extraction rate, lanthanum will be incorporated into the DH crystals before they are extracted by the ion exchange resin. An indication of this dependence was already given by SIM9 and SIM10, in which an increasing rate constant of the ions in the resin resulted in a higher extraction efficiency (figure 9.10). Similarly, a decrease of the growth rate of DH would result in an increase in extraction efficiency and a lower lanthanum concentration in DH. Figure 9.14 shows the uptake of lanthanum by DH
for a growth rate constant for DH of $10^{-8}$ m/s (SIM15) and that with a growth rate constant of $10^{-7}$ m/s (SIM7).

\[ \text{Figure 9.13. The overall lanthanum concentration in DH for } K_{\text{IR, Ca}} \text{ is 1 (SIM7) and 0.1 (SIM14).} \]

\[ \text{Figure 9.14. The overall lanthanum concentration in DH during recrystallization with simultaneous ion exchange extraction with } k_G \text{ is } 10^{-7} \text{ m/s (SIM7) and } k_G \text{ is } 10^{-8} \text{ m/s (SIM15).} \]

The extraction efficiency of lanthanum from DH, which was 96% for SIM7, is much higher than that found in the experiments described in chapter 7. This is probably due to the fact that not all lanthanides and other cations are taken into account in the simulations. These ions are also extracted by the resin and compete with lanthanum for the limited sites on the ion exchange resin. Also, the CSD differs from that taken in the simulations. Further, parameters, like the distribution coefficient of lanthanum
in DH, and affinity coefficients of the resin for the ions may be less optimistic than taken in the simulation. Nevertheless, the simulations show which parameters influence the extraction efficiency. It can be concluded that the extraction efficiency would increase when more selective ion exchange resin with respect to the impurities is taken with smaller beads and more open structures. Better experimental results would also have been gained in less acidic solutions, and with lower growth rates of DH.

9.4.5 Continuous recrystallization with simultaneous ion exchange extraction

The recrystallization reaction is simulated in a stirred vessel with a feed flow entering and a product flow leaving the continuously operated recrystallizer, like in the industrial production process. The kinetic parameters and initial composition of the slurry were taken like those in SIM5 (paragraph 9.4.2, SIM4 in table 9.1, 9.2, and 9.3 plus lanthanum). Also the composition of the feed is like that of SIM5, except for the mass fraction DH. No DH is present in the feed solution. The distribution coefficient, $K_{DH,La}$, was taken 10. The properties of the resin equal those used in SIM7 (table 9.4). The flow rate and volume of the recrystallizer were taken as in the experiments performed with ion exchange resin described in chapter 8. They are presented in table 9.7. For the simulation 'with resin b' twice the amount of resin was taken as in the laboratory experiments, which are represented in 'with resin a'. The amounts were chosen so that the residence time in the recrystallizer remains equal.

Table 9.7. The flow rates into the recrystallizer used in the simulations with and without ion exchange resin.

<table>
<thead>
<tr>
<th>Feed rates [kg/h]:</th>
<th>Without resin</th>
<th>With resin a</th>
<th>With resin b</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>2.8</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>HH</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>resin</td>
<td>0.7</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

For the recrystallization without ion exchange resin, the mass fraction of DH in the calcium sulfate phase increases until it becomes constant at 88% in the crystallizer and product. The concentration lanthanum in the DH also increases (it starts at 0, because the crystallizer is filled with 5 wt.% pure DH), until it reaches a steady value of $10^4$ kg/kg. This is much higher than the experimentally found $1.7 \times 10^{-5}$
kg/kg. This is the result of the concentration lanthanum in the acid, which was taken a factor 10 higher than that in the industrial phosphoric acid.

The concentration of lanthanum in DH, acid, and ion exchange resin during simulated recrystallization with simultaneous ion exchange extraction is plotted in figure 9.16 (the concentration lanthanum in HH remains $10^{-4}$ kg/kg).

![Graph showing concentration of lanthanum](image)

**Figure 9.16.** The concentration lanthanum in DH, on the resin, and in the acid, during continuous recrystallization with simultaneous ion exchange extraction (with resin a in table 9.7).

The concentration lanthanum in the DH decreases from $10^{-4}$ kg/kg without ion exchange extraction to $1.4 \cdot 10^{-5}$ kg/kg with ion exchange extraction. This is a reduction of 86%. In the laboratory experiments, the reduction was only 44%. This may indicate that the affinity coefficient for lanthanum or the rate constant are too optimistically chosen. With rate constants of a factor 10 lower for hydrogen, calcium, and lanthanum, the simulated lanthanum concentration in DH would approach the 44% reduction found experimentally. Lowering only the affinity coefficient of lanthanum, $K_{IR,La}$, with a factor of 10 ($K_{IR,La}$ becomes equal to $K_{IR,Ca}$), results in a decrease of 39% of lanthanum in DH with simultaneous ion exchange extraction. More probably, the lower experimental extraction efficiencies are the result of the competition with other lanthanides and other cations for the available ion exchange sites, mentioned before in paragraph 9.4.4.

Adding twice the amount of resin to the feed and crystallizer results in a further decrease of the concentration of lanthanum in acid and in DH (with resin b in table 9.7). The concentration lanthanum in the acid decreases to $7 \cdot 10^{-7}$ kg/kg and that in DH to $7 \cdot 10^{-6}$ kg/kg. As for batch recrystallization, the extraction efficiency in continuous recrystallization will increase with smaller beads, with more open
structures of the beads (less DVB), with higher affinity for the impurity ions, and with decreasing growth rate of DH.

9.5 Conclusions

For the simulation of the recrystallization and the distribution of the impurities a computer program, Crystals, was used. This program is developed to simulate (re)crystallization processes dynamically, like the recrystallization step in the phosphoric acid process. The uptake of impurities by the newly formed crystals was described by a constant distribution coefficient. Also equations describing extraction processes were included. This makes it possible to simulate (re)crystallization in the presence of impurities, that may be simultaneously removed from the mother liquor by ion exchange extraction or solvent extraction.

A semi-quantitative simulation of the recrystallization indicates that the conversion is more efficient in 3 smaller tanks with a recycle loop from the 3rd to the 1st tank than in 1 tank with a large residence time. The introduction of the recycle loop also increases the stability of the recrystallization process.

The simulations of the recrystallization with simultaneous ion exchange extraction indicate that the extraction efficiency of impurity ions would increase with increasing amount of resin, decreasing growth rate of DH, a more open structure of the resin (higher rate constants), higher affinity for the impurity ion, and smaller resin beads. The extraction efficiency would also be higher when applied in a less acidic solution than the industrial phosphoric acid.

Acknowledgement

André van Delft of Delftware Technology BV, The Netherlands is acknowledged for programming Crystals.

References

1. Delft A. van, Crystal software, Delftware Technology BV, The Netherlands.

Chapter 10

Economic Evaluation of Ion Exchange Extraction during Industrial Recrystallization

By extracting lanthanides during the recrystallization of calcium sulfate hemihydrate to dihydrate (DH, gypsum), ores of igneous origin with high concentrations of lanthanides and low radioactivity become suitable for wet phosphoric acid processing. Using these ores, the radioactivity level in the gypsum byproduct will be lower than the generally accepted limit of 150 Bq/kg for application of gypsum as building material.

Due to the unfavorable equilibrium between the stripping solution, nitric acid, and the resin (distribution coefficient of 0.46), the extraction process is not economically feasible yet. The costs exceed the profits with 6.25 €/t gypsum. If a stripping solution could be found with a more favorable equilibrium (distribution coefficient of 1), the profits will exceed the costs. For a stripping solution of 17 €/t and a distribution coefficient of 1.07, the profits exceed the costs with 3 €/t gypsum resulting in a profit of 3.8 M€/a.

The investment costs for simultaneous ion exchange extraction during the recrystallization were estimated to be 4.3 M€.
10.1 Introduction

In chapters 7 and 8, it was shown that lanthanides can be removed during the recrystallization of calcium sulfate hemihydrate (HH) to dihydrate (DH, gypsum), an existing step in some of the industrial phosphoric acid production processes (see chapter 1) by adding commercially available ion exchange resin. Due to the addition of ion exchange resin, lanthanides released from the dissolving HH crystals are taken up from the phosphoric acid solution resulting in a low concentration in that solution and consequently a low concentration in the newly formed gypsum crystals. Table 10.1 shows the extraction efficiencies, \( \eta \) [%], gained for some lanthanides during a continuously operated recrystallization with the addition of 250 g resin/kg phosphoric acid slurry.

**Table 10.1.** The extraction efficiencies, \( \eta \) [%], for some lanthanides gained during continuous recrystallization of HH to DH in the presence of 250 g ion exchange resin/kg phosphoric acid slurry.

<table>
<thead>
<tr>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Eu</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>28</td>
<td>20</td>
<td>18</td>
<td>13</td>
<td>14</td>
<td>17</td>
<td>14</td>
<td>8.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Due to the removal of lanthanides, which hamper the gypsum growth as is discussed in chapter 8, the phosphoric acid production processes will be able to use also phosphate ores with a high amount of lanthanides making the process less dependent on the type of ore they can use.

Extraction of lanthanides makes it possible to use also igneous rocks, like Kovdor and Kola. These ores have a high concentration of lanthanides, but a low concentration of radioactive elements, like radium. The composition of Kovdor is shown in table 10.2. Using only these ores can result in a gypsum product with a radioactivity level lower than 150 Bq/kg, which is the limit set by the Dutch Ministry of Environmental Affairs for application of gypsum in the building industry.

Until now, the production processes can only operate by mixing igneous rocks with sedimentary rocks. These rocks, like Jordan, contain low amounts of lanthanides, but their amount of radioactive elements is higher. The composition of Jordan ore is also shown in table 10.2. Using a mixture of 65% Kovdor and 35% Jordan ore resulted in a successful operation of the production process and gypsum with a radioactivity level of 190 Bq/kg. To acquire a gypsum product with a radioactivity level lower than 150 Bq/kg, the gypsum needs additional treatment. Kemira Agro Pernis developed the ProGips process [1]. In this process, a small fraction of fines, which
contains most of the radioactivity, is separated from the gypsum product. The radioactivity of the product becomes less than 100 Bq/kg and can be used in the building industry.

**Table 10.1. The compositions of the igneous rock, Kovdor, and the sedimentary rock, Jordan.**

<table>
<thead>
<tr>
<th></th>
<th>Kovdor</th>
<th>Jordan</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅</td>
<td>%</td>
<td>38.5</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>0.25</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/kg</td>
<td>0.002</td>
</tr>
<tr>
<td>As</td>
<td>mg/kg</td>
<td>1.5</td>
</tr>
<tr>
<td>Σ HM</td>
<td>mg/kg</td>
<td>40</td>
</tr>
<tr>
<td>V</td>
<td>mg/kg</td>
<td>20</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td>100</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>400</td>
</tr>
<tr>
<td>Ti</td>
<td>mg/kg</td>
<td>2000</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td>400</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>12000</td>
</tr>
<tr>
<td>Σ REM</td>
<td>mg/kg</td>
<td>1378</td>
</tr>
<tr>
<td>Ra_eq</td>
<td>Bq/kg</td>
<td>85</td>
</tr>
</tbody>
</table>

The properties and economics of the ProGips process are described by Penders et al [1]. The investment costs of the ProGips process for the production of 900 kton/a are estimated to be 16 M€ (1.04 € = 1 USD) and the variable and fixed costs are estimated to be 5.25 €/t ProGips. The projected sales price is 6.25 €/t. In this chapter, an economic evaluation of the recrystallization step with simultaneous ion exchange extraction of lanthanides is made.

