

Extraction of Ca(OH)₂ from industrial by-products for the use in a passive-DAC system for negative emissions

Master's thesis in Innovative Sustainable Energy Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Passive DAC system constructed in Word, showing the principle of using $\text{Ca}(\text{OH})_2$ to capture CO_2

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Abstract

Industrial alkaline by-products, originating from the steel and mining industry are produced in large amounts in Sweden and globally. These materials may contain significant fractions of MgO and CaO, in addition to other elements, e.g. Fe, Al, and Si. In a recently proposed passive-DAC system, hydrated CaO ($\text{Ca}(\text{OH})_2$) can be utilized to capture CO_2 from the atmosphere leading to negative emissions. In this work an experimental study on the $\text{Ca}(\text{OH})_2$ extraction from steel converter slag (LD-Slag), blast furnace slag and mine tailings is conducted due to a high CaO content of 32-43% in these materials.

An experimental set-up is proposed in which a chemical solvent extracts the Ca-ions from the by-products followed by a two-stage pH adjustment to separate impurities and precipitate the final slaked lime. Two different solvents, HCl and NH_4Cl , are compared in their extraction behavior for the three different industrial waste products. A preliminary literature study provided knowledge about the parameters and methods used in this study. Liquid filtrates and solid residues were analyzed using ICP-OES and XRD respectively to obtain data for the different ion and phase compositions.

It was found that HCl extracted calcium more effectively compared to NH_4Cl . However, the HCl solvent did not selectively extract calcium which results in the additional leaching of impurities, such as iron, magnesium, aluminum and vanadium. The pH-swing separated the non-desired ions but also led to a loss of calcium for the HCl case. Therefore only 71-83% of the extracted calcium could be used to produce $\text{Ca}(\text{OH})_2$ compared to 90-100% for the NH_4Cl case.

The total yield of slaked lime was more substantial for the HCl case in all three by-products. However, the results for NH_4Cl are competitive for the mine tailing and blast furnace slag, which makes this solvent interesting with respect to its high selectivity and no impurity leaching. In all cases a pure $\text{Ca}(\text{OH})_2$ was obtained which validates the method. The results indicate that impurities are effectively separated and could provide an additional value if utilized as a side stream. Further research should address the regeneration of the extraction chemicals to enhance the economical feasibility of the process. In addition the utilization of the slaked lime in the passive-DAC system would require continuing investigation of the necessary properties.

Keywords: passive-DAC, industrial alkaline by-products, LD-Slag , Blast furnace slag, Mine tailings, Calcium extraction, $\text{Ca}(\text{OH})_2$ precipitation

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Lastly, I want to thank my girlfriend for joining me here in Sweden and being very supportive in all situations.

Julian Scheer, Gothenburg, July 2022

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
DAC	Direct Air Capture
HCl	Hydrochloric acid
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
IEA	International Energy Agency
LOD	Limit of Detection
MC	Mineral Carbonation
NaOH	Sodium hydroxide
NH ₄ Cl	Ammonium chloride
NH ₄ OH	Ammonium hydroxide
PCC	Precipitated Calcium Carbonate
(P)-XRD	(Powder)-X-Ray Diffraction
Slag2PCC	Process in which slag products are utilized to produce PCC

Nomenclature

Below the nomenclature of terms and symbols that have been used throughout this thesis are listed:

Terms

Extractant	Chemical used to extract calcium from the waste materials
Filtrate	The liquid obtained after filtration
Filter cake	The material which is retained by the filter
Leachate	Solution containing dissolved ions
Residue	The solids making up the filter cake
Solvent	Chemical used to extract calcium from the waste materials

Symbols

r^2	Coefficient of determination
K_{sp}	Solubility Product
D_f	Dilution factor
ΔH_R	Reaction Enthalpy [$\frac{kJ}{mol}$]
M	Molarity [$\frac{mol}{l}$]



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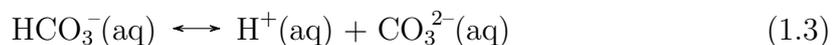
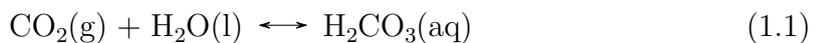
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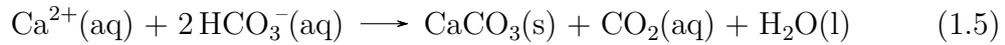
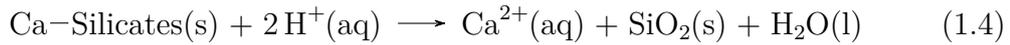
Introduction

In future scenarios the goal of many countries is to reach net zero carbon dioxide emissions by 2050 which contributes to limiting the average global temperature increase to 1,5°C [5]. A significant contribution to this target can be provided by a transition to a clean energy system supported by negative emission technologies which counter-balance the residual emissions still present in a net-zero emission scenario [6]. In many 1,5°C scenarios, CCS- and negative emission technologies are required amongst which direct air capture (DAC) systems are predicted to be scaled-up in the future [7]. More specifically in the "Net Zero Emissions by 2050" scenario from the IEA, DAC technologies are predicted to have already a capacity of capturing 85 MtCO₂/year by 2030 [8]. A novel passive-DAC approach, proposed by Abanades et al., could contribute to the needed solutions for negative emission technologies by using slaked lime and the concept of passive carbonation [1].

1.1 Direct air capture (DAC) through passive carbonation

In nature, passive carbonation occurs in the form of chemical weathering of silica rocks. It describes the reaction of CO₂ and H₂O, forming soluble carbonic acid (H₂CO₃)(Reaction 1.1). In equilibrium reactions protons (H⁺) are released by the deprotonation of carbonic acid to form the intermediate bicarbonate ion (HCO₃⁻) and the carbonate ion (CO₃²⁻)(Reaction 1.2 & 1.3) [9]. The calcium ions from naturally occurring Ca-Silicate minerals are extracted by the protons into the soil and water systems (Reaction 1.4). The natural occurring carbonation reaction (1.5) which fixes the CO₂ in a stable mineral form is presented by Ca-ions reacting with HCO₃⁻. Due to the very alkaline pH values required for CO₃²⁻ being stable ([10] & [11]) it is not dominant educt in the weathering process. Hereby, CO₂ is released resulting in a total aqueous carbonation reaction (1.6) in which one mole of carbon dioxide is bound by one mole of Ca-Silicates ([11] & [12]).





Bringing forth a passively occurring process with no additional energy input indicates a suitable carbon capture solution. However, the drawback of natural chemical weathering is the time it takes for the carbonation to occur. For this reason, Mineral Carbonation (MC) is introduced in research as an enhanced and accelerated method of the weathering process [13].

An important aspect of MC is the source material which should contain Ca- or Mg-oxides. Both have a great affinity to selectively capture CO_2 ([1]). These metal oxides are naturally present in silicates such as olivine, orthopyroxene, clinopyroxene, serpentine and wollastonite ([13] & [14]). Besides the application of MC in geological underground (in situ) formations of such silicates, research has also focused on above-ground (ex situ) MC. Here, such reactive Ca- or Mg-oxides would be extracted and in a further step the carbonation can occur in a solid/gas or aqueous/gas system [13].

When applying this multi-step procedure of calcium extraction followed by the carbonation, the concept is referred to as indirect mineral carbonation ([13]). Here the Ca-ions are first dissolved from the source material with help of a solvent and in a further step the CO_2 is chemically bound. The latter stage precipitates out calcium carbonates (PCC) which can be used as a carbon storage or as a product in the cement industry. Many studies have worked on such a PCC production process ([15],[16],[17],[18] and [19]). However, a big drawback of this concept is the necessity of a high concentrated CO_2 stream. Although many mining, heat and power, steel-making and cement industry sites provide such a point source for post combustion carbon capture, the metal-oxide source and the CO_2 stream are not always at the same location and would require additional transportation.

To be more independent from a high concentrated CO_2 stream direct air capture (DAC) provides a suitable alternative carbon capture solution [20]. Therefore, Abanades et al. ([1]), proposes a passive-DAC system as an alternative CO_2 sequestration method. It intends to avoid the high energy penalties of state-of-the-art DAC-systems while additionally no high concentrated CO_2 stream is required. In active DAC systems large volumes of air are forced through a liquid or solid sorbent. To regenerate the sorbent, heat is applied to release the CO_2 . The energy penalty related to such DAC systems, would not be needed in a passive-DAC system.

In the proposal, CO_2 from the air is captured by exposing porous structures of $\text{Ca}(\text{OH})_2$ to ambient air. The porous precipitate would selectively capture carbon dioxide from the air in a faster rate than the naturally occurring weathering process.

In addition calcium hydroxide is mechanically stable to be pelletized and shows favorable carbonation kinetics compared to non-hydrated CaO ([1],[21],[22]).

The great advantage of this approach would be the local production of $\text{Ca}(\text{OH})_2$ from by-products and the local manufacturing of structures to passively capture CO_2 [1]. This could be highly applicable for instance in the mining industry, with a significant number of mines in remote locations, but with production of large quantities of Ca-rich by-products. The concept is illustrated in Figure 1.1:

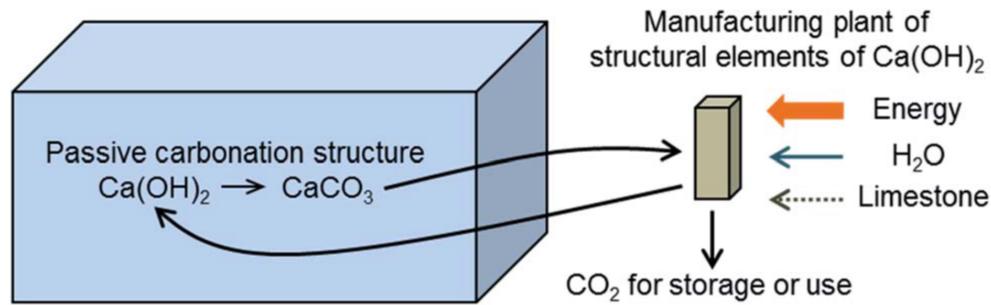


Figure 1.1: Passive carbonation structure [1]

In the system natural limestone or carbonated sorbent provide the calcium source. The low cost of both materials is promoted by the authors [1]. An oxy-fueler regenerates CaO from the source material followed by a separation of pure CO_2 and hydration of the metal oxide to form $\text{Ca}(\text{OH})_2$.

The utilization of natural limestone, demanding additional mining, is rated critically in this work. The great availability of calcium bearing by-products from the industry, motivate a different choice of source material. In addition, an energy intensive calcination process is not favored in this work, hence pursuing an alternative, chemical extraction of calcium which will be discussed in detail in the following section.

Overall, the extraction of a low cost product like CaO can be an economical challenge. It is likely that such a process is not cost competitive due to the extensive use of extraction chemicals. However, it is the utilization of industrial waste by-products which can contribute to circularity of resources as such materials could contain many other components which could be of value to recycle.

Ca^{2+} -ions would be dissolved in a comparable procedure to the PCC approach mentioned above. Moreover, to produce the desired $\text{Ca}(\text{OH})_2$ to be used in the passive-DAC system a further neutralization stage would be needed to precipitate out a solid product. In a further step the calcium hydroxide can be processed, comparable to Figure 1.1, to follow a dry and passive carbonation if exposed to the ambient air [23].

1.2 Calcium Extraction

The precipitation of $\text{Ca}(\text{OH})_2$ requires the prior calcium extraction from the provided alkaline waste materials. Such calcium extraction has been broadly studied ([24],[18],[19],[25] and [14]) with respect to sequestering CO_2 in a following carbonation process to produce PCC. Much less research has been done with respect to precipitation of Ca- or $\text{Mg}(\text{OH})_2$.

Different parameters influence the chemical kinetics of the calcium extraction which were closely investigated to select appropriate conditions. To increase the economic value of the extraction process its efficiency and selectivity is most important [26]. Hereby, the particle size, temperature, choice of solvent and its concentration, the solid to liquid ratio (SLR) and agitation play a major role according to Said et al. ([27]). On the other hand Mattila et al. argues that the freshness of the slag, the SLR and the solvent concentration is of great importance while reaction temperature does not have a great effect on the calcium extraction [18]. In this study the focus was put on a low energy consumption which motivated the reaction temperature to be at ambient conditions. Although agitation showed a great benefit [27] however, it was not used in this study, to reduce the complexity of the experimental set-up.

Choice of Extraction Agent:

In the literature many extraction agents were applied at various concentrations. However, the most common and popular ones are Ammonium chloride (NH_4Cl) and other ammonium salts ([19],[28],[17]), Hydrochloric acid (HCl) ([26],[25],[29]) and Acetic acid (CH_3COOH) ([15],[24],[25]) which were used in many studies. Lee et al. found that the application of Acetic acid led to a low filtration rate [26] while Crom et al. experienced filter clogging due to silica deposits [15]. Kodama et al. argued that Acetic acid would result in a pH of 5,32 after the extraction of calcium from $2\text{CaO}\cdot\text{SiO}_2$ (Larnite), a phase often present in slag products. This pH level would also extract other ions such as magnesium and manganese [25] which is not in favour of a high calcium selectivity. HCl was viewed as an extractant which also extracts additional impurities such as iron and silica at room temperature [29] however, it was favored by Lee et al. due to its higher calcium extraction efficiency [26]. The very commonly used calcium solvent NH_4Cl is stated to be very selective regarding its calcium extraction with values up to 99,6% [25]. The solvent performs great in combination with a PCC carbonation process due to the alkaline environment after the extraction. In case of HCl additional NaOH would be needed to create a comparable environment after extraction [17].

