Recovery of valuable metals from spent HEV NiMH battery leach solutions

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Abstract

As the demand on resources is increasing worldwide, the process of recycling material has become more important. The specific recycling of metals used in car batteries, and more specifically in the large batteries used in hybrid electric vehicles, is a rising concern where the industrially implemented recycling processes concerning these batteries that exist today are often highly pollutant and energy consuming. In the present study, an alternative hydrometallurgical recycling process of the previously and to some extent presently widely used battery type for hybrid electric vehicle applications, namely the Nickel Metal Hydride (NiMH) battery, has been investigated. The focus was to evaluate different routes of recovering Ni, Co, Mn, Zn, Al and residual Y from a NiMH battery leach solution as obtained in a priorly conducted leaching study. Three different possible products were chosen for closer investigation, a mixed metal hydroxide where all of the metals would be precipitated together, a new NiMH cathode material where a controlled precipitation of Ni, Co and Zn together would be implemented and last a pure Ni salt product where a selective separation of Ni from the other metals would be required. Two of the three products, the mixed metal hydroxide and the pure Ni salt, were found suitable for the specific system and it was concluded that a pure Ni salt production would be most justifiable. The separation of Ni from the other metals present in the solution was here proposedly achieved by an extraction process using supported liquid membranes. A mathematical model was used in Matlab in order to evaluate the separation efficiency and to determine the optimum process conditions for the extraction process and a hydroxide precipitation experimental study was conducted in order to determine both the process streams in the production of a mixed metal hydroxide and the solution behavior during the pH increase in the Ni salt production extraction process. The results suggested a low loss of valuable metals and due to this, both the process of producing a mixed metal hydroxide and the process of producing a pure Ni salt could be found to be economically justifiable.
# Table of Contents

Table of Contents  
I  
List of Figures  
IV  
List of Tables  
VI  
Nomenclature  
VIII  

1 Introduction  
1  

2 Battery chemistry and composition  
2  

3 Industrial recycling of NiMH batteries  
3  

4 Background and project goals  
4  

5 Techniques for Ni and Co recovery  
6  

5.1 Solvent extraction  
6  

5.2 Supported liquid membrane  
8  

5.3 Precipitation  
11  

5.4 Electrowinning  
13  

6 Technique comparison  
14  

7 Precipitation of mixed hydroxide product  
18  

7.1 Method evaluation  
18  

7.2 Experimental  
23  

7.2.1 Equipment  
23  

7.2.2 Chemicals  
24
7.2.3 Experimental procedure ........................................ 24
7.2.4 Results and discussion .................................................. 26
7.3 Proposed process ............................................................ 33

8 Cathode material synthesis .................................................. 34
  8.1 Method evaluation ......................................................... 35
  8.2 Experimental ............................................................... 36
    8.2.1 Equipment ............................................................ 37
    8.2.2 Chemicals ............................................................. 37
    8.2.3 Experimental procedure .............................................. 38
    8.2.4 Results and discussion .............................................. 39

9 Ni salt production using a supported liquid membrane .................. 40
  9.1 Process modeling ......................................................... 41
    9.1.1 Model modifications ............................................... 44
    9.1.2 Results and discussion .............................................. 47
      9.1.2.1 Constant feed pH .............................................. 49
      9.1.2.2 Different stripping solution pH .............................. 50
      9.1.2.3 Different membrane area ...................................... 53
  9.2 Proposed process ........................................................ 54

10 Process evaluation ......................................................... 56
  10.1 HEV NiMH batteries in Sweden ........................................ 56
  10.2 Batch- or continuous operation ....................................... 57
  10.3 Mass balance calculations ............................................ 58
    10.3.1 Leaching and REE removal process ............................... 59
    10.3.2 Mixed hydroxide production process ............................. 62
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic picture of the flat sheet supported liquid membrane process [20].</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Potential revenues of different products that could be obtained by recovering 100% of the respective metals from the NiMH battery leach solution calculated per battery.</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>Equilibrium concentrations of the different metals in the sulphate leach solution and their respective precipitation behavior as a function of pH.</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Equilibrium concentrations of the different metals in the chloride leach solution and their respective precipitation behavior as a function of pH.</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Sulphate complex concentrations present in the sulphate leach solution as a function of solution pH.</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>Chloride complex concentrations present in the chloride leach solution as a function of solution pH.</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Titration curve showing the change in solution pH as a function of added mmol of NaOH.</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>ICP results from the samples taken after 10 min precipitation time showing the precipitated fraction of each metal at different solution pH.</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>ICP results from the samples taken after 20 h precipitation time showing the precipitated fraction of each metal at different solution pH.</td>
<td>29</td>
</tr>
<tr>
<td>10</td>
<td>Process schematic of the proposed mixed hydroxide product route.</td>
<td>33</td>
</tr>
<tr>
<td>11</td>
<td>Pourbaix diagrams of Ni, Co, Mn and Zn in the NiMH leach liquor from sulphuric acid leaching (constructed in Medusa) The red markings in the diagrams show the selective Mn oxidation window.</td>
<td>37</td>
</tr>
<tr>
<td>12</td>
<td>ICP results from the oxidative precipitation on Mn from NiMH battery leach liquor.</td>
<td>39</td>
</tr>
<tr>
<td>13</td>
<td>Transport mechanism of the metals across the membrane in the SLM process [20].</td>
<td>42</td>
</tr>
<tr>
<td>14</td>
<td>Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time.</td>
<td>48</td>
</tr>
<tr>
<td>15</td>
<td>Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at constant feed pH=5.5.</td>
<td>49</td>
</tr>
</tbody>
</table>
Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at a starting stripping pH of pH=-1. ................................................................. 51

Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at a starting stripping pH of pH=0.5. ................................................................. 51

Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at a starting stripping pH of pH=1.2. ................................................................. 52

Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time using a membrane with an area 10 times larger than the area of the equipment specification. ............ 53

Process schematic of the proposed Ni salt production route. ............ 54

Estimated recycling demand of HEV NiMH batteries in Sweden. .... 57

Process schematic of the leaching and REE removal process, as proposed by the leaching study with an associated system boundary used in the calculations. ................................................. 59

Process stream compositions and volumetric increase of the reagent in the leaching and REE removal process. ................................. 61

Process stream compositions and volumetric increase of the reagent in the mixed hydroxide route process. ................................. 62

Process stream compositions of the reagent in the Ni salt production route process. ................................................................. 64
List of Tables

1  Chemical composition of the electrode materials by mass percent (nd = not detected).  ........................................ 4
2  Metal concentrations in the resulting NiMH battery leach liquor as obtained from concurrent anode and cathode leaching and REE removal by precipitation.  ........................................ 5
3  Current market values of different end products (2017).  ....................... 15
4  Added amount of metal salts in the preparation of the 200 ml synthetic solution used in the hydroxide precipitation experiment.  ....................... 24
5  Resulting metal concentrations of the synthetic solution as used in the hydroxide precipitation experiment.  ....................... 24
6  Total amount of added NaOH in terms of volume and concentration in the controlled increase of the leach liquor solution pH.  ....................... 27
7  Compositions of the three precipitates taken at different pH during the hydroxide precipitation experiment.  ....................... 31
8  Precipitated fraction of metals after increasing the solution pH to pH=5.5.  ....................... 32
9  Added amount of metal salts in the preparation of the 200 ml synthetic solution used in the oxidative precipitation experiment.  ....................... 38
10 Resulting metal concentrations of the synthetic solution as used in the oxidative precipitation experiment.  ....................... 38
11 Equilibrium constants used in the simulation.  ....................... 46
12 Diffusion coefficients used in the simulation.  ....................... 46
13 Parameters used in the simulation of the batch flat sheet SLM process.  ....................... 46
14 Metal concentration in the resulting leach solution after the pH increase to pH=5.5.  ....................... 47
15 Advantages and disadvantages of batch contra continuous processes [64].  ....................... 58
16 Total amount of elements that enter the recycling process, using one battery pack as base.  ....................... 60
17 Metal composition of the mixed hydroxide product in the Ni salt production route.  ....................... 66
Resulting chemical revenue and cost of the two different suggested separation routes and the two leaching routes on the basis of one recycled battery pack.

Yearly revenue from the possible obtained products of recovering the metals present in the leach solution minus the chemical costs associated with the different suggested processes. In the conversion of USD to SEK, the current exchange rate of 8.12 SEK/USD was used.
Nomenclature

FSSLM  Flat Sheet Supported Liquid Membrane
HEV   Hybrid Electric Vehicle
HFSLM Hollow Fiber Supported Liquid Membrane
ICP-OES Inductively Coupled Plasma-Optical Emission Spectroscopy
LCA   Life Cycle Analysis
MHP   Mixed Hydroxide Product
NiMH  Nickel Metal Hydride
PHEV  Plug-in Hybrid Electric Vehicle
REE   Rare Earth Element
SLM   Supported Liquid Membrane
SX    Solvent Extraction
UHT   Ultra High Temperature
XRD   X-Ray Diffractometer
1 Introduction

With the steadily increasing demand on resources worldwide, recycling has become more and more important in both economical and environmental aspects. One area of concern is the recycling of spent batteries. The rapid technological advancement, where today new electrical devises become available on the market everyday, has drastically increased the importance of batteries for electricity storage and as a consequence, the recycling of valuable battery material has become an important topic in both the industry and among researchers. One of the efforts to improve the situation is the European Commission Directive 2006/66/EC which contains legislations and directives regarding battery handling and recycling including the demand that all collected batteries should be recycled (Article 12(1)(b)) [1]. In addition, requirements on recovery efficiencies for different battery types are stated. On mass basis, lead-acid batteries must be recycled at a minimum of 65 %, nickel-cadmium batteries a minimum of 75 % and other battery types at a minimum of 50 %, including casings and fluids.

The most valuable and desirable material to recover from a spent battery is the metal compounds within the electrodes. This is mainly because the chemistry of the battery often require metals of which the global reserves are sparse but also because, in some cases, the metals can be toxic to the environment if not disposed of properly. The latter is something that researchers try to steer away from by replacing old battery technologies with new ones, using less harmful chemistry.

The Nickel Metal Hydride (NiMH) batteries has recently become more popular as a replacement for the previously widely used nickel-cadmium batteries because of environmental concerns regarding the intrinsic toxicity of cadmium. The battery is rechargeable, reflecting on its application areas such as power tools, mobile phones, vehicles etc. Additionally, the technology allows for much higher capacities than its precursor, making it a clear choice in many applications. Much of the success of NiMH batteries stems from Toyota’s decision to use this technology in their bestselling electric hybrid car model Prius. The decision has lead to a great increase in Hybrid Electric Vehicle (HEV) NiMH battery production worldwide, resulting in a large present recycling demand of valuable NiMH electrode materials.

In a typical recycling process of a HEV NiMH battery, the battery is firstly discharged and thereafter disassembled in order to separate the electrodes from the other compartments of the cell. The valuable metals in the electrodes can then be retrieved by using pyrometallurgical (e.g. smelting) or hydrometallurgical (leaching) methods and then further refined into sellable products. The conventional pyrometallurgical methods have the advantage of being easy and cost effective in large scale but the energy requirements in these processes are large and therefore hydrometallurgical routes, requiring less energy, have been widely investigated. Even though hydrometallurgical methods require less energy, these processes are complex and often require several different chemicals, adding to the cost of the system as well as increasing the importance of stream recycling and proper waste handling.
Apart from chemical consumption, e.g. of acids, one of the main challenges in hydrometallurgical recycling of NiMH batteries is the recovery of pure nickel (the main constituent in the electrodes) that can later be used as precursor in the production of new electrode material. In order to reach a high purity Ni product, the resulting mixture of metals has to be treated such that Ni is separated from the other metals, where the main issue is the separation from cobalt (also one of the main constituents and valuable products). Ni and Co behave similarly in solution where they tend to precipitate together as either hydroxides or sulphides and have similar standard reduction potentials. The refining steps of a spent NiMH battery leach liquor become even more complex when other electrode metals are introduced, such as manganese and zinc, which tend to follow Ni and Co.

2 Battery chemistry and composition

In NiMH batteries the energy is stored in hydrogenated metal alloys (metal hydrides) in the negative electrode (anode). During discharge, the metal hydrides undergo deprotonation, releasing electrons. This is induced by the alkaline electrolyte that is connected to both the anode and the positive electrode (cathode) where protonation occurs. The two electrodes are separated by a permeable separator material, preventing short circuiting while allowing for proton transfer. The electrolyte is usually a KOH solution [2].

The following reactions represent a simplification of the chemistry involved in a NiMH battery discharge (left to right direction) and charge (right to left direction).

The anodic reaction, where M is the metal alloy:

\[
MH_x + OH^- \rightleftharpoons MH_{x-1} + H_2O + e^- \quad \text{(I)}
\]

The cathodic reaction:

\[
NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \quad \text{(II)}
\]

The overall reaction:

\[
NiO(OH) + MH_x \rightleftharpoons Ni(OH)_2 + MH_{x-1} \quad \text{(III)}
\]

The precise chemical composition of the anode and cathode differ between manufacturers and battery type but generally the main components in the anode are a mixture of Rare Earth Elements (REEs) and Ni while the cathode is composed of Ni as hydroxides together with Co and Zn. A commercial cathode powder typically consist of spherical $\beta$-Ni(OH)$_2$ doped with around 1-5 wt% Co and Zn respectively for improved characteristics and stability of the cathode material [3].
Apart from hydrogen storage capacity, the hydriding/dehydriding temperature, volumetric changes, hysteresis (battery aging) and isotherm pressure are important properties of the anode material in battery applications [2]. Different metal hydride alloys have been investigated for this purpose and they are commonly classified based on a component $A_xB_y$ system based on their composition and crystal structure. Among the different configurations, the two most commercially applied alloys in NiMH cells are the $AB_5$ types ($A=$lanthanides and other REEs, $B=\text{Ni, Co, Al, Mn}$) and the $AB_2$ types ($A=\text{Ti, Zr}, B=\text{V, Ni, Cr, Co, Mn, Al, Sn}$) [4].

3 Industrial recycling of NiMH batteries

Regarding the recycling industry of batteries, there are several companies that collect and recycle the material but often a company specializes in one or two battery types, where different processes are often required in the recycling of different material. Many of the companies that recycle batteries today have a history within or are active in the mining industry where the processes used are similar to that of extracting metals from ores. Here, the equipment and experience already exist within the company and batteries are regarded as an extra resource where metal contents are high. One of these companies, and also one of the leading companies within the recycling of NiMH batteries, is Umicore, Belgium. Through their Umicore Battery Recycling division, the Ultra High Temperature (UHT) furnace in Hoboken has the capacity of recycling 7000 metric tons of NiMH and Li-ion batteries per year [5]. The applied technique includes a smelting process where a metal alloy containing Co and Ni is produced as well as a slag containing the REEs. The metal alloy is further refined in a subsequent step through hydrometallurgical treatments including sulphuric acid leaching and solvent extraction, where the metals are converted into new cathode material for Li-ion batteries as $\text{Ni(OH)}_2$ and $\text{LiCoO}_2$ [6] [7]. The slag is mainly sold off to be used in the construction industry but the company collaborates together with Solvay, a Belgium chemical company, in order to recover the REEs. Another leading NiMH battery recycling actor is the North American Retriev Technologies Inc., former Toxco Inc, which uses a pyrometallurgical process to produce metal alloys to be used in stainless steel production [8]. In the Glencore company Nikkelverk in Norway, NiMH batteries are recycled through a combination of smelting and hydrometallurgical processing using hydrochloric acid as leaching medium. In the refining process, precipitation, solvent extraction and electrowinning techniques are employed in order to produce high purity Co, Ni and Cu metals [9]. In Europe, the recycling company SNAM, based in France, is currently responsible for the recycling of Toyota’s HEV NiMH batteries. SNAM uses a purely pyrometallurgical route including pyrolysis, distillation and metal refining in the recovering of the material but the company is currently investing in a hydrometallurgical unit to optimize the recycling performance [10]. The main end product from the NiMH batteries is as of today a Ni/Fe alloy that can be used in stainless steel production.

As can be seen, the majority of companies that collects and recycles batteries today
employ pyrometallurgical methods in order to recover the valuable metals. The techniques perform well where high yields are obtainable and the processes are rather simple. However, the pyrometallurgical processes have received a lot of critique during the last decade as the concern regarding the human impact on the environment is increasing where these processes consume a lot of energy which is usually associated with high levels of pollution. As a consequence of the new way of viewing processes from an environmental point of view, these old processes that has been used in the mining industry for a long time are by many considered as techniques used in the past and new hydrometallurgical methods are being under investigation in many companies as to replace the existing technology.

4 Background and project goals

As part of a project on metal recovery from spent HEV NiMH batteries through hydrometallurgical routes (i.e. no conventional smelting), this thesis work proceeds from the work of Korkmaz et al. on three different routes of leaching and REE removal [11].

In their study, the electrode material was separated from the casing by hand and the anode and cathode were then leached separately. The composition of the electrodes was determined by total dissolution of the anode and cathode and subsequent ICP-OES analysis and it was determined that the battery was of AB₅ type. The resulting composition of the electrode material is shown in Table 1.

Table 1: Chemical composition of the electrode materials by mass percent (nd = not detected).

<table>
<thead>
<tr>
<th></th>
<th>Ce</th>
<th>Co</th>
<th>La</th>
<th>Mn</th>
<th>Nd</th>
<th>Ni</th>
<th>Pr</th>
<th>Y</th>
<th>Al</th>
<th>Fe</th>
<th>Zn</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode (wt%)</td>
<td>nd</td>
<td>5.46</td>
<td>nd</td>
<td>0.11</td>
<td>nd</td>
<td>76.47</td>
<td>0.43</td>
<td>0.09</td>
<td>0.14</td>
<td>3.70</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>Anode (wt%)</td>
<td>6.22</td>
<td>4.96</td>
<td>19.88</td>
<td>4.33</td>
<td>2.63</td>
<td>54.18</td>
<td>2.40</td>
<td>0.71</td>
<td>2.02</td>
<td>0.09</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>Cathode + anode (wt%)</td>
<td>3.11</td>
<td>5.21</td>
<td>9.94</td>
<td>2.22</td>
<td>1.32</td>
<td>65.33</td>
<td>1.20</td>
<td>0.57</td>
<td>1.06</td>
<td>0.12</td>
<td>0.54</td>
<td>2.07</td>
</tr>
</tbody>
</table>

It can be seen that Ni, by being the main constituent in both the anode and the cathode material, has potentially high economic value in the recycling process of NiMH batteries and the same can be said about Co, where the content is relatively high in both electrodes. The REE (Ce, La, Nd, Pr and Y) content in the anode is also high which is why the removal of these were one of the main purposes in the separating step of the study. The REEs could in the study be successfully separated through precipitation, leaving next to all Ni, Co, Mn, Al, Zn and Y in solution at pH=0.3.

In the study, two leaching techniques were tested and evaluated for the dissolution of the electrodes at atmospheric pressure, one using sulphuric acid and one using...
hydrochloric acid. The highest leaching recovery from respective route were obtained by using an acid concentration of 2 M at 90°C for both the anode and the cathode. The elevated temperature was required in order to improve the dissolution of Ni. After 4 hours of leaching time, above 99 % Ni recovery was observed in all materials except in the anode leaching with hydrochloric acid where a recovery of 95 % was obtained. The dissolution of REEs was high, above 95 %, in all experiments at higher temperatures apart from the anode leaching with sulphuric acid, where the recoveries reduced to 60-80 % due to metal sulphate precipitation. The recovery of Co was consistently around 90 %.

In addition to the two leaching routes, a third route using a combination of mixing with concentrated sulphuric acid and roasting was tested and evaluated. By using this technique, all of the REEs were easily dissolved in water and separated whilst Ni and Co together with Mn, Al and Zn stayed in their solid forms as metal oxides. The main advantages of this procedure over leaching were the the small amount of leach liquid required together with a full recovery of the REEs since the anode could be easily dissolved. The drawbacks are the heat requirement in the roasting process and the potential complications in subsequent refining steps where the resulting metal oxides are hard to redissolve.

