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Extraction of rare earth elements from grey mud using hydrochloric acid

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Norwegian University of
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Acknowledgement

First I would like to extend thanks to my supervisor Jafar Safarian for being a great mentor throughout the process. His mentorship has encouraged me work responsibly and individually to solve problems. I would also thank my co-supervisor Fabian Imanasa Azof for always being available to help when needed with lab training and questions. Additionally, I would like to thank the technical staff at department of chemistry, mainly Syverin Lierhagen for his analysis of the samples from my experiments. Lastly, I would like to thank the people in the SiManTi group for being a good arena to learn from other researchers and aquire knowledge.

Abstract

The Bayer process used for production of alumina is not very sustainable, with a large production of the residue red mud. The residue poses significant environmental challenges with its storage in landfills. An alternative, more sustainable production route is via the Pedersen process. This process is researched as a part of an EU-project, ensuring, with the main goal of having zero waste production of alumina in Europe. A part of this is to investigate the possibility of recovering rare earth elements (REEs) from one of the by-products of the process, grey mud. This thesis explores the feasibility of REEs recovery from grey mud through literature, thermodynamics and experimental work. Additionally, it forms a basis for possible further work on the topic.

Sammendrag

Bayer prosessen som brukes til produksjon av aluminiumoksid er ikke veldig brekraftig på grunn av stor produksjon av avfallet rødslam. Dette avfallet skaper miljøutfordringer på grunn av sin nødvendige lagring på land. En alternativ og mer brekraftig produksjonsrute er via Pedersen prosessen. Denne prosessen er bakgrunnen for et forskningsprosjekt for EU, som har som hovedmål å oppnå en produksjonsrute med produksjon av null avfall i Europa. En del av dette prosjektet er å undersøke muligheten for å utvinne sjeldne jordarter fra biproduktet kalt "grey mud" som produseres i denne prosessen. Denne avhandlingen undersøker muligheten for utvinning av sjeldne jordarter gjennom litteratur, termodynamikk og eksperimentelt arbeid. I tillegg legger den til grunn for mulig videre arbeid på temaet.

Table of Contents

Acknowledgement	i
Abstract	ii
Sammendrag	ii
Table of Contents	iv
List of Tables	v
List of Figures	vii
Abbreviations	viii
1 Introduction	1
2 Literature Review and theory	3
2.1 Rare earth elements	3
2.1.1 Chemistry	4
2.2 Alumina production	4
2.2.1 Bayer process	4
2.2.2 Pedersen process	6
2.3 Previous work	8
3 Thermodynamic modelling	9
3.1 Thermodynamic modelling	9
4 Experimental	13
4.1 Equipment and materials	13
4.2 Experimental methods	14
4.2.1 Grey mud leaching	14
4.2.2 Analysis	15

5	Results and discussion	17
5.1	Grey mud leaching	17
5.2	Recommendation for further work	20
6	Conclusion	23
	Bibliography	24
	Appendix	27
6.1	Experimental data	27
6.2	Risk assessment	28

List of Tables

2.1	Estimation of the grey mud composition (Vafeias et al. (2018)).	7
4.1	Overview of the experimental parameters used during leaching of the grey mud. For HCl content the weight percent of the leach solution is included.	14
5.1	The extraction yield from grey mud compared to the original content of the slag. The percentages are the normalized version of the calculated yield from the data in Appendix 6.1	20
6.1	Raw data for the ICP-analysis for the leachate solutions from the leaching of the grey mud.	27

List of Figures

2.1	The lanthanide contraction (Gupta and Krishnamurthy (2005)).	5
2.2	A simplified overview of the Bayer process	5
2.3	A simplified overview of the Pedersen process.	6
3.1	Enthalpy of the leaching reaction from HSC 9.0 software.	10
3.2	Gibbs free energy of the leaching reaction from HSC 9.0 software.	10
4.1	The grey mud produced from calcium aluminate slag.	13
4.2	The digestion furnace used in the experiments, where mixing is achieved through swinging of a plane where the vessels are placed.	14
5.1	The extraction yield of hydrochloric acid leaching of grey mud for the rare earth elements, with the parameters provided in weight percent and solid:liquid ratio. These percentages are calculated based on the initial slag composition.	19
5.2	The extraction yield of hydrochloric acid leaching of grey mud for some relevant elements, with the parameters provided in weight percent and solid:liquid ratio. These percentages are calculated based on the initial slag composition.	19

Abbreviations

HREEs	=	Heavy rare earth elements
ICP-MS	=	Inductively coupled plasma mass spectrometry
LREEs	=	Light rare earth elements
NTNU	=	Norwegian University of Science and Technology
REE(s)	=	Rare earth element(s)

Chapter 1

Introduction

Alumina is an important material with increase in production in the past, and a important usage in the production of aluminium Safarian and Leiv Kolbeinsen (2016). Most of the world's alumina is produced through the Bayer process, where Bauxite is used as the aluminium source. One of the main drawback of this process is the large production of red mud, a residue that pose environmental threats due to its storage on land but also additionally results in some loss of aluminium from the bauxite.

An alternative sustainable process is the Pedersen process, where no waste is produced and all the bi-products have known applications in other industries. Research into this process is currently performed as a part of an EU-prject, ensureal (www.ensureal.com). The main goal being a zero waste production of alumina in Europe. Researchers working on this project is investigating the different process steps to optimize the overall process to be energy efficient and more profitable. The project also include smaller projects, such as the recovery of rare earth elements.

Rare earth elements are a group of 17 chemical elements that have an increasing demand and growing interest due to uses in technology such as permanent magnets, batteries and catalysts. Contrary to what the name may indicate their occurrence is not rare compared to other elements, but the existence of economically exploitable minerals are. Additionally, the main producer is China, meaning the EU is very much dependant on import to cover its demand. As a consequence it is desirable to find secondary or other sources for REEs production. One option is the recovery of REEs from bi-products of other industries, like alumina production.