Concentration and SLR:

Other parameters linked to the extraction agent would be its concentration and the SLR. It was found that for 2M NH_4Cl the calcium extraction is limited when utilizing a SLR of 60 g/L or 120 g/L [30]. In addition, Said et al. stated that a 2M concentration of NH_4Cl would lead to the additional extraction of other elements

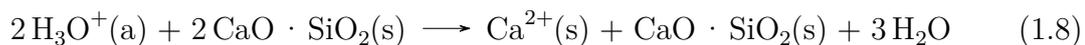
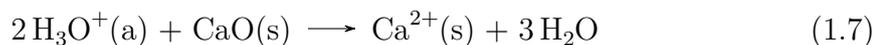
such as iron and manganese [31]. In case of the demand for high purity in the PCC this would not be beneficial. A reduction in SLR or increasing solvent molarity would solve the stoichiometric limitations. Therefore, lower SLR at a given concentration provide the highest extraction efficiencies [30]. Despite that, many studies still apply a SLR of 100 g/L which can be explained by the large reactor volume which is needed in case of lower SLR values ([19],[17],[31],[18]).

Solvent regeneration:

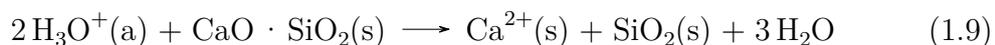
The performance of a chemical extraction and precipitation demands large amounts of chemicals per tCO₂ captured [32]. These solvents therefore represent a significant economical factor and the regeneration or recycling abilities of such would add an influential factor in the choice of the solvent. For the recycling of HCl and NaOH, electrolysis could be an option according to Teir et al. [32] who investigated the carbon fixation by producing hydromagnesite from serpentinite. In a Slag2PCC process proposed by Said et al. [31] the NH₄Cl solution could be recovered after the carbonation stage. This led to the recycling of the solvent in the extraction stage making the method economically feasible.

Stoichiometric extraction:

The Ca-extraction from alkaline waste materials, applying such solvents, only occurs for certain calcium bearing complexes. In the case of steelmaking slags Mattila et al. mentioned that the dissolution of calcium occurs according to the following reactions [18]:



Based on reactions 1.7 & 1.8 and the known CaO concentrations of the slag material one can calculate the stoichiometric amount of slag needed to be fully dissolved at a given concentration of a solvent. However, Owais et al could achieve a higher yield than expected from these reactions and added a third reaction 1.9 which dissolves calcium from calcium silicate ([28],[30]):



Knowing that e.g., 1 mol NH₄Cl or HCl produces 1 mol H₃O⁺, the stoichiometric amount of extracted calcium can be calculated.

Particle size:

The last parameter to be mentioned here is the particle size. The smaller it is, the larger the surface area which results in a greater extraction performance. In addition, the calcium content in finer particles is also higher which would benefit the process ([18]). In most studies particle sizes $<250\mu m$ were used and only really fine particle sizes could be achieved by additional milling.

1.3 $\text{Ca}(\text{OH})_2$ precipitation

As described in the previous section many studies extracted calcium in order to produce high purity PCC. However, the missing link between the novel passive-DAC proposal in the beginning of the introduction and the effective calcium dissolution from alkaline by-products is the $\text{Ca}(\text{OH})_2$ precipitation.

In all studies that have been investigated on this topic pH regulation was used to exceed the solubility of calcium. Um et al. showed that at 25°C a high alkaline condition is needed to precipitate out calcium hydroxide from CaCl_2 in $\text{NaOH-H}_2\text{O}$ solutions while increasing the reaction temperature could lower the required pH level [2]. Figure 1.2 presents the findings of the author's study. The experimental results and the chemical modelling follow the same trend which indicates that an increase in reaction temperature (25°C - 90°C) enables precipitation of $\text{Ca}(\text{OH})_2$ at lower pH values. As can be seen, the required pH for the precipitate to occur at 25°C is 12,5. NaOH was used as a control variable to reach the desired condition after the calcium dissolution. The same base has been used by Lee et al. in his study on a pure $\text{Ca}(\text{OH})_2$ precipitate for carbonation purposes using 2M HCl as an extractant. The optimal condition was $\text{pH}=13$ at room temperature [26]. The same author also focused on the separation of impurities which got leached out in the calcium extraction process. In his pH swing method an intermediate condition of $\text{pH}=9,52$ was effectively removing less soluble complexes like $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ by adding ammonium hydroxide (NH_4OH). A high Ca yield of 99,9% after the removal of impurities and a pure portlandite precipitate was the result of his study.

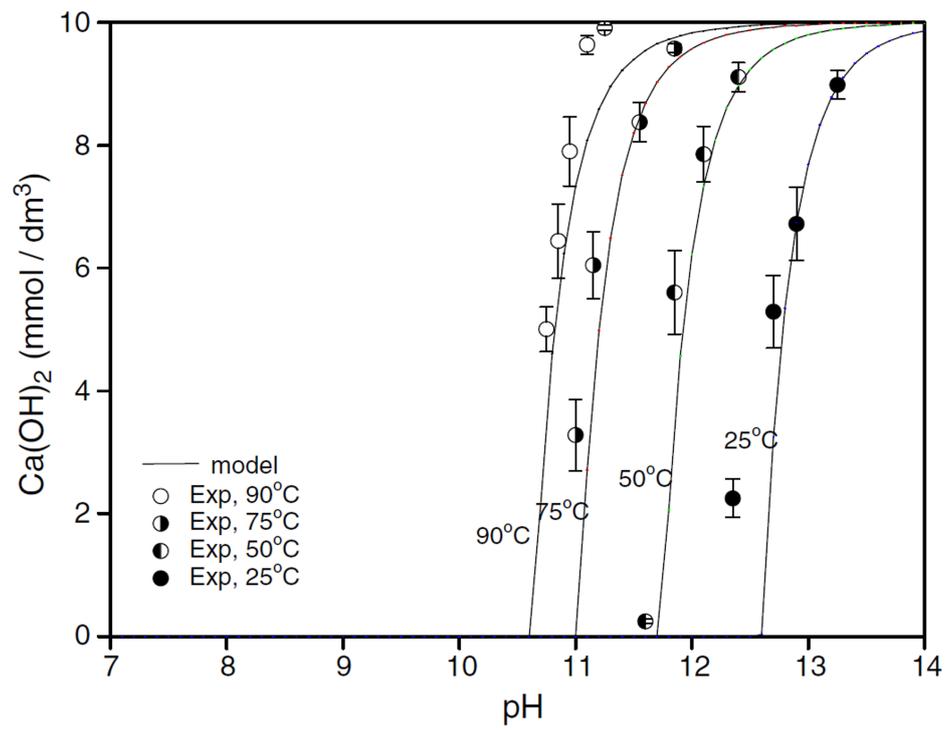


Figure 1.2: Effect of reaction temperature on precipitation behavior of Ca(OH)_2 studied by Um et al. [2]

2

Objective/Motivation

A novel DAC process was introduced which utilizes precipitated $\text{Ca}(\text{OH})_2$ which can result in negative CO_2 emissions. Alkaline waste materials could provide the calcium source for that. Although source materials such as calcium carbonate are cost-competitive today, the utilization of by-product streams from the mining- and steelmaking industry would create a value for the CO_2 intensive industries. Further, as there are many other impurities in such materials, such as Fe, Al, Si, and V, an optimized process may be able to also provide pathways for utilization of "rest" streams with high concentrations of these elements. From the studied literature a process for calcium extraction and $\text{Ca}(\text{OH})_2$ precipitation is proposed by applying two different extractant agents (HCl and NH_4Cl) using three different by-products from the mining- and steelmaking-industry. The validity of the process is investigated by focusing on the following three objectives:

- The assessment of the leaching and precipitation behavior of $\text{Ca}(\text{OH})_2$ between the investigated materials, applying selected methods
- The influence of the material composition on the impurities in the residues
- A pure quality of the precipitated portlandite ($\text{Ca}(\text{OH})_2$)

2. Objective/Motivation

3

Materials & Methods

3.1 Limitations

The provided alkaline waste materials are enriched in calcium bearing phases, while magnesium and its precipitates were not put into focus. Still, it should be noted that Mg could also be utilized for carbonation, as the MgCO_3 is a stable product at ambient conditions. The proposed experimental method is therefore optimized to precipitate $\text{Ca}(\text{OH})_2$. To assess the calcium extraction efficiency, conversion and total precipitate yield a total material digestion provides quantitative data to be the reference for further mass balances. In this study the reference is given by the leached ion concentration after the extraction.

3.2 Analysis methods

3.2.1 XRD analysis

The original samples, residual filter cakes and precipitates were analyzed using Powder-X-Ray Diffraction (XRD). The dried residual slags and precipitates provided a poly crystalline structure suitable for PXRD. The instrument used in this work is the D8 Discover Bruker. As an X-Ray source it is using a copper source in the setup of 40 V / 40 mA. The X-ray source as well as the detector are motorized, and the sample holder is stationary. This configuration is referred to as "theta-theta" and the geometry in which the source and the detector operate is Bragg Brentano. In the experiments, the same sample holder was employed, and no rotation was used. The motorized scattering knife was operated at an automated distance to the sample. This device prevents instrument background and air-scattering to occur by being lowered from the top towards the sample. The detector (Eiger2) was used in 2D mode while the angle coverage was 10-90 degrees, screening at an angle stepsize of 0,02 (two theta degrees, 2Θ)

3.2.2 ICP-OES - ion composition

The assessment of the ion composition in the filtrate was done using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). The method allows to analyze aqueous samples by exciting the ions in a plasma. Each chemical element has a characteristic wavelength which can then be detected. To determine the final concentration a calibration curve for each element is needed. The ions of interest

in this study are aluminum, magnesium, silicon, iron, manganese, vanadium, and chromium. A standard solution containing each element in a known concentration of 0, 5, 10, 50 and 100ppm was used to create the calibration curve. The filtrate samples taken after each filtration step in the experimental procedure (stage 1-3) were diluted to match a comparable concentration which would be in the range (0-100ppm) of the calibration curve. As a diluent 0,5M HNO_3 and 0,5M HCl (spiked with Yttrium) was used. The dilution is dependent on the highest ion concentration in the filtrates, being calcium. However, due to a missing total composition of the industrial by-products the calcium concentration could only be estimated by given values from literature and the suppliers. These values lead to a first estimate of diluting each sample 5000 times to reach a comparable concentration of 0-100ppm. In a second conduction of measurements a dilution of 500 was used to compare the results and detect ions which were below the limit of detection (LOD) in the first findings.

3.2.3 Medusa-Validation of solubility of impurities

XRD peaks and ICP-OES measurements analyze the results of the two experimental methods. To support the findings of impurity precipitation the software Medusa (Make Equilibrium Diagrams Using Sophisticated Algorithms) is used. It can add certainty whether precipitates of previous dissolved impurities occurred at given conditions or not. Based on the known solubility products (K_{sp}) at 25°C, the hydronium and hydroxide ions the software can calculate which species of a given ion concentration are dominant at a certain pH. If a solid precipitate is the dominant species at the pH level of stage 2 and matches the identified precipitate from the measurements it would add reliability to the results. As the second stage is aiming for an alkaline environment at pH=9.52 the concentration of hydroxide ions influences the precipitation.

In the software a chemical system is created by first adding the ions of interest while hydronium ions are included by default. In a next step the concentration of the added ions is determined and taken from the ICP-OES measurements. In a log[Conc.]-pH diagram the equilibrium calculations show the dominant species for the range of pH values 1-13. In the discussion chapter such diagrams are shown (Figure 5.1-5.4) and discussed regarding the outcome of the experiments.

3.2.4 Calculation methods

In this study three different alkaline waste materials of various composition are compared in the leaching behavior and precipitation of $Ca(OH)_2$. The Ca-extraction of the solid sample in an acid solvent is conducted in stage 1. A pH swing method would then allow the fall out of impurities (stage 2) and the final precipitation of portlandite (stage 3). The following calculation methods describe how the data from the ICP-OES got processed in order to present comparable results.

3.2.4.1 Ion concentration in filtrate

In stage 2 & 3 of the experimental procedure the pH environment was adjusted by bases to separate impurities and precipitate $\text{Ca}(\text{OH})_2$. 2M NH_4OH and 1M NaOH elevate the pH to 9,52 and 13 respectively. However, the two solvents being a weak and strong acidic solution extract different ion-species and -amounts from the industrial by-products. Therefore, the pH environment varies between the measurements and varying volumes of chemicals have to be added during stage 2 & 3. It leads to non-similar dilutions which affect the measured ion-concentrations by ICP-OES. A dilution factor has to be introduced to correct the data and allow comparison between them.

This factor expresses the ratio between the final volume after adding the base (V_{final}) and the volume of the filtrate send to the individual stage from the previous one ($V_{\text{previous stage}}$). All further results are then based on these corrected ion concentration values.

$$D_f = \frac{V_{\text{final}}}{V_{\text{previous stage}}} \quad (3.1)$$

The ion-concentration values measured by ICP-OES for stage 2 or 3 are then multiplied with the corresponding D_f to be comparable with the non-diluted ion-concentration in stage 1.

3.2.4.2 Calcium conversion

The proposed experimental method results in the dissolution of calcium ions. In order to compare the extraction and $\text{Ca}(\text{OH})_2$ precipitation performance, the conversion of dissolved calcium ions to actual precipitated portlandite is calculated. It therefore only shows the efficiency of precipitation for the Ca which was extracted and not for the Ca which is totally present in the by-product:

$$\text{Conversion}_{\text{Calcium}} = \frac{C_{\text{Ca,stage2}} - C_{\text{Ca,stage3}}}{C_{\text{Ca,stage1}}} \quad (3.2)$$

The difference in normalized concentrations between stage 2 & 3 represent the amount of portlandite which precipitated out when adding 1M NaOH according to ICP-OES measurements. Comparing this difference to the initial amount of dissolved calcium ions from stage 1 provides the calcium conversion after extraction. It does not consider the original Ca-content in the waste residue due to the fact that only literature and supplier information are available for the total chemical composition of the investigated materials.

