This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Owais, M.; Järvinen, M.; Taskinen, P.; Said, A.

Experimental study on the extraction of calcium, magnesium, vanadium and silicon from steelmaking slags for improved mineral carbonation of CO₂

Published in:
Journal of CO₂ Utilization

DOI:
[10.1016/j.jcou.2019.02.014](https://doi.org/10.1016/j.jcou.2019.02.014)

Published: 01/05/2019

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Owais, M., Järvinen, M., Taskinen, P., & Said, A. (2019). Experimental study on the extraction of calcium, magnesium, vanadium and silicon from steelmaking slags for improved mineral carbonation of CO₂. *Journal of CO₂ Utilization*, 31, 1-7. <https://doi.org/10.1016/j.jcou.2019.02.014>

Experimental Study on the Extraction of Calcium, Magnesium, Vanadium and Silicon from Steelmaking Slags for Improved Mineral Carbonation of CO₂

Owais, M.^{a,*}, Järvinen, M.^a, Taskinen, P.^b and Said, A.^a

a Aalto University, School of Engineering, Department of Mechanical Engineering
Sähkötieteen tie 4J, P.O. Box 14400, 00076 Aalto

b Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, 00076 Aalto

* Corresponding Author. Email address: muhammad.owais@aalto.fi, tel: +358 50 4102644.

Abstract

In this paper X2PCC (Calcium containing material X to Precipitated Calcium Carbonate) process wherein a steelmaking slag is used as a source of Ca for mineral carbonation of CO₂ was studied. Mineral carbonation refers to binding of CO₂ into mineral carbonates, here CaCO₃. In the process, we first dissolve Ca selectively from the slag, then separate the solid phase and finally, bubble CO₂ into the solution to make precipitated calcium carbonate CaCO₃. Based on our current understanding, the extraction step limits the process feasibility. In the experiments, ammonium chloride (NH₄Cl) water solution was used as an extracting solvent with varying concentrations of 0, 0.5, 1 and 2 mol/L using slag to solvent ratio of 100 g/L. The main objective of this study was to determine the optimal concentrations of solvent and particle size for leaching out calcium from the slag. Tests were performed at room temperature with varying particle size and solvent concentration. The extraction behaviors of different size fractions of the slag, 0–50 µm, 50–74 µm and 74–125 µm were studied. Dissolution results showed that with high solvent concentrations calcium extraction efficiency increases but at the same time, other elements are leached, such as vanadium, silicon and magnesium that act as impurities in the subsequent carbonation stage. It was found that with the largest particles, Ca extraction becomes limited by mass transfer and the availability of Ca from the particle. Our hypothesis is that the surface layer of the particles gets blocked by reaction products and stops the reaction. With the smallest particle size, before the surface gets blocked, more calcium could be extracted and the maximum extraction efficiency was not reached.

Keywords: Ca-extraction, Steel slag, Slag2PCC process, Mineral carbonation

1. Introduction

The energy demand in the world is increasing rapidly leading to an increase in greenhouse gas emissions. This is currently a matter of great concern for developed and underdeveloped countries. Annual global direct CO₂ emission 2016 was 35.8 Gt, which is approximately 23 % more than the average annual emissions during the last decade, 2000–2009 [1]. We study the use of mineral carbonization as an option for storing the CO₂ in a valuable product, Precipitated Calcium Carbonate CaCO₃/PCC. Mineral carbonation has many long term advantages, such as long-term stability and production of a valuable product of high quality. Mineral carbonation storage is a permanent method as it does not require post monitoring [2, 3]. In addition to this, our process helps to recycle Ca back to use and significantly reduces the need to mining of virgin limestone.