This thesis aims investigate the feasibility of recovering REEs from the bi-product grey mud from the Pedersen process. Additionally it aims to fill some of the information gap available on grey mud. This is achieved through literature review, thermodynamic calculations and experimental work.

Literature Review and theory

2.1 Rare earth elements

The REEs are the fifteen lanthanides (elements of atomic number 57 to 71), scandium and yttrium (Voncken (2016)). The REEs typically exhibit similar properties and usually occur together in natural deposits, and although their occurrence is not as rare as the name may indicate, economically exploitable deposits are. Additionally, they exist in mixtures rather than as pure rare earth compounds. Hence they occur in different quantities in different minerals, but mostly as oxides. Their importance for modern society has only increased in later years, especially being important part of a greener future due to use in permanent magnets, batteries for electric cars, and catalysts

The inclusion of scandium is discussed in some sources, where some choose to exclude it from the REEs. The reasoning given is a difference in behaviour between scandium and the other lanthanides in geochemical systems, and scandium occurring in other forms than the lanthanides in bauxite and bauxite residue (Vind et al. (2018)). An additional source indicate that Sc is closer in geochemical behaviour to the ferromagnesian transition elements (Fe, V, Cr, Co and Ni) because of a smaller atomic radius (Voncken (2016)). The same source further notes that the difference in behaviour is not as prominent in aqueous systems. For the purpose of this thesis scandium is included in the term REEs, but it is important to note that these factors exist and must be considered. Furthermore, the REEs are commonly divided into two groups, light rare earth elements (LREEs) and heavy rare earth elements (HREEs) based on their atomic weight.

The main production of REEs are in China, and many depend on their exports to cover their demand Voncken (2016). The dependence on China became more apparent in 2009 when China changed its position towards the market. The introduction of production quotas, export quotas, and export taxes with more caused anxiety for manufactures dependant on these resources. As a consequence, the focus on finding new sources for REEs have increased in newer years as a way to meet an increasing demand and decrease the depen-

dence on the Chinese production.

How critical the REEs are is defined by the European Commission based on economic importance for the EU and the risk of supply disruption (Mathieux et al. (2017)). In this report the REEs are defined as being critical raw materials. The supply risk is connected to China being the main supplier, making the rest of the market dependant on its exports. As a result the supply chain has previously been categorized as weak. The economic importance is connected to the high demand in industry and difficulty in finding suitable substitutes for the REEs. An additional issue connected to the production of rare earths is the so-called balance problem (Binnemans and Jones (2015)). This describes the reason for the difference in prices for the individual REEs where some are much more valuable than others. This is due to an imbalance between the abundance of individual REEs and their individual demand, where some are oversupplied and others have a high demand. Ensuring a secure and stable supply of REEs to Europe is one of the main motivations behind recent projects funded. Ensuring is one such project. Even though the main goal is not connected to REEs, valorization of grey mud may be achieved through REEs recovery.

2.1.1 Chemistry

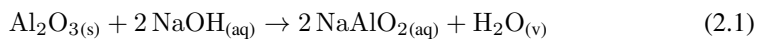
The REEs are most commonly trivalent (3+), although cerium may form 4+ ions and europium, ytterbium, and samarium may form 2+ ions (Voncken (2016)). A phenomenon connected to the REEs are the so-called lanthanide contraction, which is the observed decrease in ionic radius from La^{+3} to Lu^{+3} (Behring et al. (2014)). This trend is illustrated in Figure 2.1. This figure includes the trivalent states, which are the most stable valence state for most of the REEs, as well as some alternative valency states. This trend is attributed to the insufficient shielding of the electrons, where the effective nucleus charge experienced by the outer electrons increases with the increase in atomic number (Gupta and Krishnamurthy (2005)). Consequently, the contraction increases along the lanthanide series. The lanthanide contraction is connected to features of the REEs' chemistry.

2.2 Alumina production

The alumina production is an important industry, especially to the aluminium production. The prominent process used is the Bayer process, although an alternative process named the Pedersen process has previously been used.

2.2.1 Bayer process

The Bayer process was invented by Carl Josef Bayer in 1888-1892 (Safarian and Leiv Kolbeinsen (2016)). A simplified overview of the process is shown in Figure 2.2 (Sellaeg et al. (2017)). The first step consists of the digestion of bauxite and lime using caustic soda (NaOH). The main reaction may be written as:



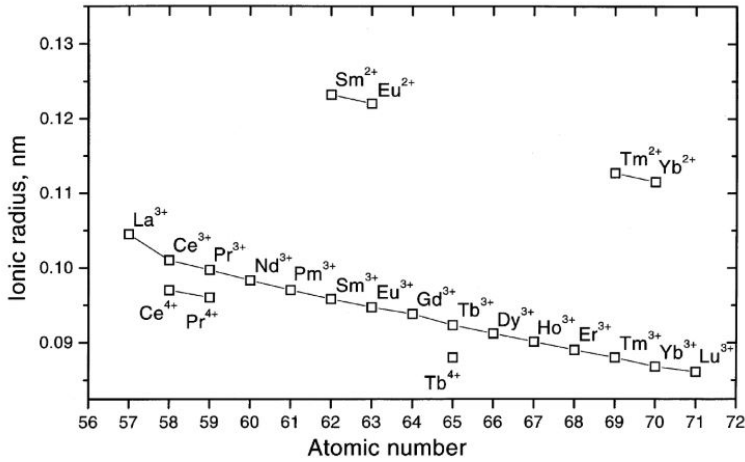


Figure 2.1: The lanthanide contraction (Gupta and Krishnamurthy (2005)).

