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Detailed performance analysis of the wet extractive grinding process for higher calcium yields from steelmaking slags

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ABSTRACT

In this paper, the wet extractive grinding method for efficient recovery of calcium from steelmaking slags was studied. This work supports the Sustainable Development Goal of UN, SDG12: Responsible Consumption and Production by reducing the need for virgin limestone and aiming to circular solutions. The extraction is the first step in our pH-swing process, wherein CaO from the slag using a NH4Cl-water solvent is dissolved. After filtering the solid phase, CO2 is bubbled into the Ca-rich solution to produce precipitated calcium carbonate (PCC). Traditional mechanical mixing for extraction stage is found problematic since it requires energy intensive preliminary fine-grinding to be effective. Effects of the processing time (1.25–20 min), and the slag-to-solvent ratio (SLR = 30–120 g/L) were studied here in detail in the extractive grinding process. Inductively coupled plasma-atomic emission spectroscopy (ICP-OES), energy-dispersive X-ray spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analyses were used for the detailed physical and chemical characterization of raw and residual slag powders. Results showed that Ca-yield increases from 35 to ~70% via the EG process as comparison with mechanical mixing. Results also show that the rate of the process also significantly increased.

1. Introduction

United Nation’s Sustainability Development Goal, SDG12: “Responsible consumption and production” aims to decrease the consumption of virgin raw material resources, increase the re-use and recycling, and focus on developing circular economic solutions [1]. This current paper focuses on the recovery and recycling of CaO from industrial side and waste products, here from the steelmaking slags. The main aim is to offer a significant circular economy solution for CaO/CaCO3 business sector and to reduce emissions from lime production.

Total global annual limestone consumption is 15 000 Mt of which 2.3% is used for the direct production of lime, CaO [2]. While CaO is produced in the lime kiln, already 275 Mt of CO2 is released from the limestone. Additional CO2 is released from the fuel that is used for heat generation in the lime kiln. 60% of the lime produced is used in metallurgical applications. The annual production of steelmaking slags is ~130 Mt, containing ~65 Mt of CaO [3]. Here, the main aim is to recover a significant share of this CaO from the steelmaking slag and use it as raw material for production of PCC, precipitated calcium carbonate. The first step in the X2PCC process is to ground the slag, or other CaO bearing material, into fine powder, preferably down to 0–250 µm. Then, CaO from the slag powder is selectively extracted using a NH4Cl-water solvent, and the slag leaching residue is removed by filtering the solution. Finally, CO2 from flue gasses is bubbled through a clean Ca-rich solution to precipitate calcium oxide as CaCO3, PCC. PCC as such already serves as a CO2 storage. However, since the annual production of slags is in the order of 130 Mt [3], and if they contain ~50%, i.e., 65 Mt of CaO, from which we can extract typically 50%, it will allow us to bind annually 26 Mt of CO2, which is only ~0.1% of total global CO2 emissions. To improve the CO2-capture potential of the PCC produced from the X2PCC process, this PCC could be used as a make-up chemical additive in the Ca-looping CO2-capture process. PCC would be fed into the calciner reactor together with the circulating sorbent loaded with CO2. Bound CO2 is then released via a decomposition reaction. Then, the released CO2 could be fed into permanent deep underground storage or used as a raw material in CCU applications [4,5]. After releasing and storing the CO2, CaO is recycled back to the carbonator, where it captures new CO2, and the cycle is then continued. The potential of this concept is initially discussed in the Section 3.5 and analyzed in detail in our future work.

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The main product of the X2PCC process, PCC, is a valuable product utilized in the paper and board, paint, plastic, brick, and cement industries, and it can also be recycled back to steelmaking or even fed into CCS/CCU processes, as described above. The most important parameters that define the applicability of the PCC product in these industries are the particle size, crystal shape, purity, and whiteness. Regarding the extraction step in a process that aims to produce clean and high-quality PCC, it is important to maximize the selectivity of the Ca extraction, and to minimize the dissolution of other elements such as Si, Mg, and Fe, which can affect the quality of the PCC. In addition to this, the yield should be maximized to increase the supersaturation of Ca in the precipitation step to produce PCC of known morphology and extremely large particle size. As will be discussed in Section 3.5, if PCC was used as a sorbent, most of these requirements would not be present, which would greatly simplify the processing in X2PCC, making the process much easier to control, and the main focus should be on maximizing the PCC yield. This will be studied in our future work in more detail.