The present study proceeds these findings and focuses on evaluating the possibilities of recovering Ni and the other metals present in the battery leach liquor as obtained after either hydrochloric acid- or sulphuric acid leaching. The results will be based on the possibility of implementing a larger scale operation in Sweden and hence, the Swedish market of HEV NiMH batteries is regarded as the recycling demand.

The resulting NiMH battery leach liquor that is obtained after the leaching and the subsequent precipitation of REEs is relatively similar in both the case of sulphuric acid- and hydrochloric acid leaching. This leads to the conclusion that the leach liquor metal concentration, which is the input concentration to the subsequent separation of the present study, can be validly determined by looking at the composition of the electrodes whilst considering both the precipitation results and the added amount of NaOH in the precipitation, in order to account for the volume change of the system. In the present study, the concentration of the leach liquor that was set as a basis in the calculations was the concentration that would have been obtained had both the anode and cathode been leached together. The metal concentrations of the resulting leach liquor after REE removal can be seen in Table 2.

| Table 2: Metal concentrations in the resulting NiMH battery leach liquor as obtained from concurrent anode and cathode leaching and REE removal by precipitation. |
|----------------|---|---|---|---|---|---|---|---|---|---|---|
|                | Ce | Co | La | Mn | Nd | Ni | Pr | Y  | Al | Fe | K  | Zn |
| [g/dm³]         | -  | 1.94 | -  | 0.83 | -  | 24.38 | -  | 0.21 | 0.39 | -  | -  | 0.77 |
| [mol/dm³]       | -  | 0.033 | -  | 0.015 | -  | 0.42 | -  | 0.0024 | 0.014 | -  | -  | 0.012 |

As can be seen from Table 2, the main constituent in the leach solution is by far the Ni and the second most dominant metal is the Co, who’s amount adds up to around
8 % of the amount of Ni. The table tells us that if no further separation is made, the end product will have high concentrations of impurities and hence, in order to increase the product value, a subsequent separation process could prove beneficial. In addition to Ni and Co, smaller amounts of Mn, Zn and Al are still in the solution as well as trace amounts of Y. These metals will also have to be considered in the evaluation and decision making regarding separation methods.

5 Techniques for Ni and Co recovery

The process of recovering metals from spent batteries is a widely discussed topic in today’s hydrometallurgical community. Several techniques have been thoroughly investigated over the years and deciding on a specific process is influenced by factors like economy, environmental concerns and end product quality and application. In this section, the different techniques and their ongoing research in the recovery of Co and Ni from spent battery leach liquor are discussed.

5.1 Solvent extraction

Several studies have been made on the matter of separating and purifying Ni and Co via liquid-liquid extraction, or Solvent Extraction (SX). In SX, separation of two or more solutes, for example metal ions, is accomplished by the partitioning of the solutes between two immiscible liquid phases through mixing of the two. The phases often consist of one aqueous and one organic liquid, the diluent. In most SX systems, the organic solvent includes an extractant that increases the separation and in some systems, modifiers are added to prevent third phase formations [12]. The extractant is synthesized such that it selectively forms complexes with the solutes in the aqueous solution, thereby increasing the metals’ solubility in the organic phase. Since this is essential for the separation, parameters that influence (1) the formation of organic complexes and (2) the equilibrium conditions such as temperature, pH and extractant concentration are of great importance when designing such a process. When the desired metals to be extracted have been loaded to the organic phase, they can be readily stripped from the organic by contacting it with an aqueous phase with conditions suitable for the reverse effect of the organic loading (e.g. lower pH), regenerating the organic phase to be used again.

The extent of the extraction of a solute is quantified by its distribution ratio (D), which is the ratio of the total concentration of the solute in the organic phase divided by the total concentration of the solute in the aqueous phase during the loading.

To quantify the separation of two or more solutes, the separation factor (SF) is often used in the literature. The separation factor is given by the ratio of the D values of the different solutes and it is defined to be >1. For example, in a system containing Co and Ni where mainly Co is extracted by the organic solvent; SF$_{Co/Ni}$
equals \( \frac{D_{Co}}{D_{Ni}} \) [12].

For the specific separation of Ni and Co from spent NiMH battery leach liquid, trying to find a suitable extractant has been the main approach among researchers and two main methods have been shown to yield the best results. Depending on the leach solution, extraction by acidic chelating extractants or extraction by anion exchangers can be used. The latter have the ability to reach high levels of separation where only a limited number of metals form anionic complexes to be extracted but the narrow window of specific conditions under which the complexes form requires precise control of the conditions. A general mechanism of which metal ions in solution are being extracted by an anion exchanger extractant can be seen below.

\[
(MX_z)^{m-} + yB_b^{b+}X_b^{-} \Leftrightarrow (MX_z)^{m-}B_b^{b+} + yX_b^{-}
\]

Where M is the metal ion to be extracted, X is the anion and B is the organic extractant. The method is commercially being used to some extent in chloride solutions, where it has been shown that the anionic species being extracted is CoCl\(^4-\) by extractants such as Adogen 283 and Alamine-336. Problems associated with the technique include the fact that even though Ni does not form chloro anions, other contaminants often present in NiMH battery leach solutions (Zn, Fe, Cu etc.) do and also, an excess of chloride ions is needed in the solution, adding to the cost of the system [13]. Where the research on extraction of Co and Ni by anion exchangers is scarce, the extraction by acidic chelating extractants has been widely used and many different application areas have been investigated over the years. The acidic chelating extractants works well in acidic aqueous solutions where the mechanism of extraction is governed by a proton transfer as can be seen in the general reaction of the extraction below.

\[
M_{(aq)}^{z+} + m(HA)_p(\text{org}) \Leftrightarrow MH_{mp-n}A_{mn(\text{org})} + nH_{(aq)}^{+}
\]

The applicability of the technique on slightly acidic solutions has made it the choice of many mining industries and high selectivities are reachable. In a study on the separation of Co and Ni from sulphate solution, Devi et al. compared the separating ability of three different acidic extractants in kerosene, namely Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), D2EHPA (di-(2-ethylhexyl) phosphoric acid) and PC 88A (2-ethylhexyl 2-ethylhexyphosphonic acid) [14]. Among the three, Cyanex 272 showed the most promising results with a separation factor of 3936 at pH=6.85. PC 88A however, required less amount sulphuric acid for the metal recovery stripping stage and the separation factor of the extraction was 1042 at pH=5.75. D2EHPA displayed larger indication of co-extraction of the metals with a maximum separation factor of 9.37. This is in accordance with other researches, showing that the separation factor of Co and Ni increases in the order of phosphoric (D2EHPA) < phosphonic (PC 88A) < phosphinic (Cyanex 272) acids [13]. The effectiveness of Cyanex 272 has also been reported by Rodrigues et al. in a study on metal recovery from spent mobile phone NiMH batteries [15]. The separation of Co and Ni was
in their research accomplished using a $0.6-0.7 \text{ M (}=20\text{ vol\%})$ Cyanex 272/kerosene solution at $\text{pH}=5.7$, yielding a separation factor over 1000. The separation involved no modifier agent of the organic phase and the process was run at room temperature.

Using the extractant labeled Cyanex 272, which is a dialkyl phosphinic acid, has several times been proven to be an adequate method for separating Co from Ni in both sulphate and chloride solutions and it is currently the favored technique in industrial applications [14] [15] [16] [17]. The exceptional Co and Ni separating ability of the extractant is no more coincidence since it was originally produced for the specific purpose of the separation of the two. There are however problems associated with the extractant. Even though it selectively extracts Co over Ni, commonly occurring contaminants in spent battery leachates such as Mn and Zn are prone to being extracted together with Co. This adds to the cost of the separation since a precipitation of Co and Ni and re-leach is often required prior to the extraction in order to meet the purity demands of a high value product [18]. An alternative way of removing impurities prior to the separation of Co and Ni is to implement another extraction step using D2EHPA in kerosene as described in a study conducted by Zhang et al. [19]. In the study, D2EHPA was successfully used for the separation of Al, Zn, Fe, Mn and REEs from a NiMH sulphate leach liquor with low co-extraction of Co and Ni. The system consisted of a two stage counter-current batch process and a scrubbing step of the organic phase in order to retain any co-extracted Co and Ni. After the extraction of impurities, Co was extracted from the leach liquor using Cyanex 272 and after stripping followed by precipitation using oxalic acid, the final product quality of Co and Ni reached 99.6 % and 99.8 % respectively.

The SX process requires the two phases to be properly mixed and this is usually made possible with the usage of equipment such as mixer-settlers or different mixing tower set-ups. These are well tested techniques within the mining industry and several equipment configurations exist, making both batch and continuous processes possible. However, since the organic solvent is mixed with the aqueous phase in order to increase the extraction, an occurring problem with these processes is the loss of solvent. This loss can be attributed to the low but still apparent solubility of the organic solvent in water as well as to not achieving 100 % phase separation before disregarding the aqueous phase. The latter is a consequence of the formation of stable multiphase emulsions, often referred to as crud, which is a common problem in larger scale SX systems. Since the organic solvents used for these processes are rather costly, the problem is often associated with high operating costs.

### 5.2 Supported liquid membrane

An alternative to the above mentioned mixing processes used in SX is to make use of the Supported Liquid Membrane (SLM) technique instead where the organic solvent loss can be reduced substantially. In an SLM process, a thin layer of the organic solvent is suspended between two aqueous phases of different compositions and the solvent is immobilized by an inert microporous support material. The inert
support material is usually a hydrophobic polymer which allows the liquid phases to be separated in the process, preventing water transfer. The suspended organic solvent (containing the extractant) is in this process acting as a semipermeable membrane, hence the name liquid membrane, since the metal ions will be loaded to the organic on the feed side, transferred through the membrane on the count of concentration gradients and then stripped from the organic phase on the stripping side. In the SLM process, the choice of membrane type is also important where two of the mainly used and discussed types are the flat sheet membranes (FSSLM) and the hollow fiber membranes (HFSLM). The hollow fiber membranes are constructed as pipes where the outer wall is a non-permeable material such that the liquids are kept inside the module. Inside, there are several small fibers which are made of the microporous support and the suspended organic solvent. The feed- and the stripping aqueous phase are then passed, usually in a counter-current manner, on each side of the tubular membranes, allowing for the extraction. The main advantage of the HFSLM process is the large interfacial area which allows for high extraction efficiencies.

![Schematic picture of the flat sheet supported liquid membrane process](image)

Figure 1: Schematic picture of the flat sheet supported liquid membrane process [20].

The construction of a flat sheet membrane is shown in Figure 1. The two sides of the membrane represent the feed- and stripping aqueous phase which both have to be well agitated during operation. The process is easy to handle in a batch system and the simplicity of the system is the main advantage when it comes to the flat sheet membranes. When comparing the extraction efficiencies of the flat sheet- and hollow fiber membranes, the hollow fibers yield the best results but still the flat sheet construction is well within acceptable values which makes both configurations justifiable [21].

In a process using an acidic chelating extractant, such as Cyanex 272, the extraction is driven by the proton concentration gradient over the membrane, allowing for extraction from the feed side of the membrane to the stripping side [20]. Due to this,
it is important to avoid concentration polarization between the membrane interphase and the aqueous bulk by continuously keeping the two aqueous phases well agitated. Since the solvent inventory is much smaller in comparison to conventional mixer-settler processes, the problem of crud formation is reduced. The same goes for the problem of organic dissolution in the aqueous phase where much lower amounts of organic solvent can be used for the same amount of extracted metal, allowing for a substantial decrease in solvent loss. It is however important to note that the loss of solvent can not be entirely eliminated by using the SLM technique. There are still some factors that might cause the organic solvent to leak out of the membrane support which ultimately leads to a decrease in extraction rate and efficiency. This membrane degrading process can be attributed to factors such as the presence of a pressure gradient over the membrane (both osmotic and physical), the solubility of the organics in the aqueous phase, the wetting of the support pores by the aqueous solutions or the emulsion formation of the organics in the aqueous phase induced by shear forces [22]. Since these phenomena reduce the separation over time, they have to be accounted for in a large scale operation. A way of coping with the problem in a continuous operation is to continually add new organics to the feed side together with applying a small pressure difference over the membrane with the higher pressure on the feed side. In such a system, the higher pressure on the feed side will prevent the organic liquid membrane from being lost in the aqueous feed solution as well as refill the organics that are lost in the stripping solution.

One of the greatest advantages of using the SLM technique for the extraction process is that the two steps of first loading the organic solvent with the metals and then stripping the organic in order to recover the metals can be combined into one process. This is because in the SLM process, both the loading and stripping take place simultaneously and continuously during the extraction. The advantage of this is that the equilibrium limitation, that leads to the high organic handling in the conventional solvent extraction processes, is eliminated by the continuous stripping of the organic in the SLM process [20].

The technique is very promising and many researchers regard it as the replacer of the mixer-settlers that are being employed today. There are however some problems with the technique in the upscaling that limits the membranes to smaller scale operations. One major problem is the instability of the membranes in terms of long time operation. As stated above, the organic solvent is by different factors lost in the continuous operation of an SLM process which ultimately decreases the extraction efficiency over time. This has lead to a slow progress of the technique in large scale applications since the membranes have to be continuously replaced, adding to the cost of the system. Another problem that is associated with the membranes is the swelling of the membranes during loading which can cause severe damage to the equipment if not taken into consideration. However, despite these challenges, the advantages of the SLM process over the conventional SX systems, using e.g. mixer settlers, makes the choice in the membrane technology justifiable, especially in smaller scale operations [20].
5.3 Precipitation

Metal precipitation is the process of extracting metals from a solution by tampering with parameters that influence the present metal complexes' solubility, leading them to precipitate as a solid salt. Through this technique, separation of metal ions in a solution can be achieved by varying the pH of the solution where the solubility of the salts at different pH differ between the metals. Precipitation, applied in metal separation processes, has the advantage of having low complexity and low operational costs when cheaper precipitants are used but the largest drawback is the selectivity of the technique. Since several metals in solution precipitate over a relatively large pH range, the impurity concentrations are often high in the product precipitate [13]. The selectivity of the separation is highly influenced by the choice of added precipitant where different precipitants are selective to form precipitates with different metal ions based on the stability of the resulting metal salt.

When it comes to precipitation of metal ions from solution the most straightforward approach is NaOH addition, creating a solid metal hydroxide product. The technique is effective in the removal of solvated metal ions but the selectivity is low due to the fast release of hydroxyl ions, creating locally high pH values. Additionally, the hydroxide solubility of the divalent Ni, Co, Zn and Mn ions present in battery leach solutions are similar, increasing the risk of simultaneous precipitation, lowering the purity of the final product. Instead, the use of complexing agents can be employed to recover the metals selectively. The reactant dimethylglyoxime (C\textsubscript{4}H\textsubscript{8}N\textsubscript{2}O\textsubscript{2}), that is often used as chelating agent in gravimetric analyses of Ni, has been successfully used in the selective precipitation of Ni from leached Li-ion cathode material [23]. The studies confirm that the complexing agent can be employed in the leach liquors from Li-ion scrap material, typically containing equal amounts of Ni, Co and Mn oxides, and a Ni separation of up to 98 % can be achieved. The resulting nickel-dimethylglyoxime precipitate is treated in a subsequent acid dissolution step where the Ni is redissolved, leaving the regenerated dimethylglyoxime in the solid phase to be reused. One problem with the technique is the bulkiness of the precipitate which creates difficulties in solid-liquid separation. Also, since dimethylglyoxime is insoluble in water and only barely soluble in ethanol, a thought process would require the addition of large volumes of ethanol, which could potentially affect the solubility of the other metal ions and would also be inconvenient from a process point of view. By estimating the needed volume of a solution of dimethylglyoxime in ethanol it is found that around 20 times larger volume than that of the initial leach liquid in the specific case of NiMH battery recycling is required, based on a stoichiometric addition of dimethylglyoxime with regards to Ni and the solubility of dimethylglyoxime in ethanol being 1.3 g/g ethanol [24]. In conclusion, the Ni content in the leach liquor is too high in order for the technique to be applicable in the present study.

A precipitation technique that is increasingly being considered in separating Ni and Co from sulphuric leach liquor is mixed hydroxide precipitation using caustic calcined magnesia as neutralizing agent for pH adjustment. The process is enhanced by
the addition of mixed hydroxide precipitate seeds in order to increase the selective precipitation of Ni and Co over contaminants, especially Mn. By using magnesia instead of NaOH or NH\(_4\)OH as neutralizing agent, the seeding effect of Ni(OH)\(_2\) can be improved, increasing the percentage of Ni precipitation as well as the crystallinity of the precipitate [25] [26]. This is possible due to the slower hydroxyl ion release that occurs when magnesia is added as precipitant, creating a more controlled precipitation with lower local supersaturations as compared to NaOH addition [27]. In a U.S. patent, different solutions containing Ni, Co and Mn, magnesia was successfully used as neutralizing agent in the selective precipitation of Ni and Co over Mn [28]. The research repeatedly reports Ni and Co recoveries over >90 % whilst Mn maintained in solution with a small precipitation percentage of around 10-15 %. No seeding was used in the process. This technique however, is problematic since it involves the addition of yet another metal ion to the solution, namely Mg, which increases the difficulty in downstream separations. As a consequence, high levels of Mg contamination in the end products are common, lowering the value of the product and creating a need for Mg separation if the product is to be used in the production of new batteries.

Where hydroxide precipitation is more prone to precipitate impurities such as Mn together with Co and Ni, mixed sulphide precipitation has been shown to produce higher purity precipitates from leach liquors [29]. In a study on selective precipitation of metals in leach liquors from ocean nodules, Jandová et al. selectively separated Co and Ni from a mixture of solvated metals using (NH\(_4\))\(_2\)S as precipitant [30]. The precipitant was added dropwise to the solution, containing a mixture of Ni, Co, Mn, Fe, Zn and Cu and the pH was measured. The results showed that both NiS\(_{(s)}\) and CoS\(_{(s)}\) formed at pH=3 while MnS\(_{(s)}\) precipitated in the alkaline pH range. Not mentioned in the report is the particle size distribution which is a recurring problem with this technique. The low solubilities of the metal sulphides easily creates high levels of supersaturation in the mixture, causing the precipitation process to be dominated by homogeneous nucleation. This promotes the formation of fine particles which creates difficulties in the subsequent liquid-solid separation, rendering process control outermost important. Another problem associated with mixed sulphide precipitation is the evolution of H\(_2\)S gases in acidic condition, creating a hazardous environment.

In order to further refine Co and Ni separately, conventional methods include re-leach and solvent extraction. An alternative route has recently been proposed by the University of Queensland Hydrometallurgy research group in which selective leaching is used for the separation of Ni from Co and Mn. The method includes the addition of an oxidant during the re-leach of mixed hydroxide precipitates in order to selectively oxidize Co and Mn into trivalent cations, thereby stabilizing them in the solid phase [31] [32]. In the proposed process, the mixed hydroxides are successfully leached in H\(_2\)SO\(_4\) together with the addition of Na\(_2\)S\(_2\)O\(_8\) as oxidizing agent, resulting in a trivalent Co and Mn hydroxide solid while Ni is selectively solubilized. The process shows potential as a cost effective and easy alternative for separating Co and Ni compared to conventional solvent extraction but the method is still on a research stage.
Using an oxidant to selectively oxidize Co(II) into Co(III) over Ni in order to lower the solubility of Co has been under investigation before [33] [34]. By adding the oxidant sodium hypochlorite (NaClO) together with NaOH to a solution of hydrochloric acid leached Li-ion cathode material, Joulié et al. successfully separated Co and Ni through selective precipitation of Co(OH)₃. The best results were obtained when using a NaClO/Co ratio of 3 at pH=3. The precipitated Co(OH)₃ and the final Ni(OH)₂ had a purity of 90.25 wt% and 96.36 wt% respectively [34].