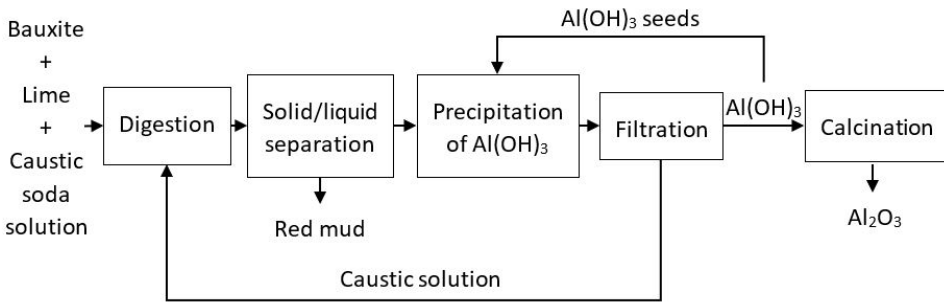
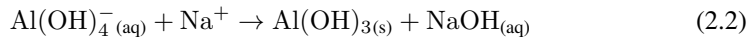
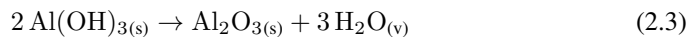


Figure 2.2: A simplified overview of the Bayer process

This yields a saturated solution with insoluble impurities. The solids are separated from the solution, resulting in the production of the residue red mud. Currently, there are no industrialized uses for this residue and it is discarded. Precipitation of aluminum hydroxide ($\text{Al}(\text{OH})_3$) is then achieved through the addition of $\text{Al}(\text{OH})_3$ seed crystals, the caustic soda solution is also reproduced:



The caustic soda is recycled and reintroduced back into the process in the initial digestion step. After filtration some of the produced $\text{Al}(\text{OH})_3$ are used as seeds, while the others are calcined to produce alumina:



The main disadvantages of this process the production of red mud which pose environmental treats due to its need for storage as no industrialized applications exists. Currently

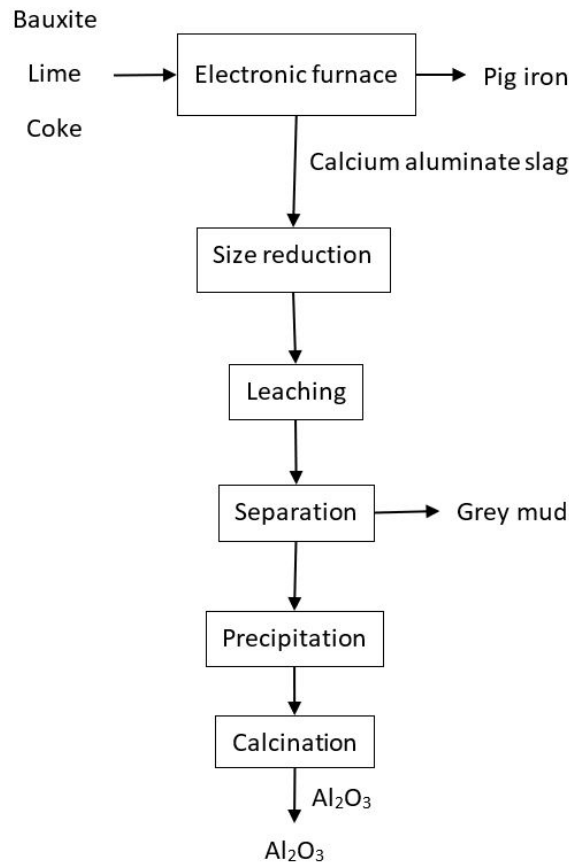
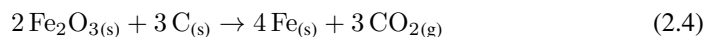


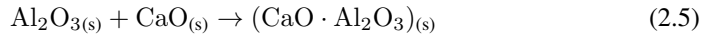
Figure 2.3: A simplified overview of the Pedersen process.

the stored residue is around 2.7 billion tonnes, with an annual increase of about 120 million tonnes (Klauber et al. (2011)). It is primarily stored in long-term storage, and even with extensive research into utilization, no industrial utilization appear to exist.

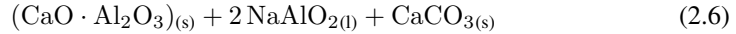
2.2.2 Pedersen process

The Pedersen process was patented by Harald Pedersen in 1920, and used in Hyanger, Norway between 1928-1969 (Miller and Irgens (2016)). During its use it had an annual production of around 17 000 metric tonnes (Safarian and Leiv Kolbeinsen (2016)). A simplified overview is shown in Figure 2.3. In this process bauxite together with lime and coke undergo a smelting reduction producing pig iron and calcium aluminate slag. The main reactions of this step is reduction of iron oxides and slag formation:





The slag is used for the alumina extraction, while the pig iron may be used in other industries. The slag's size is reduced appropriately and then digested in sodium carbonate solution (Na_2CO_3) to extract alumina. This leaching can be described as:



The solution is filtrated and the remaining undissolved solids is the grey mud. The solution is further used for precipitation of aluminium hydroxide and calcination, similarly to the Bayer process. The grey mud produced is expected to consist of mainly calcium carbonate, as indicated by the reaction in which it is created. Additionally, it will most likely contain some undissolved phases.

The grey mud has an estimated composition as shown in Table 2.1. The main component is as mentioned the calcium carbonate. The other components are the results of incomplete leaching of alumina and additionally unleachable minor phases.

Table 2.1: Estimation of the grey mud composition (Vafeias et al. (2018)).

Compound	Content
CaCO_3	77 %
Al_2O_3	8 %
SiO_2	8 %
CaO	2 %
Sodium losses	2 %
Inactive elements	3 %

Compared to the Bayer process, the Pedersen process is more sustainable with no unusable waste produced. The grey mud's high calcium content makes it usable in cement industry or in agriculture, and compared to red mud it doesn't contain iron and has a low alkalinity (Vafeias et al. (2018)). The amount of grey mud produced will be around two times as much as the produced alumina based on data from the process in Norway. (Miller and Irgens (2016)) Due to its composition mainly being calcium based it may be possible to utilize it directly. (Vafeias et al. (2018)) It could also be decomposed to lime and CO_2 for use in the industrial application to lower costs. Additionally, it contains REEs and may possibly be a secondary source, which is the basis of this thesis.