**10.2 Design basis**

The ion exchange resin is added to the recrystallizers. Figure 10.1 shows a schematic overview of the current recrystallization section of the one-filter HDH process and figure 10.2 shows the process adjusted for recrystallization with simultaneous ion exchange extraction.
Figure 10.1. A schematic representation of the recrystallization section of the one-filter HDH process.

Figure 10.2. A schematic representation of the recrystallization section of the one-filter HDH process with simultaneous ion exchange extraction.

Addition of ion exchange resin

In the first recrystallizer, already 85% of the HH is recrystallized to DH. To remove the lanthanides from the calcium sulfate solids, the presence of ion exchange resin in the first recrystallizer is essential. So, the ion exchange resin will be added to the first recrystallizer and moves with the phosphoric acid slurry through the other recrystallizers.
The calculations were performed with 56 t/h of ion exchange resin added to the recrystallizers, reducing the residence time of the gypsum slurry from 210 min to 196 min. With 445 t/h of untreated slurry added to the first crystallizer, the amount of resin becomes 125 g resin per kg of untreated phosphoric acid slurry.

The system was not optimized for the type of resin used. As is mentioned in chapter 7, the resin also extracts calcium ions. A more selective resin with respect to lanthanides will require less resin to achieve high extraction efficiency.

Separation of the ion exchange resin

After the recrystallization, the ion exchange resin must be separated from the slurry to be regenerated and reused. Separation based on a difference in size by sieving is not possible. The needle shaped crystals formed in the one-filter HDH have an average size of 90 μm, but can be as large as 1 mm. The ion exchange resin used during the research has a size of 525 ± 50 μm. The cheaper Dowex Marathon strong acidic ion exchanger, also with sulfonic acid functional groups, has a size of 600 ± 50 μm.

Separation by settling is possible. The densities of DH, product acid, recrystallizing slurry, and ion exchange resin are listed in table 10.3.

Table 10.3. Densities of DH, product acid, recrystallizing slurry (33% DH, 50% product acid, 16% ion exchange resin), and ion exchange resin.

<table>
<thead>
<tr>
<th></th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH</td>
<td>2.32</td>
</tr>
<tr>
<td>product acid</td>
<td>1.28</td>
</tr>
<tr>
<td>slurry</td>
<td>1.49</td>
</tr>
<tr>
<td>ion exchange resin</td>
<td>1.20-1.22</td>
</tr>
</tbody>
</table>

The density of the ion exchange resin is smaller than that of the acid, which indicates that the resin will float on the acid, whereas DH solids will settle at the bottom of a settler. So, the ion exchange resin can be skimmed from the slurry, whereas the slurry can leave the settler at the bottom.

As is already mentioned in chapter 7, the recrystallization rate increases strongly when lanthanides are extracted. It is assumed that the decrease in residence time from 210 minutes to 196 minutes due to the addition of ion exchange resin is compensated by the increase of the recrystallization rate and no additional crystallizers are needed. It is even assumed that the recrystallization rate increases so
much that the 4th crystallizer can be used as settler. The addition of 56 t/h ion exchange resin and usage of the 4th recrystallizer as settler will decrease the total residence time with 30%.

To transform the 4th recrystallizer to a settler, a drain should be added to the bottom of the vessel, through which the gypsum slurry leaves the settler. The ion exchange resin leaves the settler through the already existing overflow. A skimmer to lead the resin to the overflow can be fixed to the existing stirrer bar.

With the resin, also some adhering phosphoric acid will leave the settler. Therefore, the ion exchange resin will be washed on a filter before entering the regeneration section. The ion exchange resin will be washed with water that will be reused for the washing of the gypsum to maintain the water balance in the production process.

*Filter*

The ion exchange resin beads are uniform of size and have therefore a good filterability. The filtration of ion exchange resin was compared to that of sand [2]. A sand feed consists of 10-15% solids with a size of 20 mesh (d=840 μm) and 34-72% of 65 mesh (240 μm). With a suitable type of vacuum filter, the filtration capacity ranges from 2 to 16 t·m⁻²·h⁻¹. Due to the uniformity of the resin beads, it is expected that 16 t·m⁻²·h⁻¹ can be reached. This would require a filter area of 3.5 m². Washing the resin 3 times after filtration of the phosphoric acid will require a total filtration area of 14 m².

The filtration unit contains pumps, 4 vacuum pumps for the filtration and a pump for wash water to wash the resin beads. These pumps consume electricity. It is estimated that the pumps consume 40 kW each to a total of 200 kW.

*Regeneration of the ion exchange resin*

The ion exchange resin will be regenerated in a column, in which 20wt% nitric acid flows counter currently to the resin from bottom to top. Tests on the stripping performance of 20wt% nitric acid were disappointing. The distribution coefficient $K_{NO}$ [-] of lanthanum

$$K_{NO} = \frac{[\text{Ln}]_{\text{HNO}_3}}{[\text{Ln}]_{\text{IR}}}$$

10.1,

is only 0.47. This indicates that for the recovery of 90% of the ions from the resin, the flow of stripping solution, $\Phi_S$ [m³/s], should be at least 1.9 times the flow of ion exchange resin, $\Phi_{IR}$ [m³/s]. With this ratio, the number of equilibrium steps
necessary to achieve 90% recovery is infinite. Taking a ratio \( \Phi_S/\Phi_{IR} \) of 1.2 times the minimum, the separation factor \( S \),

\[
S = \frac{K \cdot \Phi_S}{\Phi_{IR}} 
\]

becomes 1.08. The required number of equilibrium steps can be calculated with the equation of Kremser [3],

\[
f = \frac{S - 1}{S^{N+1} - 1} 
\]

with \( f \) the amount not recovered (10%) and \( N \) the number of equilibrium steps, which becomes 6.6. The flow of stripping solution becomes 2.3 times the flow of ion exchange resin. Due to this, the concentration of lanthanides in the stripping solution becomes not as high as was hoped for. For example, the concentration of lanthanum on the resin is 150 ppm before regeneration. The concentration in the stripping solution becomes only 50 ppm (0.005%). The total amount of lanthanides in the stripping solution becomes only 0.01%, which is too low for economic recuperation. Nevertheless, the value of the stripping solution loaded with lanthanides is related to the price of monazite ore, which contains 55% of lanthanides. The profit gained by the loaded stripping solution, \( P_{HNO} [\text{€/t}] \), is calculated with

\[
P_{HNO} = \frac{[\Sigma Ln]_{HNO_3}}{[\Sigma Ln]_{monazite}} \cdot P_{monazite} 
\]

with \( P_{monazite} \) the value of monazite [€/t].

With the unfavorable equilibrium, calculations were performed on the regeneration of the current resin with nitric acid. The throughput of resin is 56 t/h, resulting in a throughput of nitric acid of 129 t/h to gain a recovery of 90%. The height of an equilibrium step, \( H [\text{m}] \), is determined with the Glueckauf equation [4] for the elution of trace quantities

\[
H = 1.64r + \frac{(K_{NO} - \beta)}{K_{NO}^2} 0.144r^2v + \left( \frac{K - \beta}{K} \right)^2 \frac{0.266r^2v}{D(1 + 70rv)} + \frac{D\beta\sqrt{2}}{v} 
\]

with \( r \) the resin bead radius [m], \( \beta \) the fraction of void volume in the column [-], \( v \) the velocity [m/s], \( D \) the intraparticle diffusion coefficient [m²/s], \( D \) the diffusion coefficient in solution [m²/s]. The first term accounts for the finite particle size of the resin beads, the second for slow particle diffusion, the third for slow film diffusion, and the fourth for longitudinal diffusion. The fraction of void volume in the column is the fraction of nitric acid in the column. The fraction of nitric acid was
taken 0.4. With this and the throughputs, the velocity of nitric acid is 1.6 times the velocity of ion exchange resin. The velocity \( v \) is the slip velocity of the resin in the nitric acid. The diffusion coefficient of lanthanum in a diluted solution equals \( 0.62 \cdot 10^{-9} \text{ m}^2/\text{s} \). The intraparticle diffusion coefficient of a trivalent ion was estimated from data presented by Helfferich [4]. A coefficient of \( 10^{-12} \text{ m}^2/\text{s} \) was found for trivalent yttrium in a resin with a capacity of 4.9 meq/g (also the capacity that was used here), but with a divinylbenzene (DVB) content of 12%. The resin used here has a DVB content of 8%. It was also shown that the coefficient increases with a decreasing amount of DVB, about a factor of 10 from 12 to 8% DVB in case of yttrium. So, the intraparticle diffusion coefficient was estimated to be \( 10^{-11} \text{ m}^2/\text{s} \). With these figures, the rate-determining step is the intraparticle diffusion. The diameter of the column(s) and the height of the equilibrium steps (and thus the height of the column), is determined by the velocity of the ion exchange resin and the nitric acid. With a velocity of 0.65 cm/s of the ion exchange resin, the height of an equilibrium step becomes 0.76 m and the column(s) become 5.0 m long. To reach the required throughput, the area of the column(s) has to be 4.9 \( \text{m}^2 \).

Pumps are used to pump the nitric acid through the columns. These pumps consume electricity. It is estimated that the pumps consume 40 kW each. With 3 columns, this sums up to a total of 120 kW.

**Others**

The ion exchange resin has to be transported from the settler to the regeneration column and from the regeneration column to the first crystallizer. Trough shaped conveyor belts will be used for this. It is assumed that belts with a total length of 50 m are sufficient. The total resin flow from the regeneration columns to the 1st recrystallizer is 46 \( \text{m}^3/\text{h} \). With a rate of 1 m/s and a belt with a diameter of 500 mm, the height of the resin layer will become 2.4 cm. This is thought to be acceptable. A conveyor belt consumes electricity. This is estimated to be 10 kW.

Further, some resin is purged and fresh resin is added to the process, continuously. With 56 t/h of resin added to the recrystallizers, the amount of resin in the 3 recrystallizers and 1 settler becomes 730 ton. It is assumed that the amount of resin in the entire process is twice this amount, 1460 ton. The resin purge is chosen only to be 0.06 t/h. This indicates that the resin is refreshed every 3 years or after every 920 recrystallizations.
10.3 Economics

Ore

Because lanthanides, which retard the growth of DH, are removed, cheaper ores with more lanthanides can be used. Until now, Jordan and Kovdor ores were used. These ores cost 62 €/t. By using Kola ore, 5.2 €/t can be saved [5] resulting in a saving of 520 €/h.

Gypsum

By using an ore with a low amount of radioactivity, the gypsum byproduct will have a radioactivity level lower than the required 150 Bq/kg set for application in the building industry. According to Penders [1], the gypsum sales price is estimated to be 6.25 €/t. The total amount of gypsum product is 159 t/h, resulting in a profit of 994 €/h.

Resin

In the process, a total amount of resin of 1460 tons is present. A Marathon Dowex resin costs 1920 €/t [6]. The investment on resin becomes 2.8 M€. With a purge of 0.06 t/h, the variable costs on resin become 117 €/h.

Separation of the resin

It is estimated that the transformation of the 4th recrystallizer to settler will cost about 0.1 M€.

The costs of a continuously operated 15 m² vacuum filter with constant vacuum are 0.18 M€ (AISI 316) without pumps, etc [7]. To account for all necessary pumps and tubing, this amount is multiplied with 3.7 [8] and the estimated investment costs become 0.68 M€.

