Energy Conversion

Enhanced Calcium Extraction From Steel Converter Slag Using Wet Extractive Grinding And Comparison With Traditional Mechanical Mixing

Selective extraction of Ca, V, Si and Mg

Muhammad Owais

Aalto University

DOCTORAL
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Abstract

This thesis belongs to the field of process engineering. The goal of this research is to develop an effective recovery method for calcium from industrial waste streams to produce precipitated calcium carbonate, PCC. This would reduce our dependency on virgin raw material resources, reduce CO2 emissions and offer a pathway to circular economy by closing material loops in industrial processes. We focused on the utilization of steel converter slag as a source of calcium for the pH-swing process named as X2PCC (X refers to Ca-bearing materials). As the first process step, we extract calcium from steelmaking slag using aqueous ammonium chloride solvent and separate solids by filtering. In the second step, the Ca-rich solution is treated with CO2 gas to produce precipitated calcium carbonate (PCC).

The main scientific objective of this thesis is to experimentally analyze phenomena in Ca extraction step and develop process solutions for increasing the Ca dissolution rate and yield. As a part of the work, we developed the new wet extractive grinding (EG) method. Traditional mechanical mixing (MM) process is first briefly explained and then compared with the new wet extractive grinding process. The carbonation step was left out of the scope of this thesis. In this thesis, the effects of various process parameters on the performance of these two techniques are systematically and quantitatively investigated.

The first part (paper I) focuses on the experimental study on the traditional mechanical mixing with respect to particle size distribution and strength of the solvent. Aqueous ammonium chloride (NH4Cl) was used as an extracting solvent with concentrations of 0-2 mol/L. The slag to solvent ratio was constant 100 g/L for all experiments. The main objective of this part was to determine the optimal concentrations of solvent and particle size for leaching out the maximum amount of calcium from the slag. All the tests were conducted at ambient pressure and temperature. The extraction rate of different size fractions of the slag, 0–50 µm, 50–74 µm and 74–125 µm were studied. If was found that the smaller the particle size, and the higher the solvent molarity, the higher the yield of Ca. We found that Ca extraction is limited by the mass transfer and the availability of Ca within the large particles. We proposed a mechanism that the surface layer of the slag particles could be get blocked by reaction products, mainlySiO2, and this stops the reaction. This would explain the lower yield in the larger particles.

The second part (papers II and III) of the work focuses on the new wet extractive grinding method and optimizing it for the maximum extraction efficiency of calcium from steel slag. Extractive grinding was compared with our traditional mechanical mixing to give better understanding of the performance of our new extractive grinding method, and to study the effects of the different process parameters on the calcium extraction and dissolution of other trace elements such as V, Si and Mg. Physical and chemical characterization is performed for the analysis of particle morphology before and after the extraction. Here, we found that with our new method we can achieve up to 73 % Ca-extraction efficiency as compared to below 40 % in MM. EG process, that combines grinding and extraction stages, reduces the overall energy requirement of the process. There are two mechanism that makes this possible: the processing time reduces due to reaction surface grinding effects and the Ca yield also significantly increases.

The main scientific contribution of this thesis is in identifying the limiting factors in the Ca extraction stage and presenting and analyzing the new wet extractive grinding method. We were able to show that with the EG method, Ca yield increased from 35 to 73%, processing time decreased from earlier used 30 to 5 min. To obtain Ca yield higher than 70% via mechanical mixing, energy intensive fine grinding is required. With EG method, based on preliminary calculations, energy saving can be up to 56 % compared to fine grinding and mechanical mixing path. We also found that EG method does not significantly affect the particle size distribution, which means that there are fewer filtering issues expected, compared with the fine-grinded slag. We are presenting unique data on the effects of solvent molarity, slag to solvent ratio, particle size distribution, process time. These will be later used in the actual process design and feasibility analysis.

Finally, we studied also initially a concept for the integration of CO2-capture Ca-looping integrated with our X2PCC process. Initial results show that CO2 capture potential of the process could be significantly increased by this. This will be further studied in our future work and we will evaluate what would be the optimal use for the PCC produced in terms of circular economy and environment.

Keywords Ca-extraction, wet extractive grinding, CO2 Sequestration, steel slag

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Tutkimusala Process Engineering

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Tiivistelmä

Tämä väitöskirja kuuluu prosessitekniikan tutkimusalaan. Tutkimuksen laajempi tavoite on kehittää tehokas menetelmä kalsiumin talteen ottamiseksi teollisuuden sivu- ja jätevirroista ja valmistaa tästä saostettua kalsium karbonaattia (PCC). Tämä askel vähentäisi riippuvuuttamme neitseellisistä raaka-aineista, vähentäisi fossiilisia CO2 päästöjä ja veisi alan kehitystä kohti kiertotaloutta sulkemalla materiaalikiertoja. Työssä keskityttiin teräskuonaan X2PCC prosessimme raaka-aineena. X viittaa tässä materiaaleihin, jotka sisältävät runsaasti kalsiumia. X2PCC-prosessimme ensimmäisessä vaiheessa kalsium liuotetaan selektiivisesti ja kiintoaines suodatetaan pois. Puhtaaseen kalsiumliuokseen puhalletaan sen jälkeen CO2 kaasua, jolloin tuotteena syntyy saostettua kalsiumkarbonaattia, CaCO3.

Työn tieteellinen tavoite oli tutkia kokeellisesti kalsiumin liuotusta ja siihen liittyviä ilmiöitä sekä kehittää menetelmää, joilla prosessia saataisiin tehostettua. Osana työtä kehitimme uuden märkäjauhatukseen perustuvan liuotusmenetelmän (EG). Perinteistä mekaanista sekoitusmenetelmää tutkittiin ensin ja sen jälkeen vertailtiin uuteen EG menetelmään. Karbonointivaihe rajattiin työn ulkopuolelle.

Työn ensimmäinen osa (Julkaisu I) keskittyy mekaaniseen sekoitukseen ja kuonan kokojakauman ja liuottimen vahvuuden vaikutusten tutkimiseen. Vesiliukoista ammoniumkloridia (NH4Cl) käytettiin liuottimena vaihtelemalla sen molaarisuutta välillä 0-2 mol/L. Kuona-liuotinsuhde oli vakio 100 g/L kaikissa kokeissa. Tavoite oli löytää parametrit, joilla Ca-saanto kuonasta saadaan maksimoitua. Kokeet tehtiin ilmakehän paineessa ja huoneen lämpötilassa. Kuonajauhe seulottiin mekaanisesti kokoluokkiin 0–50 µm, 50–74 µm ja 74–125 µm. Havaittiin että mitä pienempi partikkelikoko ja mitä suurempi molaarisuus, sitä korkeampi Ca-saanto. Hypoteesimme on, että suurilla partikkeleilla Ca-saantoa rajoittaa aineensiirto ja kalsiumin saatavuus reaktioiden käyttöön. Ehdottamassamme reaktiota rajoittavassa mekanismissa reaktiotuotteet, pääasiassa SiO2, tukkii huokoset ja hidastaa reaktiota olennaisesti. Tämä ilmiö selittäisi suurempien partikkelien matalamman Ca-saannon.

Työn toinen osa (julkaisut II ja III) keskittyvät uuteen märkäjauhatusliuotukseen ja sen parametrien optimointiin teräskuonalla. Uutta menetelmään verrattiin mekaaniseen sekoitukseen, jotta saataisiin parempi käsitys uuden menetelmän eduista eri prosessiparametreillä. EG menetelmää karakterisoitiin kemiallisesti ja fysikaalisesti ja tutkittiin kuonan morfologian muutoksia prosessin aikana. Havaittiin, että uudella EG menetelmällä on mahdollista kasvattaa saantoa mekaanisen sekoituksen alle 40 % arvosta yli 70% tasolle. EG menetelmässä yhdistetään jauhatuksen teho sekä liuotusvaihe. Tällöin prosessin läpimenoaika pienenee huomattavasti ja saanto kasvaa. Tämän ansiosta energian kulutus myös pienenee huomattavasti.

Väitöskirjan tieteellinen kontrobuutio on, että pystytiin identifioimaan Ca-liuotuksen kontrolloivia mekanismeja sekä kehitettiin uusi märkäjauhatusliuotus menetelmä. Pystyimme näyttämään, että EG menetelmällä Ca-saanto nousi 35 % arvosta 73% tasolle, prosessiaika lyheni 30 minuutista 5 min tasolle. Jotta vastaava saanto saataisiin aikaiseksi mekaanisella sekoituksella, täytyisi kuona jauhaa erittäin pieneksi (<50 µm), vaatien paljon aikaa ja energiaa. Alustavien laskelmien mukaan energian kulutus voisi olla 50-60% alhaisempi uudella menetelmällä. Havaitsimme myös, että EG menetelmä ei juuri vaikuta partikkelikokojakaumaan, joka tarkoittaa sitä, että hienoksi jauhetun kuonan tapauksessa esiintyviä suodatukseen liittyviä ongelmia on huomattavasti vähemmän. Työssä on myös esitetty suuri määrä täysin uusia mittaustuloksia molaarisuuden, partikkelikoon, kuona-liuotinsuhteen ja prosessiajan vaikutuksista prosessin käyttäytymiseen, joita voidaan käyttää tulevaisuudessa teollisen kokoluokan prosessin suunnittelussa, optimoinnissa ja taloudellisen kannattavuuden arvioinnissa. Työn lopuksi teimme vielä alustavia laskelmia CO2 talteenottopotentiaalin kasvatusmahdollisuuksista. Alustavien tulosten mukaan, jos X2PCC prosessi yhdistettäisiin Ca-looping CO2 talteenottomenetelmään ja käyttämällä valmistamaamme CaCO3:a talteenottoprosessin sorbenttina, hiilidioksidin talteenottopotentiaalia voitaisiin kasvattaa merkittävästi. Tätä tutkitaan tulevaisuudessa laajemmin ja arvioidaan PCC tuotteemme parasta käyttökohdetta kiertotalouden ja ympäristön kannalta.

Avainsanat Ca-extraction, wet extractive grinding, CO2 Sequestration, steel slag
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Preface

This study was carried out at the lab in Energy Conversion Research Group at Aalto University. The research was funded by Renlund Foundation and the funding by the Dean, School of Engineering, Aalto University.

I would like to show my gratitude to everyone who supported me throughout my thesis work. First and foremost, I am extremely grateful to my supervisor, Professor Mika Järvinen for his continuous support, encouragement, and insightful comments. He has given a valuable time in instructing me how to write a paper, how to search for literature and how to analyses data in detail. I would also like to thank to all my co-workers and acknowledge that without their support and contributions, this work could have been very difficult: Roza Yazdani, Arshe Said, Pekka Taskinen. A very special thanks to all technical staff, Vadim Desyatnyk and Hannu Revitzer.