Ensuring as is previously mentioned focused on the Pedersen process as an alternative production route for alumina. The REEs aspect is interesting as the grey mud is enriched in REEs compared to the bauxite ore. Therefore, the extraction of the REEs previously to the grey mud being used in other products may be beneficial and provide a source for REEs.

This thesis will therefore attempt to say something about the feasibility of the extraction of REEs from grey mud using hydrochloric acid. This will mainly be achieved through some literature review, thermodynamic modelling, and experimental work.

2.3 Previous work

This study is a continuation of the work described in the project "Extraction of rare earth elements from grey mud" written as a specialization project that is a part of the master degree coursework for materials science and engineering at Norwegian University of Technology and Science (NTNU) (Salvesen (2018)).

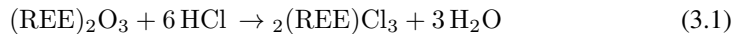
The project consisted of a literature review where hydrochloric acid was chosen as the acid to be used in the thesis based on it probably yielding a high extraction for the REEs. Additionally, calcium aluminate slag from Greek bauxite was used to produce grey mud that was further characterized using SEM, ICP-MS and XRD. The leaching of the slag to produce grey mud indicated that most of the REEs remained in the grey mud, which is optimal for further recovery.

Thermodynamic modelling

3.1 Thermodynamic modelling

This section presents some relevant thermodynamic calculations that are relevant to assess the feasibility of the leaching reactions. The thermodynamic modelling was performed using HSC 9.0 software.

For the calculations it is assumed that the REEs occur as oxides in the grey mud. For simplicity a general leaching equation for hydrochloric acid is as shown in equation (3.1). Where the REE denotes any of the rare earth elements.



The calculated thermodynamic data are graphically shown in Figure 3.1 and 3.2 for the Gibbs free energy and enthalpy change respectively. The calculations were performed with 1M as a basis. The negative value in both Gibbs free energy and enthalpy means dissolution is expected to occur during leaching for all of the REEs, except Lu. The figures show a close relation between most of the REEs, where they appear to have very similar values. The main difference is observed for Sc and Lu. Hence it may be expected that there will be an observable difference in their behaviour compared to the others. Since Sc has a less negative value it is possible that a lower dissolution may be observed. The graph also include calcium carbonate, the main component in grey mud. It has a less negative value than the REEs and may indicate that under the right conditions, the REEs may dissolve before the calcium carbonate. This would be favourable with the respect of producing a high content residue containing most of the REEs, but little calcium carbonate.

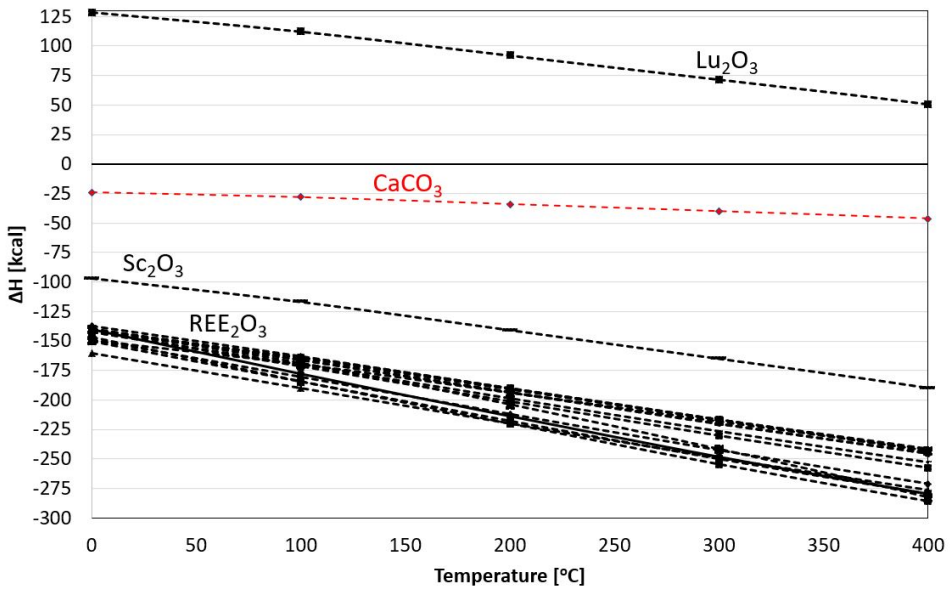


Figure 3.1: Enthalpy of the leaching reaction from HSC 9.0 software.

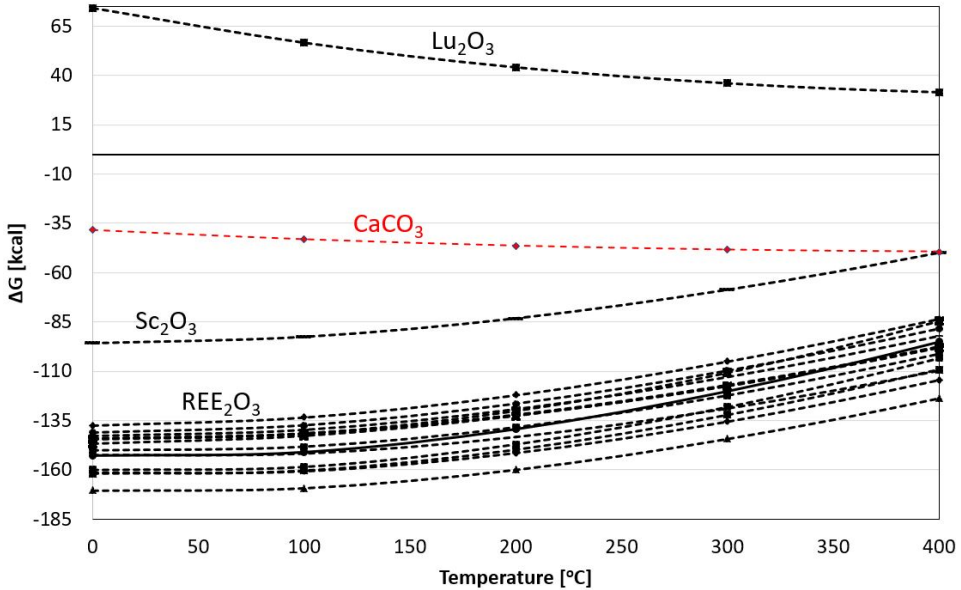


Figure 3.2: Gibbs free energy of the leaching reaction from HSC 9.0 software.