Regeneration

For the regeneration, 3 columns with a diameter of 1.5 m and a length of 5 m were chosen. According to the Dutch Association of Cost Engineers [7], the price of such a column is 58 k€ per column (AISI 304L). This amount is multiplied with a factor of 3.7 to account for pumps and other necessary supplements [8]. The total investment becomes 0.64 M€.

The price based on 100% nitric acid [9] is 102 €/t. The price of water [7] to dilute the nitric acid to 20% is only 0.04 €/t, resulting in a price of 20% nitric acid of 17
€/t. The amount of nitric acid is very large, resulting in very high costs for the regeneration, 2260 €/h.

The value of the loaded stripping solution is related to the value of Monazite ore. Monazite ore contains 55% of lanthanides and it costs 760 €/t (1997) [10]. For this calculation, the value of nitric acid with 0.01% lanthanides will become 0.14 €/t. This would result in a yield of 18 €/h.

Conveyor belts

A conveyor belt with a width of 500 mm and a length of 50 m costs 26 k€ [7]. To account also for the purges, supply, and transportation of resin from the settler to filter and consequently to regeneration columns, this amount is multiplied with a factor of 2.6 [8]. The estimated investment of all transportation is estimated to be 66 k€.

Electricity

7 Pumps, which are estimated to consume 40 kW each and a conveyor belt consuming 10 kW, results in a total of 330 kW of electricity. The electricity costs [7] are 0.06 €/kWh, resulting in 19.8 €/h.

Concluding

Tables 10.4, 10.5, and 10.6 show the investment costs, the fixed costs and the variable profits/savings and costs of recrystallization with simultaneous ion exchange extraction.

To make simultaneous ion exchange extraction economically feasible, another stripping solution, in which the lanthanides can be concentrated more, should be found. The next part will indicate the influence of the stripping solution on the economic feasibility.

The variable savings/profits and costs result in a loss of 5.3 €/t gypsum. With the fixed costs the loss becomes 6.03 €/t gypsum. Thus, the extraction process is not economically feasible. The bottleneck of the extraction process is the stripping of the resin as can be concluded from table 10.6. If a stripping solution with a more favorable distribution could be found, the extraction process can become economically feasible, as will be illustrated in the next paragraph. From contact experiments, it was found that a stripping solution of CaNO₃ already resulted in a more favorable equilibrium.
Table 10.4. Investment costs for the simultaneous extraction of lanthanides during the recrystallization reaction.

<table>
<thead>
<tr>
<th>Investment [M€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>Filter</td>
</tr>
<tr>
<td>Transformation of 4&lt;sup&gt;th&lt;/sup&gt; recrystallizer to settler</td>
</tr>
<tr>
<td>Regeneration columns</td>
</tr>
<tr>
<td>3 columns d=1.5 H=5</td>
</tr>
<tr>
<td>Belt conveyors</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

Table 10.5. Fixed costs for the simultaneous extraction of lanthanides during the recrystallization reaction.

<table>
<thead>
<tr>
<th>Fixed costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manpower 7</td>
</tr>
<tr>
<td>Maintenance 5%</td>
</tr>
<tr>
<td>Depreciation 10%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
<tr>
<td>Per ton gypsum</td>
</tr>
</tbody>
</table>

Table 10.6. Variable costs and savings/profits of ion exchange extraction of lanthanides during the recrystallization reaction.

<table>
<thead>
<tr>
<th>Savings/Profits</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>4.2 M€/a</td>
</tr>
<tr>
<td>Gypsum</td>
<td>8.0 M€/a</td>
</tr>
<tr>
<td>Resin</td>
<td>0.94 M€/a</td>
</tr>
<tr>
<td>20% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>18 M€/a</td>
</tr>
<tr>
<td>20% HNO&lt;sub&gt;3&lt;/sub&gt; containing 0.01% Ln</td>
<td>0.14 M€/a</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.16 M€/a</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>12.34 M€/a</td>
</tr>
<tr>
<td>Per ton gypsum</td>
<td>9.7 €/t gypsum</td>
</tr>
<tr>
<td><strong>Profit-Costs</strong></td>
<td>-5.3 €/t gypsum</td>
</tr>
</tbody>
</table>
The investment on the ion exchange resin is high compared to that of the equipment. A more selective resin might result in a lower amount of resin necessary to extract the lanthanides. However, a specialty resin will also be more expensive.

*Sensitivity of the costs with respect to the stripping solution*

Table 10.6 showed the variable costs. Due to the high amount of nitric acid necessary to regenerate the ion exchange resin, ion exchange extraction is economically not feasible. Reduction in the necessary amount of stripping solution can make ion exchange extraction economically feasible. To indicate this, table 10.7 shows the influence of the amount of stripping solution on the costs/profits per ton of gypsum. The table is only an indication, because the costs of the stripping solution were taken 17 €/t, the price of 20% nitric acid. The appropriate stripping solution may have a higher cost price.

Table 10.7 shows that the savings/profits already exceed the costs when using a ratio $\Phi_s/\Phi_{IR}$ of 1:1. For such a ratio, the distribution coefficient has to be at least 1 (for 20% nitric acid only 0.47 for lanthanum). For this calculation a distribution coefficient of 1.07 was applied. Also if the stripping solution loaded with lanthanides does not have a sales value, at a ratio of 1:1, the profits also exceed the costs.

Taking also the fixed costs into account, the profit for a ratio $\Phi_s/\Phi_{IR}$ of 1:1 (distribution coefficient 1.07) was found to be 3 €/t gypsum resulting in a profit of 3.8 M€/a.

*Table 10.7. The profits minus costs as a function of the amount of stripping solution to recover the lanthanides after extraction during recrystallization.*

<table>
<thead>
<tr>
<th>$\Phi_s/\Phi_{IR}$ [-]</th>
<th>Costs [€/h]</th>
<th>Profits [€/h]</th>
<th>Profits-Costs [€/h]</th>
<th>Profits-Costs [€/t gypsum]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR + HNO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:0.5</td>
<td>2075</td>
<td>1591</td>
<td>-484</td>
<td>-3</td>
</tr>
<tr>
<td>1:1</td>
<td>1096</td>
<td>1591</td>
<td>495</td>
<td>3.1</td>
</tr>
<tr>
<td>1:2</td>
<td>607</td>
<td>1591</td>
<td>984</td>
<td>6.2</td>
</tr>
<tr>
<td>1:5</td>
<td>313</td>
<td>1591</td>
<td>1278</td>
<td>8.0</td>
</tr>
<tr>
<td>1:10</td>
<td>215</td>
<td>1591</td>
<td>1376</td>
<td>8.7</td>
</tr>
</tbody>
</table>
10.4 Conclusions

The regeneration of the ion exchange resin with 20% nitric acid is not favorable enough to make extraction of lanthanides during the recrystallization economically feasible. Due to the low affinity of nitric acid for the lanthanides ($K_{NO}(La) = 0.47$), the amount of nitric acid must be at least 1.9 times the amount of resin. This also results in an HNO$_3$-Ln product after regeneration with only a low concentration of lanthanides. In the calculated case, the loss becomes 6.03 €/t gypsum.

To make the extraction process economically feasible, a stripping solution should be found with a higher affinity for the lanthanides resulting in a distribution coefficient of 1 or higher. Less stripping solution is needed and the lanthanides are more concentrated in the stripping solution. With a ratio of stripping solution to ion exchange resin of 1:1 (distribution coefficient 1.07), the profits/savings exceed the variable and fixed costs with 3 €/t gypsum, resulting in a profit of 3.8 M€/a.

The investment costs are estimated to be only 4.3 M€.

References

Chapter 11

Development of Ion Exchange Bars for Transverse Flow Ion Exchange Modules

For the treatment of slurries, like the phosphoric acid slurry, in transverse flow ion exchange modules, rigid ion exchange bars are needed to avoid cracking of the bars.

Three different bars were made, bars of commercial ion exchange resin beads glued on Hastelloy C-276 bars, bars of ground commercial ion exchange resin polymerized in polystyrene (PS) with divinylbezene (DVB), and bars of PS with DVB that were functionalized with sulfonic acid groups.

After repeated exposure to industrial phosphoric acid, also the most resistant glue softened and swelled. This made the glued bars unsuitable for the treatment of the test system, the phosphoric acid slurry.

Warping of the PS-DVB bars during functionalization with sulfuric acid was prevented by a 0.8 mm Hastelloy C-276 support. The maximum ion exchange capacity was determined to be 1.2 meq/ml for bars with 6% DVB. Analyses showed that only the surface of the bars was functionalized and it is therefore thought that further research may result in higher capacities.
11.1 Introduction

In chapters 7 and 8, the recrystallizing slurry is treated by adding ion exchange resin beads to the stirred vessel, in which the recrystallization of calcium sulfate hemihydrate (HH) to gypsum (calcium sulfate dihydrate, DH) is performed. The disadvantage of adding resin beads to the slurry is that the beads have to be separated from the solid gypsum particles again, before they can be regenerated and reused. This separation can be accomplished by using a difference in density or a difference in size.

To save an additional separation step to recover the resin beads from the solids and avoid possible contamination of the product with the resin, an apparatus, in which the ion exchange groups are immobilized, was wished for. A module with ion exchange bars, instead of beads, would be a promising potential apparatus for the treatment of slurry streams. The flow in such a module should be perpendicular to the orientation of the bars, as in the transverse flow hollow fiber membrane contactors described in chapter 6. With transverse flow, the feed solution flows from top to bottom of the module. This makes it possible to design a module, in which no dead areas and thus settling of solids occur as is described in chapter 2. In parallel flow, the feed solution enters and leaves the module with an angle of 90° creating dead areas. This will result in settling of solids and eventually in clogging of the module.

For the treatment of the phosphoric acid slurry (chapter 1) by transverse flow ion exchange modules, rigid and chemically resistant ion exchange fibers or bars are needed. However, no commercial fibers or bars with an appropriate length and rigidity were found. Only fibers of polypropylene with small islands of polystyrene, which can be functionalized with sulfonic acids, were found in literature [1,2]. However, these fibers are only commercially available in lengths of 0.2 to 1.0 mm. Another disadvantage of polypropylene fibers is their flexibility. Earlier experience with a transverse flow module with flexible hollow polypropylene fibers showed cracking of the fibers at the connection point with the housing caused by the vibrating movement of the fibers in the slurry and the force of the slurry on the fibers.

For the transverse flow ion exchange module, in which the orientation of the fibers or bars is perpendicular to the direction of the process stream flow, rigid ion exchange bars are required to handle process streams with considerable amounts of solids.
To create these rigid bars, three different production ways have been investigated;
i) commercial ion exchange beads have been glued on support wires,
ii) commercial ion exchange resin beads have been grinded and mixed with styrene and divinylbenzene (DVB) to polymerize in a mold to bars, and
iii) styrene and DVB were polymerized in a mold to bars and subsequently functionalized with sulfonic acid groups, similar to the preparation of ion exchange beads [3,4].

This chapter describes the preparation and properties of the developed ion exchange bars. The ion exchange bars were tested on their applicability for the treatment of the test system, the phosphoric acid slurry, by contacting them with clear industrial phosphoric acid of a two-filter HemiDiHydrate (HDH) production process. The next chapter will describe the application of the bars in a transverse flow ion exchange module for the extraction of impurities during the recrystallization of HH to gypsum in phosphoric acid.