3.2.4.3 Ca(OH)₂ precipitation

The ion concentrations obtained from the ICP-OES and the initial filtrate which was collected after the 20 min batch reaction in stage 1 enabled the theoretical calculation of the amount of precipitate (3.3). The concentration values have been corrected with the dilution factor (D_f). The multiplication with the volume of original filtrate in stage 1 ($V_{Filtrate,stage1}$) then results in the total amount of calcium precipitated as Ca(OH)₂. The factor of 1,85 converts the mass of calcium ions to mass of calcium-hydroxide ions. It represents the molar masses of both (Calcium: 40,08 g/mol ; Calcium-hydroxide: 74,08 g/mol).

$$Precipitate_{Ca(OH)_2} = (C_{Ca,stage2} - C_{Ca,stage3}) * V_{Filtrate,stage1} * 1,85 \quad (3.3)$$

These results could then be compared with the amount of precipitate which was measured in the lab. Both values were measured in units of grams.

3.3 Materials and sample-preparation

3.3.1 Three different waste materials

In this project three different industrial by-products have been used:

1. Linz-Donawitz slag (LD-Slag) or steel converter slag is a by-product from the steelmaking process and originates from the Linz-Donawitz process in which the pig iron is treated before being send to the Basic Oxygen Furnace (BOF). In Sweden the annual production of converter slag is estimated to be >300kton/a [3]. The material was provided by SSAB Merox and from studies conducting elemental analysis of the LD-Slag, a total elemental composition could be used and displayed in Table 3.1
2. The second industrial by-product (Petrit T) resembles a slag product produced in the blast furnace. It was provided by the Swedish company Höganäs AB, which produces metal powders for the powder metallurgy industry [33]. During smelting a calcareous by-product, tunnel kiln lime is produced which becomes Petrit T after further process steps. These include the reduction of the carbon content and an increase in its free lime content. Besides calcium and silicon being the main phases it also shows a significant content of iron and aluminum (Table 3.1). The annual production of Petrit T by Höganäs AB is estimated to be 17000-20000 t/a. [4]
3. A third industrial by-product (Tara Mining) was provided by one of the largest zinc mines in the world, operated by the new Boliden AB in Ireland. The underground Tara Mine produces large amount of mine tailings which are comprised of a high calcium and silicon content from the limestone ore body.[34]

These materials were in a fine powders form with a large weight fraction below a particle size of 250 μ m apart from LD-Slag (52,7 wt.%). In Table 3.2 the cumulative

Table 3.1: Elemental composition provided by literature and suppliers for LD-Slag [3], Petrit T [4] and Tara Mining

Material	Ca (wt.%)	Fe (wt.%)	Si (wt.%)	V (wt.%)	Mn (wt.%)	Mg (wt.%)	Al (wt.%)	Cr (wt.%)
LD-Slag	30,7	15,4	4,7	1,5	2,3	5,4	0,8	0,2
Petrit T	26,4	4,9	8,4	-	-	-	4,8	-
Tara Mining	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

weight fraction for each investigated material is shown. A particle size distribution of $90-250\mu\text{m}$ was chosen for the extraction experiments so that a significant fraction of the sample was used while a large surface area was ensured. Previous studies worked with $< 90\mu\text{m}$ LD-Slag samples while in other studies the use of particles $< 250\mu\text{m}$ also showed good extraction behaviors ([18] and [16]). It can be generally expected that small particle sizes would have a more rapid and more effective dissolution rate. To validate that statement, the effect of particle size is investigated on the LD-Slag sample using NH_4Cl as the solvent. The same experimental procedure is conducted with a particle size distribution of $0-90\mu\text{m}$ and the outcomes between both particle ranges is compared in the results chapter.

Table 3.2: Cumulative wt.% of sieved samples

	LD-Slag	Tara Mining	Petrit T
μm	cumulative wt.%		
<1180	100	100	99,4
<710	100	100	98,4
<500	100	100	97,2
<250	52,7	90,3	82
<150	15,7	28,7	57,7
<90	2,3	5	40

3.4 Experimental setup

3.4.1 Stage 1: Calcium extraction

In this study two well-known calcium extraction agents have been applied. Hydrochloric Acid (HCl) and Ammonium-chloride (NH_4Cl). The reason for HCl is its higher known calcium extraction performance compared to NH_4Cl . Although NH_4Cl is expected to extract less calcium for the same given concentration it was found that the solvent could be reused when producing PCC [31] and that less impurities will be dissolved [19]. HCl showed the best calcium selectivity at concentrations of 2M or higher [26]. To compare the two solvent the same concentration of 2 mol/L was used for HCl and NH_4Cl .

Furthermore, extraction time and SLR had to be defined. 100g/L was in the range of many studies [26] and was adopted in this study. The extraction time was chosen to be 20min which was relatively short compared to other studies but due to the choice of particle sizes $< 250\mu\text{m}$ the extraction time was agreed to be sufficient. As mentioned in the introduction this study is striving to find an effective $\text{Ca}(\text{OH})_2$

precipitation method which considers also other impurities in the process and which should not be handicapped by a larger energy penalty. Therefore, the whole procedure has been conducted at room temperature and atmospheric pressure.

Once the parameters have been selected 100ml of the solvent and 10g of alkaline waste material in the right size range have been mixed for 20 min in a batch reactor with a magnetic stirrer operating at 800rpm. The pH and temperature values have been monitored at five time-steps, $t=0\text{min}$, 1min, 5min, 10min and 20min. After the extraction the sludge was filtered through a $2\text{-}3\mu\text{m}$ filter using a vacuum pump. 50ml of the filtrate was send to stage 2 while the rest was collected to be analyzed with ICP-OES (Figure 3.1). The residue in the filter cake was dried at $120\text{ }^\circ\text{C}$ for 6h and its moisture loss was monitored. The dried residue could then be analyzed using XRD. Figure 3.1 presents an overview of the three stages which include the extraction of the Ca, the impurity separation and the final product ($\text{Ca}(\text{OH})_2$) precipitation. A more detailed description of each stage is given in Figure 3.1.

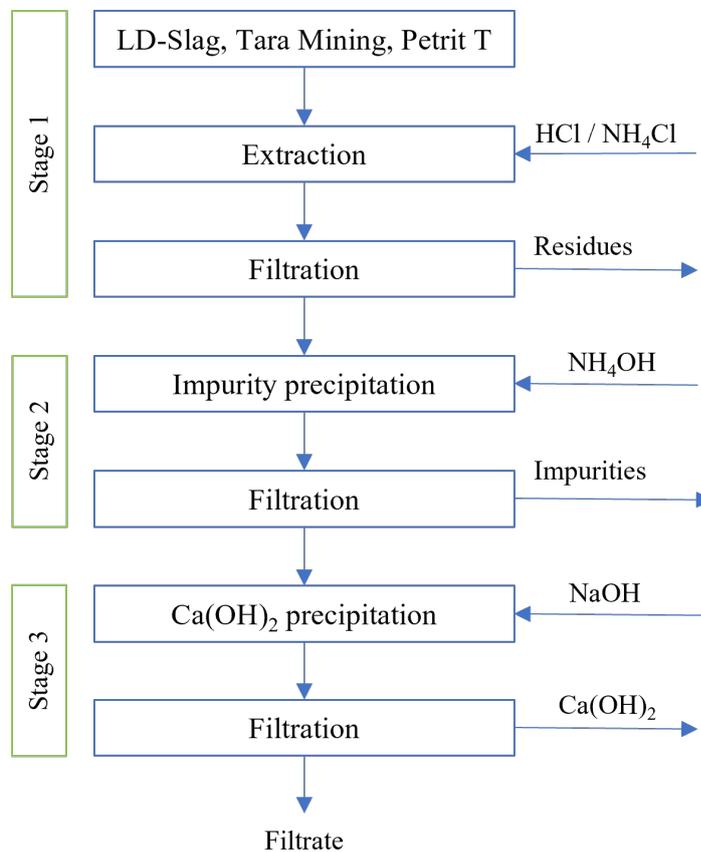


Figure 3.1: Flow diagram of the experimental method used for each alkaline waste material

3.4.2 Stage 2: pH adjustment and precipitation of impurities

In this stage a weak base (2M NH_4OH) is added to the filtrate of stage 1. The same batch reactor setup as in the previous stage has been used. The purpose the pH adjustment is to increase the pH to 9,52 which was determined to be optimal for precipitating out less soluble species which are present in the solution [26]. After reaching the desired pH level the solution was again vacuum filtered with a 2-3 μm filter. If a residue was present it was dried at 120°C for 6h. 50ml of the filtrate were send to stage 3 while the rest was kept for ICP-OES analysis.

3.4.3 Stage 3: Selective precipitation of $\text{Ca}(\text{OH})_2$

In the final stage, a strong acid (1M NaOH) was added to reach a pH=13 in order to precipitate out $\text{Ca}(\text{OH})_2$. The filtration and drying method were the same as in the previous stages. Temperature and pH were monitored in addition to the amount of base added to the filtrate.

4

Results

The chemical composition of the three samples revealed the presence of calcium bearing phases and the following results will use the extracted calcium ions in stage 1 as the reference for evaluation. This chapter describes the results achieved for the different parameters which were adjusted and investigated in the project.

4.1 Chemical composition

The chemical composition of the alkaline materials was assessed by the analyses of XRD scans. In Figure 4.1 the three original material scans are presented. The peaks for Petrit T and Tara Mining are very distinct whereas the LD-Slag sample appears to be more heterogeneous.

The mine tailings from the Tara Mine show a significant content of Limestone and Dolomite (7). These two complexes are likely to come from the rock which the ore was embedded in.

In the blast furnace slag (Petrit T) the calcium is present in free lime and Ca-Al-silicates. As in the case of the mine tailings, SiO_2 is also one of the dominating phases in the diffractogram. These results match the provided elemental composition from the supplier (Table 3.1).

The heterogeneous LD-Slag contains most detectable peaks amongst the three industrial by-products. Most calcium is present in Limestone (3), Larnite (4), and slaked lime (8) while Iron oxide (6) also matches the peaks. Therefore, Ca- and Fe-bearing phases are most significant which is in agreement with the elemental composition from Table 3.1 in which both elements are expected to have the highest weight percentage.

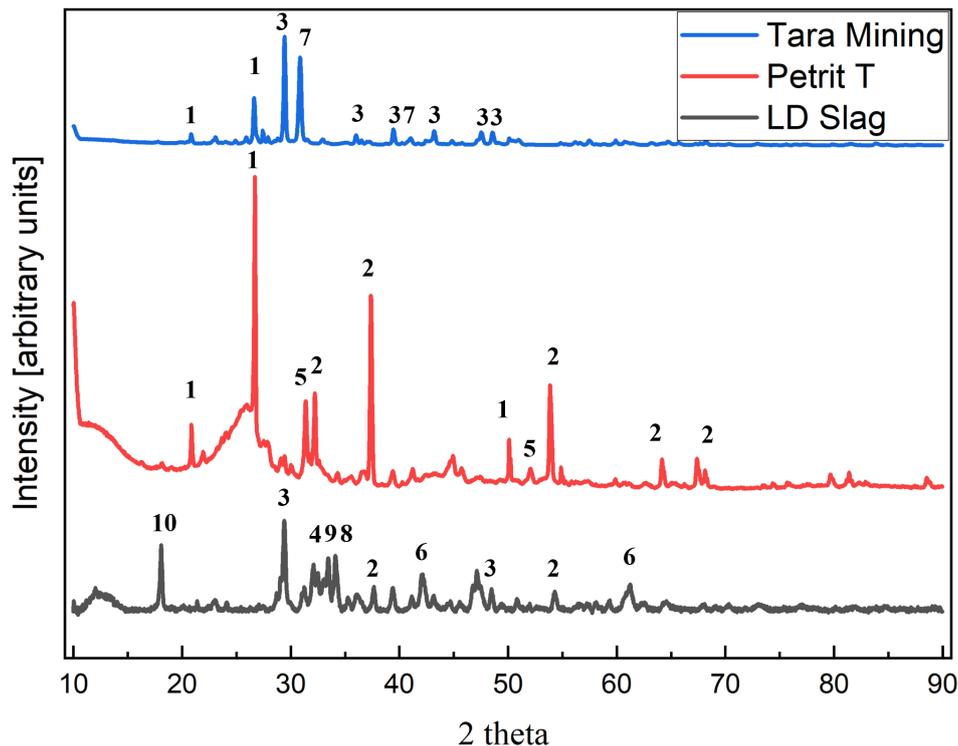


Figure 4.1: chemical composition of the provided waste materials as determined from X-ray powder diffraction analysis: SiO_2 (1), CaO (2), $CaCO_3$ (3), Ca_2SiO_4 (4), $Ca_2Al_2SiO_7$ (5), FeO (6), C_2CaMgO_6 (7), $Ca(OH)_2$ (8), $Ca_2Fe_{1,66}O_5V_{0,34}$ (9), $Al_7Ca_6O_{16,498}$ (10)

4.2 Effect of solvent (NH_4Cl vs. HCl)

This section describes the influence of the different solvents on the experimental outcome. Depending on which extraction agent has been used, the pH of the filtrate varied from 0,08-1,31 (HCl) and 7,3-9,52 (NH_4Cl) for the different waste materials. Thus, the amount of added base in stage 2 differed between the different samples.

4.2.1 Dissolved calcium

As already explained in the previous chapter two samples containing calcite had to undergo calcination to represent the fresh state. Then a comparison in calcium extraction for both solvents was possible. The results of the calcined samples was used for further evaluation of the Portlandite precipitation. Therefore, the calcium conversion from Stage 1 to the final Stage 3 has to be determined. Following the calcium concentrations evolving over the stages of the experiment showed similar trends. In Figure 4.2 the calcium concentrations are given for each stage and each method. Due to the absence of residues in stage 2 for the NH_4Cl method the concentration-values for stage 1 & 2 are very similar. Only the non-calcined LD-Slag sample shows a great difference in these stages. In both methods all the calcium from stage 2 is precipitating due to the very alkaline conditions (pH 13). The HCl method shows

greater calcium concentration differences between stage 1 & 2 which could relate with the precipitation of residues during the latter stage. These residues contain calcium bearing phases which would explain the reduction in calcium concentration.