I would also like to show special gratitude to all the members of the Energy Conversion Research Group for their encouragement and inspiration. I cannot imagine a better working environment than this group. I consider myself lucky to get a chance to work here and learn from my colleagues.

I would like to express my sincere gratitude to my father Muhammad Hassan and my beloved sister and brother, Shahida and Salman for their persistent affection and moral support throughout my whole life. I would like to extend my special thanks to my wife Farheen Ayaz Padela and my daughter Zoya Owais and my son Zaid Owais, for their continuous support, patience, and encouragement throughout the period of my doctoral studies. I know, you (Farheen) had to share all my stress, made more sacrifices than you are expected to do. Writing this thesis would never be possible without your sacrifices, especially for taking care of Zoya and Zaid (our daughter & son). Further gratitude to my friends, family members, and everyone else who supported and inspired me during my study.

In the end, to my life-coach, my mother Roshan Bano: I dedicate this thesis to you because I owe it all to you. Many Thanks!

Toronto, Canada. October 08, 2021

Muhamad Owais

Contents

List of Abbreviations and Symbols

BOF	Basic oxygen furnace
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
FTIR	Fourier transform infrared spectroscopy
GCC	Ground calcium carbonate
ICP-AES	Inductively coupled plasma- atomic emission spectroscopy
PCC	Precipitated calcium carbonate
SEM	Scanning electron microscope
SLR	Solid to liquid ratio
XRD	X-ray diffraction
SLAG2PCC	Traditional process of extracting calcium oxide from the steel converter slag using mechanical mixing
X2PCC	Process of calcium containing material X to precipitated calcium carbonate
EG	Extractive grinding
MM	Mechanical mixing

Symbols

T	Temperature (°C)
P	Atmospheric pressure (atm)
M	Molarity (mol/L)
V	Volume (cm^3)
pH	the negative logarithm of H^+ ion activity

Greek letters

λ	Stoichiometric coefficient
X_{ext}	Extraction efficiency
ρ_w	Density of water (g/cm^3)

Chemical compounds and minerals

$CaCO_3$	Calcium carbonate
$CaCl_2$	Calcium chloride
$Ca(OH)_2$	Calcium hydroxide; milk of lime; portlandite
CaO	Calcium oxide
Ca_2SiO_4	Larnite
Ca_2SiO_3	Wollastonite
Fe_xO_x	Several oxides of Iron
H_2O	Water
MgO	Magnesium oxide
MnO_2	Manganese dioxide
NH_3	Ammonia
NH_4Cl	Ammonium chloride
SiO_2	Silicon dioxide; silica, quartz
V_xO_x	Several oxides of vanadium

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals.

1. Muhammad Owais, Mika Järvinen, Pekka Taskinen, and Arshe Said. 2019. Experimental study on the extraction of calcium, magnesium, vanadium, and silicon from steelmaking slags for improved mineral carbonation of CO_2. Journal of CO_2 Utilization, vol. 31, pp. 1–7, May 2019, DOI:

10.1016/j.jcou.2019.02.014.

2. Muhammad Owais, Roza Yazdani, and Mika Järvinen.2020. Wet extractive grinding process for efficient calcium recovery from steelmaking slags. Journal of Chemical Engineering and Processing - Process Intensification, vol. 151, p. 107917, May 2020, DOI:

10.1016/j.cep.2020.107917

3. Muhammad Owais, Roza Yazdani, and Mika Järvinen. 2021. Detailed Performance Analysis of the Wet Extractive Grinding Process for Higher Calcium Yields from Steelmaking Slags. Chemical Engineering and Processing - Process Intensification Volume 166, September 2021, 108489, DOI:

10.1016/j.cep.2021.108489

Author’s Contribution

The author of this thesis has formulated and conducted almost all the experimental work presented in this thesis. In addition, the author of the thesis with the help of the co-authors has written and analyzed the results presented in all of the publications.

Publication 1: The author designed the study with support from Prof. Mika Järvinen. The author was responsible for performing the analyses with the help and support of Prof. Mika Järvinen. Prof. Pekka Taskinen and Arshe said provided guidance in the overall review and editing process of the article. The author was responsible for writing the article, with contributions from all co-authors.

Publication 2: The author of this thesis conducted the laboratory experiments, analyzed the results, and wrote the paper with the help of Prof. Mika Järvinen. The other co-author, Roza Yazdani participated in reviewing and editing of this paper.

Publication 3: The author of this thesis designed the laboratory experiments, analyzed the results, and wrote the paper with the help and guidance of Prof. Mika Järvinen. The second co-author, Roza Yazdani done scanning electron microscope and Fourier-transform infrared spectroscopy (FTIR) analysis for the samples and helps in reviewing and editing of the paper.

1. Introduction

The present thesis consists of this overview part and the three accompanying publications. The main scientific findings of this thesis have been reported in detail within the attached publications. The purpose of this short overview is to provide a reader with a brief introduction to the research area, and also to outline some of the main findings of the publications.

This thesis belongs to the research field of chemical process engineering. In particular, the research focuses on the utilization of steel converter slag as a source of calcium to develop a process through the experimental setup for enhance calcium oxide extraction from the slag through the X2PCC process. Also, to optimize the process parameters for both MM and EG processes, to make the industrial processes sustainable by utilizing waste, reducing CO_2 emissions and to make the processes economically viable for large scale industrial application.

1.1 Background and Motivation

Mitigating the impacts of global warming has emerged as a great challenge of the present century [1]. Greenhouse gases (GHG) such as CO_2 emissions is the main cause to be linked with global warming [2]. In 2018, it is estimated that ~37 Gt of CO_2 emitted alone just from the burning of fossil fuels [3]. Fig. 1 illustrates the CO_2 emissions from the burning of fossil fuels by individual countries. It is evident that the European Union (EU) is also predicted to increase the emissions in the near future [4]. Due to the COVID-19 pandemic, it is estimated that energy demands reduced by 6 % in 2020 compared to normal emissions [5] , reducing the demand growth of the last five years. This pandemic will result in reduce (GHG) emissions. However, it will again take 5 years for the world to catch CO_2 emissions to pre-pandemic levels. If something is not done rapidly, we will lose this window to reduce emissions [5]. The world is ready for change as we cannot live the same way as the pre-pandemic world. We need to act fast to mitigate emissions caused by rapid population and change our traditional behavior.

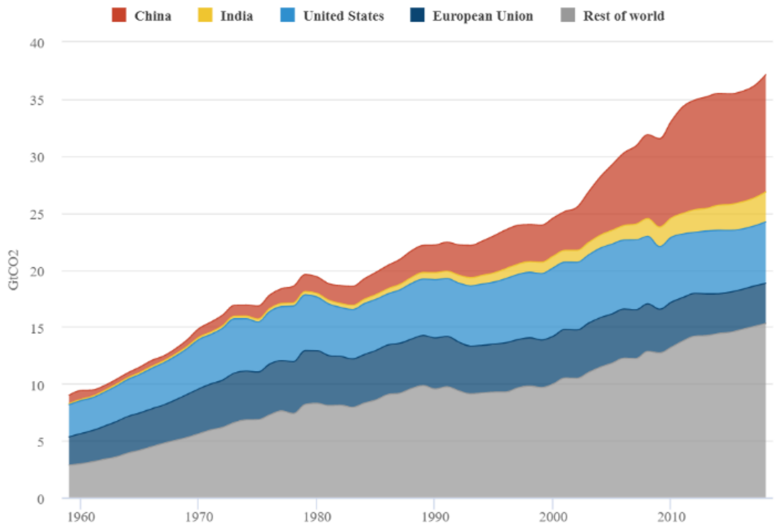


Figure 1. Annual CO_2 emissions from fossil fuels by country, 1959-2018 [4]

The Intergovernmental Panel on Climate Change (IPCC) suggested that human activities have caused approximately 1.0 °C of global warming above pre-industrial levels, which is likely to increase 1.5 °C between 2030 and 2052 if we continue to increase at the same rate [6]. Fig. 2 illustrates a good understanding of anthropogenic GHG emissions within a century Vs increase in temperature.

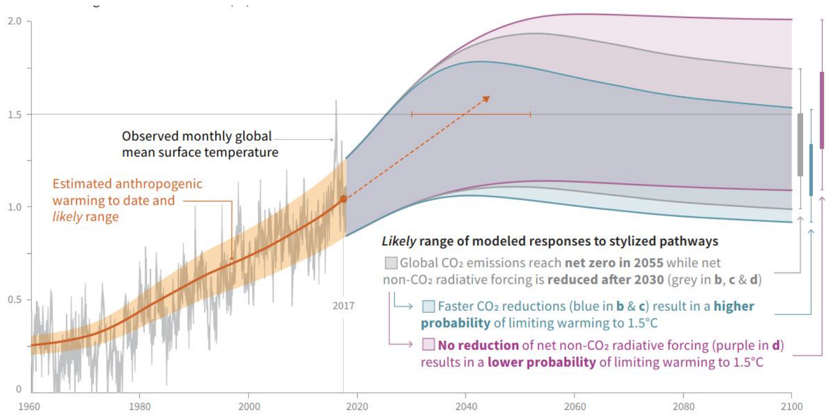


Figure 2. Global warming 1960-2100 (°C) [5]

Human activities have contributed significantly to climate change by adding CO_2 and other heat-trapping gases into our atmosphere. These GHG emissions result directly in trapping more heat from the sun and results in a rise in the earth's temperature [7]. From the industrial revolution till today, we are manufacturing and consuming exponentially. The global population is estimated to reach 10 billion by 2050, which will require a surge in energy demand and the mining of new raw material resources [8].

The global economy is mostly linear, which means we extract raw materials from the earth for production of goods. As a result, create large quantities of waste which has a negative impact on our environment. We need alternative technologies to make global economy circular and make our industrial processes cyclic to keep relying less on virgin extraction of raw material. According to the EU commission, there is a surge in the global material extraction, as it is reported that it is increased 14 times from 1990 to 2015 from 6 to 84 GT, respectively. It is forecasted that it could increase up to 184 GT in 2050. [9] Many mining resources are depleting, and mining activities generate hazardous wastewater containing poisonous heavy metals whose disposal is a threat to fresh and groundwater sources as to our environment. These activities also create a high surge in energy demand due to the burning of large reserves of fossil fuels for mining and refining phases.

Therefore, the linear model of production has to be abandoned and carbon capture utilization (CCU) and storage (CCS) should be utilized in industrial manufacturing to reduce GHG emissions and waste. In Finland, the circular economy is gaining great attention and the government is not focusing on increased production of manufacturing and goods. Rather, products are shared, rented, repaired, maintained, upgraded, recycled, and waste is reused among industries to keep the processes sustainable [10].