11.2 Characterization

11.2.1 Extraction ability

For characterization of the ion exchange bars, the volumetric maximum capacity is determined by titration. However, the effective capacity will differ from the maximum capacity. It also depends on the solution, from which the impurities are extracted. To test the performance of the ion exchange bars, the extraction efficiency, $\eta$ [%], is determined after equilibration of the bars with clear industrial phosphoric acid by

$$\eta_A = \frac{[A]_{\text{before}} - [A]_{\text{after}}}{[A]_{\text{before}}} \cdot 100\%$$

11.1,

with $[A]$ the concentration of an impurity ion A in the acid [mg/kg], before indicating the concentration before and after indicating the concentration after equilibration. The summation of the extraction efficiencies for all cations indicates the effective capacity of the resin for removal of impurities from the phosphoric acid test system.

For the extraction of impurities from industrial phosphoric acid, the selectivity of the resin for an impurity ion with respect to calcium is very important. The concentration of calcium, which is not considered an impurity ion, in the acid is high compared to that of the impurities. Therefore, it is preferred that the ion exchange bar/resin has a
very low affinity for calcium. The affinity difference between calcium and an impurity ion is indicated by the separation factor, S [-],

\[ S = \frac{\eta_A}{\eta_{Ca}} \]  

11.2.

The subscript Ca refers to the calcium ions. The higher the extraction efficiency and separation factor, the better the performance of the ion exchange bar with respect to the extraction of impurities from industrial phosphoric acid.

11.2.2 Mechanical strength

Due to the transverse flow, a pressure drop occurs over the ion exchange bars. The pressure drop, \( P_w \) [Pa], is calculated with

\[ P_w = C_w \cdot \frac{1}{2} \cdot \rho \cdot v^2 \]  

11.3,

with \( C_w \) the resistance coefficient [-], and \( v \) the velocity of the slurry [m/s]. The density, \( \rho \), of the phosphoric acid slurry with 0.2 kg calcium sulfate particles per kg slurry is \( 1.25 \cdot 10^3 \) kg/m\(^3\) (experimentally determined). The resistance coefficient depends on the Reynolds number, \( Re \) [-],

\[ Re = \frac{v \cdot d}{v} \]  

11.4,

with \( d \) the diameter of the bars [m], and \( v \) the kinematic viscosity [m\(^2\)/s]. The kinematic viscosity is \( 4.8 \cdot 10^{-6} \) m\(^2\)/s [5]. For a velocity of 1 cm/s, the Reynolds number becomes 6.25, resulting in a resistance coefficient of 4 [6]. For a velocity of 1 m/s, the Reynolds number becomes 625, resulting in a resistance coefficient of 1.2. With equation 11.3, the pressure drop over a single bar was calculated to be 0.25 Pa for a slurry velocity of 1 cm/s, and 750 Pa for a slurry velocity of 1 m/s. Equation 11.3 is only applicable for one single bar. For a staggeredly packed module, the calculated pressure drop over one bar can be estimated by multiplying it with a factor of 1.5 [7].

The force on a single bar, \( F \) [N], is determined with

\[ F = P \cdot A \]  

11.5,

with \( A \) the cross section of the bar [m\(^2\)]. For a bar with a diameter of 3 mm and a length of 5 cm, the force becomes 0.13 N with a slurry velocity of 1 m/s.
11.3 Materials for Ion Exchange Bar Preparation

11.3.1 Commercial ion exchange resin

As is shown in chapter 3, lanthanides can be extracted from industrial phosphoric acid with D2EHPA (di-(2-ethylhexyl)phosphoric acid) in kerosene and Nacure 1052 (didodecylnaphtalenesulfonic acid) in heptane. Heavy metals, like lead, copper, cadmium, and mercury are selectively extracted with Cyanex 302 (bis-(2,4,4-trimethylpentyl)-monothiophosphinic) and Cyanex 301 (bis-(2,4,4-trimethylpentyl)-dithiophosphinic acids).

Unfortunately, ion exchange resin with thiophosphinic acid functional groups was not commercially available. After consulting suppliers of ion exchange resin, some commercially available resins have been tested for the removal of lanthanides or heavy metals from industrial phosphoric acid, like Duolite GT 73 with thiol groups for the removal of heavy metals, Amberlite IRC718 with iminodiacetic groups for the removal of lanthanides, and Amberlite IR120 and Dowex C-500 with sulfonic acid groups for the removal of both heavy metals and lanthanides (the results for Dowex C-500 and Amberlite IR120 are presented in chapter 3). Duolite GT 73 and Amberlite IRC718 did not show any extraction of heavy metals or lanthanides. Therefore, it was decided to continue this research with resins with sulfonic acid functional groups like Dowex C-500 and Amberlite IR120, although these groups are not very selective.

An advantage of the usage of the sulfonic acid groups is that the functionalization of polymers is common knowledge [3,4,8] and very easy to perform. Preparation of bars by polymerization followed by functionalization with sulfonic acids would therefore be relatively easy. Using sulfonic acid functional groups for the three different kinds of bars makes it possible to compare their properties. Further, the properties of the bars can be easily compared with those of commercial ion exchange resin.

The ion exchange resin Dowex C-500 was chosen for the preparation of bars with glued ion exchange resin on wires and of bars from grinded ion exchange resin. Further, it was used as a reference for the performance of the bars. Table 11.1 shows the properties of the Dowex C-500 resin.

It should be kept in mind that the ion exchange resin and bars would perform better, if more selective ion exchange groups could be applied, like thiophosphinic acid groups for the extraction of heavy metal ions.
Table 11.1. The properties of Dowex C-500 ion exchange resin.

<table>
<thead>
<tr>
<th>Properties of Dowex C-500 resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>strong acidic sulfonic acid functional groups (pK&lt;&lt;0)</td>
</tr>
<tr>
<td>capacity 4.9 meq/g or 1.9 meq/ml</td>
</tr>
<tr>
<td>spherical beads</td>
</tr>
<tr>
<td>diameter approximately 465 - 635 μm</td>
</tr>
</tbody>
</table>

11.3.2 Support wires

Hastelloy C-276 has been chosen as a support material for the glued bars, because of its chemical resistance to the industrial phosphoric acid solution [9,10]. Further, the attachment of glue on metals is relatively easy. Polymers were not tested, because either the attachment of glue on a polymer is difficult or the polymer is not resistant to the industrial phosphoric acid process stream, as is schematically shown in table 11.2 for some common polymers. Another disadvantage of the polymers is that they bend more easily than metal wires with the same diameter.

Hastelloy wires with diameters of 1.6 and 2.0 mm were used as support material. Wires with smaller diameters could not be used, because the ion exchange beads were too large to glue uniformly on these wires. Another disadvantage of the wires with smaller diameters is that they bend easily, causing cracking of the glue and loss of the ion exchange resin.

Two groups of glues show a good chemical and thermal resistance, which are important properties for the bars, epoxy resins and polyurethane's [17]. Searching within these groups, three different glues looked promising, the epoxy resins Araldite 2014 (Ciba Geigy), Araldite 2011 (Ciba Geigy), and the polyurethane Sitan 2100 (Gijsman Epoxy Produkten, The Netherlands) [18,19].

11.3.3 Polymerized bars

Polymers of polystyrene (PS) crosslinked with DVB are chemical resistant, also to the industrial phosphoric acid solution as was already proven in chapter 3. They are, dependent on the degree of crosslinking, hard and resistant to mechanical breakdown and attrition [8]. Further, the polymerization is very easy to perform. Another advantage of the PS-DVB polymer is the possibility of attaching different functionalization groups to the solid matrix, thus changing extraction properties and selectivity of the ion exchange resin. Polysulfon and polyetheretherketon that also can be easily sulfonated have the disadvantage that they have to be pretreated to

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make them rigid, and mechanical and chemical resistant. This makes the fabrication of these bars more difficult and time consuming.

Table 11.2. Chemical and thermal resistance of some common polymers, and the possibility of attaching epoxy resin and polyurethane to the polymer [11-16].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Resistance to 50%</th>
<th>Resistance to 50%</th>
<th>Thermal resistance</th>
<th>Attachment to PU</th>
<th>Attachment of epoxy resin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₃PO₄ at 20°C</td>
<td>H₃PO₄ at 80°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDPE</td>
<td>+ / -</td>
<td>-</td>
<td>+ / -</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>+ / -</td>
<td>+ / -</td>
<td>+ / -</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>PVC-C</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Nylon 6.6</td>
<td>+ / -</td>
<td>-</td>
<td>+ / -</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>PVDF</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PTFE</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

with: PU = polyurethane, HDPE = high density polyethylene, PP = polypropylene, PVC-C = chlorated polyvinylchloride, PVDF = polyvinylidenefluoride, PTFE = polytetrafluoroethylene,

with: ++ very good, + good, + / - moderate, - bad, -- very bad.

The PS-DVB bar will be functionalized with sulfonic acid groups, because the functionalization is common knowledge and easy to perform. Further, the performance of such bars can be easily compared with commercial ion exchange resin with sulfonic acid functional groups, which are richly available.

11.4 Experimental

11.4.1 Glued ion exchange resin on support wires

The ion exchange bars are made by putting a thin layer of glue on metal wires manually after roughening the wires with sandpaper. This is followed by careful attachment of the resin beads on the surface, trying to keep as much ion exchange surface as possible available for the extraction.

Three hardening methods were tested;

i) the glue was hardened in an oven of 80 °C for 30 minutes,

ii) the glue was hardened in water at 80 °C for 30 minutes,
iii) the glue was hardened in a beaker that contained a small amount of water, which was not in contact with the wires. This beaker was placed in an oven of 80 °C for 20 hours.

After hardening of the glue, the bars were saved in tap water for 24 hours at room temperature. Pictures of the glued ion exchange resin were made with Scanning Electron Microscopy (SEM).

11.4.2 Grinned ion exchange resin bars

The commercial ion exchange beads are grinned with a pestle, and sieved resulting in particles with a maximum size of 45 μm. These particles are mixed with a solution of styrene with 8% DVB as a crosslinker and benzoylperoxide as initiator. The homogeneous mixture of ion exchange material is casted in a mold and put in an oven to polymerize for 12 hours at 90 °C.

11.4.3 PS-DVB ion exchange bars

For the preparation of the PS-DVB ion exchange bars a mold was designed. With this mold, polymer bars are prepared without air bubbles by applying vacuum before polymerization. Figure 11.1 shows the design of the mold.

For the preparation of straight bars, as will be discussed later, Hastelloy C-276 wires with a diameter of 0.8 mm are added to the styrene-DVB mixture in the mold before polymerization. An important feature of the mold is that the support Hastelloy C-276 wires are centered perfectly in the polymer bars.

The following steps are taken to make PS ion exchange bars from styrene with DVB as a crosslinker and benzoylperoxide as initiator:

- polymerization in a mold for approximately 12 hours at 90 °C
- treatment with a swelling agent in most cases, i.e. toluene, dimethylsulfoxide, chloroform or 1,1,1-trichloroethane
- functionalization by contacting the bars for at least 12 hours with concentrated sulfuric acid at 100 °C
- cooling down the bars in the concentrated sulfuric acid for at least 20 hours
- step-wise dilution of the concentrated sulfuric acid to avoid large strains in the bars [20]
- treatment of the bars with 2 N sodium chloride for 1 hour
- functionalization of the bars by contact with 2 N hydrochloric acid or nitric acid for 1 hour
- washing of the bars with a small amount of tap water to remove the excess of hydrochloric acid or nitric acid before characterization.