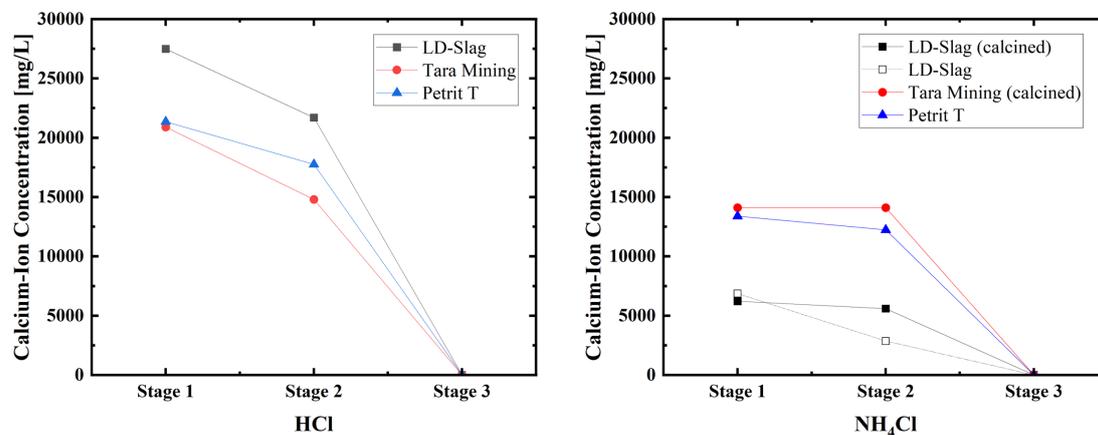


Figure 4.2: Calcium concentrations evolving over the three stages for solvent HCl (left) and NH₄Cl (right)

4.2.2 Calcination

In Figure 4.2 the ICP-OES results of the extracted Ca concentrations are presented. The method applying NH₄Cl as a solvent showed different results depending upon if the material was calcined or not. The reason for calcining LD-Slag and Tara-Mining was its limited Ca extraction and the presence of calcite (CaCO₃) in the original sample (Figure 4.1,A.4 and A.6). Only other phases like free lime, portlandite or larnite could be dissolved by NH₄Cl which limited the extraction compared to the HCl solvent, as shown in Figure 4.3(left).

In case of the Tara Mining material the limestone (CaCO₃), which makes up a large weight fraction of the material (Table 3.1), is likely to originate from the rock material which gets extracted and processed together with the ore.

However, for the LD-Slag material the limestone content can be related to the freshness of the material. When the by-product originates from the steelmaking process it contains free lime, slaked lime or lime silicates, but no limestone due to the high temperatures (1600-1650°C) being present in the furnace [35]. Being stored on a pile usually exposes the material to natural carbonation processes with CO₂ in the air, which would result in calcium carbonate in the outer layer of the pile. To restore the state in which there will be free lime or slaked lime present, the samples had to be calcined. Due to no detectable Ca extraction from the Tara Mining material using NH₄Cl, the material was also calcined to see the potential of available calcium oxide.

4. Results

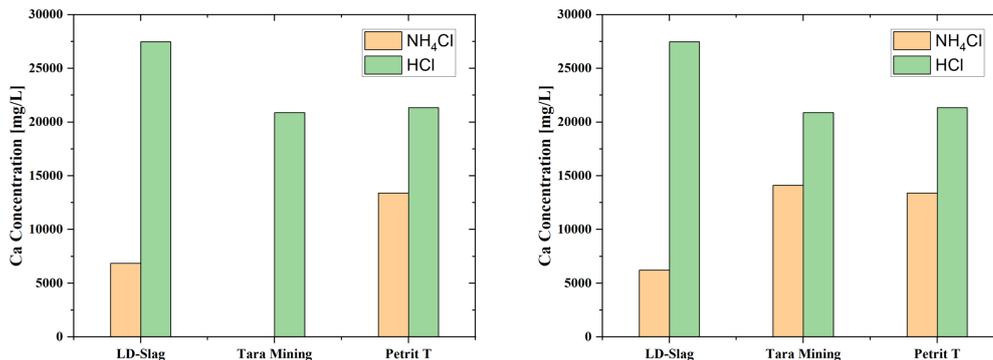


Figure 4.3: Dissolved Ca-ion concentrations for both solvents. Results of non-calcined (left) and calcined (right) materials

After the calcination, which was conducted at 950°C for 5h, the Ca extraction increased for the calcined Tara Mining but showed slightly worse results for the calcined LD-Slag sample (Figure 4.3(right)). The reaction is highly endothermic ($\Delta H_R = +168,5 kJ/mol$) and can be described the following [36]:



According to the previous equation no calcite should be present in the calcined Tara Mining material and the presence of CaO should result in a higher calcium extraction for the NH₄Cl solvent. After the extraction the solid residues contained insignificant amounts of calcite according to the XRD measurements (Figure A.6) while calcium being only present in more complex minerals such as Gehlenite. In addition, instead of the Mg-bearing mineral dolomite the residues of the calcined Tara Mining sample contained MgO which indicates that dolomite has also been affected by the calcination. It could lead to a false assessment of impurities in the further stages. Therefore, it was important to apply the results from the calcined Tara Mining material only on the calcium extraction performance. The assessment of impurity extraction and separation was conducted on the data obtained from the non calcined samples in which minerals such as dolomite have not been affected.

After dissolving the calcined LD-sample in ammonium chloride and extracting the calcium the solid residue was composed of similar phases as the non-calcined sample apart from limestone. A more detailed composition of the calcined and non-calcined samples and residues are listed in the appendix (Figure A.3-A.6).

In case of the Petrit T sample only free lime (CaO) was present from the beginning which allowed for a relative high extraction value using NH₄Cl and did not require calcination.

The results show that calcining the materials only had an effect on the Ca-extraction using NH_4Cl as a solvent. The method using HCl did not encounter any issues dissolving CaCO_3 and therefore calcining the materials did not show a great effect on the extraction performance.

4.2.3 Calcium conversion

This section provides the results about how much calcium got converted into final $\text{Ca}(\text{OH})_2$ precipitate. As the chemical composition of the three industrial by-products was only presented from literature values and suppliers' information the exact ion composition for the investigated samples was not available. The conversion rate is defined in Equation 3.2 and relates to the amount of calcium extracted in stage 1.

Table 4.1: Calcium conversion of both methods

	LD-Slag [%]	Tara Mining [%]	Petrit T [%]
2M HCl	79	71	83
2M NH_4Cl	90 (calcined)	100 (calcined)	91

In Table 4.1 a clear difference in conversion between the two methods is visible. Although a higher concentration of calcium ions was dissolved with the 2M HCl (Figure 4.2) the conversion is lower compared to the NH_4Cl method. This matches the observation from the results of dissolved calcium in the beginning of this chapter, in which the ion concentration decreased for the HCl method in stage 2. This loss of calcium being present in the filtrate prohibited a high conversion rate whereas between 90-100% of the dissolved calcium in the NH_4Cl experiments was converted and precipitated according to ICP-OES measurements.

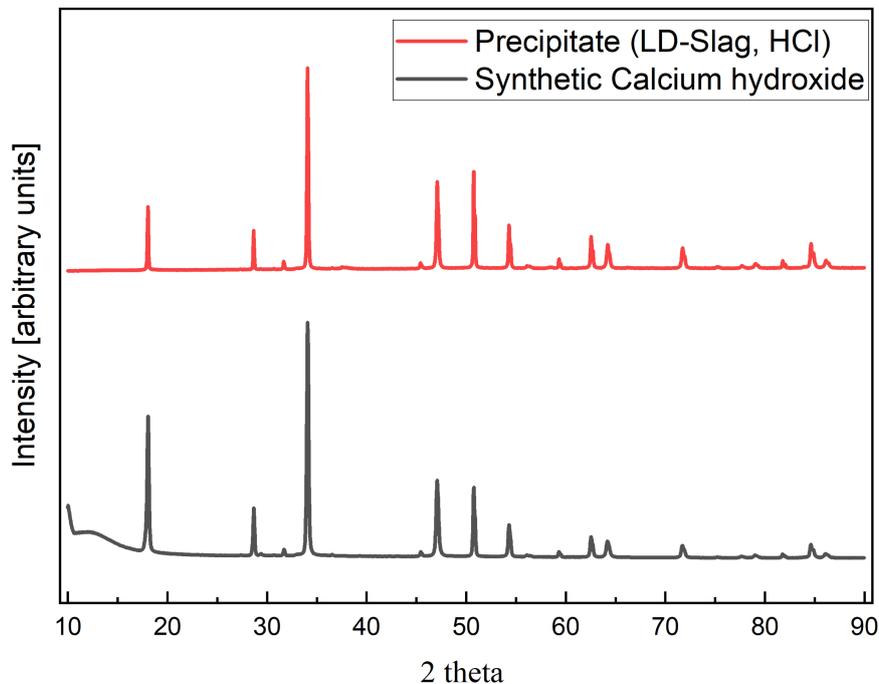
In Table 4.2 the total calcium extraction for both solvents is presented. It is derived from the stage 1 values in Figure 4.2 and the known volumes of filtrates. To determine a total chain efficiency of the process based on the available amount of calcium in the materials it is assumed that HCl extracted all available calcium from the samples, resulting in a extraction efficiency of 100%. Therefore, the total chain efficiency for the HCl method equals the calcium conversion rate from Table 4.1. Based on the previous assumption the extraction efficiency for NH_4Cl is determined by the relation of extracted calcium from NH_4Cl and HCl . Both the extraction efficiency and calcium conversion (Table 4.1) from the NH_4Cl method would result in the total chain efficiency which is now based on total available calcium. It is visible that a higher total chain efficiency can be obtained with the HCl method (71-83%) compared to the NH_4Cl method (34-64%). In the next section the amount of precipitate will be compared between the two methods.

Table 4.2: Total chain efficiency (based on ICP-OES measurements) assuming that HCl dissolves all available calcium

		LD-Slag (calcined)	Tara Mining (calcined)	Petrit T
Total extracted calcium (HCl, stage 1)	[g]	1,6	2,0	2,0
Extraction efficiency HCl (assumed)	[%]	100		
Total chain efficiency HCl (extraction eff. * calcium conversion)	[%]	79	71	83
Total extracted calcium (NH ₄ Cl, stage 1)	[g]	0,6	1,3	1,3
Extraction efficiency NH ₄ Cl	[%]	37	64	61
Total chain efficiency NH ₄ Cl (extraction eff. * calcium conversion)	[%]	34	64	56

4.2.4 Ca(OH)₂ precipitation

Adding 1M NaOH to raise the pH to 13 created an alkaline environment in which calcium hydroxide precipitates out [2]. The precipitate was analyzed by XRD. In all six cases regardless of the extraction agent, the identified peaks of the precipitate match very well with Ca(OH)₂ from the database. An example of the final precipitate of extracting calcium with HCl from LD-Slag can be seen in Figure 4.4. Therefore, a comparable purity can be assumed due to a minimum of deviating peaks.

**Figure 4.4:** XRD diffractogram of precipitate after stage 3 (LD-Slag, HCl case) (red) in comparison with synthetic calcium hydroxide (black)

In Figure 4.5 the difference between the theoretical and gravimetric measurements can be seen. The latter measurements have been conducted in the lab after the precipitate was separated from the supernatant liquid after stage 3. Before scaling, it was dried at 120°C for 6h. The theoretical results are based on equation 3.3 in which the measured concentrations from ICP-OES are corrected and multiplied with the initial volume of filtrate after extraction.

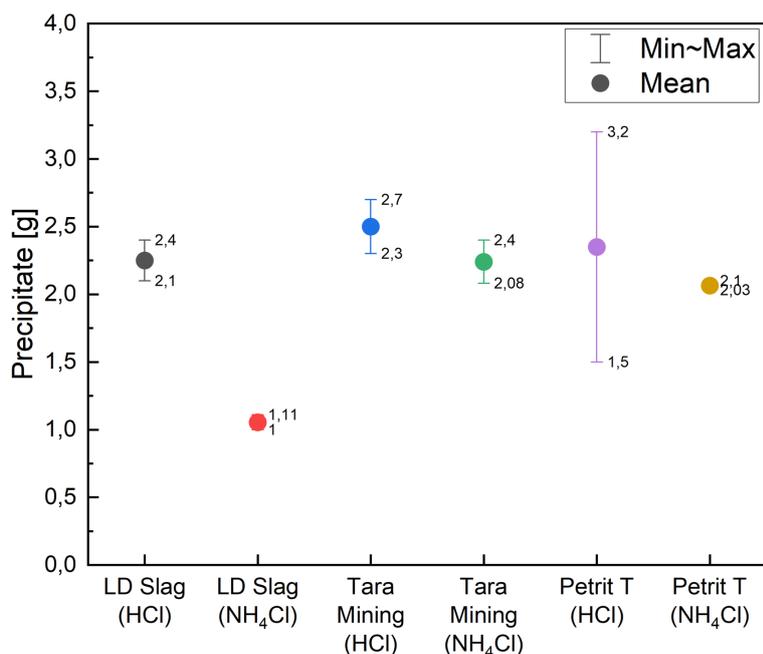


Figure 4.5: Difference in gravimetric and calculated values for the amount of the precipitate

Apart from the data points for LD-Slag (NH₄Cl) the ICP-OES values are always greater compared to the measurements in the lab. The biggest deviation was found for the Petrit T (HCl) sample with a difference of 100% compared to the lab measurements. The other deviations showed a range from 3,4%-17% compared to the lower values. Although the calcium conversion, as defined in equation 3.2, was lower for the HCl method, a greater total chain efficiency (Table 4.2) resulted in an increased yield of precipitate for the LD-Slag and the Tara Mining sample. For the Petrit T results (HCl) the measurements in the lab showed that less precipitate was found compared to the NH₄Cl method although the ICP-OES measurements would state the opposite. The biggest difference between the results of the two solvents can be seen for LD-Slag. The calcined material showed a weak extraction performance of 23% (Table 4.2) which matches the final low amount of precipitate when being extracted with NH₄Cl. The amount of precipitated Ca(OH)₂ from LD-Slag (HCl method) resulted in more than double the amount compared to the other solvent which correlates with the total efficiencies from Table 4.2.