1.2 Climate change, CCS and CCU technologies

As we have discussed earlier, climate change is linked with GHG emissions. According to IPCC, CCS, especially BECCS (Bioenergy based CCS) and CCU are the techniques that help in mitigating GHG emissions and reduce the impact of climate change [11-12]. CCS is defined as integrated techniques comprising of capture, transportation, and geological storage of CO_2. CCS includes post and pre-combustion separation of CO_2 from other gases produced at industrial installations to produce high purity CO_2. It is followed by transportation which involves the compression of CO_2 into the denser medium and transmission from the capture location to the storage facility where it is injected into the sub-surface rock formation at the deep depths and marine locations, EOR. CCU refers to the capture and the use of feedstock as the production of useful chemicals. CCU can be deployed at an industrial scale and can be integrated into the existing industrial facility. For example, it is used in the EU in the fertilizer industry for the production of melamine and urea-based glues and resins. [11] The [13] IPCC also has predicted that CCS and CCU technologies are compatible with current energy infrastructure and these techniques have a great potential to reduce the GHG emissions. These techniques can help in creates negative GHG potential.

1.3 Steel industry and steel slag

The steel industry has a vital role in the modern economy. It produces products that are important to the functioning of the wider economy. Steel is multifunctional and most adaptable material for example for the construction and car industries. Steel is also considered to be a sustainable material due to its high recycling capability. Globally, crude steel production is estimated to reach 1.9 billion metric tons by 2021 [14]. While EU is the second-largest producer of steel with 11 % of global output and providing millions of jobs directly and indirectly [15]. It is also predicted that steel production is to increase in near future.

The production of steel is known to be an energy-intensive process and cannot rely solely on electrification, and it emits huge CO_2 emissions by burning fossil fuels [11]. In 2018, On average 1 ton of steel production emits 1.85 tons of CO_2, which accounts for 8 % of total global CO2 emissions by the steel industries [16]. In addition, it generates a byproduct of 400 Mt/a of steelmaking slag that contains a high amount of calcium oxide [17]. Fig. 3 shows the overall production of steel from blast furnace slag to steel products.

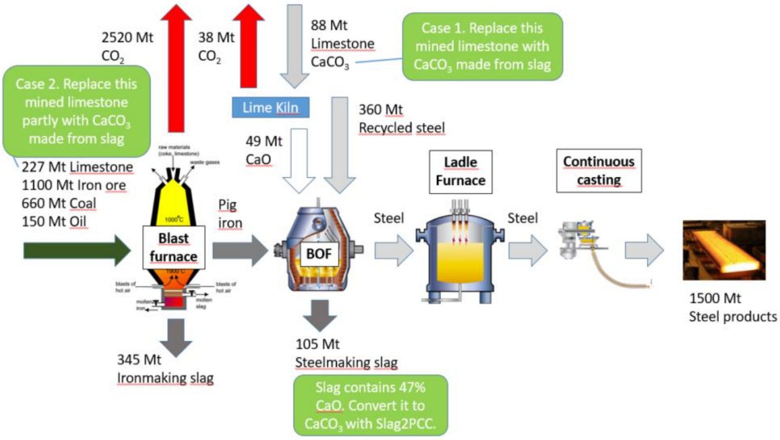


Figure 3. Flow diagram of steel manufacturing, case of CaO recycling in steelmaking.

As it is illustrated in Figure 3, we need $CaCO_3$ as a fluxing agent in the blast furnace (BF) and in the basic oxygen furnace (BOF). Moreover, steel slag is produced as a byproduct that contains ~47 % CaO. In order to make this whole process cyclic, we come with a solution with our X2PCC process. Here, we first extract CaO from steel slag and second reacts with CO_2 gas for the production of valuable product such as precipitated calcium carbonate (PCC) [18-20]. This process can create negative CO_2 potential in steel production. In the meantime, our reliance on extracting virgin $CaCO_3$ mining is reduced significantly. We will discuss this process in more detail in our coming sections.

1.4 Mineral Carbonation

Mineral carbonation is the method of reacting minerals (CaO or MgO) with CO_2 gas for the production of mineral carbonates. It is divided into two categories, i.e., direct, and indirect. Direct refers to the reaction of CaO or MgO directly with CO_2 gas for mineral carbonate formation. While indirect carbonation refers to the extraction of Ca or Mg from the mineral first and then reacting with CO_2 gas later in the carbonation stage [21]. Here, we have focused on Ca and indirect mineral carbonation. Eq. 1 and 2 refers to the simplified global extraction and carbonation reaction as following:

$$2CaO \cdot SiO_2(Ss) + 4NH_4Cl(a) + H_2O(l) \leftrightarrow 2\,CaCl_2(a) + 4NH_3(a) + 2H_2O(l) + SiO_2(s)\downarrow \quad (1)$$

$$2\,CaCl_2(a) + 4NH_3(a) + 2CO_2(a) + 4H_2O(l) \leftrightarrow 2CaCO_3(s)\downarrow + 4NH_4Cl(a) \quad (2)$$

CCS via mineral carbonation is known to be a permanent storage method for CO_2 storage [12]. As mineral carbonation is thermodynamically stable under normal conditions and does not require post monitoring as compared to other CCS methods such as geological storages [9].

1.5 Mechanical mixing and wet extractive grinding

Slag2PCC or X2PCC (Calcium containing material X to Precipitated Calcium Carbonate) is a pH-swing process whereas a steel making slag is used as a source for calcium oxide for the mineral carbonation of CO_2 [22-23]. Here, steel slag slabs are first grinded into smaller particle by large ball mills preferably 0-250 µm. This 0-250 µm steel slag particle size is used for all the cases (MM and EG).

First, we extract calcium oxide from a steel converter slag using aqueous ammonium chloride. Second, we react this rich calcium oxide solution by bubbling into CO2 gas. As a result of this, it produces precipitated calcium carbonate (PCC) . The overall yield of calcium oxide in the extraction step is an important step for process feasibility. It is found that the extraction process during mechanical mixing limits the further extraction of calcium oxide from steel slag and therefore, it requires some other techniques to enhance the rate of calcium oxide extraction [23–27].

Wet extractive grinding is a process improvement of our previous X2PCC process. In wet extractive grinding, we combine extraction and grinding of steel slag into a single process. This process is suitable for enhanced recovery of calcium oxide from the slag, and it requires less energy as compared to fine grinding for mechanical mixing which makes this process feasible for large scale industrial application.

1.6 The objective and scope of this work

The main objective of this research is as follows:

- To formulate a new process for the enhanced calcium oxide recovery from the steel converter slag.
- Process optimization of wet extractive grinding process for enhanced calcium oxide recovery and to make this process economically viable.
- To support the Sustainable Development Goal of united nations, SDG-12: Responsible Consumption and Production by reducing the need for virgin resources and aiming to rely more upon inventing circular solutions.
- To compare our new wet extractive grinding method with our traditional X2PCC process (Mechanical Mixing, MM).
- To understand the complexity of steel slag particles by analyzing chemical and physical properties during the process.
- Reaction mechanism of CaO and other species in steelmaking slag such as V, Si and Mg and their extraction rate with CaO species.
- To analyze the selectivity of ammonium chloride solution towards CaO species and its varying solvent concentration in depth for all processes.

For this reason, I conducted a laboratory-scale study to investigate the effect of various process parameters such as Solid-to-liquid ratio (SLR), Molarity (M), reaction time (t), and steel slag particle size distribution. In addition, a brief study performs for the washing of residual slag and analyzed elemental impurities of wash water after the extraction stage to develop a waste-water system.

1.7 Publication objectives

In the publication I, the X2PCC process only is described. In this, the effect of different molarities 0, 0.5, 1 and 2 mol/L of NH_4Cl using the SLR of 100 g/L of steel slag is analyzed. Initially, the original slag of 0–250 is sieved into three categories of 0–50 µm, 50–74 µm and 74–125 µm and studied for the best size suitable for enhanced extraction.

In publication II, the main objective was to study the new wet extractive grinding and compared it with the traditional X2PCC process. I also compared three different cases for process feasibility namely:

1) Mechanical mixing extraction with original grind slag A (0–250 µm).
2) Mechanical mixing extraction with fine dry-grind slag B (0–50 µm).
3) The new extractive wet grinding process with original slag A (0–250 µm).

In publication III, the focus is to further develop the EG process, also, to compare it with the X2PCC process using only original slag (0–250 µm). In addition, I studied the effects of the processing time (1.25–20 min), and the slag-to-solvent ratio (SLR = 30–120 g/L) for both processes. In this study, I also investigate briefly the chemical and physical characteristics of initial and residual particles by using various techniques without destroying the particle's morphology. This study provides an insight of the change in steel slag particle structure after the extraction stage in real-time and the requirements of the process optimization that needed in near future for further extraction of trace elements such as vanadium (V).

Earlier, it is pointed out that the extraction step is the rate-limiting step, and this study involves only the extraction step, and the carbonation step was considered to be out of the scope of this research. However, the utilized processes are state-of-the-art, many of which have not been investigated and implemented before in the context of the extraction process (X2PCC). Moreover, the optimization of the process parameters for process feasibility in the lab study is combined in a novel fashion, which is done for the first time in the context of the X2PCC and EG process in the doctoral thesis. There are no similar research experimental study of the new wet extractive grinding process and mechanical mixing for the calcium oxide extraction from steel slag.

1.8 The outline of the thesis

The thesis is divided into the chapter as follows. In Chapter 2, an overview of the materials and methods that are considered important in this research is presented. In chapter 3, a brief summary of the main findings and scientific contributions of the thesis are presented. In the end, Chapter 4 summarizes scientific contributions combined with future works and directions are explained. The main part of this thesis is compiled in the Publications I–III attached in the appendix section.

2. Material and Methods

This chapter provides an overview of the materials and methods that are considered in this research. The specific methods and their details are presented in the accompanying publications.

2.1 The extraction of calcium from steel converter slag

X2PCC is a pH-swing process, the main idea of this process comprised of extraction and followed by carbonation. Here, we discussed only the extraction step. Extraction was performed in this study by two processes namely: mechanical mixing and wet extractive grinding.

For the mechanical mixing process, steel slag, fly ash or other suitable Ca-bearing minerals or waste materials are finely ground into the particle size preferably of 0–250 μm. First, CaO from the steel slag is extracted selectively using NH_4Cl-water solvent, and the slag leaching residue is removed by filtering the solution. This is followed by the carbonation stage. Fig. 4 shows a simplified process description. For the sake of simplicity, here 50% extraction and 100% carbonation efficiency were assumed for typical description of the process. According to Fig. 4, 1 t production of PCC consumes 2.24 t of steel slag and 0.44 t of CO_2.