As a source of calcium for carbonation, the X2PCC (referred also as Slag2PCC) pH-swing process could utilize several different industrial waste materials such as steel slag or the combustion fly ash [4, 5]. To give a perspective, 1.7 Gt of steel was made globally in 2017 and on average 1.8 tons of CO₂ were produced per ton of steel [6]. The production of steel is a very energy and material intensive process based predominantly on fossil fuels. Thus the iron and steel industry is a significant source of anthropogenic CO₂ accounting for around 6.7% of global emissions [4, 6]. In the coming decades there will be constant growth in the steel production, thus CO₂ emissions from the iron and steel industry as a whole will increase unless efforts are made to reduce them. Based on [4], production on 1 ton of steel produces also 0.34 ton of iron and steelmaking slags as the solid by-product. This results in the overall amount of 575 Mt slag production annually, from which the fraction of steelmaking slag is 150 Mt. Slag is formed from the oxides of impurity elements present in pig iron such as Si, Mn, Mg, and in the case of stainless steelmaking, valuable Cr, that are formed during steelmaking. One major component of the steel slag is calcium oxide, CaO that is fluxed in the slag to remove silicon and phosphorus, and to improve slag fluidity. CaO is produced traditionally from virgin limestone by heating it in the lime kiln up to > 900 °C, resulting the reaction $\text{CaCO}_3 + \text{heat} = \text{CaO} + \text{CO}_2$. This reaction creates additional CO₂ that can easily be captured by our process.

The fundamental idea of the X2PCC pH-swing process studied here is very simple. Firstly, steel slag, fly ash or other suitable Ca-containing waste materials are ground into fine powder, preferably to 0–50 µm. Secondly, CaO from the powder is selectively extracted using, in our case, a NH₄Cl-water solvent and the slag leaching residue is removed by filtering the solution. In the subsequent step, CO₂ is bubbled through Ca-rich clean solution to form precipitated calcium carbonate PCC [4, 5]. PCC is a valuable product that we can sell to paper and board, plastic, cement or steel industries. During the carbonation, the ammonium chloride lixiviant is re-generated and can be used again for the extraction [4, 5]. See Fig. 1 for a simplified process description and flow sheet. Here 50% extraction efficiency and 100% carbonation efficiency was assumed for simplicity. Based on Fig. 1, production of 1 t of PCC requires 2.3 t of slag and consumes 0.44 t of CO₂.

Figure 2. Process schematic of the X2PCC pH swing flow sheet. Extraction and carbonation efficiencies are assumed 50 and 100 %, respectively.

At first, we will present a short summary of earlier studies and research, and based on these, the remaining research questions will be formulated. Kodama *et al.* [5] presented the pH swing process wherein aqueous NH_4Cl solvent is used to selectively extract Ca from industrial residues such as steel slag or end-of-life concrete, and then precipitate Ca from the solution as carbonate. This process is here referred as X2PCC. What makes this process especially suitable for this purpose, is the special behavior of the pH. During extraction, the solution changes from acidic to basic, pH increasing from 4.6 to 9.4 and from this it decreases down to 7.26 during the carbonation. Kodama *et al.* [5] also found that the selectivity of NH_4Cl water solution for Ca extraction was very high 99.6 and Ca conversion 60% for the studied slag. They also found that the smaller the particle size, the higher the temperature, the longer the residence time, the higher the surface area of the slag, the higher the Ca conversion rate. The results showed that this process is a prospective one from the viewpoint of low power consumption compared with the previously reported processes, though it has problems related to high cost of crushing the slag and the recovery and supply of NH_3 . The global simplified reactions in the pH swing process are the extraction reaction Eq. (1) and the carbonation reaction Eq. (2). Symbol $\downarrow$ refers to precipitating substances, (s) to solid phase, (l) to liquid and (a) to an aqueous solution.

The loss of ammonia should be minimized, and therefore, keeping the temperature and therefore the NH_3 vapor pressure low is necessary. Kodama *et al.* [5] also suggested that a cooling recovery tower should be used after the extraction reactor to capture gaseous NH_3 and water.

Teir *et al.* [10] studied the use of natural Ca and Mg containing rock minerals and iron and steelmaking slags as raw materials, and mineral and organic acids and bases as solvents for Ca/Mg extraction and capturing CO₂ by carbonation and producing precipitated carbonates. They found that minerals require stronger acids than slags for an effective extraction. For example, in the case of acetic acid (33% water solution), a complete Ca extraction from blast furnace slag can be obtained, 90% extraction from electric arc furnace and BOF slags, 80% extraction from AOD slag and 50% extraction efficiency from wollastonite. For the production of magnesium carbonate, MgCO₃, HCl, HNO₃ and H₂SO₄ were tested for dissolving minerals. It was found that the dissolution kinetics follows a shrinking core reaction scheme and the limiting step is the diffusion through the product layer. They suggested that in the future, extraction should be studied by adding glass beads in the dissolution stage to remove the silica product layers for better extraction efficiency. The acid based processes studied were found to be technically possible and efficient for Ca/Mg extraction, but unfortunately, the final conclusion was that the studied processes produce more CO₂ that it captures. The processes also require significant amounts of chemicals, mainly NaOH that has to be added before the carbonation stage to control pH, making it economically unfeasible. It was found that the smaller the particle size, the higher the lixiviant molarity, the higher the temperature, the higher is the extraction efficiency of Ca.