Oxidative precipitation has also been proposed in the selective removal of divalent Mn ions in different mixed metal ion solutions [35] [36] [37] [38]. Here, the idea is to selectively oxidize the Mn(II) to Mn(III)/Mn(IV) over the other metal ions and produce Mn oxides (MnOₓ). The low solubility of the MnOₓ then leads them to precipitate even from low pH solutions, creating a product with low concentrations of contaminants. In the redox reaction, the reduction potential of the different possible metal ion oxidations in the solution is crucial where the electric potential of the solution determines whether an oxidation is possible or not. MnOₓ precipitation techniques utilize the fact that the standard reduction potential of Mn(III)/Mn(IV) is lower than that of Ni, Co and Zn and has low pH dependence [39]. In the process, an oxidizing agent with slightly higher reduction potential than that of Mn(III)/Mn(IV) must be used at a pH where the oxidations of Ni(II), Co(II) and Zn(II) are subtle in order to create a high purity precipitate. If a too highly oxidizing agent is used, the electric potential will be high enough to oxidize the MnOₓ further into MnO₄⁻ ions, leading the Mn back into solution.

5.4 Electrowinning

Electrowinning or electroextraction is the process of extracting metal ions dissolved in a solution through electrochemical reduction of the ions onto one of the electrodes in an electrical cell. This technique has been applied in the mining industry for many years and it is often regarded as a more economical alternative compared to precipitation since electricity is used for the separation rather than the addition of chemicals [40] [41]. The end product differ as well where precipitation yields metal salts while electrowon metals wind up in the form of pure metals or metal alloys, depending on the composition of the solution. In a mixture of more than one metal in solution, the reduced metal product composition and yield depend on a variety of factors including pH of the solution, temperature, current density, purity and metal ion concentration [42]. In order to selectively reduce one metal and thereby obtaining a high purity product in such a system, the reduction potentials of the ions have to be considered, where two ions with similar reduction potential in a solution will be reduced in a similar matter.

Selective electrowinning can be achieved in for example solutions containing divalent ions of Ni and Cu, where the difference in standard reduction potential between the two ions is 0.6 V [43], but becomes more complicated in a system containing Co and Ni. In such a system, the small difference in standard reduction potential of divalent
Ni (being -0.24 V) and divalent Co (being -0.28 V) vs. the standard hydrogen electrode leads the metals to co-deposit, creating an alloy product. Hence, in this study, electrowinning is disregarded as a separation technique in the Co and Ni system but still serves as a possible process step with regards to the end product application.

6 Technique comparison

It is evident that the separation process in the recovery of metals from the leach solution will not be an easy task where the metals in solution, especially Co and Ni, behave in such a similar manner. This is of course problematic since a high purity product is often more attractive on the market than a low grade product. It is also important, from a Life Cycle Analysis (LCA) point of view, to consider the use of the potential end products. The end product application does not only affect the selling price of the product but also the process environmental impact. For instance, if the metals were recovered as an alloy to be used in stainless steel production, the process of recycling the metals yet again becomes more challenging. It would therefore be more environmentally friendly to recycle the metals into new battery production precursors than to let them be recycled into a low grade application such as stainless steel. In order to make a valid comparison between the different techniques for the recovery of metals from the resulting NiMH leach solution, one must therefore consider both the economics and the application regarding the end product since different techniques allow for different purity and composition of the end product. In Table 3, different potential products that could be obtained by the techniques stated above are listed together with their respective market price. The prices were obtained through personal contact with Chinese bulk chemical suppliers, where the requested amount were 100 kg for each compound, and the pure metal powder prices were taken from the current world commodity market.

As can be seen from Table 3, Co has a higher market value than Ni, especially as a pure metal powder. In addition, the commodity price of Co is expected to grow in the near future, increasing the economic value of recycling the metal [45]. The market price of Co(OH)$_2$ is presently lower than that of the metal powder and due to the fact that Co is mainly used in various alloy configurations, both in the steel and battery manufacturing industry, the future can be expected to follow this trend.

Even though Ni has a lower value on the market by weight, the amount of Ni within the electrodes makes it a highly valuable metal in the recycling of NiMH batteries. In forecasts on the commodity price of Ni, no drastic change within the near future can be seen [46]. From the table it can also be seen that, in contrary to Co, the price of Ni in the form of metal salts have higher market values than the pure metal. The reason for this is probably due to the large availability of Ni metal on the market, which results in a price drop. Another thing that speaks for producing a Ni salt is the fact that in the conventional process of constructing new battery material,
Table 3: Current market values of different end products (2017).

<table>
<thead>
<tr>
<th>Nickel</th>
<th>Price [USD/kg]</th>
<th>Purity [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(OH)$_2$</td>
<td>18</td>
<td>61% Ni</td>
</tr>
<tr>
<td>NiSO$_4$•6H$_2$O</td>
<td>4.5</td>
<td>22% Ni</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>16</td>
<td>40% Ni</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>12</td>
<td>44% Ni</td>
</tr>
<tr>
<td>Ni</td>
<td>10 [44]</td>
<td>&gt;99% Ni</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Price [USD/kg]</td>
<td>Purity [wt%]</td>
</tr>
<tr>
<td>Co(OH)$_2$</td>
<td>25</td>
<td>61% Co</td>
</tr>
<tr>
<td>CoSO$_4$•7H$_2$O</td>
<td>7</td>
<td>21% Co</td>
</tr>
<tr>
<td>Co</td>
<td>50 [44]</td>
<td>&gt;99% Co</td>
</tr>
<tr>
<td>Mixed products</td>
<td>Price [USD/kg]</td>
<td>Purity [wt%]</td>
</tr>
<tr>
<td>Cathode material</td>
<td>20.5</td>
<td>57% Ni, 1.5% Co, 3% Zn</td>
</tr>
<tr>
<td>MHP-1</td>
<td>16</td>
<td>31% Ni, 12.5% Co, 17.5% Mn</td>
</tr>
<tr>
<td>MHP-2</td>
<td>10</td>
<td>54% Ni, 4% Co, 2% Mn, 2% Zn</td>
</tr>
</tbody>
</table>

such as cathodes in NiMH batteries and also in some battery types, the cathodes in Li-ion batteries, the precipitation of Ni from aqueous solutions are commonly employed [47] [48]. This means that the production of a Ni salt would yield an end product that could be used directly in the production of new batteries. However, the purity demand on the Ni salts that are to be used for battery manufacturing are understandably high, requiring highly selective separation methods such as solvent extraction.

The market values of the Mixed Hydroxide Products (MHPs) differs with the composition as expected. The first mixed hydroxide product, given the name MHP-1 in the table, has a rather high value considering the low purity but this can be explained by the Co content being rather high at 12.5 % and, according to the supplier, the price of this product is almost solely dependent on the commodity price of Co. The other product, MHP-2, has the composition of the obtained product where all of the elements that are left in the NiMH battery leach solution has been precipitated as a mixed hydroxide, which can be obtained by simply increasing the pH of the solution. The price of this product could not be found since the composition is specific for just this case. However, by accounting for both the commodity prices of the different metals and the price of the high Co content MHP, the market price was estimated to 10 USD/kg as tabulated. The third mixed metal product is the material that is used in new NiMH battery cathodes, which could then be sold directly to smaller battery manufacturing companies that rely on the structure and composition of the product. The difference between the cathode material, which is basically a Ni(OH)$_2$ coated with Co and Zn, and the mixed hydroxide that is obtained by a simple hydroxide precipitation is the Mn content which affects the cathode’s performance and the structure of the two materials. In order for the product to be sold off as cathode material, the Mn would have to be removed prior to the precipitation of the product and the process of precipitation would have to be controlled by a complex agent such as NH$_4$OH to ensure the crystalline $\beta$-Ni(OH)$_2$.
phase which is dominant in NiMH cathodes [47].

In order to further assess the potential revenues from the different end products, one must start by considering the amount of metals that are present in the NiMH leach solution. The potential recovered mass of metal products can then be calculated followed by the revenues. In this work, by using the findings in the study of Korkmaz et al., the total amount and the composition of anode and cathode material in a Toyota Prius HEV NiMH battery could be used as a base in these calculations. The theoretical amount of recovered metals were obtained by assuming a 100 % recovery of each component, except for the REEs which are readily precipitated, and the molar masses were then used to calculate both the amount of product and the final product composition. This is not entirely representative of the case but since the leaching study resulted in leaching yields of >90 % for all metals, the accuracy in a comparison using the same yield for all metals is regarded as acceptable. The calculated potential revenues from different end products in the metal recovery process from the NiMH battery leach solution are summarized in Figure 2. The results from the leaching study made by Korkmaz et al. showed that one battery pack contains a total of 14.38 kg electrode material with the associated wt% as in Table 1, and this was set as the base in the revenue mass balance calculations.

![Potential revenues](image)

**Figure 2:** Potential revenues of different products that could be obtained by recovering 100 % of the respective metals from the NiMH battery leach solution calculated per battery.

From the results stated in Figure 2, one can see that the revenues per battery that comes from the pure Co products, i.e. CoSO$_4$•7H$_2$O, Co(OH)$_2$ and Co metal, are low in comparison to the other products. The highest revenue is obtained when Co is recovered as a pure metal which is a consequence of the high commodity price of the metal, but from the figure it is evident that even so, this does not exceed the lowest Ni product revenue. This means that even though the Co product have the
highest market value, the small amount of the metal in the battery and the resulting leach solution results in a low revenue compared to the other potential products. Based on these findings the separation of Co into highly pure products will not be prioritized in the present study.

The resulting revenues suggest that the two most valuable products that are obtainable from the leach solution are either a pure Ni salt, preferably NiCO$_3$ or Ni(OH)$_2$, or a new cathode material which is the crystalline $\beta$-Ni(OH)$_2$ coated with Co and Zn. Both these end products are commercially used in the manufacturing of new batteries which closes the loop of battery to battery recycling. The product of pure Ni metal yields a much lower revenue and thus, electrowinning is not justifiable in this case even though the process is regarded as rather clean with the use of less chemicals. Electrowinning could instead be used in a case where the Co content is high enough to obtain a comparative revenue.

The main advantage of choosing a process path that yields a Ni salt as the end product is the resulting revenue. The revenue is by far the highest in this case where not only would the Ni be able to be sold off as a high purity product but also would the Co, together with the other metals as a mixed hydroxide, where the Co content would be high. The only disadvantage in this process is the need for a highly selective separation technique that can yield a pure enough Ni solution, free from Co and other impurities to a maximum of around 0.1 %, which is the overall standard at the Chinese market from where the prices were obtained. From the literature review, the separation technique that exceeds all others in product purity regarding the separation of Co from Ni is the extraction processes which can also be cheap if the extractant loss can be minimized since the organics can be easily reused. Because of this reason, extraction was chosen as a technique to be further investigated for the separation and recovery of pure Ni salts from the NiMH battery leach solution. As the solvent extraction processes have the problem of crud formation and consequently large amount of expensive solvent loss, the supported liquid membrane technique was primarily chosen for the extraction.

Even though the pure Ni salt products seem to yield the highest revenues in this case, the process of producing new cathodic material for new NiMH batteries is still justifiably applicable. Where the market value of this product, which can be seen in Table 3, is higher than all the pure Ni products, this results in a high revenue since the product essentially is Ni(OH)$_2$, allowing for a large amount of product per recycled battery. The higher market value is higher because of the direct usability of the product in battery cathode manufacturing, compared to the Ni salts which in the same sought application has to be redissolved and synthesized into cathodic material. Because of this, it was chosen to also further investigate the possibility of implementing a process of producing new cathode material from the NiMH battery leach solution. By doing so, the need for a highly selective Ni separation is eliminated since the Ni, Co and Zn can be simultaneously precipitated in the synthesis of NiMH cathode material [49]. The only issue in applying the process on the recycled NiMH battery leach solution is the relatively high Mn content. Commercial NiMH cathodic material are free from Mn and thus, including the Mn in the end product
could ultimately result in a non sellable product. Hence, the Mn would have to be removed prior to the cathode material synthesis in such a process. The technique that was chosen for the selective removal of Mn from the leach solution was oxidative precipitation which has been proven to work on other types of solutions containing Mn(II) \[35\] [36] [37] [38].

Another possibility is the production of a co-precipitated mixed hydroxide (MHP-2). The main disadvantage of producing such a product is the low quality and purity of the recovered material. The resulting mixed hydroxide has no application in the industry so the product would in this case have to be sold off to another company that has the capacity to refine the metals further and hence, the product revenue will be low. The advantage however, is the simplicity of removing all metal ions together and thereby producing a sellable product. This route will also be considered as a possibility of recovering the valuable metals from the NiMH battery leach solution in the present study.

7 Precipitation of mixed hydroxide product

The production of a mixed hydroxide can be justified both by the simplicity of the involved procedure and by the, surely relatively low but still apparent, potential revenue from such a product. The simplicity of the production of the mixed hydroxide is because the need for a separation between the metals is eliminated and hence, less process steps are required. It is however important to consider the separation of some of the metals present in the leach solution since the price of the product is correlated to the amount of impurities in the end product material, meaning that if some metals can be separated from the solution beforehand, the selling price of the end product would be higher and such the revenue. In order to make an assessment of the technique of raising the pH of the solution by the addition of OH\(^-\) ions, the KTH developed program Medusa was used. Through Medusa it is possible to get an overview of the solution characteristics where the program provides a database of numerous equilibrium data which are used to conduct calculations on the given system and hence, the program can be used to predict the outcome of changes in the solution parameters such as pH. Additionally, the program can be used to calculate the equilibrium conditions where a complex reaches its supersaturation limit and is therefore being precipitated from the solution as a solid, which was the purpose for the use of the program in this work.

7.1 Method evaluation

In order to evaluate the method of separation from the leach liquor, figures showing the precipitation behavior of each metal were constructed in Medusa. Calculations were made on both the system leached with hydrochloric acid and with sulphuric acid in order to compare the different solutions and their respective response to a thought
pH increase. The input metal concentrations were the same as the concentrations in the resulting leach liquor and the concentration of chloride- or sulphate ions in the respective system was obtained by assuming total dissolution of the 2 M acid which was used in the leaching and whilst also accounting for the volume increase induced by the precipitation of REEs as described in the leaching study [11]. The hydroxide precipitation of the metals from the resulting leach solution is described in Figure 3 and Figure 4, where both the chloride- and sulphate systems are represented.

Figure 3: *Equilibrium concentrations of the different metals in the sulphate leach solution and their respective precipitation behavior as a function of pH.*

As can be seen from the figures, all metals present in the leach solution form hydroxide complexes that can be readily precipitated from the solution given that the pH is high enough. This can be said about both the chloride and the sulphate solution. As can also be seen, there seem to be no apparent differences in the hydroxide precipitation behavior of the metals between the two solutions even though the free
Figure 4: *Equilibrium concentrations of the different metals in the chloride leach solution and their respective precipitation behavior as a function of pH.*

Metal ion concentration is generally higher in the chloride solution.

Further, the results from the literature review on the matter of hydroxide precipitation is confirmed where the separation of these metals from each other through hydroxide precipitation has before been proven to be poor. This can also be seen in the figures where the solution pH where the metals precipitate are all around pH=6-9 in both solutions. Remembering that the pH scale is logarithmic, one can conclude that separating the metals through hydroxide precipitation will prove to be really hard where small amounts of added OH\(^-\) ions will have a large impact on the solution pH in this region. Additionally, there are more than seldom problems associated with the addition of base in these processes since, if not agitated properly, OH\(^-\) concentration gradients will form and create spots of high pH which leads all
the metals to locally precipitate together. It can therefore be concluded that the product using the route of hydroxide precipitation is a mixed metal hydroxide rather than pure metal salts.

It is however noticeable that one of the metals present in the solution, namely Al, precipitates already at pH=4 in both the chloride solution as Al(OH)$_3$ and in the sulphate solution as AlOHSO$_4$. This behavior is advantageous since the pH difference between the precipitation of Al and the other metals creates a possibility to separate the Al from the group, which in turn creates a mixed hydroxide product of higher value. This is also in accordance with the literature where both Al and Fe present in similar solution are often being removed by hydroxide precipitation prior to any other separation techniques. This fact can also be of use in the present work where a removal of Al prior to an extraction process would prove advantageous.

In conclusion, based on the results from Medusa, a mixed hydroxide precipitate can be readily produced from the leach liquor from both chloride- and sulphate solution by simply increasing the pH by the addition of base. It can be concluded that at pH=11-12, all of the present metals are precipitated at a fraction of close to 100 % which is sought for this route and hence, a pH of 12 is recommended as a proper value for the precipitation. Two commonly used bases for this purpose are sodium hydroxide (NaOH) and ammonia solution (NH$_4$OH) where the former is considered as a strong base and the latter is considered weak [50]. The main difference between the bases except for the addition of either Na$^+$ or NH$_4^+$ ions is therefore the release of OH$^-$ ions into the solution. In the case of using NaOH, the release is fast and spots of locally high pH are easily formed which lowers the control of the precipitation. As mentioned above, this is usually a common problem associated with precipitation where the separative ability of the method depends a lot on pH control. When pH control is crucial for the system, such when dealing with selective precipitation, NH$_4$OH can be used instead where the OH$^-$ ion release is slower, allowing for better pH control. However, since there is no need for any separation other than the separation of Al at pH=4 in the present work, there is no need for high level of pH control, where all the metals are sought to be precipitated together. Therefore, both NaOH and NH$_4$OH are justified as precipitants in this case.

The other aspect to consider when choosing a proper precipitant is the different added ions and their respective influence on the solution. In the present work, neither Na$^+$ nor NH$_4^+$ will have any effect on the cationic metals in the solution but it is important to evaluate how the added cations would affect the chlorides or the sulphates in the two leach solutions. Since the two bases form the salts Na$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ in sulphate solutions and NaCl and NH$_4$Cl in chloride solutions, the solubility of these and their supersaturation limits in the present solution need to be evaluated to ensure that these will not precipitate together with the metal hydroxides. This was again made using Medusa where a higher concentration of both anions and cations were used in order to increase the threshold of certain dissolution of the corresponding chloride- and sulphate salts, meaning where they are of no risk of precipitating from the solution. The results are shown in Figure 5.
and Figure 6.

Figure 5: Sulphate complex concentrations present in the sulphate leach solution as a function of solution pH.

Figure 6: Chloride complex concentrations present in the chloride leach solution as a function of solution pH.

As can be seen from the figures, all complexes that are present in the leach solution in the system are dissolved and no precipitation is present. This is because all the before mentioned salts have a high solubility in aqueous solutions and the concentrations of the ions in the present solution seem to be lower than the supersaturation limit, as described by the figures. It should be noted that if the Na concentration is further increased in the sulphate solution, Na₂SO₄ precipitates, contaminating the metal hydroxide product, but since the concentration at which this occurs is around twice...
as large as the concentration present in the leach solution (i.e. 4 M), the phenomenon is not a problem in this particular case.

### 7.2 Experimental

Because of the advantages of the mixed hydroxide route, complimentary experimental trials were conducted in order to verify the preliminary Medusa calculations made on the system. The hydroxide precipitation was also conducted in order to monitor the precipitation behavior of the different metals in the solution as the pH of the solution is increased. The results from the experiment could then be used to evaluate the possibility of using an extraction process directly on the leach solution since these processes, e.g. the SLM process, requires a solution pH of around 5-5.5 as can be seen in the literature review. The main concern in increasing the pH to pH=5.5 is that the high Ni concentration might lead some of the Ni to precipitate from the solution prior to the extraction in this case which would complicate the system since an additional re-leach of precipitated Ni would have to be included in order to reduce the loss. The experimental trials on the mixed hydroxide precipitation therefore aimed at answering the question whether the solution pH could be increased to pH=5.5 without any metal precipitation as well as give an increased understanding about the system during $\text{OH}^-$ ion addition. The experiments would also yield the amount of base that is needed in order to create the mixed hydroxide product from the solution, as can be seen in Section 9 in this report, making a mass balance calculation possible for the entire system from leaching to end products.

Based on the availability and easy handling, the precipitant that was selected for the experiments was NaOH. The leach liquor that was chosen for the experiments was the sulphuric acid liquor as the sulphate matrix has been shown to yield higher levels of separation in extraction processes using Cyanex 272 than systems with a chloride matrix, making the results more applicable in the extraction calculations in Section 9 of this report.