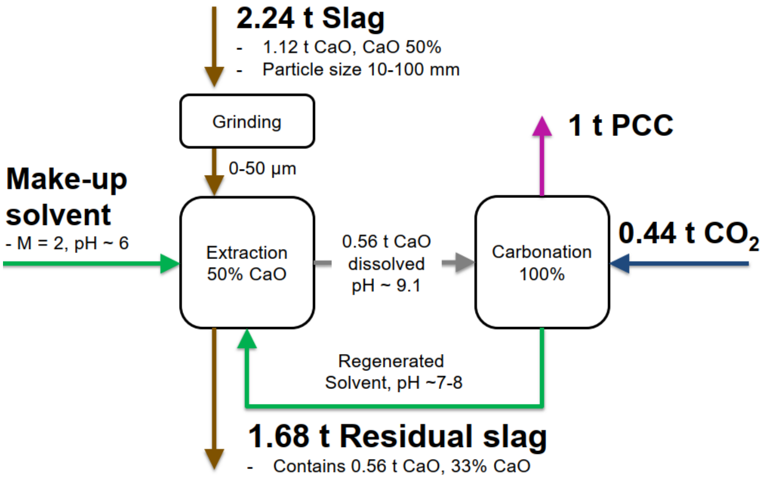


Figure 4. Process schematic of the X2PCC process flow sheet, mechanical mixing, 30% yield in extraction.

For the wet extractive grinding (EG), the extraction was performed by a new process based on combining extraction and grinding into the single step. It is carried out in a ball mill filled with required steel converter slag and ammonium chloride solution. The wet EG process reduces the further slag grinding into smaller particle of 0-50 µm step. In addition, combining extraction with grinding helps in opening slag pores which results in enhanced calcium oxide dissolution. As it is stated in Fig. 5 of the schematic diagram of the wet EG process in detail. Here, we can achieve 53-73 % extraction rate.

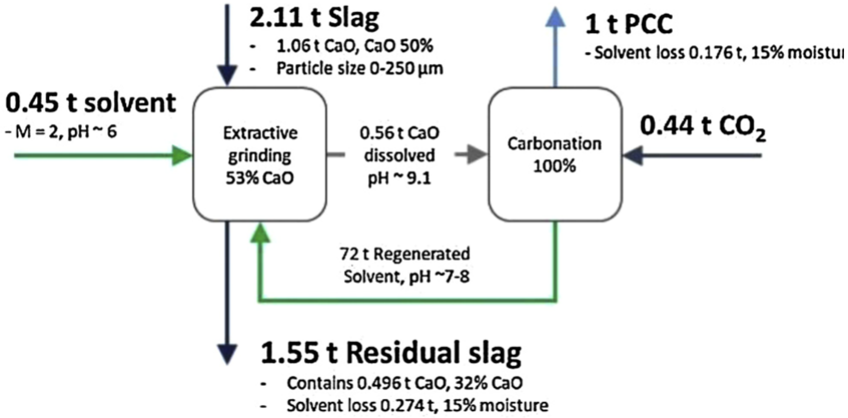


Figure 5. Process schematic of the X2PCC process flow sheet combined with extractive grinding, 53% yield in extraction.

The residual slag can be further processed for the extraction of valuable elements such as vanadium. In the later step, the carbonation stage is the same for MM and EG process. Carbonation is proceeding by the bubbling CO_2 gas into the Ca-rich filtered solution to form precipitated calcium carbonate (PCC). The carbonation reaction occurs at normal temperature by CO_2 gas with desired flow rates as per requirement. For the experimental purpose, the lab grade of higher purity CO_2 gas is used for carbonation, and further research needs to be done for using industrial grades or flu gas emissions from boilers and burners for carbonation.

PCC is a valuable product to a chemical industry that has an existing market. It can be utilized in paper and pulp making, plastic, cement, or steel industries. After the carbonation, the ammonium chloride lixiviant is filtered and can be re-generated again for the extraction stage.

2.2 Laboratory set-up of MM and EG

Mechanical mixing extraction experiments were performed in a 500 mL round-bottom glass reactor equipped with a data logger for continuous recording of pH and temperature (T). An overhead mechanical mixer was used for constant mixing of slurry. All experiments were performed at ambient conditions. The glass reactor was submerged in a thermostatic water bath during the experiments at a constant temperature of 23 °C throughout all experiments.

In all experiments, the desired ammonium chloride solvent is poured into the glass reactor, followed by mixing until the temperature and pH were stabilized. Then, the weighed slag sample was poured into the same reactor and mixed for a constant time (t) as per experiments. The extracted solution mixture was then vacuum filtered with a filter paper. Fig. 6 presents the laboratory setup of our traditional mechanical mixing.

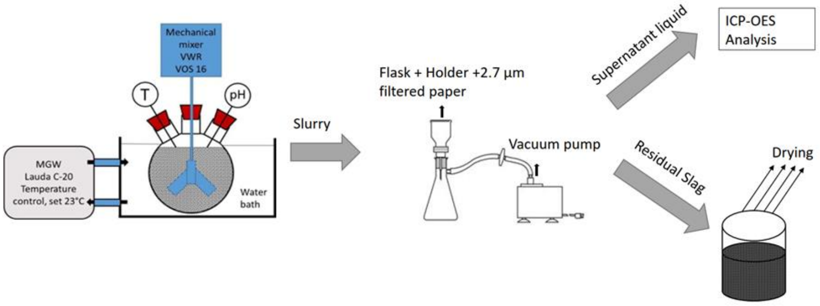


Figure 6. Laboratory set-up for mechanical mixing, filtration and followed by drying.

Wet extractive grinding experiments were performed in an AR–MINI ball mill made by Kerasil (Nurmijärvi, Finland). The mill contains a ceramic jar and lid with a rubber seal. Due to the close nature of the system, the pH was measured both before and after each experiment.

The ball mill contains 255 ceramic balls having an outer diameter of 13.5 mm, ~4.6 g each, with a density $\rho_b = 3.6$ g/cm^3. The inner dimensions (diameter × length) of the mill jar were 120 x 120 mm having a volume of 1357 cm^3. These dimensions result in a critical rotational speed of 130 rpm. The actual rotational speed used was 90 rpm, 70% of the critical value. The apparent density, ρ_a, and porosity, ε_s, of the steel slag powder were measured as 1.55 g/cm^3 and 0.46, respectively. The slag powder porosity was determined by a simple water immersion test. The solid slag density ρ_s was therefore determined to be 1.55/ (1 − 0.46) = 2.87 g/cm^3. Different milling parameters are presented in Table 1.

Table 1. Milling parameters. Mill jar volume V_0 = 1357 cm^3, solid volume of balls V_1 = 350 cm^3, total volume of bed of balls, V_2 = 650 cm^3, bed porosity ε_b = 0.462 and slag porosity ε_s = 0.46.

Parameter	Mass of slag (g)		
	15	30	60
Solid volume of slag, V_3, cm^3	5.2	10.5	20.9
Total volume of slag, V_4, cm^3	9.7	19.4	38.7
Ball filling, $J = V_2/V_0$, %	47.8	47.8	47.8
Powder filling, $f_c = V_4/V_0$, %	0.71	1.43	2.85
Interstitial filling, $U = V_4/(\varepsilon_b V_2)$, %	1.54	3.08	6.16

In all experiments, slag was mixed with 500 ml of solvent and loaded into the ceramic jar. After the experiments are performed, the ball mill was stopped, and the slurry was vacuum filtered with filter paper. The rest of the procedure was similar to the previous set-up for the mechanical mixing. A typical flow diagram of our system is illustrated in Fig. 7.

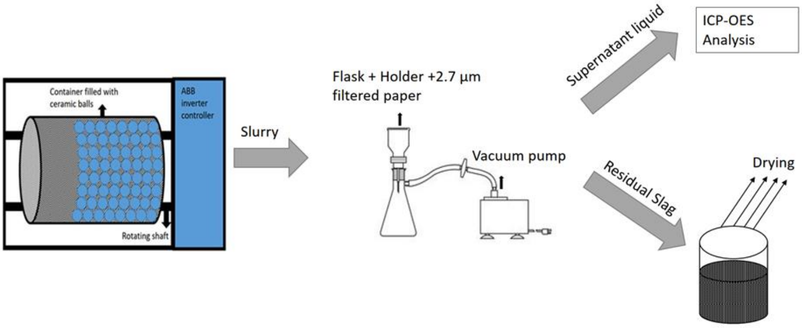


Figure 7. Wet extractive grinding set-up for extraction, filtration and followed by drying.

In the end, ~10 mL liquid Ca-rich liquid is extracted from the solution for elemental analyses. Then, the filtered residual slag cake was dried in an oven overnight at a constant 120 °C. The residual slag cake was weighed before and after drying for the total mass loss before and after extraction.

2.3 Chemical and physical Characterization

The chemical and physical composition of steel slag powder is performed in detail before and after the experiments. The elemental analysis is done for analyzing Ca, V, Si, and Mg after the extraction and for the solid slag using inductively coupled plasma-optical emission spectroscopy and inductively coupled plasma-atomic emission spectroscopy (ICP-OES, Optima 7100 DV, Perkin Elmer, U.S.A) and (ICP-AAS, Varian AA240, U.S.A), respectively.

The mineralogical phase of the original slag and the residual slag was analyzed using an X-ray diffractometer (XRD, Smartlab, Rigaku, Japan) with the operating parameters of Cu Kα radiation ($\lambda = 1.5418$ Å), and 40 kV/150 mA with a step size of 0.01° and counting time of 1 s per step.

The physical characterization of slag for analyzing morphological phase before and after is performed by using scanning electron microscope-energy dispersive spectroscopy with an accelerating voltage of 5.0 kV (SEM-EDS, Jeol, JSM–7500FA). All the slag samples for SEM were coated with a sputter coater (LECIA EM ACE600), along with a thin layer (~4 nm) of titanium/iridium before observation and analysis. Also, the 0–250 µm slag is dry fine grinding to 0–50 µm (objective size range; true size range was 0–92 µm) for detailed particle size distribution by using Beckman Coulter LS particle size analyzer. Fourier transform infrared spectroscopy (FTIR) was done on original and residual slag to identify functional groups and compounds that are present in the slag particle. This was done with a spectrometer (PerkinElmer Spectrum Two) installed with a diamond ATR crystal. The total spectrum was recorded within the range of 4000–500 cm-1, with a resolution of 32 cm^{-1} and a data interval of 1 cm^{-1} and accumulations of 12 scans.