As continuation for this work, Eloneva *et al.* [4, 11–13] studied the utilization of iron and steelmaking slags as the raw material. They tested several organics acids and three ammonium salt solutions (acetate, nitrate and chloride) as the solvent. It was found that the acetic acid was very effective solvent in the case of blast furnace slag, reaching close to 100 % extraction efficiency of Ca, with molarity of the solvent higher than 1.7 [11]. However, in the acetic acid based process, addition of NaOH was required for efficient carbonation, to keep pH high enough for avoiding reversed reaction. Therefore, the process was found economically non-feasible due to large amounts of chemicals required. The ammonium based processes were found to be CO₂ negative, showing also economic feasibility due to low prices of the raw materials and possibility of efficient solvent recycling [13]. It was found that ammonium chloride solvent concentrations greater than 1 M (mol/L) start to extract impurities, such as V, Si, Mg and Mn, from steel slags which ultimately affects the quality of the precipitated calcium carbonate [12]. It was found that the higher the solvent molarity, and smaller the slag to solvent ratio and the smaller the particle size, the higher is the Ca extraction efficiency.

Said *et al.* [14–17] continued the Slag2PCC research. The effect of ultrasound on the extraction efficiency was studied and it was found that at slag-to-solvent ratio 20 g/L and small particle size, extraction efficiency can be extremely high [16]. It was shown that ultrasonic agitation had a great impact on the extraction efficiency as it increased the rate of reaction, mass transfer and alters different reaction pathways for the reaction to occur. The steel slag used for this purpose was a test slag made from a steel converter slag with a composition of CaO of around 44.9% and SiO₂ about 22.7%. An ultrasonic cleaner created the ultrasonic energy utilized and no additional mechanical agitation was used in the leaching process. The calcium extraction efficiencies were 96 % and 38 % for 0–50 µm and 74–125 µm particle fractions, respectively. The effect of sonication can be used to break the silica gel production layer, formed in pores during the extraction of calcium. However, the feasibility of ultrasound should be studied further, as it uses a significant amount of electricity. In our recent experiments [17] the first results from a 200 liter scale pilot plant were presented and it was shown that the process also works on a larger scale [17].

Chiang *et al.* [18] suggested a three-stage process to transform blast furnace slag (BFS) into two valuable products: precipitated calcium carbonate and zeolitic materials. Calcium is first selectively extracted by organic acid leaching, followed by carbonation of the leachate to precipitate CaCO_3 . Acetic acid satisfactorily limited the leaching of aluminum, required for the subsequent synthesis of zeolites, and carbonation of the acetic acid leachate resulted in the production of PCC of varied mineralogies and morphologies, depending on the processing conditions.

Hall *et al.* [19] analyzed the calcium leaching with 2 M ammonium chloride water solvent on three iron and steelmaking slags. The results from SEM and EDX line scans showed that a silica enriched boundary region was formed at the reaction front, and the reaction continues into the core of the particle following the shrinking core reaction scheme. The main minerals in the untreated slags were found to be calcium silicates, predominantly dicalcium silicate (Ca_2SiO_4). This was followed by a complex mixture of calcium/magnesium-wustite (CaFeMnMgO) type phases and srebrodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5(\text{Ti}, \text{V})$). The results indicated that calcium silicate was more reactive component of the basic oxygen steelmaking slag (BOS), while lime bound as (CaFeMnMgO) was most reactive in hot metal desulfuration slags (HMD) and secondary steelmaking (SS) slags. Ca extraction efficiency was 37, 43 and 25% for BOS, SS and HMD slags, respectively. In addition, the selectivity of the solvent to Ca was high 95–97%.