The slope of the graph helps predict the temperature dependence for the leaching, i.e. if temperature change will give a drastic change in the leaching efficiency. The graphs in

this case are not steep and consequently it is not likely that a change in temperature will have a large effect on the efficiency. To ensure low cost of the process it may therefore be more constructive to change other parameters to see if there is a larger change observed by changing these.

Due to time limitations further calculations by varying the parameters were not performed, but may be advised to better understand the system at hand in further work.

Experimental

This chapter explains the experimental work performed as well as describing the set up and equipment used. All of the leaching experiments were performed in a digestion furnace at department of material science, NTNU. The analysis were performed by technical staff at department of chemistry at NTNU, as acknowledged previously.

4.1 Equipment and materials

The grey mud used in the experiments were produced from calcium aluminate slag originating from Greek bauxite. Complete experimental procedure for this process and characterizations of the grey mud may be found in previous work (Salvesen (2018)). The produced grey mud was leachable and no further preparations were necessary. A picture of the grey mud used may be seen in Figure 4.1.

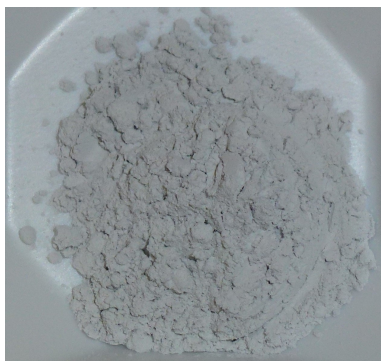


Figure 4.1: The grey mud produced from calcium aluminate slag.



Figure 4.2: The digestion furnace used in the experiments, where mixing is achieved through swinging of a plane where the vessels are placed.

4.2 Experimental methods

4.2.1 Grey mud leaching

Leaching experiments were performed in the digestion furnace TR-60 S, pictured in 4.2, using Parr acid digestions vessels. All experiments followed the same procedure, with variations only in acid concentration and liquid to solid ratio (L/S-ratio). Vessels containing the acidic solutions were placed in the furnace, which were then heated to 60°C within 12 minutes. Upon reaching the temperature, the vessel were moved from the furnace into to the fume hood where the grey mud was added. The vessels were then placed back into the furnace for the duration of the leaching with mixing achieved through the swinging plane in the furnace (see Figure 4.2). The swinging of the furnace plane was set to 46 per minute for each parallel. More specific experimental parameters may be found in Table 4.1. After leaching the liquid and solids were separated through filtration using a Bchner funnel with filtration paper assisted by a simple vacuum pump.

Table 4.1: Overview of the experimental parameters used during leaching of the grey mud. For HCl content the weight percent of the leach solution is included.

	Grey mud [g]	HCl concentration [wt %]	L/S-ratio	Temperature [°C]	Time [min]
1	0.4	10	20	60	60
2	0.4	10	40	60	60
3	0.5	18.5	20	60	60
4	0.5	18.5	40	60	60

4.2.2 Analysis

Samples from the experiments were analyzed using ICP-MS performed by Syverin Lierhagen. Samples were delivered in the original solution and further dilution and preparation was performed by the operator as necessary. The results from the analysis were normalized, using (4.1) and analyzed using Excel. The raw data of the experiments can be found in Appendix 6.1.

The normalization was performed using the formula:

$$z = \frac{x_i - \min(X)}{\max(X) - \min(X)} \quad (4.1)$$

Where X is a set of all the calculated percentages, and x_i is individual calculated percentages.

Results and discussion

5.1 Grey mud leaching

Four parallels were conducted to investigate the aspects of the dependency on L/S-ratio and acid concentration. This based on temperature reportedly not being a major factor from thermodynamic calculations. All the parallels used grey mud produced from the same batch, consequently there is not expected to be much variation in the composition from each parallel. Of the four parallels included, two parallels (1 and 2) have previously been included in the specialisation project. The choice of including them in these results is to provide a better comparison between the different parameters.

The results from the hydrochloric acid leaching is presented in terms of leaching yield, i.e. how much of the original calcium aluminate content that was leached into solution during the experiment. The results are calculated based on ICP-MS analyses, the raw data of which are included in Appendix 6.1. Normalization was performed as previously explained to avoid negative or over one hundred percent yields in the final results. The main results for the REEs and other relevant elements are presented in Figure 5.1 and 5.2 respectively.

The extraction yield as a result of hydrochloric acid leaching of grey mud for the REEs shown in Figure 5.1 has one data point that is considered an outlier. This is the data point of La for 10 wt% at a liquid to solid ratio of 40 and it will not be included in the discussion. The background for this is irregular results from the ICP-MS analysis considering this one element.

Comparing the difference extractions yields for REEs for the two liquid to solid ratio it is apparent that the difference is larger at a lower acid concentration compared to the higher. Where little difference is observed for the 18,5 wt% parallels, a much larger difference is observed for the 10 wt% parallels. However all of the parallels shows a relatively high leachability of the REEs with the main portion of extractions in the region of 70-90%.