2.4 Characterization of the material

Steel slag is mainly composed of phases formed of CaO, FeO, SiO_2 and MnO and other oxides depending on the region where the iron ore is extracted. The slag used in all the experiments was a basic oxygen furnace (BOF) converter slag from SSAB in Raahe, Finland. The original steel BOF slag used for these tests was obtained by crushing and grinding the coarse 50…200 mm slag lumps from the BOF process until they had a particle size between 0–250 µm. As reported in the paper I, steel slag was classified into different size fractions of 0–50 µm, 50–74 µm and 74–125 µm by mechanical sieve analysis in an inhouse laboratory facility. In paper II, slag analysis of these fractions is performed in detail and listed below in Tables 2 and 3.

Table 2. Elemental analysis of the sieved particle size fractions used in the experiments by ICP-AAS method, original size 0-250 µm, slag A.

Size range	0-250 µm	0-74 µm	74-125 µm	125-250 µm
Mass fraction	1	0.176	0.227	0.597
Element	(g/kg)	(g/kg)	(g/kg)	(g/kg)
Ca	331.6	335.0	333.0	330.0
Al	9.1	8.6	8.8	9.3
V	19.8	18.6	19.8	20.2
Si	52.8	40.0	48.0	58.4
Fe	175.7	175.0	178.0	175.0
Mn	17.6	18.5	17.0	17.6
Mg	10.5	9.5	10.6	10.8

Table 3. Elemental analysis of the grinded and mechanically sieved particle size fractions used in the experiments by ICP-OES method, size 0-92 µm, slag B.

Size range	0-92 µm	0-20 µm	20-32 µm	32-45 µm	45-56 µm	56- µm
Mass fraction	1	0.642	0.099	0.131	0.111	0.035
Element	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
Ca	339.0	299.0	324.0	340.0	349.0	337.0
Al	8.9	9.3	8.9	8.3	8.0	7.7
V	20.5	20.9	21.2	21.5	21.7	20.2
Si	60.5	56.0	68.1	75.1	78.6	79.8
Fe	137.0	141.5	164.0	139.0	126.0	163.0
Mn	18.5	19.5	21.7	18.7	16.8	13.9
Mg	10.5	11.4	13.8	11.6	10.5	8.7

Comparing Tables 2 and 3, it is found that ICP-AAS and ICP-OES show varying results for some species such as Si and Fe. It is worth noting that in the fine-grinded slag B, the overall Ca content is little in the smallest size fraction, 0-20 µm. If we consider the mass fraction and the total Ca amount, most of it exists in the smallest size fraction 0-20 µm, 0.624 × 0.299 / 0.339 = 57 %.

Besides, the initial composition of the slag was also calculated as oxides and is presented in Table 4.

Table 4. Slag composition calculated as oxides, %.

MnO	FeO	Al_2O_3	V_2O_5	Cr_2O_3	SiO_2	MgO	CaO	K_2O	Na_2O	Total
2.3	12.9	2.7	5.3	0.5	9.8	1.8	47.4	0.0	0.1	82.8

It is evident that the composition does not sum up to 100% of the slag, 17.2% of the mass is not covered by the analysis. It is found out that ICP-OES takes only ~ 0.2 g of slag sample for analysis which makes this error in results. For this purpose, we have analyzed the individual solid slag samples in Publication III for each experiment to be as accurate as possible. It is observed that the distribution of elements such as Al, Ca, Mg, Si, Cr and Mn throughout the original slag, possess regions with varying element density. This was also proved by energy-dispersive X-ray spectrometer.

2.5 Chemical reaction mechanism

Molarity (M) and the solid-to-liquid ratio (SLR) are the main parameters that are vital for the overall extraction reaction. These parameters are mostly affected by the stoichiometric limitations of the Ca dissolution reaction. To understand extraction reaction, we have to consider all the reactions that proceed before and after extraction. At first, solid NH_4Cl salt is dissolved in water, (a) refers to the aqueous solution. This is an ionization reaction and it occurs fast. H_3O^+ formation and its reaction with calcium are considered as a rate limiting step. Extraction reaction proceeds as follows:

$$NH_4Cl(l) \leftrightarrow NH_4^+(aq) + Cl^-(aq) \tag{3}$$

$$NH_4^+(\mathrm{l}) + H_2O(l) \leftrightarrow NH_3(\mathrm{aq}) + H_3O^+(\mathrm{aq}) \tag{4}$$

$$2H_3O^+(a) + CaO(s) \leftrightarrow Ca^{+2}(a) + 3H_2O(l) \tag{5}$$

$$2H_3O^+(a) + 2CaO \cdot SiO_2(s) \leftrightarrow Ca^{+2}(a) + CaO \cdot SiO_2(s) + 3H_2O \tag{6}$$

As it is evident from the equations that the availability of H_3O^+ ions and free CaO are the main species that alter the extraction of calcium from steel slag. Also, we found that theoretically, one mole of CaO(s) requires 2 moles of NH_4Cl. In publication III, the results show that SLR and solvent molarity should be modified in a way to keep overall reactions under the stoichiometric limit, without limiting the production of H_3O^+ ions and free CaO, which paves way for process feasibility for enhancing extraction.

2.6 Particle size distribution

Sieve analysis was also done for original steel slag to determine the particle size distribution of the coarse and fine aggregates. In this procedure, original grinded slag 0–250 µm is passed through different sieves and grouped together with the size fractions of 0–50, 50–74 and 74–125 µm sieves with a pan to analyze different aggregates present in the original slag. The corresponding Rosin-Rammler size distribution is calculated using sieve analysis to determine the differential size class i fraction. The particle size distribution of the steel slag fitted in Rosin-Rammler distribution by the equation 7 shown below:

$$F(d) = 1 - \exp\left(-\left(\frac{d}{X}\right)^q\right) \tag{7}$$

whereas

$F(d)$ = Cumulative fraction of the material by weight less than size "X".

X = Characteristic particle size

q = Constant describing the material uniformity

Particle size distributions are done to calculate the mass median diameter, Sauter mean diameter, specific surface area in the publication I and II in which the Rosin-Rammler equation is fitted with sieve analysis performed in-house and the graph will be illustrated in the summary section of publication I and II. We also calculate differential size distribution using $f(d_i)$ is the differential size class i fraction, i.e. $f(d_i)$ - $f(d_{i-1})$, and N refers to the number size (screen) classes. Please see publication I and II for more detailed results.

However, here the differential size distribution Vs particle diameter, µm, is shown in Fig. 8. This is also calculated using Rosin-Rammler by fitting parameters analyzed by Beckman Coulter LS Particle Size Analyzer.

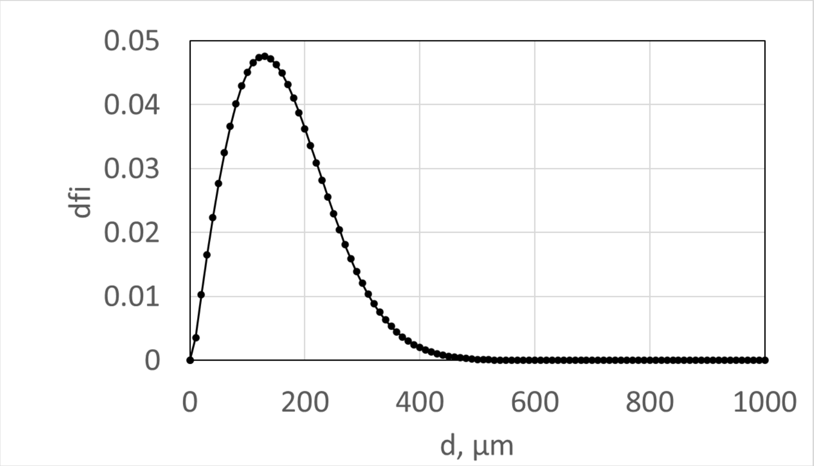
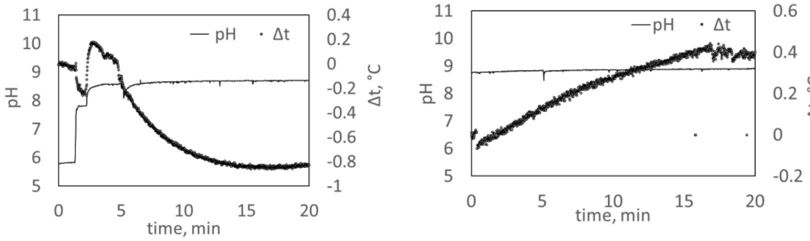


Figure 8. particle size differential distribution curve, q = 1.9558 and X =177.57.

Particle size distribution of the slag is important to understand the physical characteristics of the particle. In addition, particle size distribution tells the physical parameters such as average and mass median mean diameter, Sauter mean diameter and specific surface area to understand the physical nature of the original slag. In the end, the energy needed for grinding W (kWh/tonne) is also calculated by using the bond equation (see publication II). For this, first $d_{0.8i}$ and $d_{0.8o}$ are calculated using particle size distribution parameters by Rosin Rammler distribution.

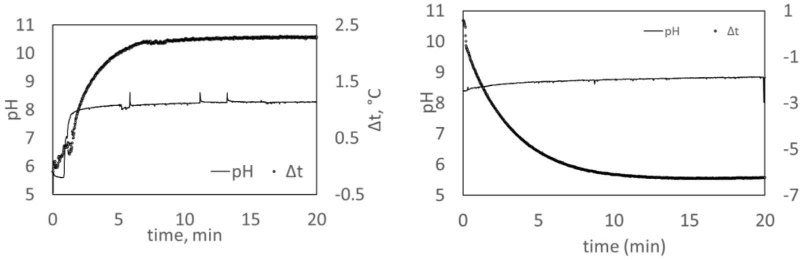
2.7 Temperature and pH profiles

Temperature and pH are measured in all the experiments in mechanical mixing using temperature and pH sensors connected to a data logger. In all the experiments, the glass reactor was submerged in the thermostated water bath, MGW Lauda C-20, at a constant temperature of 23°C to keep it constant. For both the reaction and washing stages, a VWR pH electrode (SJ 113, 662-1382), and a 1.5 mm (K-type) thermocouple, respectively, measured the pH and temperature of the experiment. A typical diagrams of the temperature and pH profile of mechanical mixing of original slag and washing of residual slag are illustrated in the below Fig. 9.



a) Temperature and pH profile (Mechanical mixing test using 0-50 µm steel slag reacting with 2 mol/L NH4Cl at SLR = 30 g/L).

b) Temperature and pH profile (Wash water test by mechanical mixing test using 0-50 µm steel slag reacting with tap water at SLR = 30 g/L).



c) Temperature and pH profile (Mechanical mixing test using 0-250 µm steel slag reacting with 4 mol/L NH_4Cl at SLR = 30g/L).

d) Temperature and pH profile (Wash water test by mechanical mixing test using 0-250 µm steel slag reacting with tap water at SLR= 30g/L).