The bars made are 3 mm in diameter and 8 cm long.

![Image of the mold](image)

**Figure 11.1.** The mold used for the preparation of PS-DVB ion exchange bars supported by a Hastelloy C-276 wire in the middle.

### 11.4.4 Characterization of the ion exchange bars

**Capacity**

For the characterization of the ion exchange bars, the maximum ion exchange capacity was determined [8] by adding 15 ml of 0.1 M sodium hydroxide to a known volume of ion exchange bar. Phenolphthalein was added as an indicator and 0.1 M hydrochloric acid was titrated until the pink solution became colorless, indicating that the solution was pH neutral.

The capacity, C [meq/ml], was calculated with
\[ C = \frac{V_{\text{NaOH}} \cdot [\text{NaOH}] - V_{\text{HCl}} \cdot [\text{HCl}]}{V_{\text{IR}}} \]

with \( V \) the volume [ml], and IR indicating the ion exchange bar. The same method was used to determine the capacity of Dowex C-500 resin as a reference.

Efficiency and selectivity

The extraction efficiency was determined by contacting approximately 1 ml of bar or resin beads with 12 g of industrial phosphoric acid (two-filter HDH process) at 80 °C in a shaking apparatus for 12 hours. In table 11.3, a typical composition of the industrial model solution is given. To facilitate analysis, the concentrations of lanthanum, cerium, europium, dysprosium, and erbium were increased with approximately 0.3 mmol/kg by adding their nitrate salts. The extraction efficiency of several ions was determined by measuring the concentration of these ions before and after contact with the bars by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The results were compared with the results of the same experiments for Dowex C-500.

**Table 11.3. Typical composition of the model solution, an industrial phosphoric acid solution from the two-filter HDH production process.**

<table>
<thead>
<tr>
<th>Concentration (mmol/kg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{PO}_4 )</td>
<td>( 8 \cdot 10^2 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>( 5 \cdot 10^2 )</td>
</tr>
<tr>
<td>( \text{Ca} )</td>
<td>30</td>
</tr>
<tr>
<td>( \text{Cd} )</td>
<td>( 5 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>( \text{Pb} )</td>
<td>( 6 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>( \text{La} )</td>
<td>( 7 \cdot 10^{-2} )</td>
</tr>
<tr>
<td>( \text{Ce} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{Eu} )</td>
<td>( 1.5 \cdot 10^{-4} )</td>
</tr>
<tr>
<td>( \text{Dy} )</td>
<td>( 1 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>( \text{Er} )</td>
<td>( 8 \cdot 10^{-3} )</td>
</tr>
</tbody>
</table>

Degree of functionalization of the PS-DVB bars

With High Resolution Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) with laser ablation system, the depth of functionalization of the polymeric bars was determined. To determine this, the bars were broken in two and the laser moved...
along the fractured surface evaporating small amounts of material as a function of the distance from the surface. An example of the laser beam path is shown in figure 11.2.

![Image](image.jpg)

**Figure 11.2.** The laser beam path for the determination of the functionalization of the ion exchange bars as a function of the distance from the surface after breaking the bar.

The evaporated material was directly transported to the ICP-MS and analyzed on carbon and sulfur content by determining intensities measured by the ICP-MS. Until now, it is not possible to translate these intensities into concentrations of sulfur in the ion exchange material, because the analyses with laser ablation cannot be calibrated yet. The carbon signal indicates the amount of material that was evaporated by the laser. It is assumed that the amount of carbon in the bars and beads is constant. Figure 11.3 shows the carbon signal during a measurement. Very clear is the hole in the bar, which results in a drop in the carbon signal. By relating the sulfur signal to the carbon signal, a relation is found between the amount of sulfur per amount of polymer. A high amount of sulfur per amount of polymer indicates a successful functionalization. The time scale on the x-axis is a measure for the distance that the laser beam has traveled, because the beam travels with a constant speed in only one direction.

Another way to determine the depth of functionalization is by shooting the laser several times on the same spot of the surface, creating a hole in the bar or bead. The laser beam will migrate deeper and deeper into the polymer and the sulfur content will be found as a function of depth. With this operation mode, there may be some distortion of the signal, because also some material of the edges of the hole may be evaporated.

This analysis was also performed on bars that were equilibrated with a solution of 50 mg/kg of lanthanum nitrate in distilled water. The presence of lanthanum as a function of the penetration depth was determined in the same way as the presence of sulfur.

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The results of the ion exchange bars were compared with results of commercial ion exchange resin beads. To determine the functionalization depth of the beads, beads were casted in an epoxy resin tablet. This tablet was scoured until the surface of the tablet showed some half through resin beads. These approximately half through beads were scanned by the laser.

![Graph showing carbon signal]

**Figure 11.3.** The carbon signal of a piece of ion exchange bar during analysis with laser ablation with simultaneous measurement with HR ICP-MS.

**Mechanical strength determination**

To get an indication of the mechanical strength of the polymerized bars, a bending test is performed. The operation of the bending test is illustrated in figure 11.4.

![Bending test illustration]

**Figure 11.4.** Illustration of the bending test for determining the strength of the polymerized ion exchange bars.

The stress at break, $\sigma_b$ [MPa], is calculated with

$$\sigma_b = \frac{3F_b}{\pi^2 d^3}$$

11.7,
with $F_b$, the force on the bar at break [N], $l$ the length of the bar between the points of support [mm], and $d$ the diameter of the bar [mm]. The diameter depends on the bar used, but was approximately 2.5 mm, and the length of the tested bar was 20.24 mm.

With equation 11.7, the point concentrated load is taken for the calculation of the stress at break. For the transverse flow ion exchange module, the load on the bars is equally divided and the stress at break will be even higher than that calculated with equation 11.7.

11.5 Results and Discussion

11.5.1 Glued ion exchange resin on support wires

Preparation

From the glues tested, only Araldite 2014 could be used for the preparation of the bars, although the glue became a little soft after contact with the industrial phosphoric acid at 80 °C. The polyurethane Sitan 1100 dissolved completely, and Araldite 2011 did not stick to the Hastelloy wire during contact with the acid.

Hardening of the Araldite 2014 glue in an oven of 80 °C resulted in loss of all resin beads after contacting the glued ion exchange bar with tap water. Due to the dry air in the oven, the beads shrunk. During contact with tap water, the beads swelled again to their original size, resulting in loosening of the beads from the glue. A solution of this problem was thought to be the hardening of the glue in water of 80 °C. The beads actually kept stuck to the Hastelloy wire, but the bars did not show any ion exchange capacity. This is probably due to a thin glue layer on the beads, as is shown in figure 11.5A. To prevent the creation of a thin glue layer on the beads and shrinking of the beads, the glue was hardened in an oven above a small layer of water, which was not in contact with the bars. The beads kept stuck to the Hastelloy wire, indicating that the surroundings were moist enough to prevent shrinking of the beads during hardening. Further, the surface of the beads that was not in direct contact with the glue was clean, as is shown in figure 11.5B, resulting in a detectable ion exchange capacity.

Capacity

The capacity of the glued ion exchange bars was determined to be 0.56 to 0.74 meq/ml, dependent on the diameter after gluing, resulting in an average of 0.66 meq/ml. It was calculated that a maximum of 1616 ion exchange resin beads with a diameter of 500 μm could be glued on a wire of 50 mm in length and 2.1 mm in thickness including a glue layer of 0.1 mm. Assuming that one quarter of the ion exchange beads sink in the glue, the diameter of the glued bar is 2.55 mm and the
volume 0.25 ml. With an ion exchange capacity of 1.9 meq/ml for the Dowex C-500 ion exchange resin, the maximum capacity of the glued ion exchange bars was calculated to be 0.79 meq/ml. So according to this very rough calculation, only about 15% of the ion exchange capacity was lost by gluing.

Figure 11.5. Ion exchange beads glued to Hastelloy C-276 with Araldite 2014 after hardening in water of 80 °C (A) and after hardening above water in an oven at 80 °C (B).

Efficiency and selectivity

In figure 11.6, the extraction efficiency of the glued ion exchange bars is compared with that of the commercial ion exchange beads. The affinity of the bars differs slightly from that of the beads, although both are (made of) Dowex C-500 resin. The capacity per volume of bar is about 2.9 times less than that of the beads (0.66 meq/ml for the bars, and 1.9 meq/ml for the resin), but the lanthanum uptake only decreased 1.7 times. So, lanthanum was taken up relatively more by the bars. Also cerium (decrease of 1.9 times), and calcium (decrease of 2.1 times) were taken up relatively more, whereas erbium was taken up less (decrease of 3.1 times). This non-linear behavior is due to the competition of cations for the active sites of the ion exchange resin, which was described in chapter 4 for Dowex C-500 in clear industrial phosphoric acid.

The separation factors depend on the number of active sites, as is shown in table 11.4. Earlier experiments with varying amounts of Dowex C-500 resin, described in chapter 3, showed comparable relations between the separation factors and the number of active sites. Due to an increasing number of active sites, the affinity sequence shifted from Ca>Eu>Dy to Eu>Dy>Ca for increasing amounts of Dowex C-500.
Figure 11.6. Extraction of lanthanides and calcium from industrial phosphoric acid at 80 °C with 1 ml of Dowex C-500 ion exchange resin and with 1 ml of glued Dowex C-500 ion exchange resin on Hastelloy C-276 wires.

Table 11.4. Separation factors of some lanthanides for 1 ml of Dowex C-500 (1.95 meq/ml) and 1 ml of glued ion exchange bar (0.66 meq/ml) after contact with 12 g of phosphoric acid.

<table>
<thead>
<tr>
<th></th>
<th>Glued bar</th>
<th>Dowex C-500</th>
</tr>
</thead>
<tbody>
<tr>
<td>active sites</td>
<td>55 meq/kg acid</td>
<td>160 meq/kg acid</td>
</tr>
<tr>
<td>La</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Ce</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Eu</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Dy</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Er</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Stability

A final test of the ion exchange bars was performed by using them in the transverse flow ion exchange module to extract impurities from the phosphoric acid solution with 200 g calcium sulfate solids per kg slurry. The transverse flow ion exchange module and the extraction efficiency of the glued bars will be described in chapter 10. During contact of the bars with the phosphoric acid, Araldite 2014 not only softened, but also swelled significantly causing loosening of the glue layer with the resin beads from the Hastelloy wire, as is shown in figure 11.7. This would eventually lead to loss of ion exchange resin. The loosening of the glue can be
avoided by leaving some space for the glue to swell, but it will remain a week spot of the bars.

Figure 11.7. Glued ion exchange bars after usage in the transverse flow ion exchange module with industrial phosphoric acid with 200 g solid calcium sulfate particles per kg slurry of 71 °C.

11.5.2 Bars of grinded ion exchange resin

Although the Dowex C-500 beads were grinded to particles with a maximum size of 45 μm, the particles were too large to avoid settling in the mold during polymerization of the styrene-DVB mixture. With the pestle, it was not possible to get particles with the same settling properties as the mixture of monomers.

No further research was performed on these bars.

11.5.3 Bars of functionalized PS crosslinked with DVB.

Preparation

The first PS bars with 8% DVB were not functionalized after contact with concentrated sulfuric acid of 100 °C, even not after contact of 72 hours. The bars did not show any ion exchange capacity. Wheaton et al [21] found that swelling of the polymer with a swelling agent prior to functionalization resulted in a more successful functionalization. Toluene, dimethylsulfoxide, chloroform, and 1,1,1-trichloroethane were taken as swelling agents, for which the effects on the bars are shortly given in table 11.5.