Lee *et al.* [20] studied the ammonium-based solvents (nitrate AN, acetate AA, chloride AC and sulfate AS) for Ca extraction from air cooled and granulated blast furnace slags. Solvent strength was varied from 0.5 mol/L to 2 mol/L and slag to solvent ratio from 10 to 30 g/L. NaOH was added before the carbonation to increase pH above 8. It was found that the Ca extraction efficiency was the highest with AN, AN and AC solvents ~52% with granulated slags. Ca extraction was much lower with the air cooled slags, 11–15%. In the case of air-cooled slags, the highest efficiency was obtained with AS lixiviant, 13–17%. It was also found that the higher the molarity and the lower the slag to solvent ratio, the higher was the extraction efficiency.

Kim *et al.* [21] presented a different version of the extraction-carbonation process wherein acetic acid pH swing process was first used to extract Ca from the slag. As discussed above, this requires pH control by adding NaOH before the carbonation. The residual slag from this process was extracted by an NH_4Cl based pH swing process to increase the extraction efficiency.

Wyersta and Komon [22] developed a one-step pH swing process using amine-based lixiviants, such as NH_4Cl . In their process, the slag and water are first mixed and then pH allowed to stabilize. After this, a substoichiometric amount of NH_4Cl was added and CO_2 gas was fed until pH decreased to 8, after which the gas flow was stopped for 30 min, allowing pH to increase and stabilize. To assure complete precipitation, gas was allowed to flow continuously until the required pH was achieved. The flow of CO_2 was continued still 10 minutes after the pH had reached 8. The experiment was finished without the gas flow, recording the pH increase for 7 minutes. The residual slag and PCC were let to separate by gravity and decanted followed by filtering. They discovered that the amount of slag required for 1 ton of PCC was 3.1–4.5 times larger in the tradition two-step X2PCC process. We assume that this calculation was based on using the same amount of NH_4Cl in both cases, which results in a low extraction efficiency in the two step process. If the two-step process is driven by 2 mol/L solvent and solid to liquid ratio of 30 g/L, very good

performance, such as 2.5–3 ton of slag per 1 ton of PCC produced, were obtained. Of course, this requires well optimized recycling of the solvent.

Mattila *et al.* [23–24] studied the Slag2PCC swing process extensively. They developed a detailed kinetic model for the extraction and carbonation steps, verified and validated it with experiments [24]. Calcium extraction rate and efficiency was found to mainly depend on the particle size and chemical properties of the slag. Rate of carbonate precipitation depended mainly on carbon dioxide flow through the reactor, mixing rate of the solution, size of gas bubbles and also strongly on the ammonia concentration in the solution. Based on their model, the recycling of the solvent and extraction stages conducted were in series [24]. They found that there is a small change in Ca and ammonium concentrations after the first cycle, but beyond that they remained constant. For the carbonation step, the recycled solvent had a minor effect. The tests with two sequential extraction reactors, both operating with fresh solvent, showed an increase in extraction efficiency from 33% to 46% of total Ca compared with the one-step extraction.

The topic of this current research paper is related to reducing carbon dioxide emissions in the atmosphere by Carbon Capture and Utilization, CCU. Based on the short review given above, there is a huge amount of development work already carried out. From the operational point of view, the higher the fraction of Ca extracted from the slag or ash, the higher the efficiency, or the yield of PCC of the overall X2PCC process will be. Therefore, the objective of this paper was to study the extraction process step in detail and systematically search for further improvement options. We also want to obtain new experimental data of the effect of residence time, particle size and molarity of the solvent to be later used as a building material for improved and validated process models. The main objective of this work was to maximize the rate and extraction efficiencies and to minimize the dissolution of other elements.

2. Materials and Methods

The extraction experiments were carried out in a 500 mL round bottom flask incorporated with pH and temperature sensors connected to a data logger. A magnetic mixer VWR VMS-A was used with 300 rpm. All experiments were carried out at atmospheric pressure. During the experiments, the reaction vessel was submerged in the thermostated water bath, MGW Lauda C-20, keeping the bath temperature constant at 23°C. Fig. 2 presents the laboratory setup. pH was continuously measured with a VWR pH electrode SJ 113, 662-1382, and temperature was measured with a 1.5 mm K-type thermocouple.

Figure 2. Laboratory set-up.