Figure 9. Temperature and pH profiles during extraction and washing stages. **(a-d)**

It should be noted that in the graphs of Fig. 9.(a & c) that pH and temperature rise at the start of the experiments. This is occurred due to the pH swing process and exothermic nature of the reaction after the addition of the slag. As the reaction progresses, temperature tends to stabilize, and there is still a little progress after 10 minutes of the reaction. While Fig. 9. (b & d) also illustrates the washings stage after 1st extraction, it shows that there are insignificant changes in pH and temperature decreases with the increase in reaction time due to the loss in energy from the solution to the water bath.

2.8 Ca-extraction efficiency

The main objective of this study is to enhance the calcium oxide extraction efficiency and to perform a detailed analysis of the parameters that are affecting ca-extraction yield. It was found during this study that the solvent molarity (M), particle size distribution, solid to liquid ratio (SLR), reaction time are the main parameters that affect calcium yield. In all publications I-III, these parameters are varied to make this process optimal and feasible, in the meantime, enhancing calcium extraction efficiency. Extraction efficiency/degrees of dissolution X_i were calculated for each study by Eq. (8).

$$X_i = \frac{c_i V}{m_i^0} \tag{8}$$

Here, c_i is the concentration of species i in the solution (g/L), V is the volume of the solvent (L) and m_i^0 is the initial mass of the element i in the steel slag (g) used in all the experiments. Tests for extraction are repeated multiple times to produce same results.

In addition, we came up with a new technology naming wet extractive grinding (EG). As classical Slag2PCC process was not feasible and there were many hindrances to enhance calcium extraction rate above 50 %. It was found that with wet extractive grinding by combining grinding and extraction, we can enhance calcium extraction efficiency up to 73 % which is required for the economic feasibility of this process. All results affecting calcium extraction efficiency will be discussed in the summary section of each publication (I-III).

2.9 Dissolution of V, Si and Mg

Dissolution of V, Si and Mg is also important as these impurities are also extracted with our aqueous ammonium chloride (NH_4Cl) solvent. It was needed to discuss the dissolution of V, Si and Mg with Ca if we try to change process parameters as above for enhancing calcium extraction. As a result, these elements are also affected by these changes and can be precipitated in the final carbonation stage as impurities, or they can remain in the solution and alter the final product quality of precipitated calcium carbonate (PCC). For this reason, the dissolution of these elements is discussed briefly in both MM and EG processes. This comparison is also needed for process development and process optimization. Parameters affecting dissolution of V, Si and Mg by process parameters will be discussed in the summary section of each publication separately (I-III).

2.10 Wash water impurities and washing stage

We also studied the washing of residual slag to remove the leftover NH_4Cl from the residual slag after drying. This process is needed for both the industrial X2PCC via MM and wet EG process to design an effective wash water purification system to make the environmental load of the process minimal. For this purpose, we performed additional wash water analysis for our publication II. The washing stage was done with 500 mL tap water, using mechanical mixing for 20 min wash duration. The rest of the process and parameters are the same as typical mechanical mixing, see Fig. 6 for more detail. Elemental analysis is also done for this wastewater using ICP-OES and it is found that it is composed mainly V, Si, Ca, and Na, also some K and Mg. Detailed analysis of this finding will be discussed later in the Publication II.

3. Publications Summary

The main scientific findings of this thesis lie within the three attached publications. Brief summaries of the publications are given below:

3.1 Publication I

In this paper, the main idea was to optimize the extraction step by finding optimum solvent's molarity and steel slag particle size for the maximum extraction and selectivity to CaO in our X2PCC process. In this study, aqueous ammonium chloride (NH_4Cl) of varying molar concentration of 0, 0.5, 1 and 2 mol/L using the solid to liquid ratio (SLR) of 100 g/L is utilized for enhanced calcium extraction. Earlier research suggests that SLR of 100 g/L is suitable with 0-2 mol/L. The maximum extraction time was fixed to be 30 minutes for all experiments. The main objective of this experimental set-up is to find the optimum solvent concentration for enhanced CaO recovery for 100 g/L and varying steel slag particle size of 0–50 µm, 50–74 µm and 74–125 µm. All the tests were conducted at an ambient temperature and pressure. In all the experiments, original steel slag of 0–250 µm was divided into three categories of the particle size distribution of 0–50 µm, 50–74 µm and 74–125 µm. This was done using mechanical sieve analysis. Later, these parameters were analyzed for particle size distribution fitted in Rosin -Rammler distribution as shown in Fig. 10.

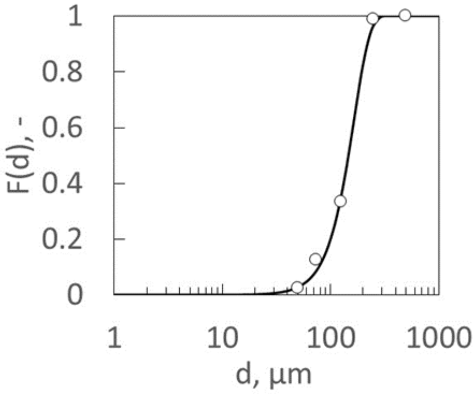


Figure 10. Particle size distribution of the steel slag, X = 165.22 µm and q = 2.9852 fitted in Rosin-Rammler distribution

According to Rosin-Rammler distribution fitted with the sieved data, the mass median diameter of the slag is found to be $d_{0.5}$ = 146 µm. Earlier, we suggested that CaO containing phase sites are the weakest parts of the slag particles. Due to these weaker sites, and we assumed that they are the most fragile sites, which is easiest to grind and have highest CaO content. However, analyzing the overall composition of the slag to calculate the overall yield from different size classes could then lead to a significant error. After chemical analysis, it is found that CaO was slightly higher in the smallest size fractions of the steel slag. In the end, it was noted that an accurate analysis of the slag was challenging due to the small sample size ~ 0.2 g. In addition, XRD analysis reveals that steel slags are composed of dicalciumsilicate (Ca_2SiO_4), dicalciumferrite ($Ca_2Fe_2O_5$) and wüstite (Fe_{1-x-y}, Mg_x, Mn_y)O_z. As an example of the results, Fig. 11 presents Ca yield as a function of the molarity.

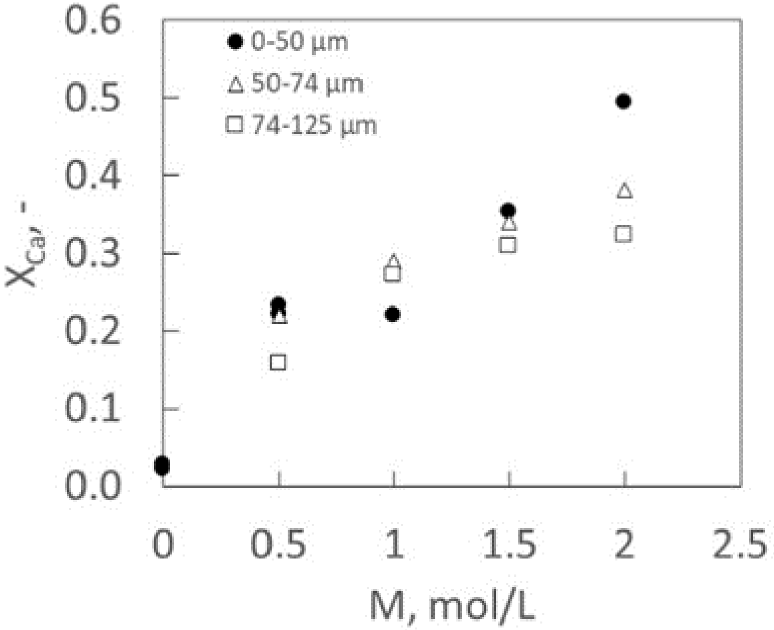


Figure 11. Extraction efficiency of Ca.

The dissolution of Ca shows that extraction efficiency increased with the increase in solvent concentration, as shown in Fig. 11. However, the dissolution pattern of other elements such as V, Si and Mg tends to increase with higher solvent concentration. These could be precipitated as impurities in the later carbonation stage, depending on their chemical characteristics. There is an optimal solvent molarity that results in high Ca yield but minimizes the dissolution of other trace elements. Results show that increase in the solvent concentration, Ca extraction is limited in the largest particles due to the mass transfer and availability of free Ca in the solid particle. Our preliminary observation is that this occurs due to the blockage of the surface layer of particles and stopped further progressing of leaching from inside of particles. In contrast, before the surface was blocked in the smallest particle most of the calcium was already extracted. The optimal concentration of the solvent and particle size is found to be 2 mol/L and 0–50 μm. The dissolution behavior of Si and V showed promising patterns. Both Si and V showed a maximum extraction efficiency and extraction rates at 1–1.5 mol/L NH_4Cl concentration except for the smallest size that showed a minimum leaching rate at 1–1.5 mol/L.

3.2 Publication II

In publication II, we aim to optimize process parameters of our classical X2PCC process in comparison with new wet extractive grinding process for process optimization. Here, we studied the process improvement of the pH-swing process referred to as X2PCC. Herein, steelmaking slag is used as a main source of CaO for the mineral carbonation using CO_2. First, we extract the CaO from the steelmaking slag using aqueous NH_4Cl of 1, 2 and 4 mol/L. Second, the solid phase is extracted by filtering, following, bubbling of CO_2 gas into the Ca-rich solution to produce precipitated calcium carbonate (PCC). In all the experiments, the SLR ratio was kept at 30 g/L; 15 g of slag dissolved per 500 mL of solvent. The SLR (30 g/L) value was calculated by our earlier experiments and economic feasibility modeling work. There are two ways to enhance extraction. It is either increase by SLR or by increasing solvent molarity. Here, This SLR of 30 g/L was chosen with regards to the high molarity test such as 2 and 4 mol/L.

As we know from our earlier work, the extraction step is limiting the process feasibility. In addition to optimizing extraction in X2PCC process, we also investigate the new wet extractive grinding process for enhance extraction of calcium oxide from steelmaking slag. For this study, we compared three cases:

1) Mechanical mixing extraction with original slag A (0–250 µm).
2) Mechanical mixing extraction with fine dry-grind slag B (0–50 µm).
3) The new extractive wet grinding process with original slag A (0–250 µm).

The new wet extractive grinding process is a combination of grinding and extraction stages into a single process. EG method has a potential to reduce the energy requirement and enhance the extraction of calcium oxide from steel slag significantly, which makes this process suitable for large scale industrial application.