#### 7.2.1 Equipment

The precipitation experiment was conducted in a 100 ml Erlenmeyer flask and the mixture was agitated using a magnetic stirrer. During the experiment, the pH was measured using an Orion Star A211 pH meter from Thermo Scientific. The mixture was centrifuged in a Sigma 3-16 l centrifuge before sampling and for solid removal and the metal ion concentrations were measured using an iCAP 7000 Series ICP spectrometer from Thermo Scientific. The scale that was used for weighing the samples was a Mettler Toledo XPE105. Additional equipment that was used includes pipettes, spatulas, beakers, stirring rods and other conventional chemical lab equipments.
7.2.2 Chemicals

The metal salts that were used in the experiment to simulate the leach solution concentrations were for all but one metal, the respective metal sulphate, i.e. \( \text{NiSO}_4 \cdot x\text{H}_2\text{O} \) (20.8-22.4 % Ni) from BDH Chemicals Ltd Poole England and \( \text{CoSO}_4 \cdot 7\text{H}_2\text{O} \) (>99.0 %), \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) (>99.0 %) and \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \) (>99.5 %) from Merck. In the case of Al, the used metal salt was \( \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} \) (>99.9 %) from Sigma Aldrich. The liquids used in the experiment were lab grade sodium hydroxide solution (4 M), sulphuric acid (95-97 %) and nitric acid (69 %).

7.2.3 Experimental procedure

Before the precipitation experiment could be commenced, a synthetic solution was made based on the results from the leaching study. In order to end up with a solution of matching metal concentrations as the leach solution (as can be seen in Table 2), the respective metal salt were weighed and added in the amounts showed in Table 4. The table is valid for the preparation of a synthetic solution of 200 ml in volume. The resulting solution composition was then measured with ICP and the resulting metal concentrations can be seen in Table 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{NiSO}_4 \cdot x\text{H}_2\text{O} )</th>
<th>( \text{CoSO}_4 \cdot 7\text{H}_2\text{O} )</th>
<th>( \text{MnSO}_4 \cdot \text{H}_2\text{O} )</th>
<th>( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} )</th>
<th>( \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added [g]</td>
<td>22.55</td>
<td>1.86</td>
<td>0.51</td>
<td>0.69</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 5: Resulting metal concentrations of the synthetic solution as used in the hydroxide precipitation experiment.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>[g/dm³]</td>
<td>26.48</td>
<td>2.03</td>
<td>0.81</td>
<td>0.8</td>
<td>0.39</td>
</tr>
<tr>
<td>[mol/dm³]</td>
<td>0.45</td>
<td>0.034</td>
<td>0.015</td>
<td>0.012</td>
<td>0.014</td>
</tr>
</tbody>
</table>

After the weighing of the samples, all the metal salts were put in a 250 ml Erlenmeyer flask and were then dissolved by adding sulphuric acid and continuously stirring the mixture using the magnetic stirrer. The sulphuric acid had been previously prepared by diluting the concentrated acid such that the pH of the acid reached a level of pH=0.3, which is the pH where the precipitation and removal of REEs are finalized in the leaching study. By doing this procedure, a 200 ml synthetic solution resembling the sulphuric acid leach solution as obtained after the removal of REEs could be made. From this solution, three samples were taken for ICP analysis in order to determine the starting value of the metal concentrations in the solution. Three samples were taken at this point as to increase the validity of the measurement.

Next, the experimental rig was set up consisting of a 100 ml Erlenmeyer flask with a magnetic stirrer bar inside which were placed on the magnetic stirrer. In order
to increase the mixing and hence reduce the risk of local supersaturation, a mixing bar was dipped in the solution and fixated, working as a baffle in the continuously agitated system. The pH meter was kept in an electrode storage solution between every measurement during the experiment and the meter was re-calibrated after each idle time longer than 10 hours. At all times, the experiments were conducted in room temperature.

As one of the aims of the experiment was to add the base as controlled as possible in order to carefully monitor the behavior at different equilibrium pH, the addition of NaOH was a slow process such that local supersaturations could be avoided as much as possible. Hence, during the whole course of the experiment, the NaOH was carefully added dropwise by using a fixed 0.1 ml pipette. Additionally, to ensure uniform dispersion of NaOH, the NaOH was added in intervals of approximately one minute in between each 0.1 ml addition. The slow NaOH addition was also necessary since the pH scale is logarithmic and at higher pH, small amounts of added NaOH can lead to a large increase in pH, rendering the experiment control unstable.

In the beginning of the experiment, a solution of 4 M NaOH was added to the solution since the pH was low enough to be able to controllably increase the solution pH with the given concentration. This was repeated until the pH reached pH=2, where the NaOH concentration was changed to 2 M instead because of the visible faster increase in pH upon NaOH addition. Subsequently, after reaching pH=3, the NaOH concentration was altered between 1-0.5 M, since the pH increase was so fast at this pH that even small added amounts of 0.5 M NaOH resulted in a rather large pH increase. During the bulk precipitation, the concentration was again changed to 4 M in order to avoid a large volume increase and this concentration was then used until the final pH was reached. The pH was measured continuously during the NaOH addition and samples for ICP analysis were taken at different pH in order to keep track of the precipitation behavior. A fraction of the solution was centrifuged during the sample taking as to ensure separation of the liquid and the solid particles. To account for the added NaOH and the removed liquid during the course of the experiment, the solution was weighed continuously before and after each sample. All of the retrieved samples were diluted 100 times in 5 % nitric acid before being analyzed because of the emission range of the ICP.

Upon reaching a desired pH for ICP sampling, the solution was first kept agitated and idle for 10 minutes before taking the sample. The solution was then left overnight while stirring and another sample was taken after 20 hours in order to study the kinetics of the precipitation. When the solution was left overnight, a cap was placed on the flask to avoid solution loss due to evaporation. This procedure was repeated during the course of the experiment. In addition to the determined and scheduled ICP sampling, additional ICP samples were taken at points in the experiment where something changed in the behavior of the solution, such as changes in pH increase velocity or changes in the solution turbidity.

During the course of the experiment, three different fractions of solids were removed by centrifugation, one at pH=4.89, one at pH=8.1 and one final at the end of the
precipitation at pH=10.81. The three solids were thoroughly washed with pure DI water, a NaOH solution of pH=8 and a NaOH solution of pH=11 respectively in the order of increasing precipitation pH. In order to determine the amount of Ni that was co-precipitated with the Al at pH=5.5 and to determine the composition of the solids, predetermined amounts of the three solid fractions were dissolved in a mixture of concentrated nitric- and hydrochloric acid as to ensure total dissolution. The metal concentrations of the three solutions could then be measured with the ICP and by knowing the added amount of solid, the results were used to calculate the solid composition by weight. Additionally, an XRD analysis were conducted in order to determine the structure of the samples.

7.2.4 Results and discussion

As a precaution for avoiding runaway pH increase during the addition of NaOH, the pH was constantly measured and plotted against the added amount of NaOH. The resulting titration curve, as can be seen in Figure 7, shows the behavior of the mixture as the pH is increased by NaOH addition. Due to the fact that the concentration of NaOH was changed during the experiment, the X-axis shows the added NaOH in the unit of mmol.

![Figure 7: Titration curve showing the change in solution pH as a function of added mmol of NaOH.](image)

It can be seen from Figure 7 that in the beginning of the NaOH addition, the pH increase is slow with regards to the added amount of NaOH. The curve is also smooth with no interruptions, indicating that no precipitation occurs in the beginning of the pH increase. The slow increase in pH between pH=0.3 and pH=2 is in compliance with the expected outcome where this is a product of the pH scale being logarithmic.
This means that at a pH of around 2, the pH will start to increase a lot faster with regards to the added amount of base while the pH increase more slowly at low pH values. Since the titration curve shows the change in pH with respect to the added amount of base, a regular titration curve, excluding any precipitation or other occurring reactions other than the pH increase, has the shape of an S-curve with the largest slope at the equivalence point which in this system is around pH=7 [51]. At pH=2, the solution pH started to increase much faster upon each new NaOH addition up until pH=4.5 where the pH increase began to slow down, as can be seen in the figure. In the titration curve, one can see that the slope is decreased at pH=4.5-5 which is an abnormal behavior from the neutral S-shaped titration curve. This indicates that the added OH\(^{-}\) ions was consumed by something in the solution upon addition and from the Medusa calculations as seen in Figure 3, it can be assumed to be due to the precipitation of Al as either Al(OH)SO\(_4\) or Al(OH)\(_3\). During the experiment, this could also be seen as the turbidity of the solution changed and a white precipitate became visible. At pH=5, the slope increased again until the solution reached pH=7, where the bulk precipitation took place, as can be seen in the titration curve. Between pH=7 and pH=9, there was a clear change in the solution turbidity and large amounts of precipitate could be seen. The color of the solid was mainly green, indicating that the Ni precipitated as either sulphates, hydroxides or both. Complete precipitation of the metals can be seen at around pH=10, according to the titration curve.

The curve in Figure 7 can be used as a guideline in the increase of the solution pH as it reveals at which points of the increase that the addition of base should be controlled more carefully. In addition, it also gives an idea of how much NaOH is needed for the precipitation. It can for instance be concluded that a total of at least 100 mmol of NaOH is needed to ensure complete precipitation of all the metals in a leach solution with a volume of 50 ml. A complete overview of the amount of NaOH in terms of volume and concentration that was added in the experiment can be seen in Table 6.

Table 6: Total amount of added NaOH in terms of volume and concentration in the controlled increase of the leach liquor solution pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>0.3→2</th>
<th>2→3</th>
<th>3→4</th>
<th>4→5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added</td>
<td>14.2 ml (4 M)</td>
<td>1.8 ml (2 M)</td>
<td>0.3 ml (1 M)</td>
<td>1.8 ml (1 M)</td>
</tr>
<tr>
<td>pH</td>
<td>5→5.5</td>
<td>5.5→7</td>
<td>7→8</td>
<td>8→11.5</td>
</tr>
<tr>
<td>Added</td>
<td>1 ml (0.5 M)</td>
<td>2.1 ml (0.5 M)</td>
<td>7.5 ml (4 M)</td>
<td>2.5 ml (4 M)</td>
</tr>
</tbody>
</table>

The results in Table 6 show a more in depth analysis of the amount of added NaOH needed in order to obtain a controlled pH increase. These results are useful when the aim is to increase the pH to pH=5.5 as in the extraction process where this pH increase requires higher levels of control than in the precipitation of the mixed hydroxide. From the table it can be seen that a total of 19.1 ml of NaOH at different concentrations is needed in order to controllably increase the pH to the desired pH.
of 5.5. The corresponding amount of NaOH in mmol can be calculated to a total of 63 mmol using the results in Table 6. The added volume corresponds to a 38.2 % volume increase where the starting volume of the experimental solution was 50 ml and it can therefore be concluded that in order to increase the leach liquor solution pH to 5.5 in a controlled manner, a reactor volume of at least 1.382 times the volume of the leach liquor solution is needed. Similarly, the volume of NaOH needed for full precipitation at pH=11.5, which can be assumed to be the same amount needed to reach pH=12, adds up to a total added volume of 31.2 ml. This would result in a 62.4 % volumetric increase in the process of precipitating all the metal together as a mixed hydroxide, requiring a reactor volume of at least 1.624 times larger than the volume of the leach solution.

As earlier mentioned, ICP samples were continuously taken during the experiment in order to be able to monitor the precipitation behavior of the metals. Samples were taken both after letting the solution rest for 10 min at each sample and additionally after letting it rest for 20 h in order to evaluate the precipitation kinetics. The results from the ICP analysis can be seen in Figure 8 and Figure 9.

![ICP results 10 min precipitation time](image)

**Figure 8: ICP results from the samples taken after 10 min precipitation time showing the precipitated fraction of each metal at different solution pH.**

From the figures, it is possible to see how the different metals behave in the mixture as the pH of the solution is increased. The first thing that can be concluded is that a full precipitation of all the metals is possible by increasing the pH to around pH=10 as was also the drawn conclusion from the titration curve in Figure 7. It can also be seen that increasing the pH further to pH=12 does not have an effect on the precipitation yield. This together with the results from the titration curve, showing that only small amounts of NaOH is needed to raise the pH from pH=10 to pH=12, leads us to draw the conclusion on setting the value of pH=12 as the final pH for the route of complete mixed hydroxide precipitation. Additionally, since both Figure 8 and Figure 9 show complete precipitation of all metals at this pH, there would be
no need to leave the solution stirring for longer than 10 min in order to obtain a full metal recovery, making the process more efficient in an upscaled production.

The kinetic of the precipitation can be evaluated by comparing the two graphs with each other, assuming that a timespan of 20 h is long enough for the solution to reach equilibrium. By comparing the graphs, one can see that all of the metals behave similarly both after 10 min and 20 h precipitation time with the exception of Mn. At pH>7, there is a significant difference in the precipitated fraction of Mn between the two figures, indicating that 10 min was not enough to reach equilibrium conditions for the Mn in the solution. Since the fraction of precipitated Mn is lower at pH>7 in Figure 8 than in Figure 9, it is suggested that the precipitation kinetics of the Mn is slow. Apart from Mn, the other metal precipitation curves are similar considering that fewer points were taken in the construction of the 20 h precipitation time graph and such, the precipitation kinetics of Ni, Co, Zn and Al can be regarded as fast.

In addition to the kinetics, the figures show the selectivity of the precipitation. An evaluation of the techniques selectivity is thought to be valid based on the experimental results in this case where the experiment was conducted under strictly controlled conditions and without any unexpected interruptions. It can be seen that the selectivity is low for Ni, Co and Mn which was the expected outcome based on the calculations in Medusa. The same can be said about Zn. Even though the graphs suggest that Zn is precipitated at slightly more acidic conditions than Ni, Co and Mn, the pH gap in between the metals is too small in order for a selective precipitation to be obtainable by this method. It is therefore concluded that if the Ni is to be recovered as a hydroxide through increasing the pH of the solution, the resulting solid product will at best be a mixture of Ni, Co, Mn and Zn. The Al is on the other hand possible to selectively recover through the process. From the figures,
one can see that already at pH=5, all the Al has precipitated from the solution while the rest of the metals remain in the solution. This means that it is possible to obtain a mixed hydroxide product essentially free from Al by first increasing the pH of the solution to pH=5 and remove the precipitate before precipitating the bulk Ni, Co, Mn and Zn metals.

The additional aim of the experimental trial, being to monitor the solution behavior during a pH increase to pH=5.5, being the feed pH of a possible extraction process with Cyanex 272, can also be evaluated from the results. In the case where the leach solution pH is increased to pH=5.5, the results show that Al will precipitate from the solution, making a solid-liquid separation step compulsory if the obtained solution is to be used in further extraction processing. From the graph, it also seems as if all the other metals have precipitated at around 10-20 % at this pH but by looking at the trend of the curve, this can be somewhat disregarded as depending on measuring errors. By following the metal precipitation behavior in Figure 8, one can see that the fraction fluctuates between 0-20 % in the interval of pH=0.3 to pH=6, meaning that a precise and accurate reading cannot be made on the constructed graphs. One must therefore regard the trend of the curve. By doing so, one can see that there at least seem to be some indication of co-precipitation of Ni, Co and Zn at pH=5.5, namely around 10 % as suggested by Figure 8. However, remembering the initial concentration of Ni as compared to Al being around 50 times bigger in weight, a 10 % co-precipitation would mean a solid product consisting of around 5 times more Ni than Al in weight. The unlikeliness of this can be confirmed by the experimental observations and outcome. In addition to the graphs, the color of the precipitate at pH=5.5 being white and black indicates something other than Ni sulphate or hydroxide which are both green, suggesting that the fluctuating fractional precipitation that can be seen in the graphs from pH=0.3 to pH=6 are in fact influenced by experimental errors, possibly in the dilution during ICP sampling. Additionally, the amount of precipitate that was recovered at pH=5.5 was not enough to accommodate for 10 % of the Ni and the rest of the metals as suggested by the graphs at this specific point. It is however likely that some of the Ni, because of the high concentration in the liquid, was co-precipitated together with the Al precipitate because of enclosure of Ni or due to adsorption of Ni on the Al solid. The precipitation of Ni can therefore not be entirely excluded at pH=5.5 but it is however likely that the fractional amount is lower than that of the graphs.

The co-precipitation of Ni can be evaluated by regarding the resulting compositions of the precipitates as stated in Table 7. In the table, the solid composition at pH=4.89 is assumed to be equal to that of a solid taken at pH=5.5 since, according to the titration curve in Figure 7, no precipitation occurred between these two values in the experiment.

By looking at the results from the solid that was taken at pH=4.89, one can see that essentially 21.3 % of the mass is Al and 10.1 % is Ni while the other metals are all below 1 %. All and all, the mass percents of all measured elements add up to a total of 43.1 % which means that more than half of the solid consist of molecules not measured by the ICP, supposedly hydroxides, hydrates or oxides. It can be seen
Table 7: Compositions of the three precipitates taken at different pH during the hydroxide precipitation experiment.

<table>
<thead>
<tr>
<th>pH</th>
<th>Co [wt%]</th>
<th>Mn [wt%]</th>
<th>Ni [wt%]</th>
<th>Zn [wt%]</th>
<th>Al [wt%]</th>
<th>Na [wt%]</th>
<th>S [wt%]</th>
<th>Σ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.89</td>
<td>0.4</td>
<td>0.6</td>
<td>10.1</td>
<td>0.7</td>
<td>21.3</td>
<td>0.6</td>
<td>9.4</td>
<td>43.1</td>
</tr>
<tr>
<td>8.1</td>
<td>3.9</td>
<td>0.6</td>
<td>48.6</td>
<td>1.5</td>
<td>-</td>
<td>0.3</td>
<td>6.2</td>
<td>61.1</td>
</tr>
<tr>
<td>10.81</td>
<td>3.7</td>
<td>1.7</td>
<td>50.5</td>
<td>1.3</td>
<td>-</td>
<td>0.1</td>
<td>3.2</td>
<td>60.5</td>
</tr>
</tbody>
</table>

however that the sulphur content is as high as 9.4 %, indicating that sulphates are present. Where metal sulphates tend to have a relatively high molecular weights due to the presence of hydrates in the structure, which can be seen by regarding the stable metal salts in Table 4, a 9.4 % sulphur content corresponds to a much higher wt% in metal sulphates. This indicates that at pH=4.89, the solid mainly consist of metal sulphates and not hydroxides as predicted by the preliminary Medusa calculations.

As can also be seen from Table 7, as the pH of the solution increases, the solid resulting precipitates contain less sulphur, indicating that metal hydroxides are more dominant in the precipitates obtained at higher pH than the one at pH=4.89. In the bulk precipitate at pH=10.81, the mass of Ni is 50.5 % and the total wt% of measured elements is 60.5 % which is a clear indication of metal hydroxides, where metal sulphates would yield a much lower metal composition, again due to the high molecular weights of the sulphates. It can therefore be concluded that the main bulk of the precipitate that can be obtained by NaOH precipitation at pH=10.81 and above consists of metal hydroxides. It should however be noted that there are still some sulphur left in the solid. This sulphur could either be a product of insufficient washing of the solids, meaning that sulphates got incorporated in the solid from the sulphuric acid as the samples were dried, or it could mean that some of the metals in the solid are present as mixed metal sulphate hydroxides. The composition of the metals however, match the composition of a mixed metal hydroxide and such, it can be concluded that the obtained product by increasing the pH of the solution to pH=10.81 or above is a mixed metal hydroxide of similar composition to the MHP-2 product as can be seen in Table 3. Additionally, as next to 0 % Na could be found in the solids, the incorporation of Na in the solid can be disregarded as a consequence of using NaOH as precipitant.

Additionally, the aim of the total dissolution test was to determine the amount of Ni that is co-precipitated with the Al at pH=5.5. This can be done by assuming that the 21.3 % of Al in the resulting solid at this pH corresponds to all of the Al that is present in the solution, i.e. assuming 100 % of Al precipitation, as could be concluded to be the case from the results in Figure 8 and Figure 9. By this assumption, the percent of each metal that is co-precipitated with the Al can be calculated by using the fractions between the metal and Al present in the original solution compared to the fractions in the solid at pH=4.89 in Table 7. The resulting percentage of co-precipitated metals at pH=4.89 and hence pH=5.5 are stated in
Table 8: Precipitated fraction of metals after increasing the solution pH to pH=5.5.