4.2.5 Leached Ions

Different leaching properties of the methods could already be seen in the previous chapters regarding calcium. A great Ca selectivity would be desired to maximize the extraction efficiency while preventing other impurities from the heterogeneous materials to be present in the filtrate, too. Therefore, the filtrates have been analyzed regarding seven further ions: aluminum, magnesium, silicon, iron, manganese, vanadium and chromium. The results are shown in Figure 4.6.

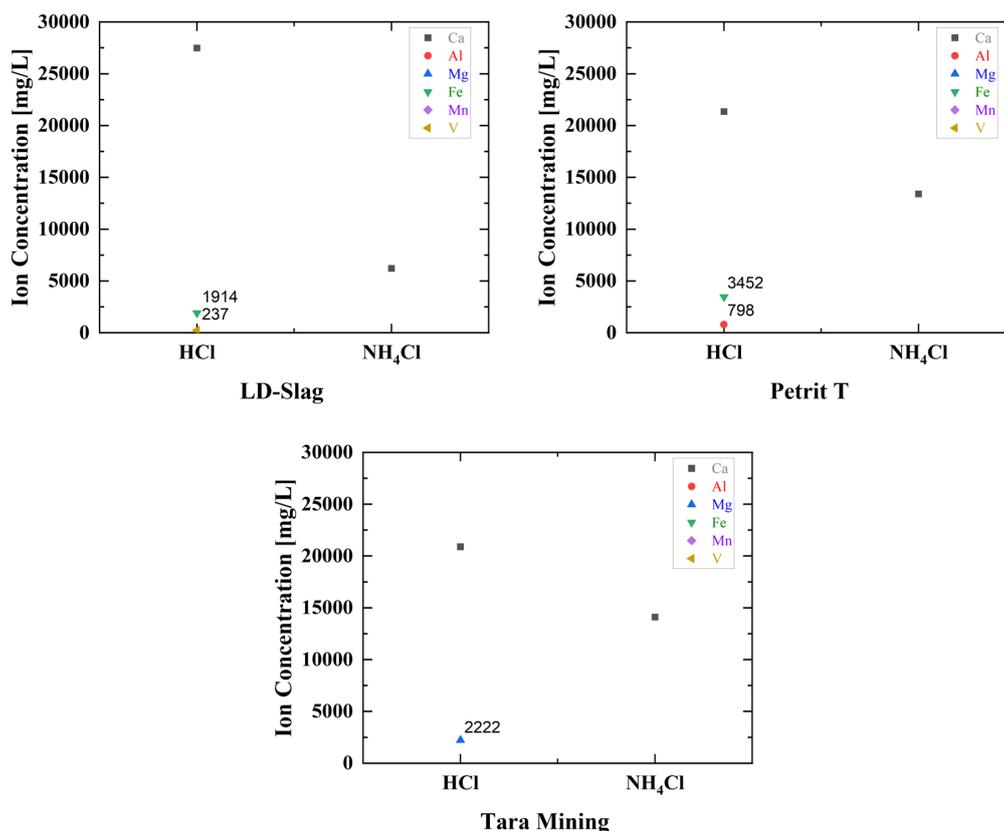


Figure 4.6: Additional ion extraction for the three industrial by-products for both solvents

Both solvents performed a very selective calcium extraction. The ICP-OES measurements did not detect any other ion concentrations besides calcium for the method using NH₄Cl. For the other solvent impurities were measured but kept below a concentration of 3500ppm. Amongst the other ions no silicon and chromium was detected and only the HCl method for LD-Slag extracted vanadium (237ppm) which agrees with the LD-Slag composition shown in Table 3.1. Iron (1914ppm) as one of the dominating elements in LD-Slag was also detected in the filtrate after stage 1. As being rich in Mg-bearing phases the only ion extracted from the Tara Mining sample was magnesium (2222ppm). For the Petrit T sample aluminum (798ppm) and iron (3452ppm) was additionally extracted from the material. In the next sec-

tion these results are further be related to the individual material composition.

4.3 Effect of material composition

In this study three very different alkaline waste materials have been studied. The effect of the phase composition, measured with XRD, of each sample is presented in this section.

4.3.1 LD-Slag

Amongst the three industrial by-products LD-Slag represents the most heterogeneous material with respect to present phases in the solid material (Figure 4.1). The method using NH_4Cl very selectively extracted calcium according to the ICP-OES results (Figure 4.6). Therefore, all detected phases in the original sample apart from CaO , $\text{Ca}(\text{OH})_2$ and $\text{Al}_7\text{Ca}_6\text{O}_{16.45}$ still remained in the residues after the extraction. Although the aluminum bearing mineral phase appeared to be dissolved, Al was not detected in the filtrate after extraction in stage 1.

The method using HCl as an extractant revealed concentrations of iron and vanadium in the leachate after 20min mixing. In the second stage the increase in the pH up to 9.52 should precipitate out less soluble species like $\text{Fe}(\text{OH})_2$ (Figure 5.1). The dried filter cake of the residue in stage 2 was analyzed using XRD and amongst other phases Fe_2O_3 and SiV_3 was detected. This finding is in accordance with iron and vanadium not being detectable after the impurity separation in stage 2 which concluded precipitation. All other ions apart from Ca and Fe were below the Limit of Detection (LOD) throughout all three stages. This contradicts the results in the XRD diffractogram of the precipitated impurities in stage 2. It showed that magnesium and aluminum bearing phases are present in the same intensity as of Fe_2O_3 (Figure A.9) and should therefore be also detectable by ICP-OES in the filtrate after stage 1 (Figure 4.6). In total the impurity precipitate also containing calcium bearing phases made up 3,09g per 50ml of filtrate from stage 1 according to gravimetric measurements. Although 100ml of solvent was used for the extraction only 60ml could be obtained after filtration due to clogging of the filter which resulted in wasting some filtrate. If it is assumed that the full 100ml of liquid is recovered, 6,18g impurities would have been separated which corresponds to 61,8% of total solids (10g).

4.3.2 Petrit T

The blast furnace slag is less heterogeneous compared to LD-Slag but has a characteristic presence of aluminum and iron compared to the other samples. In the leachate of the NH_4Cl extraction all other ions apart from calcium were below the LOD. The qualitative analysis of the XRD measurements also stated that only calcium was dissolved while other phases were still present in the residue after extraction.

Only HCl extracted also iron and aluminum which resulted in a detectable concentration in the filtrate. A light green color of the filtrate is indicating $Fe(OH)_2$ being present. Both impurities were below LOD after stage 2 which is in accordance with the aluminum and iron-bearing phases in the precipitate. Similar to the LD-Slag sample Fe_2O_3 was detected by XRD while for the aluminum bearing phase complex minerals or AlO were found. The precipitate appears to be mixture of dark red and brown crystalline structures which could indicate iron oxide and aluminum oxide (Al_2O_3). After drying the precipitate, it made up 1,51g per 50ml of filtrate from stage 1 which corresponds to 30,2% of total material used for extraction.

4.3.3 Tara Mining

The mine tailings show a characteristic high calcium and magnesium content. The NH_4Cl method extracted calcium very selectively without magnesium being detected in the leachate. No impurities precipitated in the second stage which is the same case for all three industrial by-products being mixed with this solvent.

The HCl method however, leached out a noticeable concentration of magnesium in the filtrate. A precipitate was formed when increasing the pH to 9.52. It resembles a dark brown crystalline structure which does not indicate $Mg(OH)_2$ as expected in Figure 5.4 which states the precipitation behaviour of $Mg(OH)_2$ in a simplified system. The solid impurities could not be analysed by XRD due to its moisture content even after being dried at 120°C for 6h. This would indicate a hydrophilic nature of the solid. Compared to LD-Slag and Petrit T the precipitate only made up 0,11g per 50ml filtrate from stage 1 which makes up 2,2% of the total material used.

4.4 Effect of particle size

In the literature, leaching properties were studied on different particle size distributions which showed that smaller particles allow a higher extraction performance. In this study a size distribution of 90 – 250 μm was chosen to represent a large fraction of the material provided by the suppliers, but also create a large surface area. Hereby it was seen from the previous sections that the HCl method extracted more calcium while the second solvent performed less effectively, especially for the LD-Slag sample.

To test the effect of finer particle sizes on the leaching and precipitation performance one additional experimental set-up was done for the LD-Slag sample using the NH_4Cl -method. More fines were included in the resulting particle distribution of 0 – 90 μm . In Figure 4.7 the diffractograms of the original, uncalcined LD-Slag sample (black), the residues of the old particle distribution (red) and the new particle distribution (blue) is shown.

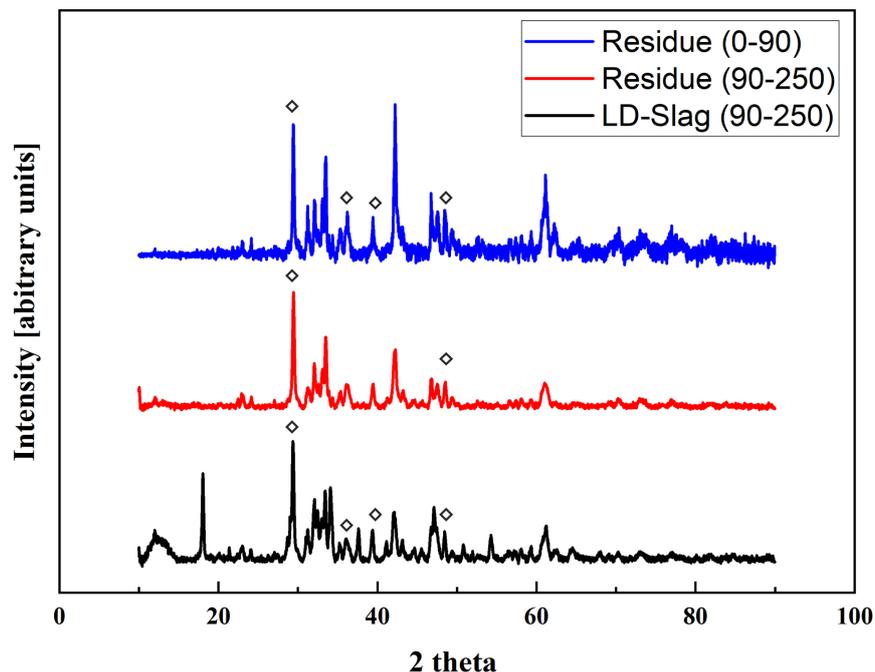


Figure 4.7: Diffractograms of original LD-Slag sample (black) and residues after stage 1 for the 0 – 90 μm (blue) and 90 – 250 μm (red) distribution applying 2M NH_4Cl . Characteristic calcite peaks marked with \diamond

It is visible that the same phases got detected from the XRD regardless of the particle distribution. In both cases the results refer to the non-calcined samples which contain a large fraction of calcite (\diamond) which does not dissolve and is found in the residues of both samples (Figure 4.7). In Table 4.3 the final precipitate of both grain size distributions was measured and calculated accordingly. It can be clearly stated that a distribution of 0 – 90 μm enabled a greater extraction performance and thus a greater amount of precipitate. For the non-calcined sample and the size distribution of 90 – 250 μm the precipitate was 54% (ICP) and 26% (Lab) less compared to the results of the calcined sample in Figure 4.5. However, the range of 0 – 90 μm obtained better results compared to the calcined samples of 90 – 250 μm . A difference between the ICP-OES measurements and the measurements from the lab can be seen in both cases with similar deviations.

Table 4.3: Effect of particle size distribution on $\text{Ca}(\text{OH})_2$ precipitate yield (after stage 3) for non-calcined LD-Slag

	Extractant	Precipitate (ICP) [g]	Precipitate (Lab) [g]
LD-Slag (90-250 μm)	2M NH_4Cl	0,52	0,74
LD-Slag (0-90 μm)	2M NH_4Cl	1,48	1,13

5

Discussion & Limitations

5.1 Stage 1: Calcium extraction

The proposed methods both selectively extracted calcium from the alkaline waste materials. Assessing the calcined samples of LD-slag and Tara Mining it was observed that while HCl extracts more calcium compared to NH_4Cl it also leached out other ions. However, focusing on the extraction performance of the two methods, the HCl extractant would be the favored solvent. This part of the study has already been conducted in many different studies as mentioned in the background chapter. The results in stage 1 followed the expected trends of other studies and therefore more focus is put on the discussion of the pH-swing method and the resulting $\text{Ca}(\text{OH})_2$ precipitation which hasn't been studied to a great extent yet.

5.2 Stage 2: Ion separation with a pH swing method

The second stage showed that impurities being extracted by the HCl solvent would effectively precipitate out. The ICP-OES measurements and XRD peak analysis matched in detecting complexes of aluminum, iron, and magnesium in the respective probes. Based on equilibrium modeling done with Medusa, a change in pH can lead to certain complexes to be dominant. In Figures 5.1, 5.2 and 5.4 all investigated ions are dominant at acidic pH. Different soluble and insoluble complexes would be formed when increasing the pH. Based on the K_{sp} at 25°C of the solid complexes ($\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$) the software predicts the pH environment in which they exceed solubility and precipitate out. Initially all filtrates from stage 1 using the HCl method started at a pH between 0,08-1,31. In all three Figures 5.1, 5.2 and 5.4 the dissolved ions (Fe^{2+} , Al^{3+} , and Mg^{2+}) are the dominant species respectively. The software has also been used to predict the solubility for vanadium species and is shown in the appendix (Figure A.2). It also indicates the same behavior for stage 2 in which the pH environment would precipitate out a solid phase of VO. The concentrations of the impurities used in these diagrams are taken from the results of the ICP-OES measurements in Figure 4.6 and converted from mg/L to mM (mmol/l).