For each parallel a lower extraction yield is observed for scandium. This can be explained by the thermodynamic calculations performed previously, where scandium had a noticeable difference compared to the other REEs. Based on this train of thought it would also be expected to see similar behaviour when investigating calcium dissolution. However, this is not the case. This may be explained by the calculations being too superficial, requiring more thorough calculations, or the large quantity difference of calcium carbonate compared to REEs may explain why the dissolution of the calcium carbonate would be more rapid. Meaning, a large weight fraction of calcium carbonate compared to other compounds may push its equilibrium forward. Further investigation into this aspect of the leaching would definitely be most beneficial in understanding how the system works.

Comparing both the rare earth extraction yield and the major elements extraction yield it appears that Sc is more attached to the Fe and Ti containing phases, while the other REEs are more closely associated with Ca. Upon researching this trend there are some indications that scandium may act differently than the other REEs in geological systems, see rare earth elements section of the literature review. However, no definitive examples related to this type of system was found to give any further explanation as to why this may occur. Anyhow, looking into the possibility of enhancing this effect may be interesting, as the result may yield a scandium rich residue without the other REEs. Hence, further purification may be much easier than purification of a residue or solution containing all of the REEs.

Comparing the calcium extraction to the rare earths it does not appear that a selective leaching is achieved. It would be interesting in further experiments to test this aspect more closely. An aspect previously discussed in the specialization project was the possibility of performing experiments where a closed lid would restrict the formed gas to escape and cause a build up of pressure. This is an interesting aspect that may be considered for further work. It was not performed in this thesis due to large amounts of bubbling occurring as the grey mud was initially added to the vessel. Consequently, the main initial formed gas was not tapped and sufficient pressure build up appeared unlikely.

The major elements in the grey mud does not appear to share an overall trend in leachability. Calcium, titanium and magnesium is mainly found in the acidic solution while iron and silicon appears to remain in the solid. Ideally these would behave in a more uniform way, such that a selective leaching of these elements or the REEs may be achieved. Since, this does not appear to be possible it would be most interesting to focus on the most abundant elements in further experiments as these make up most of the grey mud.

Due to low amount of residue produced in the experiments, no further analysis was possible to determine which phases remained in the residue. This would have been beneficial as it may provide some insight to the chemistry behind which elements remains in the residue, and if this is in accordance to the ICP-MS results. To achieve this information it may be advised to scale up the experiment to achieve a larger portion of residue that may be further analyzed and characterized. From the extraction yield it would be assumed to contain Sc, Fe, and Si as its main components. Further literature review may provide

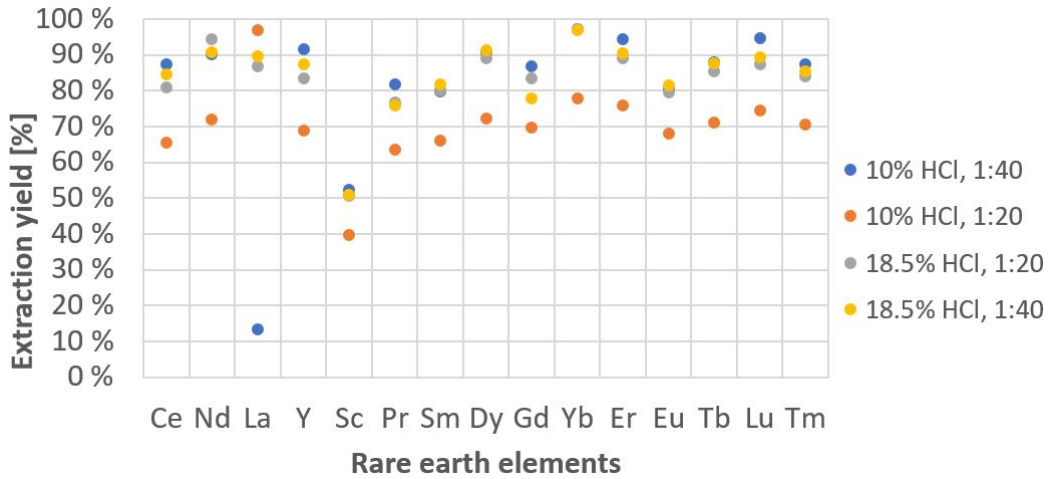


Figure 5.1: The extraction yield of hydrochloric acid leaching of grey mud for the rare earth elements, with the parameters provided in weight percent and solid:liquid ratio. These percentages are calculated based on the initial slag composition.

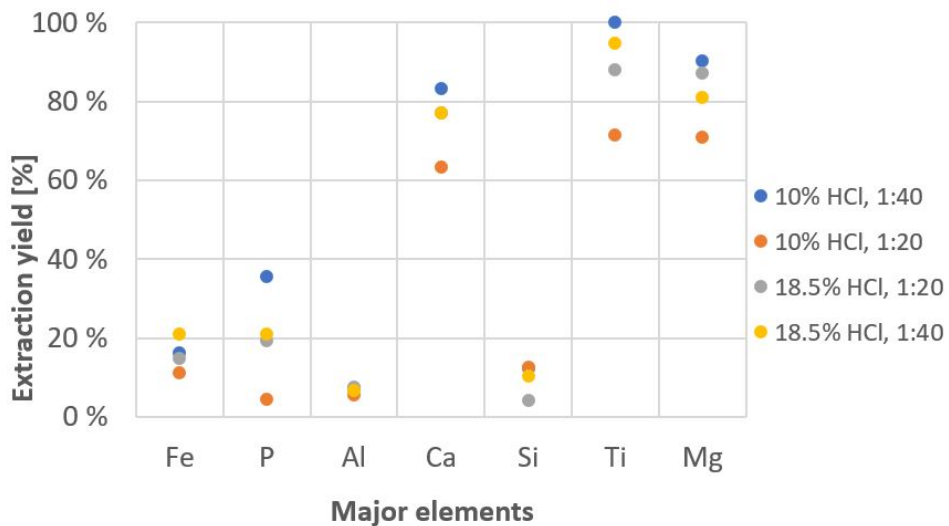


Figure 5.2: The extraction yield of hydrochloric acid leaching of grey mud for some relevant elements, with the parameters provided in weight percent and solid:liquid ratio. These percentages are calculated based on the initial slag composition.