<table>
<thead>
<tr>
<th>[% precipitated]</th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
<td>1.4</td>
<td>0.8</td>
<td>1.7</td>
<td>100</td>
</tr>
</tbody>
</table>

As can be seen from the table, when converted into wt%, the precipitation of Ni is small due to the large amount of Ni that is present in the solution as compared to the other metals. It can be seen that only around 1-2 % of each metal is co-precipitated together with the Al which means that the loss of Ni is acceptably low in the process of increasing the pH to pH=5.5. As a precaution to errors in the results, a value of 2 % loss in metals while increasing the pH to pH=5.5 is assumed based on the conducted experiments.

The results from the XRD analysis is not included in the report since no clear peaks could be seen in the spectra. This indicates that the precipitates are amorphous which would also be expected since the production of crystalline metal hydroxides needs higher levels of control than practiced in the experiment made in the previous work.

In the present study, no precipitation experiments were conducted on the leach liquor with a chloride matrix, as in the experiment using hydrochloric acid in the leaching. It was instead decided that studying the sulphate matrix liquor would gain more applicable results since the result would then also be able to be used in a possible extraction process, as can be seen in Section 9 of this report. It can however be assumed that the results from an imagined precipitation study on the chloride solution would have the same characteristics as the results obtained by the conducted study on the sulphate solution. This assumption is based on the similarity of the Medusa calculations made on the two systems. Since the pH difference between the bulk precipitation of Al and all the other metals is equally large in both systems according to the calculations, it is safe to say that a controlled pH increase to pH=5.5 can be achieved also for the chloride matrix solution with similar outcome as in the sulphate system, i.e. a 100 % precipitation of Al and a 2 % co-precipitation of Ni, Co and Zn. The mixed hydroxide product that is obtained when increasing the chloride matrix solution pH to pH=10.81 or above can also be assumed to have similar composition as the precipitate in the experiment with the exception of chlorides being incorporated in the solid matrix instead of sulphates, mainly due to co-precipitation mechanisms such as entrapment of chloride ions during the formation of metal precipitates. Additionally, since Y was not included in the precipitation studies, the trace amounts that are present in the leach solution is thought to be precipitated together with the bulk precipitate as suggested by the Medusa calculations. The introduction of oxalates in the chloride solution, which are used to precipitate the REEs in the hydrochloric acid leaching study, might have an effect on the outcome of the precipitation behavior but where the amount of added oxalates are stoichiometric with respect to the REEs in the solution, the remaining oxalate concentration after the precipitation of REEs would be small and would thus suggestively have a small effect on the solution characteristics.
7.3 Proposed process

Based on the results obtained from Medusa together with the experimental results, it can be concluded that a mixed hydroxide product can be obtained through the addition of either NaOH or NH$_4$OH. The choice of base is mainly dependent on the price, availability and the associated hazards in dealing with the two compounds since the process of mixed hydroxide precipitation is in this case not reliant on precise pH control. The proposed process schematic can be seen in Figure 10 where a block diagram has been drawn to represent the process steps.

Figure 10: Process schematic of the proposed mixed hydroxide product route.

The procedure, starting from the leach solution (either sulphate- or chloride matrix) as obtained after the precipitation of REEs, consists of the addition of base until the solution reaches pH=5, where Al and residual Fe precipitates, and then the continuing addition of base until pH=12. At pH=5 the solid precipitate is easily removed by filtration or centrifugation prior to the addition of more base. The amount of obtained precipitate in this stage is relatively small due to the small amount of Al in the electrode materials so no large revenue can be collected. It is however possible to collect several batches of precipitate and sell the precipitate to Al production companies such as the Swedish company Kubal in the city of Sundsvall where the precipitate has a high content of Al if the Fe content can be kept low during the process (Fe is not present in the electrode material but can be introduced due to corrosion of process equipment). This would prove advantageous since an otherwise waste stream would be converted into a product which, would not only have a small contribution to the final revenue of the process but more importantly decrease the environmental impact of the process where the process waste would be lowered. After the subsequent pH increase to pH=12, the mixed metal hydroxide product can be collected via filtration or centrifugation and washed and dried before being sold of as the main product of the final separation of metals from the leach solution. The washing step is implemented in order to remove as much of the soluble sulphates or chlorides as possible which originates from the leaching acid. As can be seen from Figure 2 in Section 6 of this report, the potential revenue from this product (MHP-2) is relatively large and this is mainly because of the large amount of dissolved Ni that, through this route, is converted into a solid sellable product. Potential buyers of such a product could be Ni production companies where the product would be bought for the high Ni content but still, the
content of other metals is high enough for an additional separation to be necessary before the recycled metals can be used in an end user application.

The advantages of this route lies in the simplicity and robustness due to few process steps and few added chemicals. The amount of base that is needed for the process is relatively low since, as previously mentioned, small amounts of base is needed to raise the solution pH at around pH>2 due to the logarithmic nature of the pH scale. This fact justifies the mixed hydroxide production even more where a low chemical consumption is related to both lower amounts of waste streams and lower costs. It should however be noted that a waste stream is inevitable in the process where the resulting aqueous solution after the precipitation of the dissolved metals can not be fully recycled as either a leaching medium or a precipitant solution. In order to lower both the process costs and the process environmental impact, part of the resulting waste solution might be recyclable as a precipitate solution. This is because the pH of the waste solution is high at pH=12 and thus contain a relatively high concentration of OH\(^-\) ions which could be used as to increase the pH of the leach solution. However, a recycled waste solution would have a relatively high concentration of Na ions which, as discussed in Section 7.1, could lead to the precipitation of Na\(_2\)SO\(_4\), leading to a lowered product quality. The amount of accumulated Na ions would therefore have to be considered in a process stream recycling calculation when regarding the aqueous waste solution. The amount of remaining waste solution after a thought recycling partitioning of the waste stream can be readily taken care of by a municipal water treatment plant as the resulting waste solution consist of mainly sulphates and Na ions dissolved in water, where all the problematic and sometimes toxic metals have been removed from the solution.

8 Cathode material synthesis

By producing new cathode material, using the leach liquor as precursor, the need for expensive separation methods such as solvent extraction can be eliminated. This is possible due to the fact that commercial Ni(OH)\(_2\) cathode material often contain both Co and Zn where they improve the electrode performance and stability and hence, producing a product consisting of the three metals seems promising. Considering this, it would be possible to obtain a Ni(OH)\(_2\) cathode material doped with Co and Zn from the leach liquor by co-precipitation with the addition of NH\(_4\)OH as described in a study on the recovery of valuable products from the recycling of NiMH batteries [49]. In the study, a cathode material was obtained by applying a mixed hydroxide precipitation technique directly on the resulting leach liquor. The product morphology was in the precipitation controlled by the addition of NH\(_4\)OH which is a known technique for the production of spherical \(\beta\)-Ni(OH)\(_2\) where, as in this study, the pH can be controlled by the addition of NaOH. In the study however, the composition of the resulting leach liquor differs a bit from the one that is available in the present study and hence, the technique is not thought to be directly copyable without some modifications. One of the main issues is the high Mn
concentration in the present study leach liquor that stems from the leaching of the anode together with the cathode. The high Mn content in the leach liquor would result in a relatively high Mn content in the composition of the Ni(OH)$_2$ and where this is not the standard in NiMH cathode materials, the resulting product in this case would be difficult to sell on the market. Instead, in order to obtain a product that could be sold off as a commercial Ni(OH)$_2$ cathode material, the Mn would have to be removed prior to the hydroxide precipitation. On the basis of the research on oxidative precipitation of Mn from metal ion solutions, this technique was evaluated in the present study. At the time of writing, no studies could be found on the technique used on solutions similar to those from NiMH battery leach liquors and hence, experiments were conducted in order to determine the applicability on highly concentrated Ni solutions.

8.1 Method evaluation

The experimental trials aimed towards selectively oxidizing Mn and thereby separating it from the solution through MnO$_x$ precipitation induced by the low solubilities of the Mn oxides. By doing so, the resulting leach liquor, now free from Mn, could potentially be used as starting material in the synthesis of new NiMH cathodic material, closing the loop of battery to battery recycling. In theory, this is possible if the reduction potentials of the Mn(II) ions present in the solution are lower than the corresponding Ni(II) and Co(II) reduction potentials. Since this is the case in a standardized state at 25°C and an effective concentration of 1 M for each component (single handedly measured), it is hypothesized that this also applies to the NiMH leach liquor. Below, the three competing half cell redox reactions are stated along with their respective standard reduction potential.

\[
NiO_2 + 4H^+ + 2e^- \rightleftharpoons Ni^{2+} + 2H_2O \quad E^o = 1.678 \quad [V]
\]  
\[
Co^{3+} + e^- \rightleftharpoons Co^{2+} \quad E^o = 1.83 \quad [V]
\]  
\[
MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O \quad E^o = 1.224 \quad [V]
\]

From the three reactions, one can conclude that the divalent Mn, through its comparatively low standard reduction potential, should be able to be selectively oxidized and thereby precipitated from the two other ions by an enough but not too highly oxidizing agent. In order to evaluate the possibility of selectively oxidizing only Mn in the leach liquor, the concentrations of the ions present in the solution must however be considered. This because the "real" reduction potential of a metal ion in the solution is dependent on both the solution temperature and the activities and hence the concentrations of the metals through the Nernst equation:
\[ E_{\text{red}} = E_{\text{red}}^o - \frac{RT}{zF} \log \frac{a_{\text{red}}}{a_{\text{ox}}} \]  

In the equation, \( E_{\text{red}}^o \) is the standard reduction potential of the metal ion reduction which is known and often tabulated with respect to the standard hydrogen electrode. \( F \) is the Faraday constant, \( z \) the number of electrons transferred per half cell reaction and \( R \) is the universal ideal gas constant. Apart from these constant values, the electric potential is dependent on and can be allowed to be varied by the temperature of the solution and the oxidizing/reducing compounds’ activities. It is therefore crucial to know both the concentrations of all the compounds in the solution as well as the ideality if a system is sought to be investigated. In order to assess the techniques applicability on the specific system of the NiMH battery leach liquor, the software Medusa was used to calculate the Nernst equation with the given concentrations of the system at different equilibrium pH in order to construct a diagram showing the electric potential as a function of pH. Such a diagram is called a Pourbaix diagram and by examination, one can obtain information about the expected stable complexes in the solution at different electric potentials and solution pH. The constructed Pourbaix diagrams of the leach solution at a temperature of 25°C are shown in Figure 11. The Al and Y which are present but not shown in the figure do not have any known stable oxidized forms and are therefore not affected by the oxidizing environment, as is shown to also be the case for Zn.

From the diagrams, it is clear that all three of the divalent metal ions of Ni, Co and Mn can be readily oxidized to form stable oxide complexes at enough oxidizing conditions. However, by comparing the three respective diagrams, one can see that the Mn is slightly more prone to being oxidized than the Ni and Co and hence, a selective oxidation of Mn should be possible by keeping the solution pH at 1-2 while maintaining the electric potential of the solution between 1.25-1.5 V. In order to obtain the desired electric potential, the addition of the oxidant NaClO was chosen as method, both based on previous research and the suitable standard reduction potential of the oxidant being 1.482 V.

### 8.2 Experimental

The method’s applicability was evaluated experimentally where the aim of the experiments was to study the effectiveness of selectively removing Mn from the solution. The co-precipitation of especially Ni was also examined since the concentration of Ni is much larger compared to the other metals in the NiMH leach liquor than in the solutions used in previous studies and a large co-precipitation of Ni would mean a large loss of sellable product.
8.2.1 Equipment

The oxidative precipitation experiment was conducted in a 200 ml Erlenmeyer flask and the mixture was agitated using a magnetic stirrer. The pH was measured using an Orion Star A211 pH meter from Thermo Scientific. The mixture was centrifuged in a Sigma 3-16 l centrifuge before sampling and during solid removal and the metal ion concentrations were measured using an iCAP 7000 Series ICP spectrometer from Thermo Scientific. The scale that was used for weighing the samples was a Mettler Toledo XPE105. Additional equipment that was used includes pipettes, spatulas, beakers, stirring rods and other conventional chemical lab equipments.

8.2.2 Chemicals

The metal salts that were used in the experiment to simulate the leach solution concentrations were for all the respective metal sulphate, i.e. NiSO₄•xH₂O (20.8-22.4 % Ni) from BDH Chemicals Ltd Poole England and CoSO₄•7H₂O (>99.0 %) and MnSO₄•H₂O (99.0 %) from Merck. The liquids used in the experiment were lab grade sulphuric acid (95-97 %), nitric acid (69 %) and sodium hypochlorite (0.125
8.2.3 Experimental procedure

Before the oxidative precipitation experiment could begin, a synthetic solution was prepared by weighing the metal salts such that the proportions between the metal concentrations matched the ones as in the leach solution of the leaching study. It should be noted that the total concentrations of the metals in the synthetic solution, which can be seen in Figure 10, turned out to be larger than the concentrations in the real leach solution but since the proportions between the metals in the solution were the same, the results of the experiments can be considered applicable also for the concentrations of the leach solution. The resulting synthetic solution was a 200 ml solution with the added amount of metal salts as shown in Table 9 and the resulting concentrations as in Figure 10.

Table 9: Added amount of metal salts in the preparation of the 200 ml synthetic solution used in the oxidative precipitation experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Added [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄•xH₂O</td>
<td>40.93</td>
</tr>
<tr>
<td>CoSO₄•7H₂O</td>
<td>3.17</td>
</tr>
<tr>
<td>MnSO₄•H₂O</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 10: Resulting metal concentrations of the synthetic solution as used in the oxidative precipitation experiment.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>[g/dm³]</td>
<td>46.39</td>
<td>3.39</td>
<td>1.52</td>
</tr>
<tr>
<td>[mol/dm³]</td>
<td>0.79</td>
<td>0.057</td>
<td>0.027</td>
</tr>
</tbody>
</table>

The weighed salts were put in a 250 ml Erlenmeyer flask and dissolved in 200 ml sulphuric acid of pH=3, making the synthetic solution complete. Afterwards, two experiments were conducted using the synthetic solution as precursor. The experimental setup was in both experiments established by adding 50 ml of the synthetic solution into a 100 ml Erlenmeyer flask and placing a magnetic stirrer inside. During the experiments, a plastic inert tube was dipped in the solution to serve as a baffle in order to increase the mixing. The mixture was contentiously stirred during the course of the experiments. In experiment 1 (Exp 1), the starting pH was pH=3 as in the synthetic solution and in experiment 2 (Exp 2), the pH was adjusted to pH=1.5 before adding the oxidant. This was established by adding a few drops of concentrated sulphuric acid while measuring the resulting pH of the solution. The addition of the oxidant, NaClO (0.125 M), was then carefully added dropwise to the solutions with a fixed addition rate. Through the course of the experiments, 0.25 ml NaClO was added every 3 min, allowing the solutions to be properly mixed during the addition. Samples for ICP analysis and pH measurements were continuously taken during the addition in order to monitor the precipitation and the behavior of the solutions. This was repeated until an equal amount of mol NaClO as present mol Mn in the samples had been added.
8.2.4 Results and discussion

Since the aim of the experiments was to evaluate whether Mn could be selectively removed from the leach solution without any major precipitation of Ni and Co, the change in metal concentration was monitored by taking samples for ICP analysis. In order to get a clear view over the solution behavior during the addition, several points were taken continuously during the addition and the results from the analysis can be seen in Figure 12.

![ICP results](image)

Figure 12: ICP results from the oxidative precipitation on Mn from NiMH battery leach liquor.

In Figure 12, the percentage of precipitated metal is plotted with respect to added oxidant in the unit of NaClO/Mn ratio. It can be seen that in Exp 1, where the solution pH was set to 3, the desired separation of Mn from the other two metal ions is better than at pH=1.5, but the separation is not complete in any of the experiments. Apart from the small Mn yield of 34 % the co-precipitation of both Co and Ni is evident. Keeping in mind that the starting Ni content in the NiMH leach solution is around 25 g/l and the Mn content around 0.8 g/l, a 15 % Ni precipitation corresponds to a comparatively substantial loss which unfortunately renders the process unsuitable for the application. The co-precipitation of Co and Ni can be the product of several different phenomena. As before mentioned, all three metal ions can be readily oxidized to form stable metal oxides which have low solubility in sulphate solutions. Therefore, a co-precipitation of Mn-, Co- and Ni oxides can be expected if the electric potential or the pH of the solution is not adjusted within the window of selective Mn oxidation as shown in Figure 11. This could have been the case where the pH of the solution firstly increased to around pH=4 upon the first 30 min of oxidant addition (corresponding to a NaClO/Mn ratio of 0.25) and then started to decrease as the oxidation reactions started, which involve the release of hydrogen ions as can be seen in the redox reactions in Eq. (VI-VIII). The pH increase in the beginning of the addition, owing to the alkalinity of NaClO, might have let both Co and Ni to be oxidized in accordance with the Pourbaix diagram and hence
a precipitation of all three metals would be expected. Additionally, increasing the pH of the solution also causes both Co and Ni to precipitate as their corresponding hydroxides which might also be the cause of the precipitation behavior in this case. Considering this, the pH control proves very important in the selective removal of Mn from NiMH battery leach liquor via oxidative precipitation and experiments where the solution pH is continuously monitored during oxidant addition would be needed to further refine the technique. Another problem that might not be avoidable when using the technique is the co-precipitation of metals by chemisorption of Co and Ni on the precipitated MnO$_x$ which have been proven to be problematic in previous studies [38]. The reason for this phenomenon is the sorptive behavior of the produced MnO$_x$ which is also exploited in waste-water treatment systems where MnO$_x$ is added to remove solvated metals. This sorptive behavior is a product of the negatively charge surface of the MnO$_x$ which causes metallic cations to adsorb onto the solid and thus precipitate even at low pH [52]. The precipitation of Co and Ni that can be seen in Figure 12 is thought to be a product of these three phenomena combined and together they create a Ni loss that is too high in order for the process to be economically justifiable. Based on these findings, the technique was disregarded in the present study as a possible way of recovering the valuable metals from the NiMH leach liquor. Complementary experiments could be conducted in order to try and improve the selectivity towards the precipitation of Mn but the narrow window of selectivity, combined with the problematics regarding pH- and electric potential control, makes the process stability uncertain. This would be especially problematic in battery recycling processing where the input concentrations may differ quite substantially.

Due to the fact that the effective removal of Mn was unsuccessful in the experiments, no further effort was put into producing the cathodic material using the leach solution as precursor. It should be noted however that incorporating the Mn in the cathode material and the affect it has on the cathode’s overall performance is not fully investigated and it could thus in the future prove to be unnecessary to remove the Mn prior to the cathode synthesis. If this proves to be the case within the near future and other battery manufacturers start incorporating Mn in the NiMH cathode material, this route would be a highly justifiable choice where essentially no separation would be required and the revenue would be high. In this work however, the cathode material that was considered as a sellable product was the presently commercial product which at the time of writing is free of Mn.

9 Ni salt production using a supported liquid membrane

As earlier stated, the route of producing a pure Ni salt product would yield the highest revenue and is also arguably environmentally friendly due to the fact that new cathode material can be directly produced without any further processing. It is also clear that the most promising separation technique for accomplishing this is
the extraction by the extractant Cyanex 272 which have an apparent selectivity of the other metals present in the leach solutions compared to Ni. From the Cyanex 272 data sheet, as obtained by the extractant manufacturing company Cytec, it can be seen that from both sulphate- and chloride solutions, Ni can be readily separated from Mn, Zn, Al and Co where Co has the lowest affinity to the extractant apart from Ni [53]. The experimental results stated on the company website is in accordance with other research articles where the pH of the effective separation of Co and Ni is around pH=5.5 in sulphate solutions and a bit lower, pH=4.5, in chloride solutions. This suggests that both the sulphate matrix and the chloride matrix solution could be readily processed using Cyanex 272 as extractant. However, both on the company website and from the literature review, the separation factors of Ni and Co from sulphate solutions tend to be higher than those from chloride solutions, suggesting better separative capabilities of Cyanex 272 in sulphate solutions. Due to this fact, it was chosen to further study the resulting leach liquor from sulphuric acid leaching for this route.