Reaching the pH of 9,52 in stage 2 the model shows that for all investigated impurities the dominant species would be a solid (s) or crystalline solid (cr) complex which precipitates out (Figure 5.1-5.4). However, the diagrams resemble a very simple environment at 25°C without any other ions or solid phases being present. Hence, based on these diagrams the expected separation of impurities can just be seen as

an indication for what will actually happen.

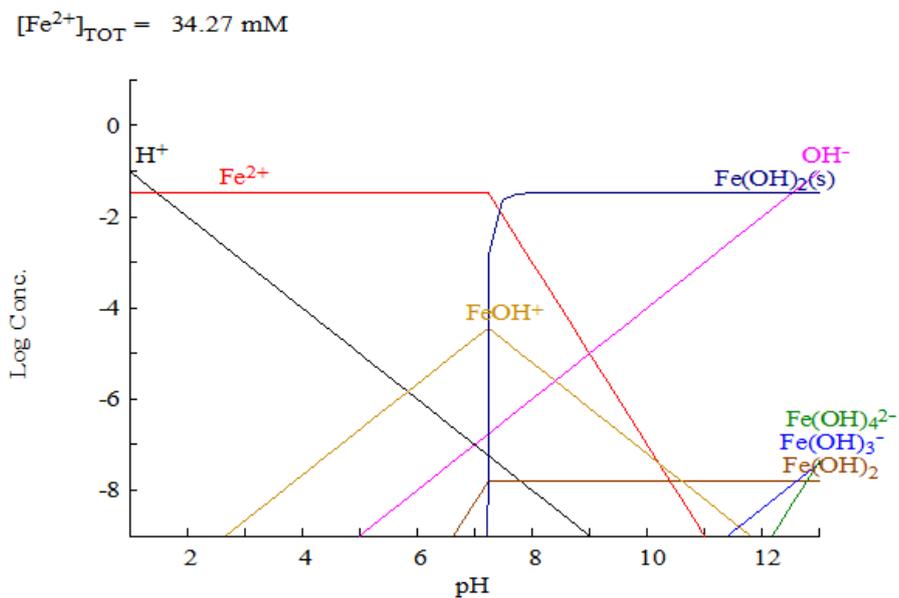


Figure 5.1: Dominant Fe-species in Log(Conc)-pH diagram

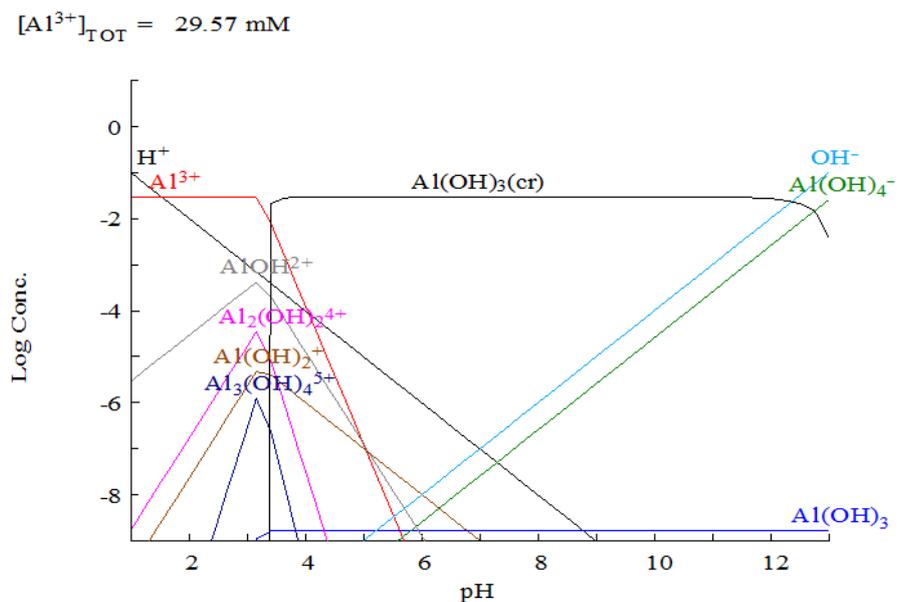


Figure 5.2: Dominant Al-species in Log(Conc)-pH diagram

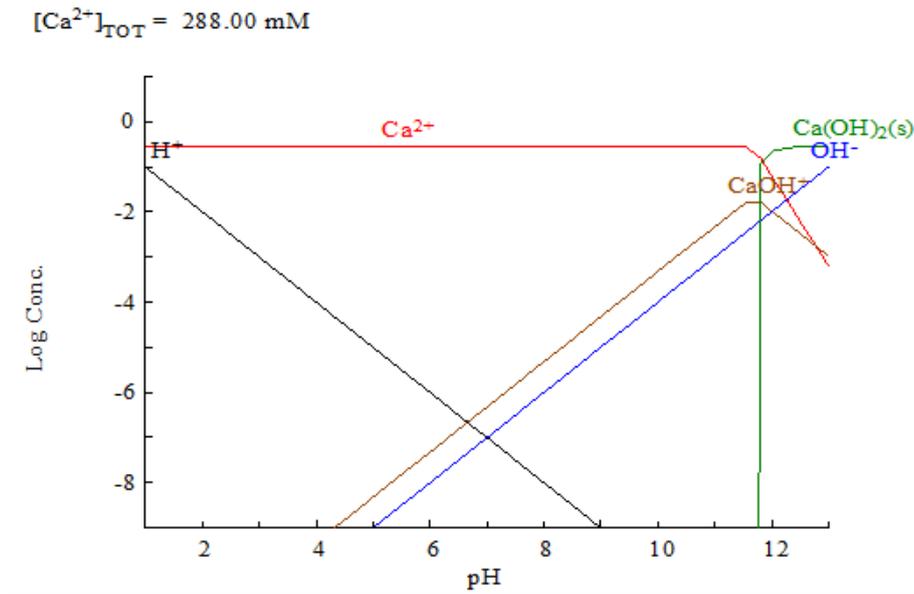


Figure 5.3: Dominant Ca-species in Log(Conc)-pH diagram

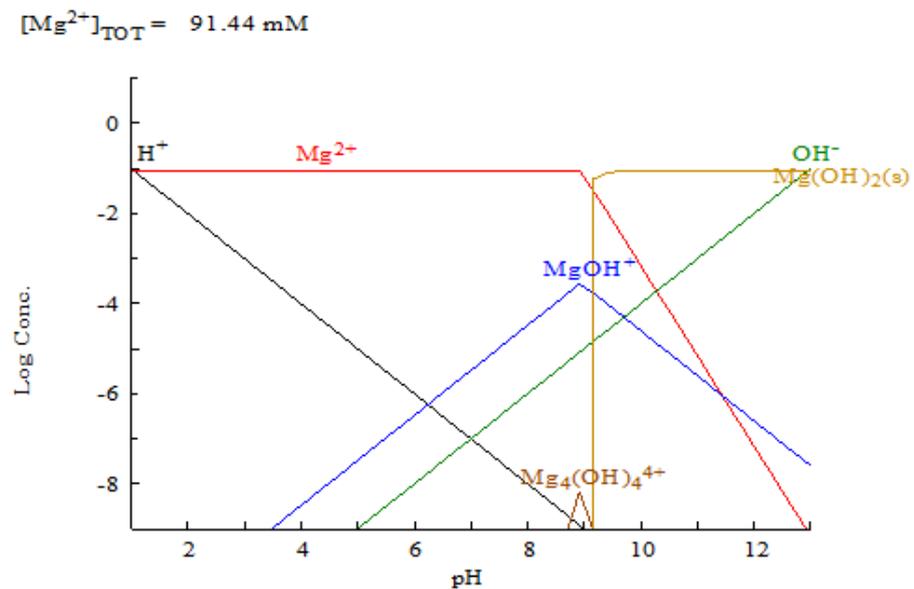


Figure 5.4: Dominant Mg-species in Log(Conc)-pH diagram

As an example, the ICP-OES measurements presented a loss in calcium for the HCl measurements between stage 1 & 2. Ca-bearing phases were also found in the precipitated impurities which contradicts the modelled trends in Figure 5.3 expecting a solid Ca(OH)_2 to precipitate out at very alkaline pH and not during stage 2. Therefore, other ions and potential filter errors can influence the separation of impurities by pH variation and don't strictly follow the modelled predictions. This observation is also supported by the findings of the NH_4Cl method which did not show any impu-

rity extraction and simultaneously there was no significant calcium loss (Figure 4.2).

This difference in the two methods is crucial when assessing the overall calcium conversion of the two methods. Although the total extraction of calcium ions is greater for the HCl extractant, the calcium conversion is lower in all three samples compared to the NH₄Cl extractant (Table 4.1). This would also indicate that the second stage would not be needed in case of the NH₄Cl method which could simplify the experimental procedure and save chemicals. On the other hand, the precipitated impurities consist of chemical elements such as iron, aluminum and magnesium which could be utilized as a by-product stream and could provide additional value to the process.

5.3 Stage 3: Ca(OH)₂ precipitation

As discussed in the previous chapter, a great difference was observed in the pH-swing for the two solvents. The total amount of precipitate would give an answer to the impact and drawback of the second stage for the method applying HCl. Figure 4.5 presents the amount of Ca(OH)₂ precipitate taken from the measurements of the ICP-OES data and the ones from the lab after drying the precipitate and weighing. The results show that the HCl method would be the favored procedure for LD-Slag and Tara Mining although the difference is only little in the case of the Tara mining sample. In case of Petrit T (HCl) the deviation between the two measured values did not allow a comparison to the case using NH₄Cl.

Overall a pure and high quality precipitate was produced in all cases which contributes to the method proposed by Lee et al. [26] by introducing an additional solvent (NH₄Cl) and testing the procedure on two additional alkaline waste materials which could be of interest for the passive-DAC system proposed here.

5.4 Sample preparation and analysis

5.4.1 sample preparation

A finer particle size distribution does not have an effect on the dissolved phases for the LD-slag sample in case of the method applying the NH₄Cl solvent. It showed a greater precipitation performance compared to the sample with a size fraction of 90-250 μ m. From literature this was observed, too [28]. Although this would encourage to use a finer particle distribution, 0-90 μ m only represent 2,3wt.% of the LD-Slag material provided for this study. The chosen distribution in this study represents 50,4 wt.% of LD-Slag, 85,3 wt.% of Tara Mining and 42 wt.% of the Petrit T sample which can be seen in Table 3.2. This effect of the particle size distribution has only been investigated on the LD-Slag sample using the NH₄Cl method to encounter additional potential of Ca(OH)₂ precipitation using the same solvent. A more detailed analysis regarding the effect of varying particle sizes could optimize the precipitation performance but hasn't been further investigated in this

study.

5.4.2 sample analysis

In this study two methods were used to analyze the results of the experimental method. Due to the presence of solid samples, residues and precipitates the analysis using XRD was favored to give a qualitative estimate of the present phases. The initial composition of the three alkaline waste materials could be assessed with the identification of characteristic peaks. However, quantitative data about the extracted ions was needed to compare the calcium conversion and the additional extraction of other ions. ICP-OES analysis could provide this information by analyzing the filtrates of each stage. It was not possible to conduct a total digestion of the original samples which would have provide the total chemical composition prior to extraction. Therefore, all quantitative results can only be referred to the total amount of extracted ions after the extraction. From literature [26] the composition of LD-Slag was used to prepare the standard solution for the eight chemical elements of interest. These standards were used for all three samples. The high content of calcium in LD-Slag required a great dilution of the probes being send to the ICP-OES instrument. To increase the chance of detecting also the low concentrations of the other ions the probes were diluted 5000 and 500 times.

Calcium ions could be identified very clearly and also followed an expected trend throughout the experimental procedure seen in Figure 4.2. However, due to the large calcium fraction diluting the samples 5000 times did detect magnesium and aluminum in a great extend but at varying trends throughout the three stages. Even increasing concentrations were measured which did not agree with the nature of the experiment in which extracted ions either precipitate out or remain in the filtrate. Errors in the filtration could lead to a bypass of small particles which would later dissolve and increase certain concentrations. To validate these results a second ICP-OES analysis was conducted with a dilution of 500 times which should also lead to the detection of additional chemical elements such as iron, manganese and vanadium.

The outcome of the second measurements showed similar trends for the calcium concentrations of the first measurements (Figure A.11). It also detected Iron in the LD-Slag and Petrit T sample which were treated with HCl which was already presented in Figure 4.6. However, all other detected concentrations from the previous ICP-OES measurements could not be validated by the second data. The calibration curves in both runs presented a coefficient of determination (r^2) between 0.96-1.00 which could not be the source of the mismatching results. It could rather be related due to the relatively large error the measurements have when detecting very low concentrations in the filtrates (first ICP-OES measurements). The probes from stage 2 and 3 are additionally diluted by the bases NH_4OH and NaOH . Therefore, the results of the second run were taken as more reliable for all ion apart from calcium. Due to the time period which passed between the two measurements potential precipitates or small particle could leach out calcium which would explain slightly higher concentrations in three of the six diagrams in Figure A.11.

5.5 General Discussion and Limitations

As mentioned in the background section, the regeneration of the extraction agents would be of great importance. The study by Said et al. concluded that NH_4Cl can be reused up to 10 times in their X2PCC process which also leaches out calcium from LD-slag but instead of a pH-swing method a carbonation step is introduced [31]. It would require additional testing of the filtrate in stage 3 to conclude the same for this study. Theoretically also HCl can be recovered using alkaline electrolysis but it would add an additional energy penalty which is not desired in this procedure [32].