At first, industrial grade ammonium chloride was dissolved in distilled water to obtain required molarities of 0.5 mol/L, 1 mol/L, 1.5 mol/L and 2 mol/L, using a 500 mL measurement bottle. The slag used for tests had a particle size between 0–250 μm . Steel slag was classified into different size fractions of 0–50 μm , 50–74 μm and 74–125 μm by mechanical sieving. The solid to liquid ratio was 100 g/L in all experiments, 50 g slag per 500 mL of solvent. The reaction time was 30 minutes and liquid samples of 10 mL were taken in every 5 minutes. Data logger reading interval for temperature and pH was one second. The experimental test matrix is given in Table 1.

Table 1. Test Matrix

Slag Size (μm)	NH_4Cl concentration M, mol/L			
	0.5	1	1.5	2
0–50	Test #1	Test #2	Test #3	Test #10
50–74	Test #4	Test #5	Test #6	Test #11
74–125	Test #7	Test #8	Test #9	Test #12

The slag used in the experiment was a basic oxygen steel converter slag from SSAB in Raahe, Finland. The slag composition was analyzed by Ahma Ympäristö Oy (ICP-AES) and Aalto University (ICP-AAS), and its chemical composition is given below in Table 2. Error of the ICP analysis was $\pm 2\%$. Table 2 also presents the mass fractions of different particle size classes and their compositions. Here we grouped together the size fractions 0–50 and 50–74 μm to 0–74 μm to have a more reliable and representative sample size. In the leaching rate studies later, the size fractions were studied separately.

Table 2. Chemical compositions of the steel slag particle fractions used in the experiments by ICP-AES and ICP-AAS methods, analysis error $\pm 2\%$.

Size range	0–250 μm^a	0–250 μm^b	0–74 μm	74–125 μm	>125 μm
Mass fraction	1	1	0.176	0.227	0.597
Element	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
Ca	356.0	331.6	335.0	333.0	330.0
Al	6.4	9.1	8.6	8.8	9.3
V	20.8	19.8	18.6	19.8	20.2
Si	52.9	52.8	40.0	48.0	58.4
Fe	133.0	175.7	175.0	178.0	175.0
Mn	18.2	17.6	18.5	17.0	17.6
Mg	10.2	10.5	9.5	10.6	10.8

a = ICP-AES, b = ICP-AAS, combined from different size fractions.

XRD results shows that steelmaking slags mainly consist of dicalciumsilicate (Ca_2SiO_4), dicalciumferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and wüstite (Fe_{1-x-y} , Mg_x , Mn_y) O_z . It can be seen in Table 2 that there are no significant chemical differences between the size fraction classes of the slag. It should also be noted that an accurate analysis of the slag was extremely challenging since the sample size in chemical analysis was only 200 mg. Particle size distribution of the slag and the corresponding Rosin-Rammler size distribution fit is presented below in Fig. 3.

Figure 3. Particle size distribution of the steel slag, $X = 165.22 \mu\text{m}$ and $q = 2.9852$ fitted in Rosin-Rammler distribution $F(d) = 1 - \exp\left(-\left(\frac{d}{X}\right)^q\right)$

Based on the Rosin-Rammler distribution fitted with the sieved data, mass median diameter of the slag was $d_{0.5} = 146 \mu\text{m}$. As far as authors are aware of, the compositions of different particle

size classes have not been reported prior to this study. Based on Table 2, the compositions of different size fractions were not the same, and Ca was slightly enriched in the smaller size fractions. This could be due to a weaker structure of the CaO phase, and easier grindability. However, the differences in Ca contents were fairly small.

3. Results and Discussion

The extraction of Ca and other elements such as Mg, V, Si from the different size classes of the steel slag was studied. Based on the earlier research [4, 5] the extraction rate is a strong function of the particle size, the smaller the size, the higher the rate and the final extraction efficiency, defined as the Ca recovered to the solution. Therefore, we focused here on the sizes smaller than 125 μm , dividing that into 3 size classes, namely 0–50 μm , 50–74 μm , 74–125 μm . However, based on the results above particles higher than 146 μm correspond to 50% of the powders mass. This would mean that in an industrial plant practice, we would grind the slag to smaller fineness in order to reach higher Ca-extraction efficiency.