The carbonization with the application of toluene, which was indicated to be a suitable swelling agent by Wheaton et al [21], was due to the fact that not only the polymer was sulfonated but also toluene, which probably resulted in a large temperature increase due to the highly exothermic reaction.
Table 11.5. The effects of different swelling agents on polymer bars with 8% DVB with respect to swelling and functionalization.

<table>
<thead>
<tr>
<th>Swelling agent</th>
<th>Effect on polymer bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>The bar is visually swollen, but fully carbonized after contact with concentrated sulfuric acid.</td>
</tr>
<tr>
<td>Dimethysulfoxide</td>
<td>No swelling can be seen, and the bars have no ion exchange properties after contact with concentrated sulfuric acid.</td>
</tr>
<tr>
<td>Chloroform</td>
<td>The bars swell very rapidly. After contact with chloroform for 20 minutes, the bars are rubbery and are destructed during contact with concentrated sulfuric acid.</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>No swelling can be seen, but the bars are functionalized after contact with concentrated sulfuric acid for 24 hours.</td>
</tr>
</tbody>
</table>

For polymer bars with 4% DVB, 1,1,1-trichloroethane could not be used as a swelling agent. The polymer bars became rubbery and contact with sulfuric acid for functionalization resulted in destruction of the bars. Only bars with 6 and 8% DVB were successfully functionalized after treatment with 1,1,1-trichloroethane.

Without using a support, it was not possible to gain straight bars after contact with concentrated sulfuric acid, as is shown in figure 11.8.

![Image](image.jpg)  

**Figure 11.8.** The polymer bars before and after contact with concentrated sulfuric acid of 100 °C for functionalization.

Therefore, Hastelloy wires of 0.8 mm were used to support the polymer bars. The
wires were added to the mold before polymerization of the monomer mixture, either in the middle or on one side of the future polymer bar. During the sulfonation of the bars with the Hastelloy wire on one side, the polymer bent and loosened from the wire, whereas for the bars with the Hastelloy wire in the middle, straight sulfonated ion exchange bars were gained.

**Capacity**

The capacity of the sulfonated PS-DVB bars depended strongly on the sulfonation time, especially the cooling down time. For a bar with 8% DVB, a sulfonation of 42 hours, including cooling down, resulted in an average capacity of 0.8 meq/ml (this is not very accurately, because it is difficult to determine the actual volume of the bar), and a sulfonation of 72 hours resulted in an average capacity of 1.0 meq/ml. This ion exchange capacity is still a factor of 2 smaller than that of the commercial resin, but already larger than that of the glued ion exchange bars.

Lowering of the DVB content to 6% resulted in an increase of the maximum capacity to 1.2 meq/ml after a sulfonation time of 48 hours including cooling down.

**Functionalization**

The PS-DVB bars are only functionalized on the surface and not in the heart of the bars. This is illustrated by figure 11.9 for a bar with 8% DVB without a Hastelloy wire as support. As mentioned in the experimental part of this chapter, the time scale can be translated into a length scale, because the speed of the laser beam is constant.

After equilibrating the bars with a solution of lanthanum nitrate, lanthanum can also only be found on the surface of the bars. This is shown in figure 11.10. The lanthanum peaks appear at the same places as the sulfur peaks, indicating that only ion exchange capacity is found on the surface of the bars where sulfur, and thus sulfonic acid, is present. It is clear that the limited functionalization also limits the ion exchange extraction of lanthanum.

For the commercial ion exchange resin beads, the entire bead is functionalized, as is shown in figure 11.11 for a scan of two resin beads. The figure shows a small dip in the intensity of sulfur, but this is the epoxy resin between the two adjacent beads.

The limited functionalization of the PS-DVB bars is the reason that the capacity of these bars is lower than that of the beads. It is expected that further research may solve the problems that cause this limited functionalization of the ion exchange bars.
Figure 11.9. The intensity of sulfur measured by ICP-MS with laser ablation for a PS bar with 8% DVB after 42 hour of sulfonation.

Figure 11.10. The intensities in counts per second [CPS] of sulfur, lanthanum, and carbon after equilibrating a functionalized PS bar with 8% DVB with a solution of 50 mg/kg lanthanum nitrate in distilled water.
Figure 11.11. The intensity of sulfur measured by ICP-MS with laser ablation for two adjacent scoured Dowex C-500 resin beads.

Efficiency and selectivity

For the characterization of the PS-DVB bars, bars with 8% DVB that were sulfonated for 36 hours were taken. These bars had an ion exchange capacity of 0.8 meq/ml. In figure 11.12, the extraction efficiency of the PS-DVB bars is compared with that of commercial ion exchange resin. Contrary to the glued bars, the affinity sequence of the PS-DVB bars equals that of the commercial resin, but the affinity has already shifted. The shift of the affinity is due to competition effects, which play a role when contacting a same amount of acid with different amounts of ion exchange active sites, as is already mentioned in chapter 4 for different amounts of commercial beads and in § 11.5.1 for the glued ion exchange bars. The amount of active sites of the PS-DVB bars is 2.4 times smaller than that of the commercial resin due to the lower degree of functionalization. However, the extraction of lanthanum only decreases 1.6 times and that of cerium 1.7 times. These lanthanides are thus more concentrated on the bars than on the resin, whereas dysprosium and erbium are taken up relatively less. The shifted affinity did not result in a different affinity sequence, because the difference between the amount of active sites of the PS-DVB bars and that of the commercial resin was not large enough. In case of the glued ion exchange bars, the amount of active sites was 2.9 times less than that of the commercial resin. Due to this larger difference in the amount of active sites, the affinity shifted more resulting in a different affinity sequence.
Mechanical strength

To gain a large mechanical strength, it is important to create bars without any cracks or air bubbles. Non-sulfonated PS-DVB bars with 8% DVB, showed a stress at break between 105 to 135 MPa, far more than the necessary 1.5 kPa for a slurry velocity of 1 m/s. After sulfonation, the stress at break decreased to a minimum stress at break of 45 MPa (highest stress at break found was 85 MPa).

![Graph showing extraction efficiency for various elements](image)

**Figure 11.12.** Extraction of lanthanides and calcium from industrial phosphoric acid at 80 °C with 1 ml of Dowex C-500 ion exchange resin and with 1 ml of PS-DVB bars functionalized with sulfonic acids.

11.6 Conclusions

For the application of the transverse flow ion exchange module, straight ion exchange bars of 3 mm in diameter and 8 cm in length have been developed by polymerizing styrene with DVB in a mold with in the middle of the bar a Hastelloy wire of 0.8 mm. The bars were swollen by means of 1,1,1-trichloroethane, before they were sulfonated successfully by concentrated sulfuric acid at 100 °C. The capacity of the bars with 6% DVB is 1.2 meq/ml, which is lower than that of commercial Dowex C-500 with a capacity of 1.95 meq/ml. The lower capacity is due to the fact that only the surface of the bars is functionalized with sulfonic acid groups. It is expected that further research would result in a better functionalization resulting in a higher capacity of the bars.

The capacity of the glued ion exchange bars is only 0.66 meq/ml (average value). Another disadvantage of the glued bars is that they are larger in diameter, so less ion exchange capacity can be inserted in the same volume of module. Further, the glue
swells during application of the transverse flow ion exchange module, which will eventually lead to loss of ion exchange resin.

Acknowledgement

Michiel Hoogerwerf is acknowledged for his perseverance and all his experimental work on the glued and PS-DVB bars. Michel van der Brink is acknowledged for his experimental work on the PS-DVB bars and the analyses on the ICP-MS with laser ablation. Jan Sterk (Faculty of Mechanical Engineering, Delft University of Technology) is acknowledged for his help with the bending tests.

References

5. Becker P., Phosphates and phosphoric acid; raw materials, technology, and economics of the wet process, Marcel Dekker, Inc., USA (1989).


Chapter 12

Transverse Flow Ion Exchange Module for the Treatment of the Phosphoric Acid Slurry

Two transverse flow ion exchange modules were developed, one for the glued ion exchange bars and one for the polystyrene-divinylbenzene (PS-DVB) bars functionalized with sulfonic acid groups. With the module with PS-DVB bars functionalized with sulfonic acid groups, up to 24% of the input amount of a single lanthanide was extracted. The amount of active groups in the module is comparable to 13 g commercial resin/kg slurry. This means that the extraction with the module is the most efficient one gained until now. This is probably due to the fact that all functional groups are present at the surface of the bars and readily accessible.

To increase the extraction efficiency of the module, more research is needed on flow of slurry streams in tube banks to determine the minimum pitch sizes, the possibility of increasing the capacity, and improving the selectivity of the bars by changing functional groups.

12.1 Introduction

In chapters 7 and 8, the recrystallizing slurry was treated by adding ion exchange resin beads to the crystallizer, in which the recrystallization of calcium sulfate hemihydrate (HH) to gypsum (calcium sulfate dihydrate, DH) was performed.

The disadvantage of adding resin beads to the slurry is that the beads have to be separated from the slurry before they can be regenerated and reused. To avoid this additional separation step, an ion exchange module, which contains ion exchange bars, is developed on laboratory scale. Another advantage of such a module, in which the ion exchange functional groups are immobilized, is the prevention of possible contamination of the product with ion exchange resin.

In the module, the feed flow is chosen perpendicular to the orientation of the bars, as in the transverse flow hollow fiber modules for liquid membrane extraction, described in chapters 2 and 6. Parallel flow is thought to be not applicable due to the presence of high concentrations of solids. In a parallel flow configuration, the feed stream enters and leaves the module with an angle of 90° resulting in dead areas where solids will settle and eventually cause clogging of the module. This is discussed in more detail in chapter 2.

For the treatment of the phosphoric acid slurry by transverse flow ion exchange modules, rigid and chemically resistant ion exchange fibers or bars are needed. Because such fibers or bars were not commercially available, ion exchange bars have been developed. The development of ion exchange bars is described in chapter 11.

Two transverse flow ion exchange modules are designed and tested for the treatment of the recrystallizing phosphoric acid slurry. The first module is developed to treat the slurry during the recrystallization of HH to gypsum with the glued ion exchange bars, which are made by gluing commercial Dowex C-500 resin beads on Hastelloy C-276 bars. The second module is of an improved design, in which bars of polystyrene-divinylbenzene (PS-DVB) functionalized with sulfonic acid are placed. This chapter describes the module designs and the results that are gained during treatment of the recrystallizing phosphoric acid slurry with the transverse flow ion exchange modules.
12.2 Module Design

12.2.1 Module for glued ion exchange bars

The module designed for the glued ion exchange bars is build up by piling up several slides, resulting in a very flexible experimental set-up. Figure 12.1 shows the design of the module schematically.

![Diagram of the module](image)

**Figure 12.1. Schematic presentation of the modular transverse flow ion exchange module for the treatment of the recrystallizing phosphoric acid slurry with glued ion exchange bars.**

The slides with an internal size of 50 times 57 mm are made of Teflon®, because of its low heat conductivity and its chemical resistance to the industrial phosphoric acid, which also contains sulfuric acid, chlorides, fluorides, etc. The low heat conductivity makes it possible to treat the recrystallizing slurry at a constant temperature of 70 °C without isolation or tracing. The slides either contain 9 or 8 ion exchange bars with an approximate diameter of 3 mm and a length of 50 mm.