In our recent study [9], a brief descriptive review of the literature related to X2PCC and wet extractive grinding was already presented, which we do not repeat here. Rather, a concise summary of the topics that are most relevant to the extractive grinding process is presented. X2PCC (or Slag2PCC) process is similar to the work done by Kodama et al. [15]. They also introduced the pH-swing process, using aqueous NH4Cl solvent to extract Ca from industrial residues such as steel slag or cement mortars. It was found that the selectivity of the NH4Cl water solution for Ca extraction is very high at 99.6%, and Ca conversion was 60% for the slag grade studied. Teir et al. [10–12] found that the dissolution kinetics of Ca follow a shrinking core reaction scheme, and the limiting step is the diffusion through the product layer. They suggested that extraction could be improved by adding glass beads in the dissolution stage to remove the silica product layers for better extraction efficiency. The effect of ultrasound on the extraction efficiency was reported by Said et al. [13]. It was found that extraction efficiency can be extremely high at a slag-to-solvent ratio of 20 g/L and small particle size. The calcium leaching of three iron and steelmaking slags with 2 mol/L ammonium chloride water solvent was studied by Hall et al. [15]. They found that a silica-enriched boundary region at the reaction front was formed, where the reaction continued into the core of the particle, following the shrinking-core reaction scheme. The selectivity of the solvent to Ca was high at 95–97%. Wang et al. [16] studied the efficiency of wet grinding for the mechanical-chemical activation of granulated blast furnace slag (BFS), when used as a substitute for cement. It was found that the size reduction of large particles largely depends on the duration of the grinding. The further reduction of small particles slows down when the milling duration exceeds 20 min, mainly due to the high viscosity of BFS slurry. Wet grinding increases the alkalinity of BFS slurries due to the dissolution of alkaline cations from BFS particle. Navarro et al. [17] studied the physico-chemical characteristics of steel slag under simulated environmental conditions. The steel slag particle size used in their process was 0–10 mm, and samples were milled and sieved to obtain a powder with particle sizes < 100 μm. The slag was characterized as a crystalline heterogeneous material made of iron oxides, calcium, and magnesium compounds (hydroxides, oxides, silicates, and carbonates), elemental iron, and quartz. The slags were porous, with a specific surface area of 11 m²/g, containing both mesopores and macropores. Steel slags contained a significant amount of portlandite, and calcium silicates are potential raw materials for CO2 long-term storage. Wang et al. [18] evaluated the self-hydration characteristics of ground granulated blast-furnace slag (GGBFS) activated by wet-grinding treatment. Reaction kinetics, mechanical properties, hydration products, and microstructure of hardened GGBFS pastes were studied. It was found that the self-hydration heat was strongly influenced by the grinding time, and that a shorter grinding time typically presented two exothermic peaks, while samples with a longer grinding duration showed only one exothermic peak. The main products of self-hydration GGBFS are calcium silicate hydrate, hydroaluminate, crystalline phases, and calcite. J. Yang et al. [19,20] investigated the utilization of high-volume fly ash in steam-cured cement mortar using wet milling. It was found that with wet grinding of cement mortar and combining with ultra-fine ash can increase the strength of cement mortar up to 50%. They used wet milling for enhancing pozzolanic reactivity of fly ash for sustainable building material. He et al. [21] used wet milling for autoclave aerated concrete waste (AACW) as supplementary cementitious material. It was found that with AACW can be used as an alternative building material with 30% replacement level [21]. The main objective of this work is to study the performance of the wet extractive grinding method for the effective extraction of calcium from steelmaking slag and to perform detailed analyses of original and residual slag by chemical and physical properties. Process optimization of the EG is conducted by varying the solid-to-liquid ratios from 30 to 60 and 120 g/L, while reaction time was varied between 1.25 and 20 mins, respectively. Here, the Ca, Mg, V and Si yields are compared and discussed between the traditional mechanical mixing and EG processes. The main hypothesis is that, by using wet extractive grinding, the extraction rate is increased since abrasion between particles and the grinding ball provide a means of keeping the surface open for deep leaching of calcium into particles. This results in enhanced extraction and efficient leaching. This hypothesis is supported by earlier research [9,10]. Here, the main aim is to maximize the rate and extraction efficiencies, and to minimize the dissolution of other elements such as V, Si, and Mg. Two cases were compared: 1) mechanical mixing extraction (MM) with original slag (0–250 μm); and 2) a wet extractive grinding process (EG) with original slag (0–250 μm).

In this paper, the focus is on the extraction step. A significant amount of earlier research has been done on optimizing the carbonation stage [6, 7,10–14], also in the high Ca yields. Earlier [8,9], it was found that the extraction stage is the main limiting factor for process optimization. In the EG process, the grinding and extraction steps are combined into a single unit, intending to increase the rate and the yield of the overall process. In addition, the aim is to decrease the overall energy consumption, as well as the reducing the intricacy of the system.

2. Materials and methods

All tests are divided into two categories: traditional mechanical mixing (MM), and wet extractive grinding (EG). These are compared briefly in [9]. For 2 mol/L solvent, 53.49 g ammonium chloride (NH4Cl) of industrial grade was dissolved in normal tap water at room temperature using a 500 mL volumetric flask. The solvent was kept at room temperature overnight to dissolve all the salt particles in the solution and to reach the room temperature. Tests were conducted using slag-to-liquid (SLR) ratios of 30, 60, and 120 g/L; we used 15, 30, 40, and 60 g of slag per 500 mL of solvent, respectively. Earlier work was performed using only 30 g/L SLR [9], and, in this study, the SLR ratio was determined by multiplying 2 and 4 times the amount of slag used by our prior research experiments. This SLR ratio is significant as it depicts the amount of slag leached by the 2 mol/L solvent. Earlier study suggested that the 30 g/L solid-to-liquid ratio, with a 1 mol/L solvent with extractive grinding, gave the highest extraction efficiency [9]. In this study, however, the solvent concentration was increased to 2 mol/L and analyzed varying SLR to optimize the ratio and extraction time. The extraction time was varied between 1.25 and 20 mins. Samples from slags and liquid products were collected and analyzed in detail.