Table 5.1: The extraction yield from grey mud compared to the original content of the slag. The percentages are the normalized version of the calculated yield from the data in Appendix 6.1

	Grey mud extraction yield			
	18.5% HCl		10% HCl	
	1 : 20	1 : 40	1 : 20	1 : 40
Ce	80.98 %	84.56 %	66.05 %	88.74 %
Nd	94.44 %	90.78 %	72.75 %	91.58 %
La	86.88 %	89.65 %	98.70 %	11.88?? %
Y	83.60 %	87.47 %	69.74 %	93.09 %
Sc	50.59 %	50.84 %	39.36 %	52.48 %
Pr	76.86 %	75.90 %	64.11 %	82.95 %
Sm	79.98 %	81.84 %	66.77 %	80.93 %
Dy	88.96 %	91.29 %	72.96 %	92.25 %
Gd	83.43 %	77.85 %	70.46 %	88.30 %
Yb	97.25 %	96.84 %	78.95 %	98.91 %
Er	89.10 %	90.52 %	76.80 %	95.96 %
Eu	79.47 %	81.38 %	68.79 %	81.68 %
Ho	-	-	-	-
Tb	85.44 %	87.63 %	71.97 %	89.49 %
Lu	87.39 %	89.36 %	75.51 %	96.44 %
Tm	84.14 %	85.49 %	71.42 %	88.86 %
Pm	-	-	-	-
Fe	14.93 %	20.96 %	11.34 %	16.25 %
P	19.45 %	21.00 %	4.36 %	35.70 %
Al	7.69 %	6.88 %	5.50 %	7.24 %
Ca	77.08 %	77.06 %	63.22 %	83.34 %
Si	4.24 %	10.28 %	12.57 %	12.34 %
Ti	88.06 %	94.76 %	71.55 %	100.?? %
Mg	87.16 %	80.88 %	70.84 %	90.34 %

some insight, but no such sources were found during the duration of the thesis to provide any further theories.

5.2 Recommendation for further work

It would be recommended for further work to spend some time setting up experiments that will yield results not included in this thesis, mainly more characterization would be favourable to be able to perform a more detailed analysis of the system. The most unanswered question from this thesis is mainly what chemical compounds remain in the residue after leaching, which may be answered if a larger batch is used to produce enough residue to be further analyzed.

The thesis is also unsuccessful in determining the major factors that may increase the selectivity and control of the overall process. This is attributed by many factors; the lack of extensive experimental work, good available literature to give hints as to what may be the cause, and little characterization of the experiments apart from the ICP-MS analysis. In the future it would be recommended to perform several more experiments at a wide range of concentrations and liquid to solid ratios to possibly determine the most impactful parameter.

Another unanswered question is the possible effect of the gas formation on the rate of calcium carbonate dissolution. It would be advised to change the equipment setup to test effect of no "ventilation" of the digestion vessel. i.e. explore the possibility of decreasing gas formation and less dissolution of calcium carbonate to see if REEs will leach more efficiently. Not possible with the current setup as a lot of bubbles were produced in the initial addition, where the lid was completely taken off.

Further thermodynamic modelling may give further insight into the nature of the experiments. Testing out different concentrations, closer to the actual concentrations achieved in the experiments could be a beneficial route to see if any additional information may be provided. Such an effort may help predict results of experiments to a more accurate degree and limit time spent doing experiments that ultimately does not yield any new information.

Overall the feasibility of REEs extraction shows potential. The setup used in this thesis was based on the literature review performed during the previously mentioned specialization project, where hydrochloric acid was chosen as it showed the highest potential of yielding a high extraction of the REEs. In hindsight it may be more appropriate to also investigate nitric and sulfuric acid as these may be easier to tailor in order to control the leaching of the different elements. For this it would be recommended to consider whether a high leachability is the most important aspect or not.

Conclusion

The present study has investigated the possibility of rare earth elements extraction from grey mud through literature review, thermodynamic calculations and experiments. The main findings indicate that there are possibilities for extraction, however the work was not extensive enough to provide a good experimental setup that will guarantee selectivity and control over the process. Hence, further experimental work and possibly thermodynamic calculations is advised to give a clearer insight into the process.

For leaching of the grey mud the overall leachability was high, mainly around 70-80% for most of the REEs. The exception being Sc, which showed a much lower extraction at around 40-50%. This was partly attributed to information achieved from thermodynamics and literature indicating that Sc may sometimes behave different compared to the other REEs.

Some general features for extraction of REEs have been found based on literature and the experimental work:

- The REEs (excluding Sc) can easily be leached from the grey mud
- The selectivity of REEs appears to be limited to Sc vs the other REEs, with little possibility of selectively dividing the other REEs
- Hydrochloric acid appears to have low selectivity towards any specific elements within the parameters tested in this thesis

The leaching results were limited due to only ICP-MS being the available for collecting information. Ideally classification of the residue after the leaching would be helpful in making any further conclusions.

The thesis also uncovered some weaknesses in the experimental setup with respect to being able to control certain parameters. Particularly the initial gas formation where large

parts of the grey mud were dissolved without the possibility of achieving a build up in pressure limited the investigation into some aspects of the parameters. A suggestion was made to alter the setup if such experiments are to be attempted in the future.

Overall the conclusion of the feasibility of the extraction is that it shows potential. The choice of using hydrochloric acid was made to achieve high extraction, but in the future investigating another acid that may possibly yield a higher selectivity may be beneficial.

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Appendix

6.1 Experimental data

The experimental data from the ICP-analysis performed for the experiments are included in Table 6.1 for the REEs and other relevant elements.