In this study, the particle size distributions for slag A and fine-ground slag B were also analyzed by both sieve analysis and Beckman Coulter LS Particle Size Analyzer, respectively. Moreover, we determined the particle size distributions for the dry ground slag (20 min duration using the same mill that was used for the EG), referred to as the slag C, and the slag D, which corresponds to the situation after the wet EG (2 mol/L and 30 g/L). This can be illustrated in Fig. 12 below.

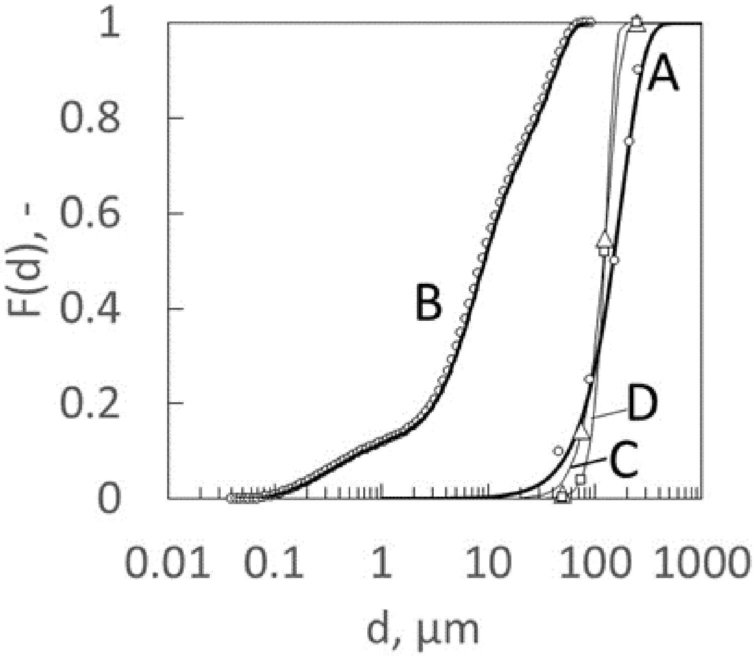


Figure 12. Cumulative particle size distributions of the slag A, B, C and D.

By fitting all the parameters from sieve analysis into Rosin-Rammler distribution, we also found the mass median diameter ($d_{0.5}$) of the slags A, B, C and D were 147.2, 8.8, 119.8 and 123.9 µm, respectively. Further, results showed that after 20 min dry grinding, there is an insignificant reduction in the size and the energy requirements for the dry grinding of slag C is negligible. Besides, specific surface area for slags A and B were found to be 27.8 and 1741 m^2/kg, respectively. This suggests that slag B has 63 times higher surface area than slag A. Due to higher surface area, this results in enhancing the extraction rate. As an example of main results from this paper, Fig. 13 shows the Ca extraction rate for MM and EG methods.

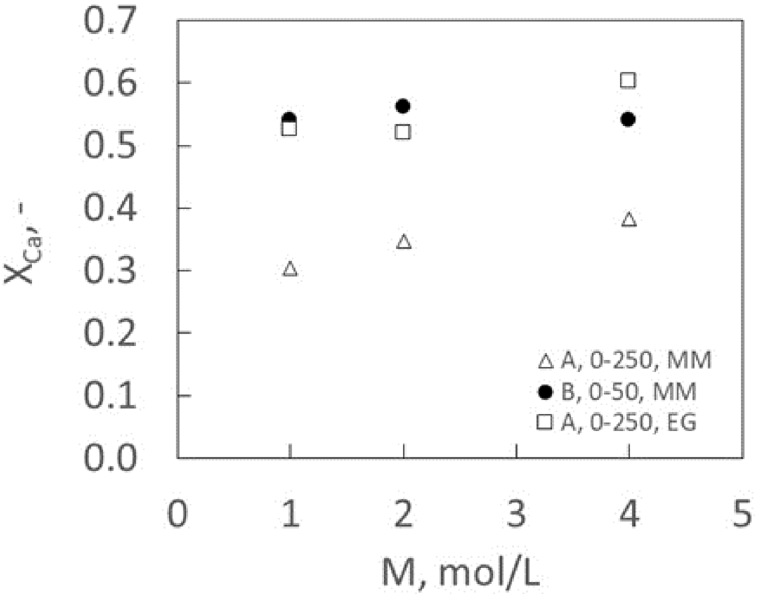


Figure 13. Ca extraction efficiency.

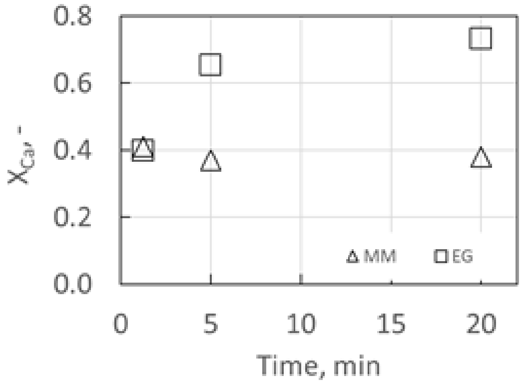
From Fig. 13 we can clearly see that dissolution of Ca for slag A with mechanical mixing process can reach a maximum extraction of 38% by varying from 1 to 4 mol/L solvent concentration. In comparison, with wet EG, the yield was found to be 52% at a molarity of 1–2 mol/L and 60% at 4 mol/L. It was found from the Bond equation, the specific energy consumption is 20- and 58.1-kW h/t for dry-grinding down to 1) 250 µm (d_{80} 230 µm) and 2) 50 µm (d_{80} 27.4 µm), respectively. Energy required for extractive grinding path 3) is 25.3 kW h/tonne (d_{80} 143.9 µm) starting from infinitely large particles. Dissolution of other impurities such as V and Si, also, reduces with an increase in solvent concentration. With fine grind slag (0–50 µm), 56 % Ca yield is achieved with 1 mol/L solvent and an increase in solvent concentration does not effect on the yield. For this study, fine ground slag is used to understand the extent to which Ca is extracted from the slag particles, if mass transfer limitations are negligible on the particle side. For our X2PCC process, we needed to analyse initially the wash water purification system. We want to have a minimal impact on the environment. Here, we propose a system that can utilize the same wastewater again for make-up solvent. For this reason, a brief analysis of wash water is done, and it was found that the main elements presents are: Ca (122–438 mg/L), Si (38–61 mg/L), V (10–27 mg/L), and Na (5.7–9 mg/L) and K (0.9–1.2 mg/L). This results are utmost important to develop the wastewater treatment system for treating this water or to use this waste-water as a make-up solvent. Here, the analysis showed that no Cr dissolution occurs within the analysis range. Also, it was important to calculate error analysis of elemental Ca mass balances. Error analysis showed that for EG and fine ground slag, errors were less than 7% and 4%, respectively. The wet EG system is sufficiently accurate and has the potential for applying at a large industrial scale.

3.3 Publication III

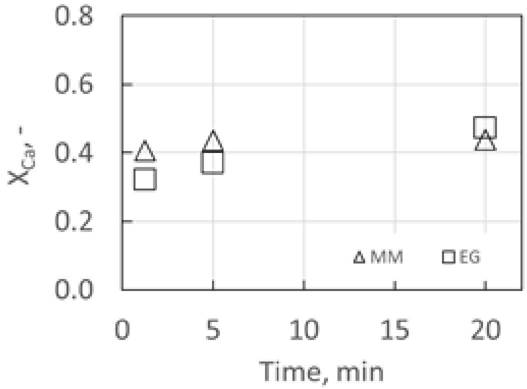
In this publication, the main aim to process optimization of our new wet extractive grinding process and comparison with traditional mechanical mixing with detailed characterization of slag particles. Here, we studied the detailed analysis of wet extractive grinding and also compared it with the traditional mechanical mixing. The pH-swing process, in this case, is the same as in the previous publication. Also, we focus only on the extraction stage. For this purpose, we studied the effect of the processing time (1.25, 5 and 20 min), and the slag-to-solvent ratio (SLR = 30, 60 and 120 g/L). In addition, different operating parameters of ball mill are calculated for in-depth analysis. We also analyzed the statistical error coming the analysis of solid slag due to small sample size. Physical and chemical characterization was performed in detail on the fresh and used slag powders. We also initially investigated the process of combing X2PCC process, for the production of sorbent (CaO) for calcium-looping CO_2 capture processes to bind CO_2 from flue gases.

As examples for the results from Paper II, Fig. 14 below presents the yield of Ca for different stoichiometries and as a function of the time.

SLR = 30 g/L, λ = 4.0



SLR = 60 g/L, λ = 2.0



SLR = 120 g/L, λ = 1.0

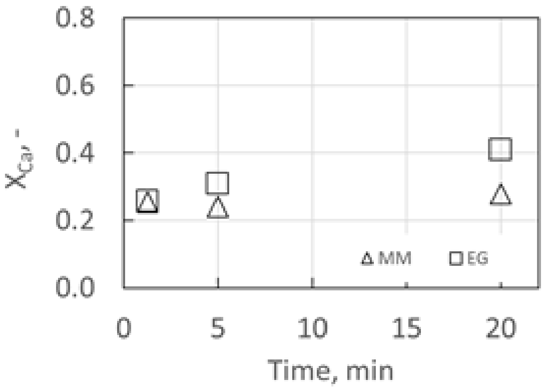


Figure 14. Extraction pattern of calcium

In publication II, it was found that with SLR = 30 g/L and M = 2 mol/L, and at 20 min yield 63% Ca, see Fig 13 for individual results. However, in this study Ca yield has reached 73% as shown in the above Fig. 13. All the tests were performed twice for result's repeatability. This occurred due to fact that only one sample used for the initial slag in our previous study. Results showed that after the first 1.25 min and 30 g/L, the Ca yield is the same for both MM and EG. In contrast, the reaction soon stops for MM. Moreover, Ca continues to dissolve and reaches a higher level already after 5 min processing for EG. In the case of SLR = 60 g/L and 120 g/L, Ca yield drops, this occurs due to existing stoichiometric limitations. It is suggested that there are not enough H_3O^+ ions present in the solution that could increase the CaO dissolution. These results are important to determine the extent to which SLRs are increase or decrease as to residence time.

We also performed preliminary analysis of using our PCC as a make-up sorbent in the Ca-looping CO_2 capture process. It was also found that PCC production by X2PCC can bind 125 Mt of CO_2 by using a total of 600 Mt of annual slag production, which accounts for 0.3% of annual global CO_2 emissions (37 Gt in 2018). However, the PCC utilization in the Ca-looping CO_2-capture as a make-up sorbent, results in binding of 1500 Mt of CO_2, i.e., ~4% of global annual emissions or over 60% of the iron- and steel-making CO_2 emissions. A typical flow diagram of the integrated X2PCC process combined with the Ca-looping CO_2-capture process is illustrated in Figs. 15 (a+b).