Furthermore, from the advantages of low solvent loss and the technique’s ability to be non-limited by the concentration equilibrium between the aqueous and organic phase, supported liquid membranes were chosen as the separation method. The liquid membrane was, on the base of the literature review, chosen to consist of Cyanex 272 in kerosene and the process that was evaluated was a batch flat sheet membrane process.

9.1 Process modeling

In order to assess the possibility of using the technique on the NiMH battery leach liquor and to optimize the conditions of the process, the process was modeled mathematically in Matlab. The modeling was limited to a three metal ion system, namely Ni, Co and Mn, due to computational constrains. This is however not regarded as a limitation since the metal ions of Zn, Al and Y which are also present in the real solution, are all more easily extracted with Cyanex 272 because of high affinities to the extractant and the concentrations of the ions are lower than those of Ni, Co and Mn in the system. Hence, a system containing Ni, Co and Mn should represent the real system where the separation factors towards Ni should, and has been proven before, to descend in the following matter: $SF_{Co} < SF_{Mn} < SF_{Zn}, SF_{Al}, SF_{Y}$.

In an SLM process, there are several steps in the extraction that influence both the yield and separation of the different metals. In contrary to conventional solvent extraction using mixer-settlers, the mass transfer and consequently the mass transfer resistance in both the aqueous- and organic phase and the interphase of the two play a key role in the final process yield. In Figure 13 the basic principle of the SLM process is described.

The passage of events in the process is that first the metal ions $M^{z+}$ reacts with the extractant on the feed side, releasing $H^+$ and forming the organic complex as
described by the complexation reaction in Eq. (V). The complex then diffuses through the liquid membrane to the stripping side where the reverse reaction takes place, consuming $\text{H}^+$ ions from, and releasing the metal ions into, the stripping solution. As can be seen from Figure 13, the extraction of metals from the feed side of the membrane to the stripping solution is governed by concentration gradients in the process, meaning that as long as there is a metal concentration gradient over the liquid membrane, the metal will be removed from one side of the membrane to the other. Additionally, in an SLM process using the acidic chelating agent Cyanex 272, the pH of the feed- and the stripping solution are essential in determining the direction of the extraction. In general terms, a lower pH at the stripping side and vice versa, a higher pH at the feed side, increases the concentration gradient of hydrogen ion over the membrane and hence the driving force of the process. This is because the metal equilibrium concentrations between the aqueous- and organic phase at the liquid membrane interphases is governed by the acidity of the two aqueous solutions in the system of Cyanex 272 extraction. Since it is possible to obtain a large driving force by only adjusting the pH of the stripping phase, a stripping phase solution with higher metal concentrations than in the feed can be obtained, thus overpassing the equilibrium metal concentration between the two sides of the membrane. It can also be seen in Figure 13 that the bulk concentration of the aqueous phases differs from the concentration at the respective side’s interphase. This is because of the formation of a boundary layer due to the continuous removal and release of metals at

Figure 13: Transport mechanism of the metals across the membrane in the SLM process [20].
the interphase which creates a concentration gradient. This is problematic since the concentration at the interphase, which is in equilibrium with the organic phase, will be lower than the bulk concentration at the feed side and vice versa at the stripping side, lowering the concentration gradient over the membrane. The thickness and impact of these boundary layers can be reduced to some degree by proper mixing but still they would have to be considered in a mathematical model. Consequently, in order to describe the overall process of extraction in an SLM system, at least the following mechanisms must be considered:

- The diffusion of metal ions from the bulk of the feed aqueous phase to the membrane-feed interphase and the counter diffusion of protons.
- The complex formation at the membrane-feed interphase according to the complexation reaction in Eq. (V):
  \[ M^{z+} \ + \ m(\text{HA})_{p(\text{org})} \leftrightharpoons MH_{mp-n}A_{mn(\text{org})} + nH^+_{(\text{aq})} \] (V)
- The diffusion of the metal complex through the liquid membrane to the membrane-stripping interphase together with the counter diffusion of organic carrier.
- The reverse complex reaction at the membrane-stripping interphase.
- Diffusion of metal ions from the membrane-stripping interphase to the stripping aqueous bulk and the counter diffusion of protons.

The five mechanisms of the extraction in a flat sheet membrane batch process have been mathematically explained and modeled by Martinez et al. using Matlab in a study on SLM processing for the separation of REEs [54]. The similarities of the extraction in the modeling study and that of the extraction of metals from the NiMH leach solution in the present study makes it possible to make use of the same model on the present system with only some minor modifications. This is because the same set-up is used and the mechanism of complex formation, namely by acidic chelating agents, are the same in both cases.

The model assumes a single boundary layer system similar to the system in Figure 13 where the resistance in the membrane is expressed as a function of the membrane diffusion coefficient and the distribution factors of the metals at the membrane feed- and stripping interphases. Additional assumptions made in the constructed model include:

- The volumes of the feed- and stripping side are constant during the process.
- The complexation reaction at the membrane interphase is fast and the complex concentrations in the membrane interphases are in equilibrium with the composition of the feed- and stripping solutions.
• The diffusion of metal ions and metal complexes are independent in the aqueous- and organic phase respectively.

The model has before been tested against experimental trials with matching results and it is therefore assumed that the model is accurate in terms of yielding reliable results that can later be verified experimentally. In the present study, the model was used in order to gain a better understanding of the system and to determine process parameters and to see whether the sought separation is possible or not.

9.1.1 Model modifications

The modifications that were made in the model in order for it to be applicable on the system in the present study are only attributed to the metals of extraction as well as the extractant and solvent. Since the mass transfer through the liquid membrane is dependent on both the viscosity and the molecular weight of the organic phase, and the membrane in the modeling study was D2EHPA in heptane, both these values were changed in the model to fit the NiMH battery leach system, where Cyanex 272 in kerosene is proposed. The other property differences of the extractants and solvents can be assumed to have no effect on the outcome since the complexing mechanism of both extractants (D2EHPA and Cyanex 272) are the same and both solvents (heptane and kerosene) are aliphatic compounds which can be assumed to be inert during the extraction.

The next parameters that had to be considered and altered in the model were the ones regarding the equilibrium between the aqueous- and organic phase. Where the mathematical model assumes a fast reaction at the aqueous-organic interphase, the equilibrium concentrations are the main parameters that influence the separation between the different metal ions and hence, finding the correct equilibrium constant for each of the components as well as establishing an accurate equilibrium expression is a crucial step. Given the complexation reaction between the metal ions in solution and Cyanex 272, the equilibrium constant for a metal ion is given by:

\[
K_{eq} = \frac{[MH_{mp-nA_{mn(org)}}] \cdot [H^{+}_{(aq)}]^n}{[M^{2+}_{(aq)}] \cdot [(HA)_{p(org)}]^m}
\]  

(2)

Where the m in the equation is a factor of how many complex carriers that takes part in the reaction per extracted metal ion and n is the number of H\(^+\) ions that are exchanged per complexation reaction. The precise reaction that shows the extraction of metals by Cyanex 272 is hard to determine since the complexation reaction can vary. In a single system, there are several different reactions of which a metal might be extracted by the extractant and hence, experiments are often conducted in order to determine a mean value of the number of extractant molecules that are involved in the complexation reaction for a specific system. For the reaction of Co and Mn, studies have shown that for dimeric extractants, which can be assumed in the case of
acidic Cyanex 272, the complex that is being extracted is $M(\text{HA}_2)_2$ by the following reaction:

$$M^{2+}_{(aq)} + 2H_2\text{A}_{2(\text{org})} \rightleftharpoons M(\text{HA}_2)_{2(\text{org})} + 2H^+_{(aq)} \quad (IX)$$

Where $M$ is again the extracted metal (Co or Mn) and $A$ is the extractant [55]. This means that for each Co or Mn in the loading of organic on the feed side, two extractant molecules (as dimers) are consumed and two $H^+$ ions are released into the aqueous phase. The reverse reaction is present at the stripping side of the membrane. In the case of Ni however, the complexation reaction is different. In a study on the equilibrium characteristics in the extraction of Ni by Cyanex 272 from sulphate media, Biswas et al. found that the extractant dependence varies between 1 and 3 with varied extractant concentration [56]. The results suggested an extractant dependence of 3 at higher concentrations (>0.1 M) while the $H^+$ dependence was consistently 2. On the account of these results, the complexation reaction of Ni in Cyanex 272 was in the present study assumed to follow the reaction as proposed by Sole et al. [55]:

$$Ni^{2+}_{(aq)} + 3H_2\text{A}_{2(\text{org})} \rightleftharpoons Ni(\text{HA}_2)_{2(\text{org})} + 2H^+_{(aq)} \quad (X)$$

Even though the precise complexation reactions are hard to determine, the above reactions can be assumed to be an approximation valid for the present system, where similar conditions have been investigated in the previous studies. On the basis of this, the mathematical simulation model was run with the assumption that 2 and 3 Cyanex 272 molecules (as dimers) were consumed in the extraction of 1 Co or Mn metal ion and 1 Ni metal ion respectively. Since the pH dependence was found to be 2 in both extraction mechanisms, it was also assumed that 2 $H^+$ ions take part in the complexation reaction of each metal.

The equilibrium constants that were used in the model were found from equilibrium studies in the literature that had been made on similar systems to that of the present study, with the exception of the equilibrium constant for Co that was found for a system of hexane as diluent instead of kerosene. However, since both hexane and the distilled kerosene, as used in the studies on the equilibrium constants of Ni and Mn, are aliphatic hydrocarbons, they are thought to have similar impact on the equilibrium conditions and such, the equilibrium constant found for Co is assumed to be valid also for the current system of Cyanex 272 in kerosene. The constants describing the equilibrium at the aqueous-organic interphase can be found in Table 11.

Additionally, the diffusion coefficients of the three metals in aqueous media were found in the literature and are stated in Table 12. It is here assumed that the diffusion of the metals through water is similar to that of the diffusion through sulphuric acid solution.
Table 11: Equilibrium constants used in the simulation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$K_{eq}$ with Cyanex 272 from $SO_4^{2-}$ solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$10^{-7.17}$ [57]</td>
</tr>
<tr>
<td>Ni</td>
<td>$10^{-11.086}$ [56]</td>
</tr>
<tr>
<td>Mn</td>
<td>$10^{-6.17}$ [58]</td>
</tr>
</tbody>
</table>

Table 12: Diffusion coefficients used in the simulation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$D_0$ in water at 25 °C [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$0.59 \times 10^{-9}$ [59]</td>
</tr>
<tr>
<td>Ni</td>
<td>$0.68 \times 10^{-9}$ [60]</td>
</tr>
<tr>
<td>Mn</td>
<td>$0.59 \times 10^{-9}$ [61]</td>
</tr>
</tbody>
</table>

The main advantage of using a software program to simulate a chemical system is the possibility to run the simulation several times with different process conditions in order to evaluate the outcome in a quick and safe way. In order to evaluate the possibility of separating all of the metals from the Ni, the parameters found in the literature were used in the simulation. These together with other physical parameters associated with the membrane support and the process set-up can be seen in Table 13. The compartment volumes and membrane area are matched such that they resemble available lab equipment which makes a complimentary experimental study possible.

Table 13: Parameters used in the simulation of the batch flat sheet SLM process.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ in aqueous phases $\bullet 10^9$</td>
<td>0.68</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>$10^{-11.086}$</td>
<td>$10^{-7.17}$</td>
<td>$10^{-6.17}$</td>
</tr>
<tr>
<td>Feed Volume [cm$^3$]</td>
<td>250</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>Membrane Area [cm$^2$]</td>
<td>-</td>
<td>9.08</td>
<td>-</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>-</td>
<td>0.85</td>
<td>-</td>
</tr>
<tr>
<td>Film thickness $\bullet 10^6$ [m]</td>
<td>2</td>
<td>150</td>
<td>2</td>
</tr>
<tr>
<td>$C_{0, extractant}$ [vol%]</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>5.5</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>T [K]</td>
<td>298</td>
<td>298</td>
<td>298</td>
</tr>
</tbody>
</table>

The parameters in Table 13 were used in the simulations with some variation in for instance aqueous pH, membrane area and initial extractant concentration in order to evaluate the best operating conditions but the ones stated in the table served as a base for the calculations. The initial metal concentrations in the feed were in all simulations the composition of the solution remaining after the precipitation of REEs and the additional precipitation of Al, while increasing the pH to pH=5.5, as determined by the hydroxide precipitation study in this report. From the results of increasing the pH to pH=5.5 by NaOH addition, the resulting metal concentrations
can be calculated by accounting for both the volume increase of 1.382 and the small amount of metal loss by 2 %. The resulting concentration of a metal in the solution that is fed to the SLM process would then be determined by:

\[ C_{m,SLM} = \frac{C_{m,ini} \cdot 0.98}{1.382} \]  

(3)

Where \( C_{m,ini} \) is the concentration of metal \( m \) in the leach solution as obtained by the leaching study and \( C_{m,SLM} \) is the resulting concentration of metal \( m \) in the feed solution. Additionally, since 100 % of the Al is precipitated from the solution, the resulting metal concentrations that are fed to the SLM system are as stated in Table 14.

Table 14: Metal concentration in the resulting leach solution after the pH increase to pH=5.5.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
<th>Y</th>
<th>Al</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/dm³</td>
<td>1.38</td>
<td>0.59</td>
<td>17.29</td>
<td>0.15</td>
<td>-</td>
<td>0.55</td>
</tr>
<tr>
<td>mol/dm³</td>
<td>0.023</td>
<td>0.011</td>
<td>0.30</td>
<td>0.0017</td>
<td>-</td>
<td>0.0085</td>
</tr>
</tbody>
</table>

As can be seen from Table 14, the Ni content in the solution is still high as compared to the other metals and a separation of all the other elements from the solution would therefore yield a relatively large revenue from the process.

9.1.2 Results and discussion

The first simulation that was run in the model was the one with fixed parameters as stated in Table 13. The results can be seen in Figure 14.

In Figure 14, the concentrations of Co, Ni and Mn in both the feed- and stripping solution can be seen as a function of process time. Remembering that both the feed solution and the stripping solution has an equal volume in the simulations, the metal concentrations in the two solutions gives a clear picture of the transfer of metals from one side to the other. Additionally, the pH of the two solutions are plotted as to show the potential variations due to the \( H^+ \) ion release and consumption as can be seen in the complexation reaction in Eq. (V). By looking at the top left graph in Figure 14, one can see that the separation of metals from the feed solution is rather low even though the system was ran for 100 h. All of the three lines seem to be strait but this is not really the case where the Ni concentration in the feed solution is much higher than the concentration of the other metals, yielding a misleading graph due to the scale of the axis. Instead, the top right graph, showing the concentration in the stripping solution, gives a better understanding of the separation in this case. Where no metals are present in the stripping solution at the start of the processes, one can more easily see the concentration increase of each metal in the stripping solution which in turn corresponds to the number of metal ions that has been transferred.
from the feed side across the liquid membrane. By examining the graph, it is clear that there is a small extraction of Co and Mn from the feed side to the stripping solution while close to zero Ni is being extracted. Consequently, there is evidently a prioritized extraction of Co and Mn over Ni in the process where, from the looks of the concentration change in the stripping, Mn is most prone to be extracted, followed by Co, leaving Ni in the feed. However, the amount of Co and Mn that are extracted using the above process parameters are still low after 100 h of process time, meaning that the main objective of the process, being to extract all the other metals from the Ni, will not be fulfilled during an acceptable process running time. The extraction kinetics would therefore have to be increased in order to make the SLM process justifiable in this application.

Another thing that can be seen from Figure 14 is the pH decrease on the feed side of the membrane. Already after 10 h of process running time, the solution pH of the feed has dropped from pH=5.5 to pH=3 due to the constant release of H⁺ ions into the solution which originates from the complexation reaction in Eq. (V). The pH decrease in the feed solution results in a lower loading capacity of the organic phase since the equilibrium metal concentrations at the feed-membrane interphase are dependent on the solution pH. As can be seen in the equilibrium equation as shown in Eq. (2), a decrease in pH and hence an increase in H⁺ ions, leads to a decrease in the ratio between the metal complex concentration in the organic phase and the metal concentration in the aqueous phase which results in a lower loading capacity at the interphase since the aqueous- and organic phase are assumed to be at equilibrium in the model. Hence, the pH must be controlled on the feed side of the membrane in order to retain an acceptable separation.
9.1.2.1 Constant feed pH

In order to evaluate the separation behavior when the feed pH is being controlled, a simulation was ran on the system where the feed pH was fixed to pH=5.5. The resulting feed- and stripping metal concentrations over time can be seen in Figure 15.

As can be seen from Figure 15, the separation of Mn and Co from the Ni is largely improved when the solution pH of the feed is fixed to pH=5.5. In fact, since the selectivity of Cyanex 272 towards Ni is so low, next to zero Ni is being extracted to the stripping side during the first 60 hours of running the process as can be seen in the top right graph, showing the metal concentrations in the stripping solution. It can be seen that in the first 10 hours of the process, both Co and Mn are being extracted together, meaning that a separation of the two using Cyanex 272 would be hard to achieve, which has been reported before. After 10 hours, all of the Mn has been extracted to the stripping solution and the process needs a total running time of 60 hours in order to additionally extract all of the Co. The co-extraction of Ni is low during the extraction of the other elements because of the low concentration of free extractant molecules in the organic phase where the main fraction of the extractant is occupied by the elements with higher affinity to the organic. Instead, the extraction of Ni is noticeable firstly after the extraction of Mn and Co is complete in Figure 15. As mentioned before, since Co is both the metal in the feed solution that has the lowest affinity to the extractant and has the highest concentration in the feed second to the Ni, a 100 % extraction of Co in the system also means a 100 % extraction of all the metals except Ni. It should be noted here that the other compounds that are present in the real solution, i.e. Zn and Y, would also have a set extraction time which could increase the total process time of extracting all the...
Co, but since the concentrations of the two missing compounds are relatively low, it is here assumed that the results of the simulation represent the process with the real solution. Since the fraction of Ni that is being co-extracted with the other metals is negligibly small, a 100 % recover of Ni in the feed solution can be assumed if the process is stopped at the time where the Co has been fully extracted to the stripping solution. Conclusively, the results suggest that a highly pure Ni solution, free from all the Mn, Co, Zn and Y, can be obtained by running the process as specified in Table 13 as long as the pH of the feed solution is controlled at pH=5.5. The controlling of the pH at this value can be employed by either continually measuring the pH and adjusting it with the addition of weak base or maybe more conveniently by the addition of a pH buffer to the feed solution. The addition of an acetate- or a citrate buffer are two options when it comes to controlling the pH at pH=5.5, where acetate buffers have been used in similar solvent extraction systems in the literature. It is therefore proposed that an acetate buffer solution is added to the feed in proper proportions to account for the H^+ ion transfer from the stripping side to the feed side of the membrane in the final SLM process.

The pH of the stripping solution must also be considered since, as explained above, it is the pH difference between the two phases that is the main driving force in the SLM system using an acidic chelating agent. In Figure 15, one can see that the stripping solution pH is slightly increased during the extraction but still the pH seems to be low enough in order for a full separation to take place, meaning that a stripping solution of pH=1 is an alternative for the process.

### 9.1.2.2 Different stripping solution pH

In order to evaluate the influence of different stripping pH, simulations were ran while changing the starting pH of the stripping side and keeping all other parameters constant as shown in Table 13. The simulation was ran at three different starting solution pH and the resulting stripping metal concentrations along with the pH change of the system can be seen in Figure 16 through 18.