Table 6.1: Raw data for the ICP-analysis for the leachate solutions from the leaching of the grey mud.



	Ce [µg/L]	Nd [µg/L]	La [µg/L]	Y [µg/L]	Sc [µg/L]	Pr [µg/L]	Sm [µg/L]	Dy [µg/L]
1	8 669.84	2 366.21	3 201.89	2 215.42	1 151.86	579.70	478.47	499.63
2	4 927.99	1 260.25	162.99	1 251.07	649.86	317.31	245.35	267.26
3	7 949.75	2 304.87	2 111.15	1 987.90	1 092.35	519.17	428.56	456.59
4	4 491.35	1 196.53	1 178.25	1 125.40	593.38	277.00	237.14	253.41

	Gd [µg/L]	Yb [µg/L]	Er [µg/L]	Eu [µg/L]	Ho [µg/L]	Tb [µg/L]	Lu [µg/L]	Tm [µg/L]	Pm [µg/L]
1	424.98	360.53	320.97	101.95	-	74.38	52.65	48.89	-
2	225.32	191.09	169.69	51.22	-	39.13	28.45	25.73	-
3	376.67	333.53	279.17	88.06	-	66.14	45.66	43.11	-
4	189.68	179.50	153.36	48.77	-	36.69	25.25	23.69	-

#	Fe [µg/L]	P [µg/L]	Al [µg/L]	Ca [µg/L]	Si [µg/L]	Ti [µg/L]	Mg [µg/L]
1	26 275.40	108.70	704 022.71	16 497 460.88	219 160.61	495 795.80	121 888.46
2	16 836.54	549.00	437 055.07	9 264 556.06	90 692.08	295 314.61	66 132.87
3	26 661.67	498.40	823 922.65	14 910 130.51	36 751.08	452 159.54	111 131.85
4	21 028.48	293.08	384 635.15	8 056 817.57	68 741.00	263 390.08	55 649.46

6.2 Risk assessment

The main results from the risk assessment performed in connection to the experimental work is summarized in the following pages.

 NTNU HSE	<h2 style="margin: 0;">Risk assesment</h2>	Responsible: Malin Salvesen	Valid to: 22.11.2019	

Unit: Department of materials science and engineering – Faculty of natural sciences - NTNU

Participants: Malin Salvesen (student), Jafar Safarian (supervisor), Fabian Imanasa Azof (co-supervisor)



Risk assesment for main activity: Master thesis for Malin Salvesen, "Extraction of rare earth elements from grey mud using hydrochloric acid"

Existing documentation used for the risk assesment:

- Hydrochloric acid (HCl) and calcium carbonate (CaCO₃) safety data sheet
- 249M Parr acid digestion vessels instrument manual – provided the limits of maximum 2g of inorganic sample and a maximum volume of 30 ml to be used in the vessel.

Personal protective equipment to be used: Glasses, lab coat, gloves (where appropriate) and closed shoes. Additionally work is performed in a fume hood as much as possible.

ID nr	Activity	Possible unwanted incident/hazard	Probability (1-5)	Consequence				Risk	Comments Proposed actions
				Health (A-E)	Enviroment (A-E)	Material values (A-E)	Reputation (A-E)		
1	Dilution of acids	Heat generation during addition of acid to water	3	A	-	A	-	A3	It is likely that heat is generated when acid is diluted as it is exothermic. The effects are limited by slow addition and caution. Using the mantra "syre i vann går ann, vann i syre blir uhyre" the likelihood is limited. Unlikely that large spills will occur due to the amounts used. Additionally, a fume hood and protective gear is used to limit consequences and likelihood of damage.
		Wrongly adding water to the acid	2	B	B	B	-	B2	
		Acid spilling	2	B	B	B	-	B2	
2	Sample preparation in Parr digestion vessel	Acid spilling when transferring diluted acid into vessel	2	B	B	B	A	B2	HCl spilling may cause skin irritation or worse, together with possible spill into sink. Protective gear and fume hood decrease the probability and concequence of the incident. CO ₂ is created in reaction between calcium carbonate and hydrochloric acid. Preparation in fume hood minimizes the likelihood.
		Inhalation of fumes from addition of grey mud to vessel containing acid	1	B	-	-	-	B1	
3	Use of the digestion furnace	Exploding vessel due to pressure build up	2	B	B	B	-	B2	A lid with a hole may be used since gas formation (CO ₂) is expected.

 NTNU HSE	Risk assesment	Responsible: Malin Salvesen	Valid to: 22.11.2019	

		High temperature	2	B	-	-	-	B2	Temperatures inside the furnace will reach 60°C, and may cause hot surfaces.
		Hot vessel to be removed after program is finished	2	B	-	-	-	B2	Vessel will be hot during removal. Normal caution is advised, together with the use of gloves to avoid burns or similar injuries.
4	Filtrations of solids from leach solution	Acid spilling when transferring vessel content into filtration equipment	2	B	B	B		B2	Likelihood and consequence minimized by the use of personal protective gear and fume hood.
5	Handling the filtrated solids	Filtrated solids are washed with water, dried and stored.							
6	Sample preparation for the ICP-MS	Acidic spilling when transferring leach solution to sample container	2	B	B	B	-	B2	Unlikely that large spills will occur due to the amounts used. Additionally, a fume hood and protective gear is used to limit consequences and likelihood of damage.
7	Disposal of waste	No waste is exposed of due to residue being stored for possible further tests and liquid solutions being sent to analysis. Only washing performed after experiments produce waste that can appropriately be disposed of in the sink.							
8	Washing of equipment	Cut due to breaking glass equipment	2	B	-	B	-	B2	Caution should be used so that glass equipment is not dropped or otherwise broken.

Final evaluation: Base don the risk assessment it is clear that the main hazards are connected to the participant performing the experiments and not a dangerous nature of the experiments itself. It is therefore important that the participant is vigilant during the performance of the experiments and are familiar and conscious of the possible hazards presented in this overview.