6

Conclusion & Outlook

In this study a possible valorization of alkaline waste materials from the mining and steelmaking industry was proposed by the production of $\text{Ca}(\text{OH})_2$ for the use in a passive-DAC system for atmospheric removal of carbon dioxide. The method took advantage of known calcium extraction agents and a pH-swing method to selectively dissolve calcium and precipitate $\text{Ca}(\text{OH})_2$. The comparison between three waste products and two solvents provided a great overview about the applicability of the method. Further, the three investigated by-products are generated in industries which have substantial direct or indirect CO_2 emissions. Here, a passive-DAC system could be of high interest. According to the targeted objectives of this project the following conclusions could be drawn from the results and discussion:

- Overall, NH_4Cl provided a more selective extraction and a greater calcium conversion of up to 100%, based on the extracted Ca. Applying this solvent also made the intermediate step of raising the pH to 9,52 redundant which would simplify the procedure in the future and additionally saves chemicals used in this stage (NH_4OH). According to the measurements in the lab it also achieved a yield of precipitate comparable to the 2M HCl method, at least for the Tara Mining and Petrit T samples. Assuming that the 2M HCl method dissolved all available calcium, the total chain efficiency of the 2M NH_4Cl method is 34-64% compared to 71-83% for the HCl method.
- Due to precipitating impurities in the pH-swing and a correlated poor calcium conversion of a maximum of 83% (Table 4.1) for the HCl solvent, the final amount of $\text{Ca}(\text{OH})_2$ precipitate only provided much better results for the heterogeneous LD-Slag sample. Therefore, 2M NH_4Cl would be the favored method for Tara Mining and Petrit T based on the complexity of the procedure and the yield of precipitate produced from the waste materials.
Despite the relatively poor calcium conversion of the 2M HCl method, the yield of final precipitate was doubled for the LD-Slag case in comparison to the NH_4Cl method which promotes the HCl extraction solvent.
- A pure precipitate was found in all cases which can be utilized in the introduced DAC system and proves the validity of the method for both solvents and all three waste materials.

It has been shown in this work that the effect of particle size on the extraction performance is significant. Adapting such important extraction parameters like

6. Conclusion & Outlook

SLR, solvent concentrations or particle sizes on a specific method and individual waste materials, could enhance the calcium leaching performance and should be considered in future work.

Reducing the costs related to large amount of extraction solvents needed, the regeneration of such and the additional value of precipitated impurities are important factors which could determine which calcium extractant is more applicable in general.

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Appendix

A.1 Particle size distribution of the three industrial by-products (Sieve curve)