3.1 Calcium conversion, pH and temperature as function of time

As an example of the leaching experiments, Figs. 5–7 present typical temperature and pH measurements for 0–50 μm size slag fraction. Fig. 4 presents the corresponding extraction efficiency curves for calcium. Extraction efficiency/degrees of dissolution X_i and their rates $\frac{dX_i}{dt}$ were calculated by the Eqs. (3) and (4), respectively.

$$X_i = \frac{c_i V}{m_i^0} \quad (3)$$

$$\frac{dX_i}{dt} = \frac{X_i^{t=5 \text{ min}}}{5 \text{ min}} \quad (4)$$

Wherein 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 slag (g) used in the experiment.

Figure 4. Extraction efficiency of Ca, 0–50 μm size fraction: 100 g/L solid to liquid ratio. 0.5, 1 and 2 refer to lixiviant molarities (mol/L)

Figure 5. pH and temperature of the solution: 0–50 μm , 100 g/L, 0.5 mol/L

Figure 6. pH and temperature of the solution: 0–50 μm , 100 g/L, 1 mol/L.

Figure 7. pH and temperature of the solution: 0–50 μm , 100 g/L, 2 mol/L.

As it can be seen from Figs. 4–7, the higher the concentration of ammonium chloride, the higher the extraction efficiency, the higher the rate of heat generation and the higher the end pH. It is interesting to see that the extraction efficiency curves of the 0.5 and 1 mol/L NH_4Cl cases overlap and they both resulted in the same final composition field. This result was verified with an additional repeated leaching test.

3.2 Effect of particle size and molarity on extraction efficiency

As a summary of all the experiments, Figs. 8a–11a presents the extraction efficiency after 30 min reaction for all size classes 0–50, 50–74 and 74–125 μm . Slag-to-solid ratio was 100 g/L in all tests. Based on the first measurement point at 5 min of each leaching test, the initial extraction rates were calculated by 1st order differentials of the recovery vs. time plot, Eq. (4), Figs. 8b–11b.

Figure 8a. Extraction efficiency of Ca.

Figure 8b. Initial extraction rate of Ca.

Figure 9a. Dissolution degree of V.

Figure 9b. Initial dissolution rate of V.

Figure 10a. Dissolution degree of Si.

Figure 10b. Initial dissolution rate of Si.

Figure 11a. Dissolution degree of Mg.

Figure 11b. Initial dissolution rate of Mg.

Figs. 8a–11a show the final extraction efficiencies of Ca, V, Si and Mg after 30 min, in varying solvent concentrations of 0.5, 1, 1.5, 2 mol/L NH_4Cl and for the particle size fractions of 0–50 μm , 50–74 μm and 74–125 μm . Generally, the extraction efficiency of Ca and Mg increased with increasing solvent concentration and decreasing particle size. When increasing the solvent concentration, extraction efficiency of Ca increased first almost linearly. This indicates that the calcium extraction is limited by the amount of solvent available in the lixiviant. With the largest particles, Ca extraction became limited by the availability of Ca from the solid particle and the increase of extraction efficiency as a function of molarity decreased, and ceased around 1.5–2 mol/L. It seemed likely that a surface layer of the particles was formed by reaction products, such as silica gel, and stopped the advancement of the reaction. With the smallest particle size, before the surface layer was blocked, most of calcium was extracted and this ended up with the higher yield. This was also discussed and partially verified already in our earlier paper, Said *et al.* [15].

In the case of smallest particles, the maximum extraction efficiency limit was not reached and linear increase in extraction efficiency can be observed up to 2 mol/L concentration of the solvent studied. Interestingly, as can be seen in Fig 8a, there seems to a local minimum at 1 mol/L solvent concentration. These same observations can be seen for Mg. This minimum was verified by additional leaching tests. In the case of the smallest particles, the maximum extraction

efficiency was not reached and in our future work, this will be studied in detail by increasing the solvent strength and minimizing still the yield of extraction of other elements from the slag. Both Ca and Mg are known to behave similarly and can be carbonated in the subsequent process step. Mg is much less reactive and it does not seem to be limited by Mg availability at higher solvent concentrations, Fig. 11a. For both V and Si, there can be a maximum in the extraction efficiency around 1–1.5 mol/L NH_4Cl concentration. In our future work, these will be studied in detail by increasing the solvent strength and minimizing the yield of extraction of other elements from the slag.