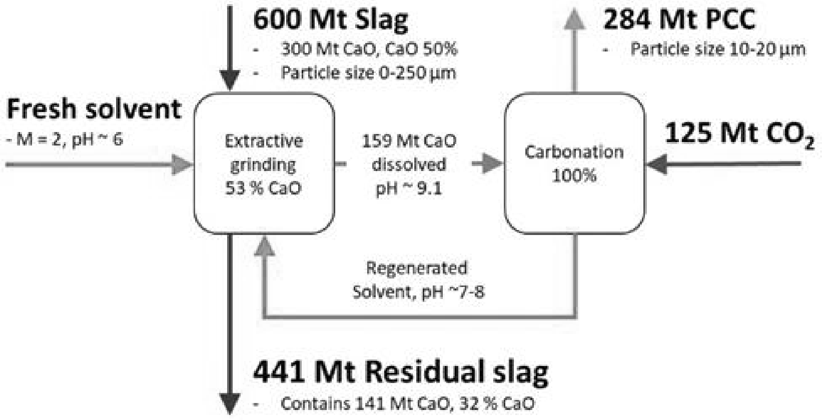


Figure 15-a. X2PCC process mass balance on an annual iron- and steel-production basis. 284 Mt of PCC is used as input for Ca-looping capture process.

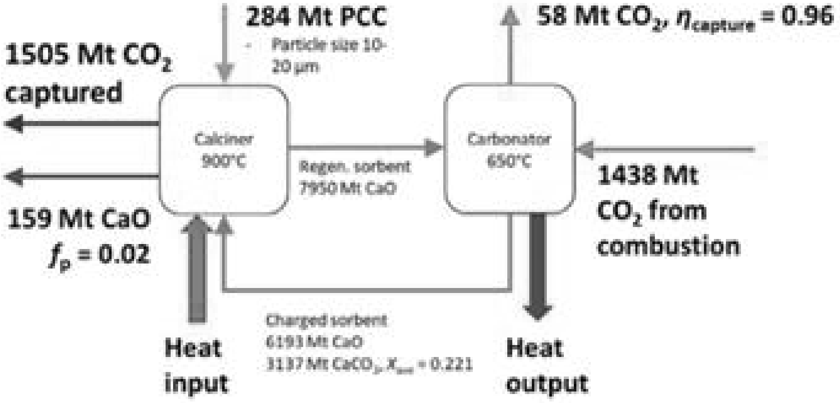


Figure 15-b. Ca-looping capture mass balance on an annual steel-production basis, 2% loss is assumed in the calciner.

4. Conclusion

4.1 Summary and scientific contributions

The main objective of this thesis was to analyze the extraction stage and to bring new understanding of the X2PCC process. For this reason, a new process is developed named as a wet extractive grinding to maximize the CaO extraction rate and minimizing the overall energy needed for the X2PCC process. In addition, a brief study is done to compare the EG with traditional MM process, also, to optimize process parameters involves in both for higher calcium oxide extraction efficiency to make X2PCC process economically viable for large scale industrial applications.

In this thesis, the effects of various process parameters affecting the wet EG step were quantitatively and systematically investigated for the first time. The thesis was motivated in part by the continuation need to develop mineral carbonation as a carbon capture and storage process (CCS). Currently, mineral carbonation research is primarily at the laboratory-scale research and needs major improvements. It is also needed to make this process a real possibility for the reduction of CO_2 emissions on a large industrial scale. Steelmaking slag-based carbonation does not have a very significant CO_2 reduction capacity. Therefore, this work contributes to the development of mineral carbonation as a CCS method, providing both experimental and process improvement for industrial-scale economic feasibility. Also, to integrate CCU with our X2PCC to utilized steelmaking slag, reducing CO_2 emissions and manufacturing of calcium carbonate as a cyclic-material for CO_2 storage in large-scale applications such as steel making.

In publication I, the optimal concentrations of solvent and particle size for leaching out calcium oxide from the steelmaking slag were analyzed in detail by using the solvent to liquid ration(SLR) of 100 g/L for the extraction step in the X2PCC process. In publication II, a new extractive grinding method for reducing energy and, enhancing calcium extraction efficiency from steelmaking slag is analyzed and compared with our traditional X2PCC process. For this, we used original slag (0-250 μm) and fine ground slag (0-50 μm) and SLR = 30 g/L. In publication III, wet extractive grinding and X2PCC process is analyzed in more detail by varying Solid to liquid ratio and reaction time. In addition, this study also gives a physical characterization of the slag particle before and after extraction.

In this thesis, the extraction stage for X2PCC is comprising of both cases extractive grinding (EG) and mechanical mixing (MM) were studied with numerous experiments on a laboratory scale with varying process parameters. A new wet extractive grinding method was proposed and analyzed in detail. It is also considered that this new EG method results in higher efficiency than the traditional MM method, where typically a handful of varying process parameters were analyzed previously in detail. Especially, the relationship between lowering SLR, reaction time, particle size distribution, the effect of solvent leaching, on the slag particle with physical and chemical characterization is studied on a completely new level for both EG and MM. To the author's knowledge, the comparison of these two methods was utilized in the present thesis for the first time in the context of extraction of calcium, Si, Mg and V from steelmaking slag. It is worth noting that there exist only a few laboratory-scale comparison studies for mechanical mixing and extractive grinding in the vast field of recovery of valuable material from waste.

The main points of this thesis are considered to be consist of the following important factors. Primarily, it is one of the brief studies on the extraction of Ca, and other elements (V, Si and Mg) from steelmaking slag via solvent leaching. A significant number of new findings was achieved, and previous knowledge was also validated by analyzing the different process parameters affecting the extraction stage.

- Traditional mechanical mixing process is discussed in detail with varying parameters.
- New wet EG process is developed for extraction of CaO from steel converter slag. This new process of wet EG is also compared briefly with traditional MM.
- Higher calcium oxide yields up to 70 % is achieved and the wet EG process parameters are also optimized during this study.
- The goal of Sustainable Development Goal of united nations, SDG-12: Responsible Consumption and Production by reducing the need for virgin resources and aiming to rely less upon inventing circular solutions is achieved during this study.
- The selectivity of ammonium chloride is checked for all processes and it was found that it is selective towards calcium bearing species and very little leaching of other elements such as Mg, Si and V.
- Chemical and physical properties of raw and residual slag is compared and analyzed in more depth in all publications.
- Prior process parameters are validated throughout this study to support our earlier hypothesis and new ideas are formulated and published in this study with chemical and physical properties validations.

This study also provides basic design parameters for developing a new wet extractive grinding process in detail to leach valuable minerals. Also, an exceptional study was done for the integration of CO_2-capture Ca-looping integrated with our X2PCC process. The factors limiting the extraction stage are:

1) System limitations of mechanical mixing
2) Solid-to-liquid ratios
3) Solvent molarity

4) Reaction time
5) Particle size distribution

This thesis paves the way for significantly enhancing extraction efficiency to make the X2PCC process economically viable and optimize process parameters for large-scale industrial application.

4.2 Future works directions and limitations

In the context of this present thesis, certain limitations can be identified during the study. Regarding the solid analysis, The ICP-OES/AAS method is used to analyze elemental composition in the original slag. This method has considered the main limitation in the actual final extraction efficiency due to analyzing a very small amount of sample approximately ~0.2 g which is not sufficient and represent a small amount of slag sample. To overcome this error, we come up with a solution, to use the same solid slag sample for conducting experiments and solid analysis from the same batch.

Another area of primary concern is the development of wastewater recycling and purification system for the X2PCC process. The system should be designed in a way to minimize environmental load and to use the same water continuously. For this reason, we analyze wash water generated in different experiments. We conclude that wash water consists mainly: Ca (122–438 mg/L), Si (38–61 mg/L), V (10–27 mg/L), and Na (5.7–9 mg/L) and K (0.9–1.2 mg/L). Another way to reduce the waste wash water is to use as a makeup water after solvent losses during filtration and carbonation stage in the solvent. This has to be analyzed further, as it could lead to an increase in the impurities in the system in the extraction stage.

Another limitation, which concerns optimization in general, is that the molarity of solvent should be increased in a way not to leach other trace impurities such as V, Si and Mg with CaO extraction. And at the same time, keeping the reaction within the stoichiometric limitations. Another important factor is to be considered to change the SLRs by increasing or decreasing to molarity of solvent. For example, in publication III, we studied the combination of 2 mol/L solvent and 30, 60, and 120 g/L SLR, producing λ values of 4, 2, and 1, respectively. We would expect that smaller values could already present stoichiometric limitations.

The following future directions are identified as a high potential for further detailed investigation. First, the optimization of continuation cycling of ammonium chloride for multiple complete extraction-carbonation cycles is needed to be investigated. These need to be investigated for the accumulation of trace impurities after every extraction and carbonation stage. The overall effect of these impurities on final quality of precipitated calcium carbonation (PCC) should be investigated since it offers the possibility of higher quality end-product.

Second, the X2PCC pH-swing process can also utilize other waste materials such as the combustion fly ash. A detailed investigation is needed to analyze the extraction of calcium and other trace impurities via MM and EG, e.g., the fly ash from the oil shale combustion from Estonia at the extraction stage. Recovery of valuable extraction of metal such as Mg and Ca have economic benefits and minimize its disposal to landfills. Accompanying research should also focuses on the waste-water purification system.

Third, the utilization of residual slag should also be investigated for further extraction of valuable metals such as V, Si and Mg. The properties of residual slag after the washing stage should also be investigated in detail for further extraction. The same framework could also be useful to apply to parallel extraction of residual slag through wet extractive grinding. Therefore, the potential for optimization of X2PCC via extractive grinding is maximized.

Finally, the combination of X2PCC with the Ca-looping CO_2-capture process should be investigated further. In this study, we assumed some preliminary estimations, we found that all 284 Mt of PCC produced (using both iron and steelmaking slags) via X2PCC process is used as a make-up chemical. It was suggested that instead of using PCC as the final storage for CO_2, higher CO_2-capture potential is achieved by using PCC in the Ca-looping process. The capture capacity increases from 125 Mt to 1505 Mt annually, which already allows ~4% capture of global CO_2 emissions (37 Gt in 2018). However, this will lead to the continue using virgin limestone for the iron and steel making industry, and no circular economy solution for closing the Ca-loop in the iron and steel industry is attained for this section. But one could think that in the scenario, steel industry would only be borrowing the CaO and then its final use is as an CO_2 capture sorbent.

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