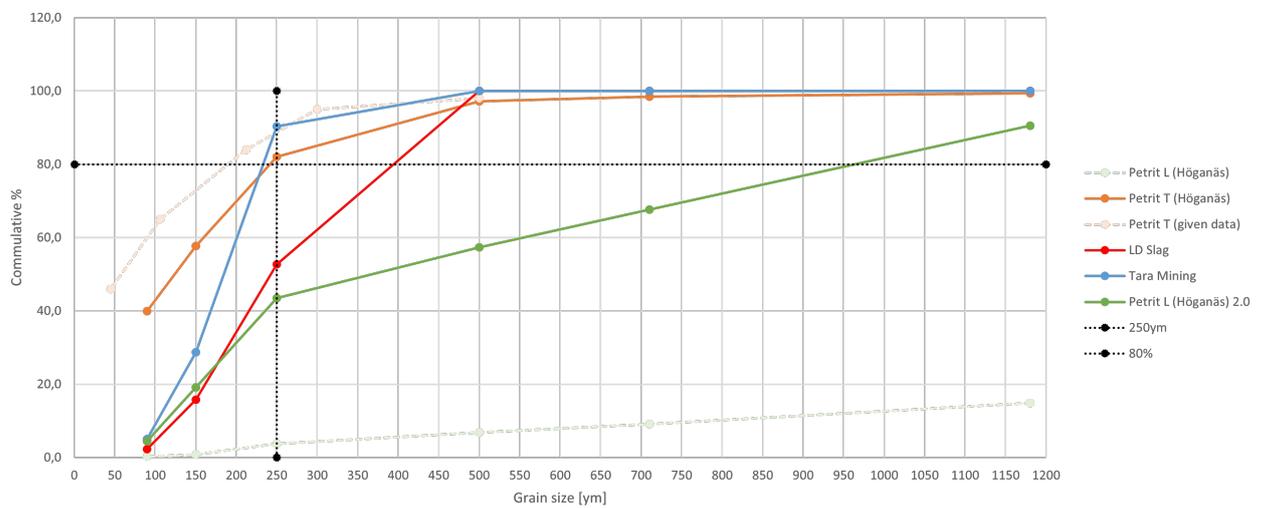


Figure A.1: Particle size distribution of the provided waste materials

A.2 Medusa solubility products used in the calculations

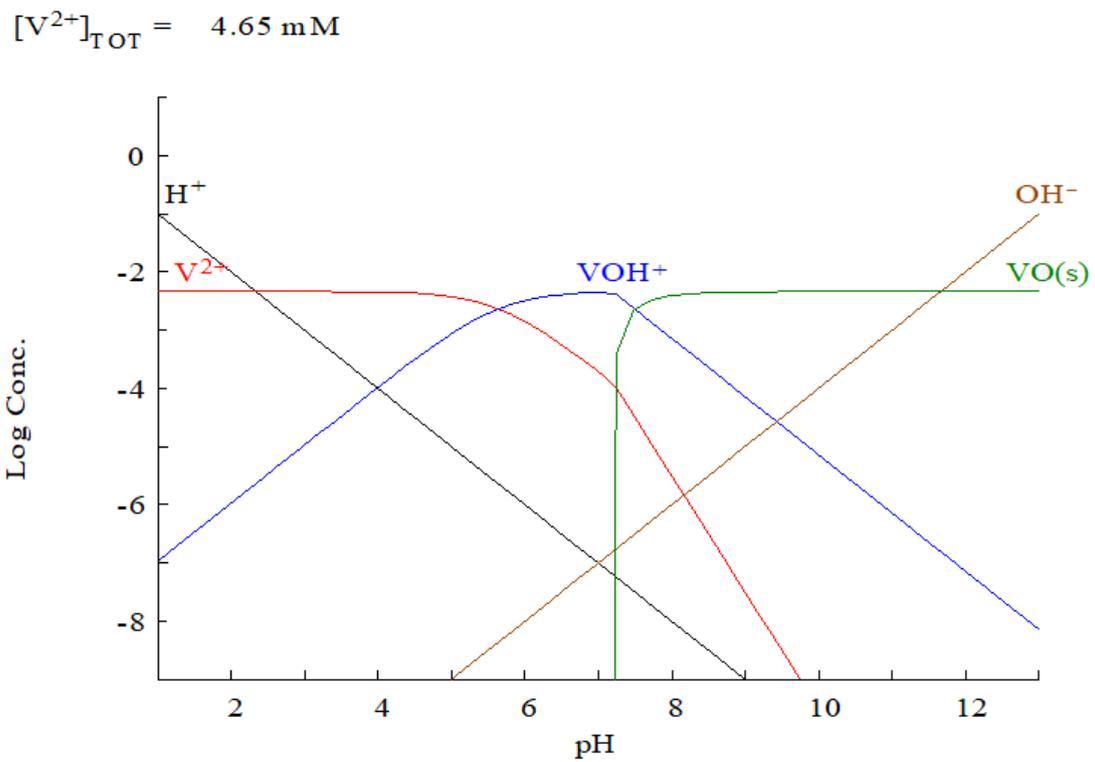


Figure A.2: Dominant V-species in Log(Conc.)-pH diagram

A.3 Calcination of LD-Slag & Tara Mining

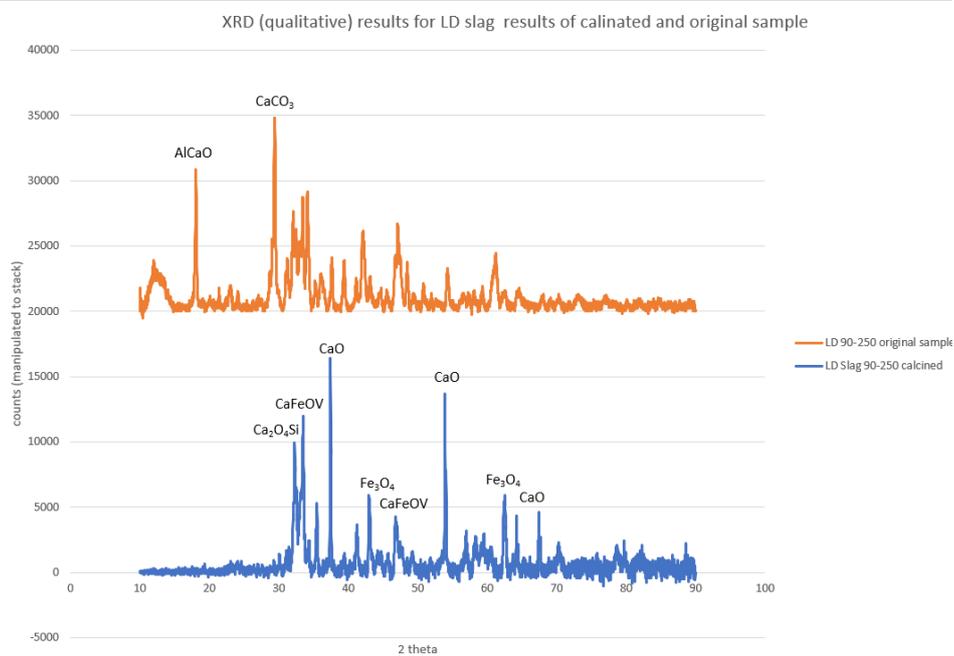


Figure A.3: Comparison of LD slag samples original and calcined

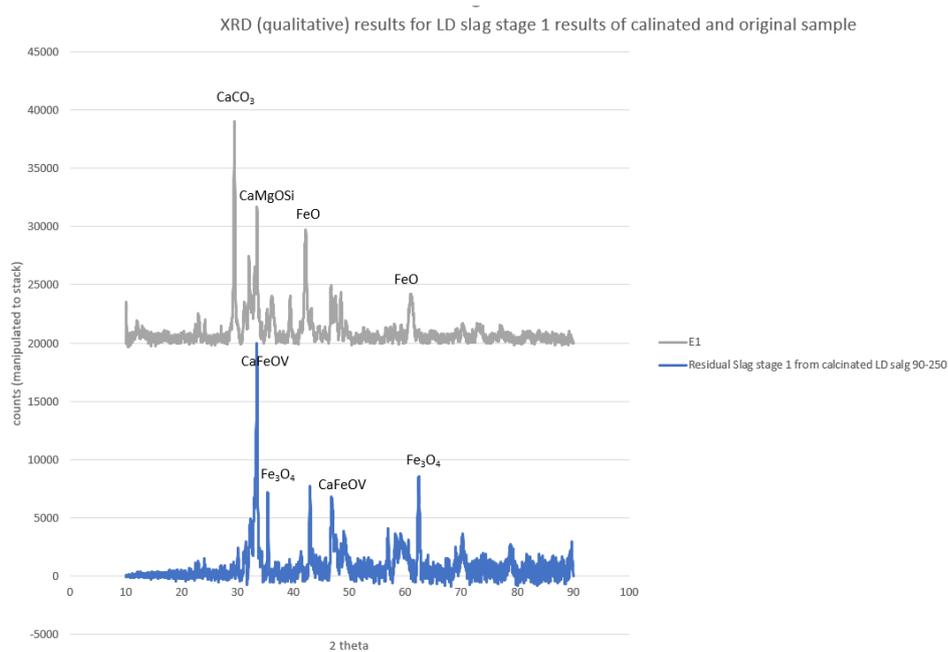


Figure A.4: Stage 1 residual slag from LD samples E1 and Calcin1

A. Appendix

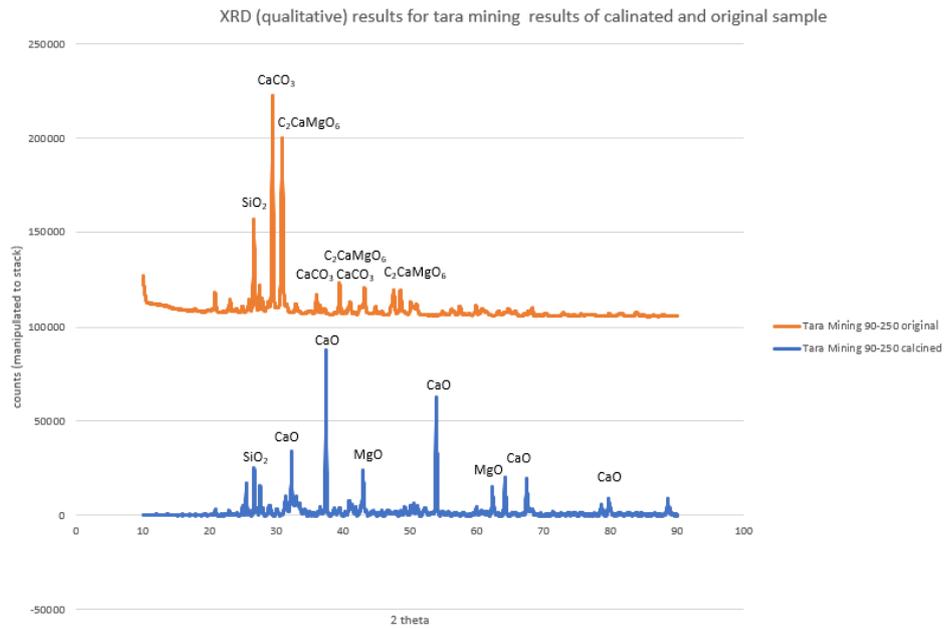


Figure A.5: Comparison of Tara Mining samples original and calcined

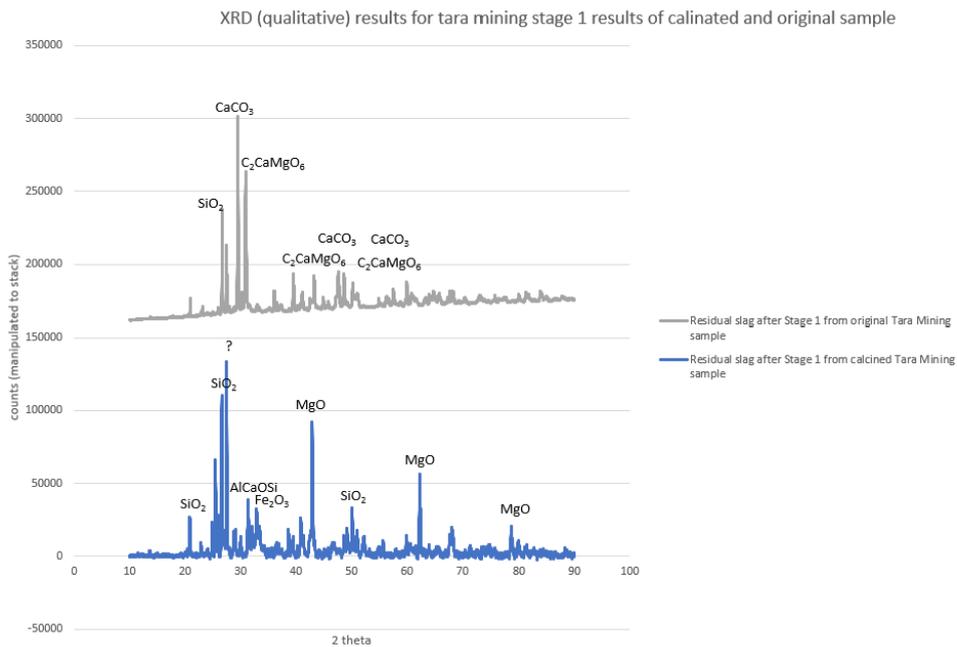


Figure A.6: Stage 1 residual slag from Tara Mining samples G1 and GC1

A.4 Effect of pH

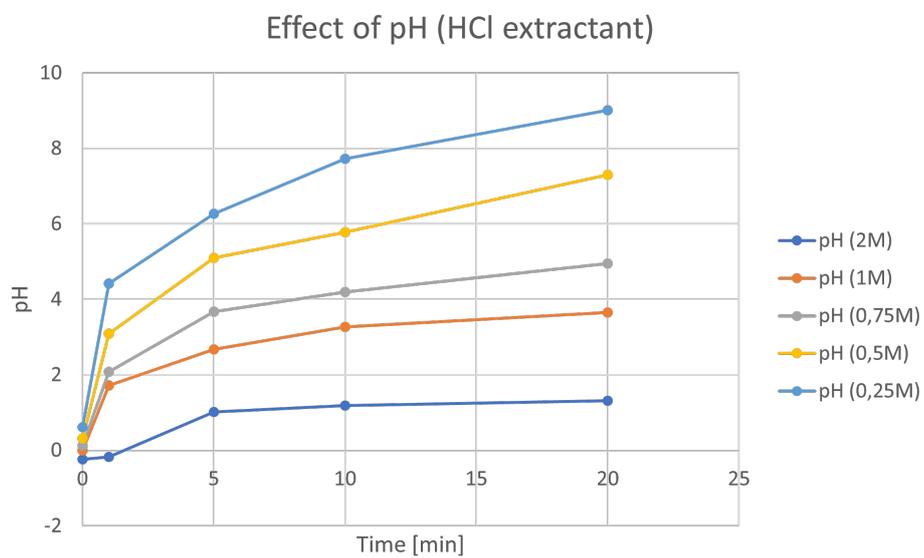


Figure A.7: Effect of pH

A.5 XRD diffractogram of Separated Impurities in Stage 2

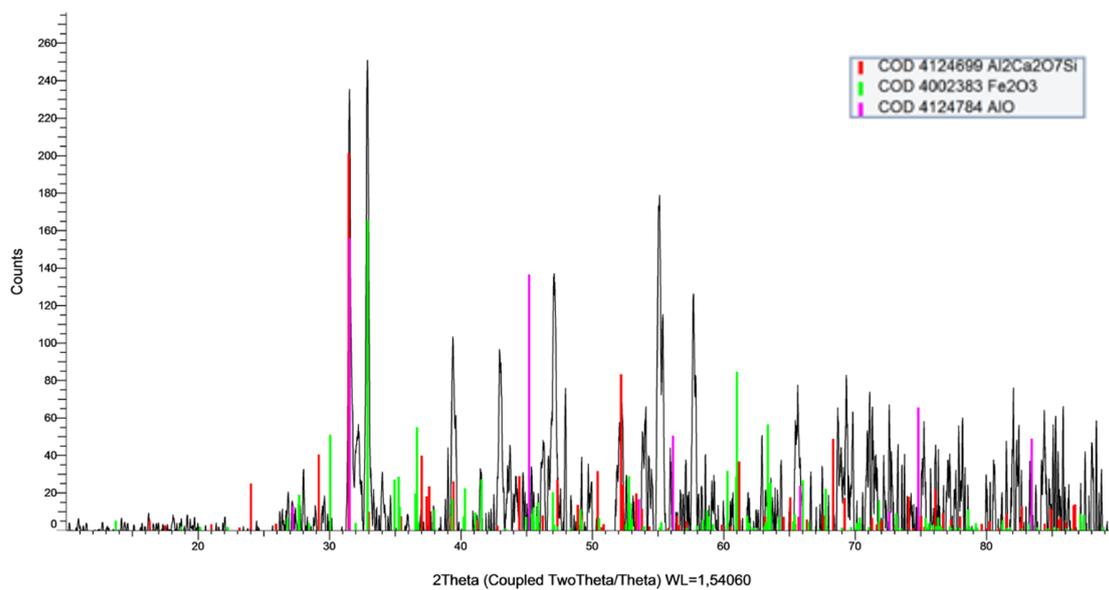


Figure A.8: Diffractogram of separated impurities of Petrit T (HCl) case

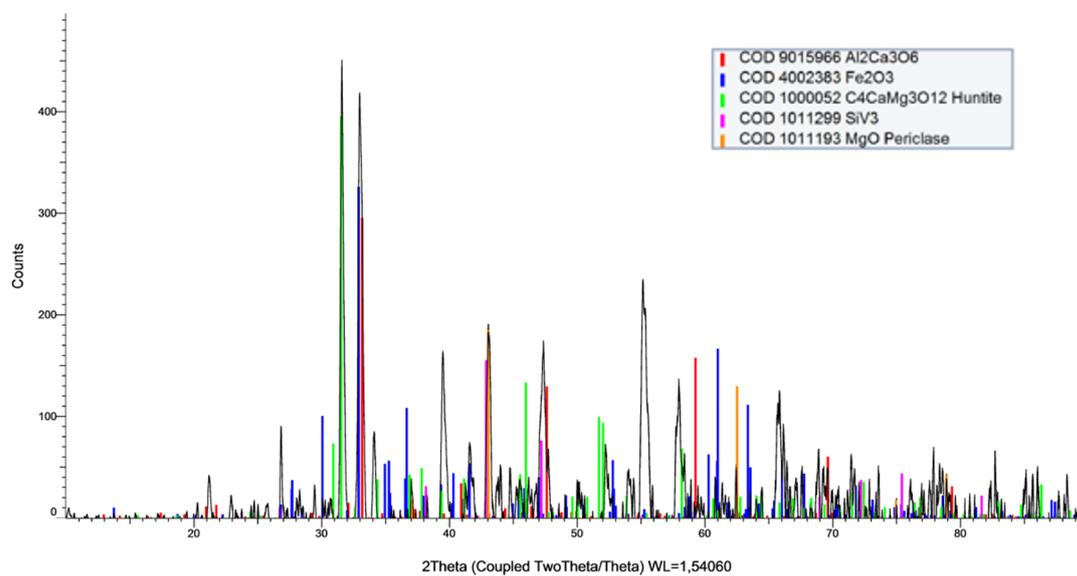
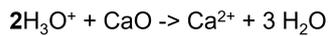


Figure A.9: Diffractogram of separated impurities of LD-Slag (HCl) case

A.6 Theoretical calculation of total calcium extraction from non-calcined LD-Slag using both solvents

Assuming that all Ca comes from CaO (CaCO₃ and Ca₂SiO₄ are not dissolved with **NH₄Cl**)



0,2mol of NH₄Cl (100ml of 2M)-> max. 0,1mol of CaO

in 50ml Filtrate for stage 2: max. 0,05mol Ca²⁺

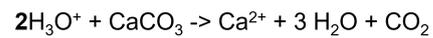
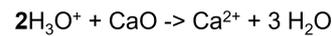
in 50ml Filtrate for Stage 3: max. 0,03mol Ca²⁺

-> max. 0,03mol Ca(OH)₂ => **2,22g Ca(OH)₂**

-> obtained precipitate: 0,38g

-> extraction efficiency: **17,1 %**

Assuming that all Ca comes from CaO and CaCO₃ (Ca₂SiO₄ is not dissolved with **HCl**)



Still 0,2mol of HCl (100ml of 2M)-> max. 0,1mol of CaO

in 35ml Filtrate for stage 2: max. 0,035mol Ca²⁺

in 20ml Filtrate for Stage 3: max. 0,0129mol Ca²⁺

-> max. 0,0129mol Ca(OH)₂ => **0,939g Ca(OH)₂**

-> obtained precipitate: 0,7g

-> extraction efficiency: **74,5 %**

Figure A.10: Stepwise calculations of potential amount of precipitate based on filtrate volumes and stoichiometry

A.7 comparison of ICP-OES results of the first and second calcium concentration measurements

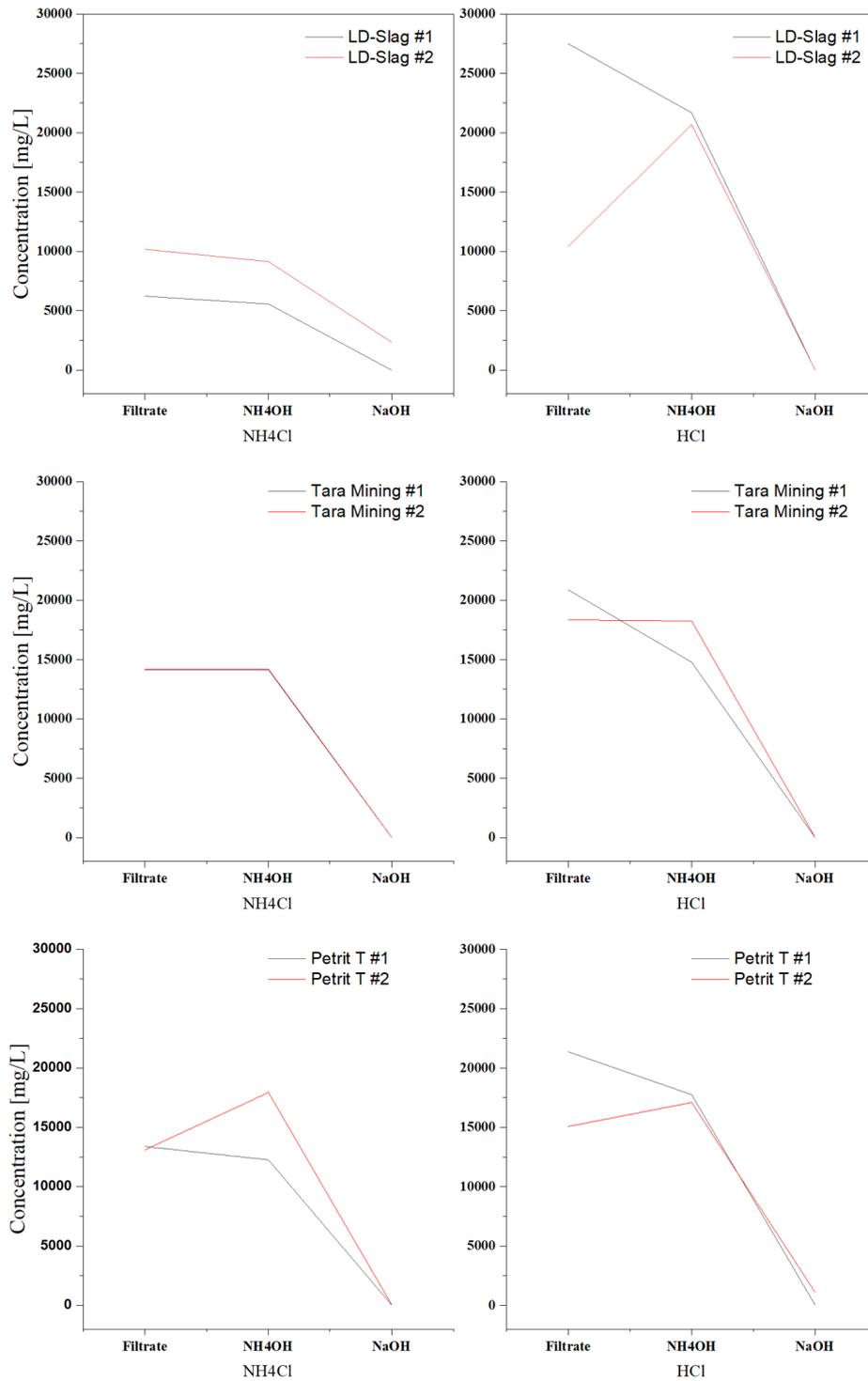


Figure A.11: Comparison of ICP-OES results of the first and second measurements

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