As can be seen in Figure 16 and Figure 17, where the stripping pH is lower than pH=1, the pH of the stripping solution is almost constant during the full separation and hence, the separation is still obtained. However, the quantity of the separation and the time needed for full separation is not affected by decreasing the stripping pH, meaning that any stripping pH equal to or below pH=1 yields the same results on the present system. As a lower pH means a higher concentration and consumption of acid and also means that more base would be needed in order to precipitate the Co, Mn, Zn and Y from the stripping solution, the higher the pH of the stripping solution, the better. Therefore, a stripping pH of pH<1 is not necessary for the present system. While regarding Figure 18, where the starting pH of the stripping solution is pH=1.2, one can see that the pH increases quite substantially during the separation. In this case, the pH of the stripping solution is increased to an extent where the separation comes to a stop, meaning that the system has reached
Figure 16: Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at a starting stripping pH of pH=-1.

Figure 17: Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time at a starting stripping pH of pH=0.5.

equilibrium between the two sides, and hence no further separation is possible. To run the process at this starting pH in the stripping phase could therefore possibly result in a lowered overall product quality where a complete separation is hindered by the increased feed solution pH during the extraction. This means that in order to obtain a pure high quality product, a stripping pH of pH<1.2 is needed. It can therefore be concluded that a stripping pH of pH=1 is suitable for the specific system at hand. It should be noted however, that in a case where the volumes are different
between the two aqueous phases, a different stripping pH might be needed since the resulting concentrations in the stripping phase will be different as the ratio between the volume of the feed and the volume of the stripping changes. A stripping pH of pH=1 can be concluded to be a suitable pH when the two volumes of the stripping and the feed are the same.

By using the results from the simulation, it can be concluded that a full separation of Ni and all the other elements in the solution can be obtained by using a batch SLM process with the specified process parameters in Table 13. If a pH buffer is added to the feed solution as to control the pH to a fixed value of 5.5, a close to 100 % separation of all elements apart from Ni can be achieved in a process time of 60 h. The co-extraction of Ni during this process time is small enough to be negligible and hence, the loss of Ni in the feed solution can be assumed to be 0 %. The proposed process can be ran on a larger scale by using several large flat sheet membrane processes in parallel but since the process time is 60 h, this would take up a rather large amount of space and equipment.

The main reason for the long process running time in the process is the small effective mass transfer area of the flat sheet membrane, where a small membrane area that is in contact with the feed results in a slow transfer of ions from one side to the other. Instead, an SLM process using a hollow fiber membrane could be used where the membrane area per unit feed volume is much higher as compared to the flat sheet membranes. As a comparison to the present system, which has a membrane area per unit feed volume of 3.63 m²/m³, hollow fiber membranes can be constructed to have a value of 10 000 m²/m³.
9.1.2.3 Different membrane area

In order to evaluate the influence of effective mass transfer area on the present system, the simulation was ran with different membrane areas while keeping the other parameters as shown in Table 13. It should be noted that this simulation can not be applied for a real system where the increased membrane area would yield physical constrains when trying to construct a flat sheet membrane with the specified dimensions. The results from the simulations on differing membrane area are therefore only to be used as an evaluative tool when comparing the affect of effective mass transfer area. The obtained results from the simulation can be seen in Figure 19.

![Figure 19](image)

Figure 19: Metal concentrations and solution pH in the two aqueous solutions in the SLM system as a function of time using a membrane with an area 10 times larger than the area of the equipment specification.

As can be seen in Figure 19, which shows the results of the simulation where the membrane area that is enlarged 10 times as compared to the value in Table 13, the process time is considerably decreased when a larger area is used. Since the same membrane thickness is used in the simulations, the membrane area increase also results in a membrane volume increase of the same magnitude, which in turn means that more extractant is available for extracting the ions from the feed solution. This is the reason for the process time being proportionally linear with regards to the membrane area in the results, since we are simply multiplying the number of membranes with 10 while still considering the same feed- and stripping volume. The results can however be used to evaluate the process time’s dependence on effective mass transfer area and clearly there is a decrease in needed time for a full separation when larger membrane areas are employed. This suggests that a process with a higher membrane area per unit feed volume, such as a hollow fiber membrane,
should be implemented in an upscaled version of the process where a process time of 60 h would most probably result in a too large investment in space and equipment.

### 9.2 Proposed process

Based on the results from the simulations on the SLM process using a flat sheet membrane together with the results from the hydroxide precipitation study, it can be concluded that a pure Ni product as well as a mixed metal hydroxide can be obtained by an SLM extraction process. Again, the choice of base needed for the feed solution pH increase to pH=5.5 is mainly dependent on the price and the availability of the bases since a controlled pH increase to pH=5.5 can be obtained by both NaOH and NH\(_4\)OH as concluded in the hydroxide precipitation study. The proposed process of producing a pure Ni salt and a mixed metal hydroxide precipitate can be seen in Figure 20. The process is here represented as a block diagram, showing the different process steps.

![Figure 20: Process schematic of the proposed Ni salt production route.](image)

In the final process, the leach solution going in to the separation is preferably the sulphuric acid leach liquor since the separation factor of the extraction is larger in solutions with sulphate matrices as compared to solutions with chloride matrices. It is therefore suggested that the sulphuric acid leaching route is employed where an SLM process using Cyanex 272 is implemented as a Ni recovery process. In the
Separation unit, the pH of the sulphate leach solution is firstly increased from pH=0.3 to pH=5.5 by the addition of either NaOH or NH_{4}OH. During the pH increase, all the Al will precipitate as mixed sulphates and hydroxides and the precipitation will cause around 2% of the other elements to co-precipitate which can be regarded as a metal loss of the system. The solid will then have to be recovered prior to the SLM process where solid particles could cause problems with clogging of the membrane support and essentially decrease the separative ability. The separation is preferably done by either a filtration- or a centrifugation process. After the removal of solids, an acetate- or a citrate pH buffer solution could preferably be added as to control the solution pH to pH=5.5. Alternatively, the feed solution pH in the SLM process could be controlled by NH_{4}OH addition by continuously measuring the solution pH and adding small amounts of base when the pH starts to drop. The choice of base for this application being NH_{4}OH is because of the slow OH^{-} ion release upon addition on the base, resulting in a more stable pH control. Next, the solution is fed to the SLM process where preferably a hollow fiber membrane process is used because of the advantages of large effective mass transfer area as compared to a flat sheet membrane process. Since the separation factors of Ni against all the other elements are really large and the loss of Ni is negligible, as concluded in the process simulations, a feed solution of pure Ni in solution together with a stripping solution of pure mixed Co, Mn, Zn and Y in solution is obtained at this process step. Both solutions are then subsequently treated with NaOH or NH_{4}OH addition in order to increase the pH of the solutions to pH=12 and thus obtaining a solid metal hydroxide product. It should also be noted here that since pure Ni, apart from sulphates and Na or ammonia, is present in the feed solution, it would be possible to alternatively produce other Ni salts from the same solution, such as NiCO_{3} which yields the largest revenue among the considered Ni salts in Figure 2 in Section 6 in this report. However, since the precipitation of NiCO_{3} was not tested in the present study, this procedure needs some future experimental evaluation in order to be proven feasible, and instead, the production of a pure Ni(OH)_{2}, yielding the second largest revenue in Figure 2, is considered in this route. Both the produced mixed metal hydroxide and the Ni(OH)_{2} can be readily separated from the mixtures by either filtration or centrifugation.

The main advantage with this route is the production of a highly pure Ni product which undoubtedly leads to the highest revenue of the proposed routes in the present study. The usage of the more expensive extractant Cyanex 272 in kerosene is in this case justified where the SLM process require low amounts of extractant as compared to conventional solvent extraction and the solvent loss can therefore be assumed to be low. Hence, it can be concluded that the process of producing a pure Ni(OH)_{2} and a mixed metal hydroxide, rich on Co, with the help of an SLM process is a promising possibility in the recovery of valuable metals from the NiMH battery leach solution.
10 Process evaluation

In order to determine the input streams to the battery recycling system at hand, the number of available batteries for recycling in Sweden will be considered.

10.1 HEV NiMH batteries in Sweden

The number of NiMH batteries used for vehicle applications in Sweden is hard to estimate where no such statistics is currently available. In addition, the fraction of these batteries that need to be recycled each year is even harder to determine where the current situation does not reflect the near future. With an average car lifetime of 16 years and the first modern HEVs being put on the Swedish market in the year 2000, the HEV NiMH batteries that need recycling today mainly come from car accidents and sometimes battery failures (the batteries are constructed to last a full car lifetime). Through personal correspondence, it was shown that Toyota Sweden collected and recycled a total of 79 NiMH batteries during 2016, which is a low number considering the total Swedish Toyota HEV fleet of over 10 000. Considering that the NiMH HEVs were introduced to the Swedish market in 2000 and that the popularity of HEVs has increased since then, an increased recycling demand of these batteries is expected within the near future. In addition to Toyota, other car manufacturers such as Honda, BMW, Volkswagen, Mercedes etc. also contribute to the growing HEV car fleet in Sweden, which at the end of 2016 was a total of 55 126 HEVs and 18 832 Plug-in HEVs (PHEV) [62]. While the new plug-in hybrids all use the Li-ion based technology, Toyota included, the NiMH battery has up until recently been the choice of technology for other car manufacturers as well in their respective HEV models. However, during the last decade, together with the breakthrough of Li-ion batteries, most car developers have started steering towards using Li-ion batteries for HEV applications instead of the NiMHs and Toyota is currently the only main manufacturer that instead has decided to refine the NiMH technology. This will ultimately lead to a decrease in recycling demand of NiMH batteries from HEVs. In summary, based on the situation today, the recycling demand of HEV NiMH batteries in Sweden is expected to grow within the near future as a consequence of car lifetime and then start to decrease due to the replacing Li-ion technology. As a collected view from both the Swedish scrap yards and the Swedish car dealerships, it was found that the durability of the NiMH batteries in HEV applications is in general high enough to survive a full car lifetime.

To quantify the future recycling demand in Sweden, an estimation was made by using the number of yearly registered HEVs in Sweden since 2002 together with a world battery market study made by Avicenne Energy [62] [63]. It is here assumed that all newly registered cars have a lifetime of 16 years, the batteries are recycled together with the car and that car accidents and battery failures have negligible effect on the results. The fraction of NiMH batteries in HEVs was obtained from
the result of Avicennes market study. The further future was not predicted in this study where the technology advancement within this area is rapid and in order to obtain reliable results, a larger study would be needed. The resulting near future recycling demand can be seen in Figure 21.

![Figure 21: Estimated recycling demand of HEV NiMH batteries in Sweden.](image)

It can be seen from the graph that the recycling demand of HEV NiMH batteries will in fact increase within the near future and a proper recycling system is therefore needed. The trend can however be expected to turn where the PHEVs, using Li-ion technology, are becoming more and more popular on the Swedish market. Additionally, if Toyota decides to follow their competitors by abandoning the NiMH technology, the recycling demand would drop drastically. Until then, the recycling demand of HEV NiMH batteries in Sweden remains according to the graph, where a yearly average of roughly 2600 batteries need recycling within the 14 year timespan.

### 10.2 Batch- or continuous operation

When considering a scaled up version of a HEV NiMH battery recycling facility in Sweden, the first thing to consider is the deciding on a batch or continuous process. As a guidance in the decisioning, a list of different advantages and disadvantages regarding the two process types are stated in Table 15.

Based on the advantages and disadvantages of the two process types, it is concluded that a batch process would suit the specific application more than that of a continuous one. The main advantage of a batch process in this particular case is a result of the Swedish market, which has previously been proven to be rather small and uncertain. In a small and uncertain market, the batch process is favored where the process is more flexible and requires relatively low investment costs. If a batch process was constructed, it would also be possible to process other batteries, such as Li-ion, using the same equipment without major modifications. Here, because of the uncertain future recycling market, a batch process could therefore be regarded as a precautionary decision where it means being adjustable to the rapidly changing market. Additionally, since stops are regular in a batch process, cleaning of the reactors can be easily carried out. Where the process involves strong acids this is a
Table 15: *Advantages and disadvantages of batch contra continuous processes* [64].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Batch process</th>
<th>Continuous process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Profitable in small scale (lower equipment costs)</td>
<td>High efficiency</td>
</tr>
<tr>
<td></td>
<td>Same equipment can be used for different process steps</td>
<td>Possibility for heat integration</td>
</tr>
<tr>
<td></td>
<td>Flexible regarding variations in the feed stream</td>
<td>Low maintenance costs</td>
</tr>
<tr>
<td></td>
<td>Possibility to produce different products with the same set-up</td>
<td>Safe operation</td>
</tr>
<tr>
<td></td>
<td>Favored in processes that have slow reaction rates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Possibility to clean equipment after each batch</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages</th>
<th>Requires strict schedules</th>
<th>Needs continuous operation to be profitable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Higher maintenance costs</td>
<td>Fouling issues in acidic processes (requires stop of production)</td>
</tr>
<tr>
<td></td>
<td>Safety issues (requires personnel responsibility)</td>
<td>Low flexibility</td>
</tr>
</tbody>
</table>

major advantage since the corrosion of equipment can be readily suppressed through continuous cleaning. The main advantage of a continuous process, being the possibility of reaching high process efficiencies due to the possibility of heat integration, is not really applicable in the proposed hydrometallurgical process where the main part of the process is carried out in room temperature. Based on the presented argumentation, a batch process is chosen for the scale up system, meaning that the proposed process steps are preferably conducted in one large, or as few as possible, vessel reactors where different process steps can be ran in the same reactor in batch based systems. In the proposed SLM process, which would most preferably be of a hollow fiber type, the process fluid could either be continuously recirculated in the hollow fiber structure until the sought separation is reached, or the length of the hollow fiber could be adjusted such that the residence time in the SLM step fits the separation criterion. The choice between the two options is influenced by factors such as cost of equipment and available space since a longer hollow fiber might take up the space needed for other equipments in the finalized process construction.

10.3 Mass balance calculations

In order to further evaluate the feasibility of implementing either the mixed hydroxide route or the route of producing the Ni(OH)$_2$ salt and a residual mixed hydroxide rich on Co, the systems’ streams must be determined in order to calculate the amount of product that can be obtained. In order to do so, system boundaries were drawn
over the different process steps and mass balance calculations were made using the data obtained from the experimental- and modeling results of the two routes. Additionally, the streams going in to and out of the leaching and REE removal process, which is the preceding process of the separation considered in the present study, were determined as to get a picture of the recycling process as a whole. The streams in this process were determined by using the results as obtained by Korkmaz et al. in the leaching studies made on the system and it was determined to use the base of one recycled battery as a base for the calculations.

10.3.1 Leaching and REE removal process

The leaching and REE removal process, using either sulphuric- or hydrochloric acid, essentially consist of two process steps subsequent to the process of dismantling and crushing the battery material. These two steps include first the process of leaching the anode and cathode material which is made at elevated temperatures as to ensure a higher leaching yield, and later a precipitation process where the REEs are precipitated as a solid and removed from the solution. The overall schematic of the preceding leaching process can be seen in Figure 22.

![Process schematic of the leaching and REE removal process, as proposed by the leaching study with an associated system boundary used in the calculations.](image)

In Figure 22, the stream going in to the system is the HEV NiMH battery as it comes when taken of its compartment in the car and the outgoing stream is the resulting leach solution which has been under investigation in the present study. From the leaching study made by Korkmaz et al. it was concluded that 1 HEV NiMH battery consist of a total of 14.38 kg anodic- and cathodic material in total and this value is therefore set as the total mass input stream of the system. Additionally, the results from the leaching study tell us the composition of the anode and cathode, which can also be seen in Table 1 of this report, and by knowing both the mass percentage and the total mass of material in one battery, the total weight of the each element going in to the system can be calculated. The resulting composition of electrode elements in the stream going in to the system (S1 in Figure 22) can be seen in Table 16.

The amount of each element in Table 16 is essentially the maximum recyclable amount in each battery pack. However, as have been seen from the experimental
<table>
<thead>
<tr>
<th>Compound</th>
<th>Tot</th>
<th>Ce</th>
<th>Co</th>
<th>La</th>
<th>Mn</th>
<th>Nd</th>
<th>Ni</th>
<th>Pr</th>
<th>Y</th>
<th>Al</th>
<th>Fe</th>
<th>K</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass in [kg]</td>
<td>14.38</td>
<td>0.44</td>
<td>0.74</td>
<td>1.42</td>
<td>0.31</td>
<td>9.39</td>
<td>0.17</td>
<td>0.08</td>
<td>0.15</td>
<td>0.01</td>
<td>0.07</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>

Table 16: **Total amount of elements that enter the recycling process, using one battery pack as base.**

Results both in the present study and the preliminary leaching study, there are material losses in each process step which have to be accounted for. The first step, where the battery is being disassembled and the electrode material crushed, has not yet been fully investigated and in order to evaluate the entire process yield, an investigation on the material losses associated with this pre-treatment step should be performed on the HEV NiMH batteries. This because the losses in these kinds of systems can be high if not properly designed, where for instance dust formation in a crusher might lead to leakage of material and adhesion of particles on the walls. In the present study, no research on the disassembling and crushing of the electrode material was available and hence, a study on material losses in the process of crushing and sieving Zn batteries was used as a reference in determining the yield of the pre-treatment [65]. In the study, a double rotary crusher was used in order to obtain a fine powdered electrode material that could, in the present process on NiMH material recovery, be regarded as a clean stream of crushed electrode material that can be readily leached. The loss of material in the crusher ranged between 5-10 % in mass for the dry battery material and hence, a mean value of 8 % loss in the first step of the process, i.e. the dismantling and crushing, was chosen in the present study.

Additionally, the material losses found in the leaching- and REE precipitation step were used in the calculation of the total mass balance of the system. The added-and resulting volume in each step were also considered since the total volume of the process reagent ultimately determines the size of the equipments needed for an upscaled process. The resulting volume increase and stream compositions of the leaching and REE removal process can be seen in Figure 23.

Figure 23 gives a rather comprehensive overview of the leaching and REE removal process steps and their respective stream compositions. One can see that some of the metals are lost during processing, the first 8 % loss is due to dust formation in the crushing of the anode and cathode material and the second loss of metals of 1 % and 10 % loss of Co are based on the findings from the leaching and REE removal study. The increased solution volume can also be seen in the bottom of the figure as the process progresses. The total volume of liquid in each process step is here also based on the experimental results from the leaching and REE removal study, where the amount of added liquid in each step contributes to an increased process volume. It should however be noted that the volumes here are approximate since in the real case, the volumetric increase is not only a function of added volume where reactions upon mixing and mixing volumes would need to be considered in order to precisely determine the process volume. Additionally, the removal of solids leads to a decrease in solution volume, which is not considered here but still, the approximated volumes gives an overview of the process volume which can be used in order to determine the
size of the equipment in a scaled up process. In addition to the calculation of material loss and volumetric increase, the amount of added chemicals needed in the process of recycling one battery was determined. In the leaching and REE removal study, a 1/20 solid to liquid ratio was used in the leaching process using a concentration of acid of 2 M. After considering the 8 % solid loss in the crushing, which leaves 13.24 kg solid for leaching per battery pack, the amount of pure sulphuric- or hydrochloric acid can be calculated, using the molar mass of the acids being 98.079 g/mol and 36.461 g/mol for sulphuric acid and hydrochloric acid respectively:

\[
V_{H_2SO_4} = V_{HCl} = 13.24 \cdot 20 = 265 \text{ [dm}^3]\]

\[
n_{H_2SO_4} = n_{HCl} = 265 \cdot 2 = 530 \text{ [mol]}\]

\[
m_{H_2SO_4} = \frac{530 \cdot 98.079}{1000} = 52.0 \text{ [kg]}\]

\[
m_{HCl} = \frac{530 \cdot 36.461}{1000} = 19.3 \text{ [kg]}\]

In addition to the acid, the amount of pure NaOH or oxalic acid, which was used for the precipitation of REEs in the sulphuric- or hydrochloric acid route respectively, was directly taken from the results in the leaching study:

\[
m_{NaOH} = 4.9 \text{ [kg]}\]

\[
m_{oxalic acid} = 7.1 \text{ [kg]}\]

The process in Figure 23 has roughly the same output whether it is sulphuric- or hydrochloric acid that is used as leaching medium and the leach solution leaving the process (stream S5 in the figure) therefore has the same composition of metals independent of which acid has been used. Since stream S5 is the stream going in to
the separation system that has been considered in this study, mass balances on the two chosen routes can be made, now knowing the input of metals and solution per recycled battery pack.