Figs. 8b–11b showed the initial leaching rates, dX/dt , based on the 5 minute experimental extraction rate values. Both Ca and Mg showed increasing rates with respect to increasing molarity of ammonium chloride and decreasing particle size, except for the local minimum for Mg at 1 mol/L and in the smallest particle size range. Surprisingly, extraction rates of both Si and V had a minimum at 1 mol/L with 0–50 μm particle size fraction but they both presented a maximum at 1–1.5 mol/L for larger particles. This will be studied further in the future work.

As the extraction step is only a part of the overall Slag2PCC/X2PCC process, we need to consider also the effects of extraction in the subsequent carbonation stage. For example, if a significant fraction of V, Mg and Si are dissolved in the leaching step, they start to accumulate in the circulating leaching solution in a continuous process without bleed and separate removal step outside the actual leaching-carbonation cycle, affecting the quality of the PCC product and also decreasing the solution potential of the solvent. This will be studied in our future work.

5. Conclusions

This work examined the extraction of calcium oxide from an industrial steel converter slag powder, and analyzed the effect of slag particle size in fractions of 0–50 μm , 50–74 μm and 74–125 μm , effect of lixiviant molarity on the extraction efficiency, rate and selectivity. The research aimed in finding the optimum solvent molarity and particle size for the maximum extraction and selectivity to Ca. Our original hypothesis was that CaO containing phase locations could be the weakest parts of the slag particles, and therefore, easiest to grind, and therefore Ca could be enriched in the smaller fractions. If we use the overall composition of the slag analyzed to calculate the yield from different size classes this could then lead to significant errors. However, this seems not to be the case as Ca was only slightly enriched into the smallest size fractions of the steel slag. The dissolution results showed that with a high solvent concentration, calcium extraction efficiency increased but at the same time, the lixiviant leached other elements from the steel converter slag, such as vanadium, silicon and magnesium that are impurities in the carbonation stage. Similar trend has also been observed and reported by us earlier e.g. [4, 6, 12 and 13]. Clearly, there is an optimal solvent molarity that gives high Ca yield but minimizes dissolution of other elements. This will be studied in our future work in detail, including a study wherein extraction and carbonation stages are repeated several times, using the same solvent, and studying the accumulation of V, Si and Mg in the solvent during continuous processing. When increasing the solvent concentration, it was found that with the largest particles, Ca extraction became limited by mass transfer and availability of Ca from the solid particle. It seemed that the surface layer of the particles was blocked from the same depth by reaction products and stopped the reaction. Opposite

to this, with the smallest particle size, before the surface was blocked, 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 extraction behavior of other elements Si and V showed extremely interesting behavior. Both Si and V presented a maximum extraction efficiency and extraction rates at 1–1.5 mol/L ammonium chloride concentration with the exception of the smallest size that showed a minimum leaching rate at 1–1.5 mol/L.

6. Acknowledgements

We acknowledge Academy of Finland (projects 258319 and 26495) and Renlund foundation for their financial support.

7. References

1. Olivier, J.G.J., Janssens-Maenhout, G., Muntean, M., Peters, J.A.H.W. Trends in global CO₂ emissions 2016 report, PBL Netherlands Environmental Assessment Agency The Hague, 2016, Netherlands, EU Commission report, 2016.
2. Pan, S.Y., Chang, E. E., and Chiang, P.C. CO₂ capture by accelerated carbonation of alkaline wastes: A review on its principles and applications, *Aerosol Air Qual. Res.*, vol. 12, no. 5, pp. 770–791, 2012.
3. Lackner, K.S. A Guide to CO₂ Sequestration, *Science*, vol. 300, no. 5626, p. 1677, Jun. 2003.
4. Eloneva, S. Reduction of CO₂ emissions by mineral carbonation: steelmaking slags as raw material with a pure calcium carbonate end product, Doctoral Dissertation, Helsinki University of Technology, 2010.
5. S. Kodama, T. Nishimoto, N. Yamamoto, K. Yogo, and K. Yamada, “Development of a new pH-swing CO₂ mineralization process with a recyclable reaction solution,” *Energy*, vol. 33, no. 5, pp. 776–784, May 2008
6. World Steel Association, World Crude Steel Production – Summary, 24 January 2018, www.worldsteel.org
7. Teir, S., Fixation of carbon dioxide by producing carbonates from minerals and steelmaking slags, Doctoral Dissertation, Helsinki University of Technology, 2008.
8. Teir, S., Eloneva, S. and Zevenhoven, R. Production of precipitated calcium carbonate from calcium silicates and carbon dioxide, *Energy Conversion and Management* 46 (2005) 2954–2979.
9. Teir, S., Eloneva, S., Fogelholm, C.J. and Zevenhoven, R. Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production, *Energy*, Volume 32, Issue 4, April 2007, Pages 528-539.
10. Teir, S., Revitzer. H., Eloneva, S., Fogelholm, C.J. and Zevenhoven, R. Dissolution of natural serpentinite in mineral and organic acids, *International Journal of Mineral Processing*, Volume 83, Issues 1–2, 4 July 2007, Pages 36-46.
11. Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.-J. and Zevenhoven, R. Fixation of CO₂ by carbonating calcium derived from blast furnace slag, *Energy*, Volume 33, Issue 9, September 2008, Pages 1461-1467

12. Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.-J. and Zevenhoven, R. Steel converter slag as a raw material for precipitation of pure calcium carbonate. *Industrial & Engineering Chemistry Research*; 47 (18): 7104-7111, 2008.
13. Eloneva, S., Said, A., Fogelholm, C.J. and Zevenhoven, R. Preliminary assessment of a method utilizing carbon dioxide and steelmaking slags to produce precipitated calcium carbonate, *Appl. Energy*, vol. 90, no. 1, pp. 329–334, Feb. 2012.
14. Said, A. CO₂ sequestration by steelmaking slags for the production of precipitated calcium carbonate - From laboratory to demonstration stage, Doctoral Dissertation, Aalto University, 2017.
15. A. Said, H.-P. Mattila, M. Järvinen, and R. Zevenhoven, Production of precipitated calcium carbonate (PCC) from steelmaking slag for fixation of CO₂, *Appl. Energy*, vol. 112, pp. 765–771, Dec. 2013.
16. A. Said, O. Mattila, S. Eloneva, and M. Järvinen, Enhancement of calcium dissolution from steel slag by ultrasound, *Chem. Eng. Process. Process Intensification*, vol. 89, pp. 1–8, Mar. 2015.
17. A. Said, T. Laukkanen, and M. Järvinen, “Pilot-scale experimental work on carbon dioxide sequestration using steelmaking slag,” *Appl. Energy*, vol. 177, pp. 602–611, Sep. 2016.
18. Y.W. Chiang, R. M. Santos, J. Elsen, B. Meesschaert, J. A. Martens, and T. Van Gerven, “Towards zero-waste mineral carbon sequestration via two-way valorization of ironmaking slag,” *Chem. Eng. J.*, vol. 249, pp. 260–269, Aug. 2014.
19. C. Hall, D. J. Large, B. Adderley, and H. M. West, “Calcium leaching from waste steelmaking slag: Significance of leachate chemistry and effects on slag grain mineralogy,” *Miner. Eng.*, vol. 65, pp. 156–162, Oct. 2014.
20. Lee, S., Kim, J.W., Chae, S., Bang, J.H. and Lee, S.W. CO₂ sequestration technology through mineral carbonation: An extraction and carbonation of blast slag, *J. CO₂ Util.*, vol. 16, pp. 336–345, Dec. 2016.
21. Kim, T.Y., Chung, S.Y., Lee, K.C. System and Method for carbon dioxide solidification, US20130078168A1, Patent application publication, March 28, 2013.
22. Wyrsta, M. and Komon, Z.J.A. Methods for producing alkaline earth carbonates. WO2015168159A1, PTC publication, November 2015.
23. Mattila, H.P. Utilization of steelmaking waste materials for production of calcium carbonate (CaCO₃). Doctoral Dissertation. Åbo Akademi University, 2014.
24. Mattila, H. P., Grigaliūnaitė, I. and Zevenhoven, R. Chemical kinetics modeling and process parameter sensitivity for precipitated calcium carbonate production from steelmaking slags. *Chemical Engineering Journal*, Volume 192, 1 June 2012, Pages 77-89.