The glued ion exchange bars are placed in a staggered configuration to enhance the contact between the bars and the slurry and avoid settling of the solid particles on the bars [1].

No literature was found on the handling of slurry streams in tube banks. No indications were found on the necessary pitches between the ion exchange bars to avoid clogging. The required pitches will be dependent on both the crystal size distribution and crystal shape. As a first assumption pitches of 10 times the
maximum industrial crystal size were taken. Based on Scanning Electron Microscopy (SEM) and crystal sizes determined with a Malvern Mastersizer, longitudinal and transverse pitches of 6 mm were taken. More fundamental research on the design of transverse flow modules for the treatment of slurry streams is described by Berends [2].

12.2.2 Module for PS-DVB bars

The transverse flow ion exchange module, designed for the treatment of the recrystallizing phosphoric acid slurry with PS-DVB bars functionalized with sulfonic acid groups, is an improved design of the first module described in the previous paragraph. To establish an evenly divided flow in the entire module, resulting in an optimum usage of the entire ion exchange bars, the angle of the module should not be larger than 8° [3]. With such small angles, the fluid follows the module wall and no dead areas, in which settling may occur, are formed. The fluid flow through modules with small and large angles is compared in figure 12.2.

Due to the small angle necessary to avoid release of the fluid from the module wall, the inlet of the module becomes very long, 27.7 cm, until a diameter of 5.8 cm, which was used in the experimental set-up, is reached. Although the angle of the outlet may be larger, up to 25-30°, without causing release of the flow from the module wall, the angle is chosen equal to that of the inlet, 8°. If the inlet and outlet of the module, which represent a volume of 0.3 L each, would be without any ion exchange resin bars, only a very small contact area per unit volume would be present in the module. Therefore ion exchange bars are already placed in the inlet and outlet, resulting in the design presented in figure 12.3.

The designed module contains about 260 m² contact area per m³ module volume. The ion exchange bars with a diameter of about 2.7-2.8 mm are placed in a staggered configuration, like in the first module. Also the pitches are taken equal to those in the first module, because no clogging appeared in that module. So, transverse and longitudinal pitches are taken 6 mm again. Figure 12.4 shows the staggered configuration of the ion exchange bars in the module.
Figure 12.2. Illustration of the influence of the angle on fluid flow in a module and usage of the ion exchange bars in these modules. The shaded areas in the right picture indicate dead areas.

Figure 12.4. The staggered configuration of the PS-DVB ion exchange bars in the improved transverse flow ion exchange module.
Figure 12.3. The improved transverse flow ion exchange module, which contains PS-DVB ion exchange bars.
12.3 Experimental

12.3.1 Procedure

Experiments have been performed with HH and phosphoric acid (0.8 M H₃PO₄ and 0.5 M H₂SO₄) from the two-filter HemiDiHydrate phosphoric acid production process. The composition of the acid and HH used for the two different ion exchange modules differs, because the industrial production process changed the composition of their feed ore. The experiments with the module with glued ion exchange bars were performed with HH and acid from a production run with 90% Jordan and 10% Kovdor ore, the other experiments with HH and acid from a production run with just Jordan ore. The differences in composition of these ores were already given in chapters 1 and 7.

The recrystallization was performed at a temperature of approximately 70 °C. The temperature drop in the module was negligible. The experiments were performed batchwise. Figure 12.5 shows a schematic draw of the experimental set-up.

![Schematic drawing of the experimental set-up for batch-wise treatment of the phosphoric acid recrystallizing slurry in a transverse flow ion exchange module.](image)

First the acid was heated, during which it was pumped through the ion exchange module. After the acid reached the reaction temperature, HH was added slowly to avoid pumping problems due to a too high solid concentration in the buffer vessel. After about 1 hour, all HH was added and a slurry with 10-15 wt% solids was pumped through the module. In figure 12.5, the slurry enters the module at the top. Also experiments were performed with a slurry flow from the bottom to the top of
the module to be sure that all ion exchange bars were in contact with the slurry. The temperature was controlled by adding a pT-100 to the buffer vessel, which was connected to a thermostat. Further, the temperatures at the inlet and outlet of the module were measured. After the recrystallization reaction, the ion exchange bars were regenerated with either 20wt% of HCl or 20wt% of HNO₃ (strip solution), and reused during a second recrystallization.

During the experiments, samples were taken. The calcium sulfate solids were separated from the phosphoric acid by filtration and washed twice with a hot saturated solution of analytically pure DH to clean the crystals from phosphoric acid and washed twice with acetone to remove the water. Removal of the water avoids further recrystallization and facilitates drying of the crystals.

To avoid settling of the crystals in the module, the superficial velocity in the module has to be higher than the settling velocity of the crystals. With a Malvern Mastersizer, it was determined that industrial HH particles had an average size of 50 μm with a maximum size 260 μm of and industrial DH particles had an average size of 80 μm with a maximum of 530 μm. The calculation of the settling velocity is given in Appendix 12.1. The settling velocity of the averaged sized particles was found to be 0.5 cm/s for DH and 0.2 cm/s for HH (spherical crystals, unhindered settling). The settling of the large HH particles is much higher, 6 cm/s. During the experiments in the modules, the formed DH particles are not as large as in the industrial process.

Glued ion exchange bars

For the first experiment, 6 slides with 9 glued bars and 6 slides with 8 glued bars were used. The amount of ion exchange resin per bar was determined to be approximately 0.15 g (see chapter 11). So, the total amount of ion exchange resin was about 15.3 g of ion exchange resin, which equals about 75 meq of functional groups. This resulted in contact of the recrystallizing slurry with approximately 19 g resin/kg phosphoric acid slurry (93 meq/kg slurry). After the experiment, the glued ion exchange bars were contacted with 20 wt% HCl solution to regenerate the resin. After regeneration, the glued bars were reused during a repeated recrystallization, in which about 19 g resin/kg phosphoric acid slurry was contacted with fresh acid and HH crystals.

A superficial velocity of 1.28 cm/s was used. With this velocity, most solids will not tend to settle, but settling of the large solids can not be excluded.
PS-DVB bars

The volume of ion exchange bars equals about 0.16 L in the 0.8 L module. The amount of slurry treated in the experiments is about 2.4 kg. With an ion exchange capacity of the ion exchange bars of 1.0 meq/ml (see chapter 9), the capacity of the module equals 65 meq/kg slurry.

The flow through the module was 30 mL/s. This resulted in a superficial velocity of 38 cm/s at the in- and outlets, and 1 cm/s in the middle. The superficial velocity in the in- and outlets is much higher than the settling velocity, also than that of the large solid particles. However, settling of the large solid particles may occur in the middle of the module.

12.3.2 Analyses

Before analyses, the calcium sulfate solids were digested with aqua regia in a microwave oven. The concentrations of several heavy metal ions were determined in the phosphoric acid, the digested calcium sulfate crystals, and the strip solution by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS). The concentrations of calcium, sulfate, and phosphate were determined by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The extraction efficiency of component A, $\eta_A [%]$, was calculated from the amount in the strip solution and from that in the input by

$$\eta_A = \frac{m_{\text{strip}} [A]_{\text{strip}}}{m_{\text{HH before}} [A]_{\text{HH before}} + m_{\text{recr. acid, before}} [A]_{\text{recr. acid, before}}} \cdot 100\%$$

with $m$ the mass [kg], $[A]$ the concentration of A [mol/kg], the subscript recr. acid indicating the recrystallization acid, and before the concentration before the recrystallization.

12.4 Results and Discussion

12.4.1 The module with glued ion exchange bars

With the module with the ion exchange bars of commercial Dowex C-500 beads glued on Hastelloy C-276 wires, only very low extraction efficiencies were gained, as is shown in table 12.1 for the lanthanides.

The extraction efficiencies are the result of the small amount of functional groups per kg slurry in the module, which is comparable with only 19 g commercial ion exchange resin per kg slurry. During batch recrystallizations with simultaneous extraction described in chapter 7, up to 21% of a single lanthanide was extracted.
with an amount of 50 g commercial resin beads per kg slurry. To increase the extraction efficiency in the module, the ion exchange capacity per volume should be increased. This can be established either by increasing the capacity of the ion exchange bars or by decreasing the pitches. A decrease of the pitch sizes may result in clogging. More research is necessary to determine the minimum pitches to avoid clogging. Increasing the capacity of the bars is not possible by gluing ion exchange beads on a support (see chapter 11).

Table 12.1. The extraction efficiencies after recrystallization in the transverse flow ion exchange module with glued ion exchange bars.

<table>
<thead>
<tr>
<th></th>
<th>1st use of bars</th>
<th>use after regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Input [mg]</td>
<td>η [%]</td>
</tr>
<tr>
<td>La</td>
<td>4.01</td>
<td>4.2</td>
</tr>
<tr>
<td>Ce</td>
<td>4.04</td>
<td>3.2</td>
</tr>
<tr>
<td>Pr</td>
<td>0.66</td>
<td>2.8</td>
</tr>
<tr>
<td>Nd</td>
<td>2.83</td>
<td>2.6</td>
</tr>
<tr>
<td>Sm</td>
<td>0.61</td>
<td>2.7</td>
</tr>
<tr>
<td>Eu</td>
<td>0.18</td>
<td>4.1</td>
</tr>
<tr>
<td>Gd</td>
<td>0.91</td>
<td>3.6</td>
</tr>
<tr>
<td>Tb</td>
<td>0.14</td>
<td>4.0</td>
</tr>
<tr>
<td>Dy</td>
<td>1.01</td>
<td>4.4</td>
</tr>
<tr>
<td>Ho</td>
<td>0.26</td>
<td>4.7</td>
</tr>
<tr>
<td>Er</td>
<td>0.84</td>
<td>5.2</td>
</tr>
<tr>
<td>Tm</td>
<td>0.12</td>
<td>5.1</td>
</tr>
<tr>
<td>Yb</td>
<td>0.70</td>
<td>5.1</td>
</tr>
<tr>
<td>Lu</td>
<td>0.11</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Another problem of the glued ion exchange bars was their stability. After the first recrystallization, 17% of the used ion exchange bars broke down, because the glue loosened from the Hastelloay wires. This was caused by swelling of the glue. Figure 12.6 shows the loosening of the glue from a Hastelloay wire in one of the slides.

The design of the module also must be improved. With experiments, in which the module was fed from the top, severe scaling occurred on the ion exchange bars in the first two Teflon® slides. This was caused by the fact that these bars were not wetted by the slurry, as was already illustrated in figure 12.2. On the bars in the slides in the
middle of the module, which are in better contact with the slurry stream, scaling was not visible with the naked eye.

Figure 12.6. Loosening of the glue with the ion exchange resin from the Hastelloy wire after treatment of the recrystallizing phosphoric acid slurry.

From the extraction efficiencies measured after a recrystallization, in which the regenerated ion exchange bars were reused, it was concluded that no severe fouling of the resin occurred. The extraction efficiencies were comparable to those measured with fresh ion exchange resin on bars, as is shown in table 12.1. Long-term experiments should be performed to determine the built up of small amounts of fouling, which may cause a decline of the extraction efficiency on the long-term.

Despite the poor flow profile in the module, no clogging appeared.