10.3.2 Mixed hydroxide production process

In the production of a mixed hydroxide, two different fractions of solids are taken out as the pH of the solution is increased, as can be seen in Figure 10 in the method evaluation section of this report. Consequently, there are two main steps in the separation process which are two precipitation steps and in order to determine the amount of retrievable product through this route, mass balances over the two steps need to be conducted in order to account for any material losses. The material losses that were used in the mass balance calculations on the mixed hydroxide route were the losses found in the experimental study which was conducted in the present study. Additionally, the volumetric increase during the addition of base was determined for each step of the process, again in order to determine the required size of equipment. The resulting stream compositions and solution volume increase of the mixed hydroxide route process are summarized and can be seen in Figure 24.

Figure 24: Process stream compositions and volumetric increase of the reagent in the mixed hydroxide route process.

As can be seen in the figure, 8.38 kg of Ni is still left in solution after the precipitation of Al has been made and can thereby be recovered as a hydroxide product through the addition of base until the pH reaches pH=12, as suggested by the hydroxide precipitation experiments in this study. The other elements that are left in solution are precipitated together with Ni, forming the mixed hydroxide precipitate (MHP-2). The composition of the precipitate can be seen in Table 7 in the results of the precipitation study, where the corresponding product is the one precipitated at pH=10.81. Assuming 100% precipitation of metals, the total amount of obtained
mixed hydroxide product from the recycling of one battery pack can be calculated by using the mass of Ni still left in the solution and the composition of Ni in the product, being 50.5 % by weight:

$$m_{MHP-2} = \frac{8.38}{0.505} = 16.5 \ [kg]$$

This product could then be sold off as one of the main products of the recycling system. Similarly, the amount of Al and co-precipitated metals as mixed hydroxides and sulphates can be calculated by knowing the total amount of precipitated Al, being 0.13 kg in Figure 24, and the composition of Al in the precipitate, being 21.3 % by weight in Table 7:

$$m_{Al\text{precipitate}} = \frac{0.13}{0.213} = 0.61 \ [kg]$$

The fraction of Al precipitate taken at pH=5 can be stored and stacked until a reasonable amount has been gathered and can then be sold off to an Al production company.

The total amount of NaOH needed for the two precipitation steps can be calculated by using the resulting amount of NaOH used in the hydroxide precipitation experiment as can be seen in Table 6. By knowing the volume and concentration of each addition, together with the molar mass of NaOH being 39.997 g/mol, the amount of pure unhydrated NaOH needed in both precipitation steps can be determined. Remembering that the experiment was conducted on a leach solution volume of 50 ml, this must also be accounted for in order to determine the amount of NaOH needed per one recycled battery pack:

$$n_{(NaOH, pH=0.3-5.5)} = (14.2 \cdot 4 + 1.8 \cdot 2 + 0.3 \cdot 1 + 1.8 \cdot 1 + 1 \cdot 0.5) \cdot \frac{356}{50} = 449 \ [mol]$$

$$n_{(NaOH, pH=5.5-12)} = (2.1 \cdot 0.5 + 7.5 \cdot 4 + 2.5 \cdot 4) \cdot \frac{356}{50} = 293 \ [mol]$$

$$m_{(NaOH, pH=0.3-5.5)} = \frac{449 \cdot 39.997}{1000} = 18.0 \ [kg]$$

$$m_{(NaOH, pH=5.5-12)} = \frac{293 \cdot 39.997}{1000} = 11.8 \ [kg]$$
10.3.3 Ni salt production process

In the process of producing a pure Ni salt, the separation of Ni from the other elements is achieved by the usage of an SLM process. Similarly as in the case of the mixed hydroxide route, mass balance calculations were done on this process as to account for the process losses as well as determining the amount of product that is obtainable by the process. The resulting metal concentrations in the different process streams in the Ni salt production route can be seen in Figure 25. The volumetric increase is not mentioned in the figure since the volumetric amount of pH buffer that is needed as well as the optimum stripping solution volume was not studied in the present study.

In the process, the pH is first increased to pH=5.5, which results in a 2 % loss of metals as they are being co-precipitated with the Al that is fully precipitated from the solution at this step. In the subsequent step, a pH buffer is added to the solution in order to keep the pH constant during the extraction in the SLM process. As could be concluded by the simulations on the SLM process, the separation of Ni from all the other elements is high when using Cyanex 272 as extractant where, according to the results of the simulations, next to zero co-extraction of Ni was observed and the loss of Ni into the stripping solution could therefore be assumed to be insignificant. However, when considering a real upscaled SLM process, it would be hard to monitor and stop the process precisely at the time where all elements other than Ni has been extracted which is the only way to obtain a Ni extraction of close to 0 %. It would more likely be the case that the process would sometimes be stopped at a time where either some of the Ni has started being extracted to the stripping solution or at a time where not all of the other elements have been fully

Figure 25: Process stream compositions of the reagent in the Ni salt production route process.

In the process, the pH is first increased to pH=5.5, which results in a 2 % loss of metals as they are being co-precipitated with the Al that is fully precipitated from the solution at this step. In the subsequent step, a pH buffer is added to the solution in order to keep the pH constant during the extraction in the SLM process. As could be concluded by the simulations on the SLM process, the separation of Ni from all the other elements is high when using Cyanex 272 as extractant where, according to the results of the simulations, next to zero co-extraction of Ni was observed and the loss of Ni into the stripping solution could therefore be assumed to be insignificant. However, when considering a real upscaled SLM process, it would be hard to monitor and stop the process precisely at the time where all elements other than Ni has been extracted which is the only way to obtain a Ni extraction of close to 0 %. It would more likely be the case that the process would sometimes be stopped at a time where either some of the Ni has started being extracted to the stripping solution or at a time where not all of the other elements have been fully
extracted. The former would in this case be preferred as the latter would result in an increased impurity level in the main product of the process and it would therefore be beneficial to run the process for a slightly longer time than needed in order to ensure complete extraction of Co and the other elements. Considering this, one must expect some extraction of Ni into the stripping solution and here, the co-extraction is therefore assumed to be 1%. This results in a metal concentration of pure Ni in the feed solution and a mixed metal concentration of all elements in the stripping solution as can be seen in Figure 25.

The amount of Ni(OH)$_2$ that is obtainable from the recycling of one battery pack can be calculated by knowing the amount of Ni left in the feed solution after the SLM process (stream S9 in Figure 25) and knowing the composition of Ni in a typical pure Ni(OH)$_2$ product as can be seen in Table 3 in this report. A total recovery of 8.29 kg Ni from one battery pack and a Ni composition of 61 % in a commercial Ni(OH)$_2$ yields:

$$m_{Ni(OH)2} = \frac{8.29}{0.61} = 13.5 \text{ [kg]}$$

The amount of mixed hydroxide that is obtained from precipitating the metals in the stripping solution can also be calculated by knowing the amount left in the the stripping solution (stream S12 in Figure 25). Here however, the composition of the end product is unknown since the only information available on the matter are the results obtained from the hydroxide precipitation experiments in this study. If Table 7 is to be used again, the Ni would have to be excluded from the composition since in the SLM process, Ni is not present to the same extent as was the case in the mixed hydroxide production and hence the total metal composition is used instead. From Table 7, one can see that in the precipitate at pH=10.81, all the metals add up to a total of 57.2 % of the total mass of the precipitate, where the remaining 42.8 % can be assumed to consist of hydroxides and residual sulphates. By knowing this, together with the fact that the molar masses of Ni, Co, Mn and Zn are relatively equal and that their respective metal ions are divalent in the sulphate solution (meaning that they can bind to equal amount of counter ions), it can be assumed that the total weight percent of metals in the mixed hydroxide, as obtained from the stripping solution, is equal to the total weight percent of metals in the precipitate, as obtained in the hydroxide precipitation experiment. From this, the total amount of obtained mixed hydroxide precipitate (MHP-1) can be calculated:

$$m_{tot, metals} = 0.09 + 0.67 + 0.28 + 0.26 + 0.07 = 1.37 \text{ [kg]}$$

$$m_{MHP-1} = \frac{1.37}{0.572} = 2.3 \text{ [kg]}$$

The composition of the resulting mixed hydroxide product can then be determined by a simple division between each metal mass and the total mass of the precipitate.
The resulting composition of the product can be seen in Table 17.

Table 17: Metal composition of the mixed hydroxide product in the Ni salt production route.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.1</td>
<td>12.2</td>
<td>3.9</td>
<td>11.3</td>
<td>3.0</td>
</tr>
</tbody>
</table>

As can be seen in Table 17, the composition of Co is as high as 29.1 % in the calculated amount of product which is around twice the amount of the 12.5 % Co in the mixed hydroxide product (MHP-1) in Table 3 in the technique comparison section of this report. This together with the fact that the price of this product was found to be governed by the commodity price of Co, suggest that the price of the mixed hydroxide product, as obtained from the stripping solution, is slightly higher than the price of the mixed hydroxide found on the market. Since the mixed hydroxide available on the market has a market value of 16 USD/kg according to Table 3, the price of the mixed hydroxide, as obtained here was estimated to at least 18 USD/kg. Most probably the price will increase even more because of the increased Co content but due to hedging reasons, 18 USD/kg is used as the selling price of the MHP-1 product.

The amount of chemicals used in the process cannot fully be determined where some practical knowledge about the SLM process would have to be gathered in order to make an accurate evaluation on the matter. The two main considerations of this nature is the amount of pH buffer that would be needed in the process and the amount of organic loss that would be present during operation. The latter could be tested experimentally by running the process for longer periods of time while regarding the organic loss but at the time of writing, research on the matter using solutions that resembles the present system could not be found and hence, the organic loss is hard to predict. Instead, this is passed on as considerations for future work. However, the amount NaOH needed for the pH increase to pH=5.5 will be considered as this could be determined in the hydroxide precipitation experiment. Additionally, the amount of NaOH needed for the precipitation of both the pure Ni salt and the mixed hydroxide will be considered as slightly higher than in the results of the bulk precipitation in the hydroxide precipitation experiment. The amount of hydroxide ions needed for the precipitation of metals would ultimately be the same in both systems since the total amount of metals are the same, but the fact that a stripping solution of lower pH is introduced to the system increases the demand on NaOH in total. By considering this, the total amount of anhydrous NaOH could be estimated:

\[ m(\text{NaOH}_{pH=0.3-5.5}) = 18.0 \ [kg] \]

\[ m(\text{NaOH}_{\text{feed+stripping}}) = 15 \ [kg] \]
Similarly, the amount of added sulphuric acid in the stripping solution can only be estimated for the current process since the optimum stripping volume is yet to be evaluated. However, since the number of H$^+$ ions that are transferred from the stripping solution to the feed solution is constant for a certain amount of metal extraction, independent on stripping volume, an estimation of needed sulphuric acid should be valid. As determined by the simulations, a stripping volume equal to the feed volume at pH=1 has enough H$^+$ ions in solution as to extract all the metal ions except Ni and hence, the amount of sulphuric acid needed for such a stripping solution would serve as a good estimation of the sulphuric acid demand of the process. By knowing the volume (here assumed to be the same as in stream S7) and pH (being pH=-1) of the solution and the molecular formula and weight of sulphuric acid, the required amount of anhydrous sulphuric acid needed in the SLM process can be estimated:

$$C_{H^+} = 10^{-1} = 0.1 \left[ \frac{mol}{dm^3} \right]$$

$$C_{H_2SO_4} = \frac{0.1}{2} = 0.05 \left[ \frac{mol}{dm^3} \right]$$

$$n_{H_2SO_4} = 0.05 \cdot 492 = 24.6 \ [mol]$$

$$m_{H_2SO_4} = \frac{24.6 \cdot 98.079}{1000} = 2.5 \ [kg]$$

11 Results and discussion

In the present study, three different separation techniques have been regarded and tested as to evaluate the possibility of recovering valuable metals from a NiMH battery leach solution with specified concentrations based on the results from a previously conducted leaching study. One of the techniques, involving the selective oxidative precipitation of Mn from the solution could be disregarded by an experimental study as the co-precipitation of Ni was high, resulting in a large amount of product loss. The other two considered techniques, being a hydroxide precipitation process and an extraction process using a supported liquid membrane, were both found to be able to produce sellable products of reasonable value on the world market.

In order to be able to compare the different techniques further, the total collected revenue of the two processes were calculated by combining the results of the mass balance calculations, which were based on the recycling of one battery pack, and the results of the conducted market study on available HEV NiMH batteries in Sweden,
being approximated to a total of 2600 recyclable batteries per year. The prices of the products and the chemicals were again collected from the Chinese market and assumed to be valid in the economical comparison. The resulting revenue of each product and the chemical costs associated with the two suggested routes of metal recovery from one recycled battery pack are summarized in Table 18. In the table, a negative sign connected to the amount of a chemical represents a need of the chemical rather than a production.

Table 18: Resulting chemical revenue and cost of the two different suggested separation routes and the two leaching routes on the basis of one recycled battery pack.

<table>
<thead>
<tr>
<th>Leaching</th>
<th>H₂SO₄</th>
<th>H₂SO₄</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount [kg]</td>
<td>-52</td>
<td>-4.9</td>
<td></td>
</tr>
<tr>
<td>Price [USD/kg]</td>
<td>0.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Revenue [USD]</td>
<td>-10.4</td>
<td>-2.0</td>
<td>-12.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching</th>
<th>HCl</th>
<th>Oxalic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount [kg]</td>
<td>-19.3</td>
<td>-7.1</td>
</tr>
<tr>
<td>Price [USD/kg]</td>
<td>0.16</td>
<td>0.56</td>
</tr>
<tr>
<td>Revenue [USD]</td>
<td>-3.0</td>
<td>-4.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixed hydroxide product</th>
<th>NaOH</th>
<th>Al precipitate</th>
<th>Mixed hydroxide MHP-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount [kg]</td>
<td>-29.8</td>
<td>0.61</td>
<td>16.5</td>
</tr>
<tr>
<td>Price [USD/kg]</td>
<td>0.4</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Revenue [USD]</td>
<td>-11.9</td>
<td>-</td>
<td>165</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni salt product</th>
<th>NaOH</th>
<th>H₂SO₄</th>
<th>Mixed hydroxide MHP-1</th>
<th>Ni(OH)₂</th>
<th>Al precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount [kg]</td>
<td>-33</td>
<td>-2.5</td>
<td>2.3</td>
<td>13.5</td>
<td>0.61</td>
</tr>
<tr>
<td>Price [USD/kg]</td>
<td>0.4</td>
<td>0.2</td>
<td>18</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Revenue [USD]</td>
<td>-13.2</td>
<td>-0.5</td>
<td>41.4</td>
<td>243</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen in Table 18, here the two leaching routes are only associated with a cost since acids and bases are consumed in the process. In the real case, an REE precipitate is produced which contributes to the total revenue of the process but since the aim of the present study is to evaluate different methods of recovering the remaining metals from the resulting leach solution after REEs removal, only the chemicals used in the leaching are considered here.

The first thing that can be concluded from Table 18 is that the chemical cost in the hydrochloric leaching route is lower than that of the sulphuric acid route and hence, in the case of producing a mixed hydroxide product (MHP-2) where both leaching routes are valid, it could be arguable to choose the hydrochloric acid as leaching acid. However, if one compares the chemical costs of the leaching process to the gained revenues associated with the recovering of Ni and the other elements, the choice of leaching route has low influence on the final income of the process as a whole. Instead, the choice of leaching process route should depend on the revenue.
of the two differently recovered REE precipitates and the hazards associated with the usage of the different acids if the chosen route for the Ni recovery is the mixed hydroxide route.

In the case of producing the pure Ni(OH)$_2$ as a main product, the total revenue of the process is even higher than in the mixed hydroxide route. This is both because of the price of the main product being higher in this process as well as the fact that two product can be obtained instead of one. The chemical cost is a bit higher because of the increased number of process steps, but the increased value of the products renders the process of producing a Ni salt more justifiable than producing the mixed metal hydroxide. As was discussed in section 9 in this report, the chosen extractant for the extraction, being Cyanex 272, works better in solutions of sulphate- than in solution of chloride matrices which lead to the conclusion that the sulphuric acid leaching route was more suited for the process. Hence, only the sulphuric acid route should be considered in the production of a pure Ni(OH)$_2$ and the residual mixed metal hydroxide rich in Co (MHP-1) by the SLM process.

Combining these conclusion about which leaching route can be used for each metal recovery route, the total revenue of the process in a whole can be calculated. This together with the amount of HEV NiMH batteries available for recycling each year in Sweden then makes the calculation of an annual revenue possible. The resulting annual revenues from the recovery of Ni and other elements present in the leach solution of each process route can be seen in Table 19.

Table 19: Yearly revenue from the possible obtained products of recovering the metals present in the leach solution minus the chemical costs associated with the different suggested processes. In the conversion of USD to SEK, the current exchange rate of 8.12 SEK/USD was used.

<table>
<thead>
<tr>
<th>Separation- and leaching route</th>
<th>Mixed hydroxide (MHP-2) H$_2$SO$_4$ leaching</th>
<th>Mixed hydroxide (MHP-2) HCl leaching</th>
<th>Ni(OH)$_2$ and Mixed hydroxide (MHP-1) H$_2$SO$_4$ leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Revenue [USD/year]</td>
<td>365 000</td>
<td>379 000</td>
<td>672 000</td>
</tr>
<tr>
<td>Revenue [SEK/year]</td>
<td>2 963 000</td>
<td>3 077 000</td>
<td>5 456 000</td>
</tr>
</tbody>
</table>

As can be seen in Table 19, the two processes of producing a mixed metal hydroxide as the main product can be seen to yield almost equal amount of revenue even though different acid leaching and REE precipitation techniques are implemented in the different processes. However, the yearly revenue from the route of producing the Ni salt and the residual mixed metal hydroxide is nearly twice as large as the gained revenue from the route of producing only a mixed metal hydroxide. Because of this, the process of producing the Ni salt as the main product through a separation using an SLM technique can be justifiably considered as the most promising route. It should be noted though, that some supplementary experimental confirmation is needed in order to fully determine the input and output streams of this process, such as the ideal amount of stripping solution, pH buffer and the amount of organic loss that would have to be considered in a larger scale process.
12 Conclusion

From the combined results of the literature study, the experimental trials, process simulations and the final mass balance calculations coupled with the product values, it can be concluded that a process of producing a Ni salt and a residual mixed metal hydroxide rich in Co is possible and would yield the highest revenue from the recycling of HEV NiMH batteries in Sweden. In order to achieve the required separation of Ni from the other elements in the battery leach solution, an extraction process using a supported liquid membrane technique would most beneficially be implemented where the extractant of the process is the commercially available Cyanex 272. The leaching process, the preceding step of the separation process considered in the present study, would here be the sulphuric acid leaching route as described in the previously conducted leaching study. The upscaled version of the process as a whole would most preferably be of batch design because of the relatively small market as well as the usage of strong acids and probable deviations in process input streams. Despite the relatively small amount of HEV NiMH batteries that need recycling in Sweden at the time of writing, the near future recycling demand is evident and a process of handling the yearly sum of 2600 used up HEV batteries has here been suggested and evaluated with promising results.

13 Future work

For future work on the process in whole, supplementary upscaling calculations as well as energy balance calculations would have to be made in order to be able to evaluate the process in a large scale design. Additionally, some supplementary experimental confirmations are needed in the supported liquid membrane process step as to fully determine the chemical loss and consumption.

14 Acknowledgements

The success and outcome of this project would not have been possible without the guidance and support from many people who have worked close to me during the course of the of my project. I would like to thank everyone at the Department of Chemical Engineering at KTH who gladly joined in discussion whenever I needed guidance or a second opinion.

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References