12.4.2 The module with the PS-DVB ion exchange bars

The new ion exchange module is designed to overcome the most apparent problems of the first one, the low ion exchange capacity in the module and the flow through the module. To increase the capacity of the module with the same pitches between the ion exchange bars, the amount of functional groups per volume of ion exchange bar had to be increased. With the Hastelloy support wire with a diameter of 1.6 mm, 28% of the volume of the glued ion exchange bars does not participate in the extraction of impurities (if taking also the glue into account, this percentage would even be higher). To avoid the necessary support for gluing the beads, PS-DVB bars functionalized with sulfonic acid groups were developed. With such bars, it should be possible to increase the ion exchange capacity of the module. However, the PS-DVB can, until now, only be functionalized at the surface resulting in a lower ion exchange capacity of the bars (1.0 meq/mL) than of the commercial ion exchange resins (1.9 meq/mL). Due to this, the ion exchange capacity of the new module with the PS-DVB ion exchange bars is lower, 65 meq/kg slurry, than that of the module with the glued ion exchange bars, 93 meq/kg slurry. If the ion exchange capacity of the bars would reach that of the commercial beads, the capacity of the second
module would become 124 meq/kg slurry, which is higher than that of the first module.

Although the amount of functional groups per amount of treated slurry was lower during the experiments with the new module than during experiments with the module with the glued bars, the extraction efficiencies were higher, as is shown in table 12.2 for the lanthanides. Table 12.3 shows extraction efficiencies measured for some other heavy metals than the lanthanides.

**Table 12.2.** The extraction efficiencies of lanthanides after recrystallization in the transverse flow ion exchange module with functionalized PS-DVB bars.

<table>
<thead>
<tr>
<th>Input [mg]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>5.20</td>
</tr>
<tr>
<td>Ce</td>
<td>8.40</td>
</tr>
<tr>
<td>Pr</td>
<td>1.19</td>
</tr>
<tr>
<td>Nd</td>
<td>4.25</td>
</tr>
<tr>
<td>Sm</td>
<td>1.04</td>
</tr>
<tr>
<td>Eu</td>
<td>0.29</td>
</tr>
<tr>
<td>Gd</td>
<td>3.37</td>
</tr>
<tr>
<td>Tb</td>
<td>0.22</td>
</tr>
<tr>
<td>Dy</td>
<td>1.84</td>
</tr>
<tr>
<td>Ho</td>
<td>0.44</td>
</tr>
<tr>
<td>Er</td>
<td>1.53</td>
</tr>
<tr>
<td>Tm</td>
<td>0.15</td>
</tr>
<tr>
<td>Yb</td>
<td>1.33</td>
</tr>
<tr>
<td>Lu</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The higher extraction efficiencies with lower ion exchange capacity can have several causes. First, the composition of the acid and HH that was fed to the module. In chapter 7, it was already shown that this could have its influence on the extraction efficiency.

Another explanation can be found in the improved design of the module. Due to the angle of 8° of the module wall, the slurry flows along the entire ion exchange bars, using all the ion exchange capacity in the module. In the module with the glued bars, the capacity present in the module was not used optimally, because the slurry did not flow along the entire bars. However, this does not explain the relatively high
extraction efficiencies compared to those gained with commercial ion exchange beads during a batch recrystallization in a stirred vessel described in chapter 7. The 65 meq/kg slurry is comparable to approximately 13 g of commercial ion exchange resin per kg of slurry. Given this low amount of active groups, the extraction with the PS-DVB bars is the most efficient one gained until now.

Table 12.3. The extraction efficiencies of some other heavy metals than lanthanides after recrystallization in the transverse flow ion exchange module with functionalized PS-DVB bars.

<table>
<thead>
<tr>
<th></th>
<th>Input [mg]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>95.0</td>
<td>9.3</td>
</tr>
<tr>
<td>Co</td>
<td>1.04</td>
<td>13</td>
</tr>
<tr>
<td>Ni</td>
<td>11.9</td>
<td>15</td>
</tr>
<tr>
<td>Cu</td>
<td>4.40</td>
<td>12</td>
</tr>
<tr>
<td>Zn</td>
<td>52.5</td>
<td>7.9</td>
</tr>
<tr>
<td>Y</td>
<td>32.7</td>
<td>12</td>
</tr>
<tr>
<td>Cd</td>
<td>10.1</td>
<td>9.8</td>
</tr>
</tbody>
</table>

The efficient extraction by the PS-DVB bars is therefore most probably the result of the fact that all active groups are present on the surface of the ion exchange resin bars, as was shown in chapter 11. Due to this, the active groups are readily accessible. In commercial beads, the active groups are divided evenly over the bead, and a significant amount of groups is present in the internals of the beads. It seems that diffusion in the resin is a rate limiting step and that the internals of the commercial beads do not participate in the extraction as actively as the groups on the surface.

For the application of an ion exchange module with ion exchange bars for the treatment of slurries, more research is required. The dead volume in the experimental set-up can be decreased, resulting in a small increase of ion exchange capacity per kg slurry.

Smaller pitches between the bars will result in a higher ion exchange capacity per volume of module. Further research may give an insight in the smallest possible pitches, which will depend on the crystal size distribution and crystal shape, for the treatment of slurry streams in tube banks.

Further, an increase of the selectivity and ion exchange capacity of the ion exchange bars will result in higher extraction efficiencies. However, the latter will not have as
much influence as first expected if only the surface is most actively used in extraction. If an ion exchange resin is more selective with respect to the impurities, the available functional groups will be used in a more efficient way and thus extract more impurities. For the removal of lanthanides, groups like that of Duolite C-467 (-CH₂-NH-CH₂-PO₃Na₂) would be more successful. For the removal of heavy metal ions like lead, mercury, and cadmium, groups with thiophosphinic acids would be more successful (but these groups are not available on solid matrices yet).

12.5 Conclusions

The extraction efficiency gained with the module with glued ion exchange bars is very low, up to 5.2% of the input amount of a single lanthanide. This is due to the low ion exchange capacity of the module compared to that during experiments performed with commercial ion exchange beads in stirred vessels described in chapter 7. Despite the 30% lower ion exchange capacity of the module with the PS-DVB bars (65 meq/kg slurry) compared to the module with glued bars (93 meq/kg slurry), the extraction is by far more efficient, up to 24% of the input amount. The ion exchange capacity of the PS-DVB module is comparable with 13 g commercial resin/kg slurry. This makes the extraction with the PS-DVB bars the most efficient one gained until now. This is probably due to the fact that all functional groups are present at the surface of the bars and thus readily accessible.

To increase the extraction efficiency of the module, more research is needed on flow of slurry streams in tube banks to determine pitch sizes, on the improvement of ion exchange capacity of the bars, and on the selectivity of the bars by changing functional groups.

Acknowledgment

Michiel Hoogerwerf is acknowledged for his work on the module with the glued ion exchange bars. Michel van der Brink is acknowledged for his work on the module with the PS-DVB bars.

References


Appendix 12.1

Determination of the Settling Velocity

The average sizes of the industrial HH and DH particles from a two-filter HemiDiHydrate phosphoric acid production process were determined with a Malvern Mastersizer. The average sizes were found to be 50 μm for the HH particles with a maximum of 260 μm and 80 μm for the DH particles with a maximum of 530 μm. However, in the module the formed DH crystals are smaller.

In systems with large amounts of solids, like the slurry used in these experiments, the settling of the particles will be influenced by the presence of other particles. However, during start-up the amount of solids is only low and no hindered settling will occur. Because the settling velocity is higher when hindrance is not taken into account, this settling velocity is calculated as an indication.

The settling velocity, $v_s$ [m/s], is estimated with Stokes law,

$$v_s = \frac{d^2 \cdot (\rho_s - \rho_f) \cdot g}{18 \cdot \eta_f} \quad \text{(A12.1)}$$

with $d$ the diameter of the particles [m], $\rho_s$ the density of the solid particles [kg/m$^3$], $\rho_f$ the density of the fluid [kg/m$^3$], $g$ the acceleration by gravity [m/s$^2$], $\eta_f$ the viscosity of the fluid [kg/m·s]. Stokes law is only applicable for viscous or laminar flow (Re<0.2). It is assumed that the particles are spherical. If not, a shape factor would have to be introduced, resulting in lower settling velocities.

With the densities of 2540 kg/m$^3$ for HH, 2310 kg/m$^3$ for DH, and 1120 kg/m$^3$ for the acid and the viscosity of the acid of 8.32·10$^{-4}$ kg/m·s (measured with an Ubbelohde at 74 °C), the maximum settling velocity of HH was found to be 6 cm/s (260 μm). The settling velocity of the average HH particles is 0.23 cm/s, that of the average DH particles 0.5 cm/s.

The Reynolds number $Re$ is calculated by

$$Re = \frac{\rho_f \cdot v_s \cdot d}{\eta_f} \quad \text{(A12.2)}$$

and is 0.2 and 0.5 for the averaged sized HH and DH particles, respectively. For the maximum sized particles, Re becomes as high as 21 and Stokes law is not applicable anymore. The calculated settling velocity is therefore only an indication.
Epilogue

It was proven that impurities could be removed by recrystallization with simultaneous extraction resulting in a cleaner liquid and a purified crystal product, although the original goal of 70-90% reduction of the impurity content in gypsum from the phosphoric acid production was not reached. This original goal of 70-90% reduction in impurity content of the gypsum to decrease the environmental impact of gypsum disposal became outdated with the development of the ProGips process by the Dutch phosphoric acid industry. Despite this, in-line extraction techniques can still contribute to a more sustainable phosphoric acid production.

With the ProGips process, which is developed by the Dutch phosphoric acid industry, 90% of the gypsum by-product becomes a useful product for the gypsum industry. By the in-line removal of impurities from slurries by extraction techniques, the amount of contaminated waste gypsum could be further reduced. Another important advantage of in-line extraction is that more flexibility is gained with respect to the ores that can be used. For example, due to the experimentally found extraction of lanthanides that are released from calcium sulfate hemihydrate, it becomes possible to consume other phosphate ores, like magmatic ores with high concentrations of lanthanides and low concentrations of radioactive elements. This will reduce the radioactivity level in the gypsum, which is a crucial product property.

Gypsum from the phosphoric acid production can become a useful product, for example, as building material. Although, the gypsum industry already uses a lot of by-product gypsum, like desulfurization gypsum, natural gypsum is still mined to meet the market demand. In some countries in Western Europe, like Great Britain, Germany, and France, restrictions were already introduced for the mining of natural gypsum, promoting the recycling of by-product gypsum. Not only in Western Europe, but also in countries, like India, China, and Brazil, recycling of gypsum from the phosphoric acid industry is an issue. The ProGips process with in-line extraction of impurities can make an essential contribution to the recycling, not only during phosphoric acid production itself, but also for the treatment of existing stacks.

For an economically feasible extraction process, the carrier or resin must be regenerated and reused. Until now, the feasibility of the in-line extraction in the phosphoric acid process is limited by the unfavorable regeneration. For an economic
feasible process, carriers and resins with more favorable chemical properties with respect to extraction and regeneration behavior should be developed.

The extraction results for the phosphoric acid slurry were limited due to the high acidity of this solution (< pH=0). In this region, effective and selective carriers and ion exchange resins are rare. For a process slurry with different chemical composition, the in-line removal by extraction may be more effective due to the availability of appropriate carriers and ion exchange resins.
Dankwoord

Dit onderzoek werd deels gefinancierd door Hydro Agri Rotterdam en Kemira Agro Pernis. Hierbij wil ik vooral de contactpersonen, Wolter Bos en Leo Penders, bedanken voor hun enthousiasme, ondanks de dreigende sluiting van de fabrieken.

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