2.1. Stoichiometric limitations

The stoichiometric limitations of the Ca dissolution reaction are vital for the selection of the process parameters, i.e. the molarity, M, of the solvent, and the solid-to-liquid ratio (SLR). The main reactions that occur in the calcium dissolution from slag are presented below. At first,
solid NH₄Cl salt is dissolved in water, (a) refers to the aqueous solution.

\[ \text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_4^+(a) + \text{Cl}^-(a) \]  

NH₄Cl is highly soluble in water, i.e., 391.8 g/L at 25 °C, and 740.8 g/L at 100 °C; these correspond to molarities of 7.3 and 13.8 mol/L, respectively [22]. The next step is the formation of the hydronium ion \( \text{H}_3\text{O}^+ \) by reaction with water.

\[ \text{NH}_4^+(a) + \text{H}_2\text{O} \rightarrow \text{NH}_3(a) + \text{H}_3\text{O}^+(a) \]  

It is noted that the ionization reaction is fast and tends to reach equilibrium. Actual dissolution of calcium occurs when these hydronium ions react with CaO(s) as follows.

\[ 2\text{H}_3\text{O}^+(a) + \text{CaO(s)} \rightarrow \text{Ca}^{2+}(a) + 3\text{H}_2\text{O} \]  

\[ 2\text{H}_3\text{O}^+(a) + 2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{Ca}^{2+}(a) + \text{SiO}_2(a) + 3\text{H}_2\text{O} \]  

\[ 2\text{H}_3\text{O}^+(a) + \text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}^{2+}(a) + \text{SiO}_2(a) + 3\text{H}_2\text{O} \]  

It is assumed that the last three reactions (3a, 3b and 3c) form the rate limiting steps. For example, Mattila et al. [33] assumed that only CaO(s) requires 2 mol of NH₄Cl. The solvent molarity and SLR define the possible to attack calcium silicate.

The stoichiometry of these reactions plays a vital role in the performance of the process. Theoretically, the extraction of one mole of CaO(s) requires 2 mol of NH₄Cl. The solvent molarity and SLR define the actual stoichiometry. This relation can be presented as follows.

\[ \lambda = \frac{N_{\text{CaO}}}{2M_{\text{NH}_4\text{Cl}}} = \frac{M}{2m_{\text{SLR}}} = \frac{M}{2SLR} \frac{M_{\text{CaO}}}{y_{\text{CaO}}} \]  

Factor 2 comes for the stoichiometric requirement. For a stoichiometric reaction, with the above definitions, \( \lambda \) is equal to 1. In our previous paper [10], SLR = 30 g/L was studied by varying molarity between 1 and 4. Using Eq. (4), this correspond to \( \lambda \) values of 2.0, 4.0, and 8.0, for 1, 2, and 4 mol/L solvent, respectively. Using the extractive grinding, the Ca yields of 55–60% were obtained with these values, showing no significant change in yield as a function of the molarity with 0–50 μm particles, where there are no major limitations on mass transfer or the availability of Ca. In the case of 0–250 μm particles, a significant decrease in the Ca yield for the larger particle size due to mass transfer limitations was found. This indicates that, within the studied range, the amount of solvent is not limiting the reaction, and there is potential for improving the process feasibility; similar results could be obtained with a smaller amount of chemical used. The similar results could be achieved with a lower value of \( \lambda \), e.g. by increasing the SLR, or decreasing the solvent molarity (M). In this paper, 2 mol/L solvent and SLRs of 30, 60, and 120 g/L, were studied, resulting in \( \lambda \) values of 4, 2, and 1, respectively. It is expectable that smaller values could already present stoichiometric limitations. It has been found [6 – 14] that the available CaO in slag particles is mostly in the form of free CaO and 2CaO(SiO₂). From the latter, only one CaO can be easily extracted using an NH₄Cl solvent due to the strong bonding in the remaining phase. In our earlier research, it was also discussed that silica gel formation also hinders solvent extraction by preventing the penetration of solvent into the reaction surface within the particle, which ultimately results in lower extraction [9 – 10]. Different techniques, such as sonication [13], can reduce this hindrance and enhance extraction. If a significant amount of the Ca is bound within 2CaO(SiO₂), then 50% of it could be easily extracted, resulting in CaO(SiO₂), which is then more inactive. In addition to this, a small amount of free CaO is available for further extraction, consequently increasing the maximal yield to 55–60%.

2.2. Mechanical mixing method

The extraction experiments were performed in a 500 mL three-neck round-bottom glass reactor equipped with pH and temperature sensors connected to a data logger. A mechanical overhead VOS-16 mixer manufactured by VWR International was used at rotation speed setting 4, corresponding to 460 rpm. The impeller is a two-blade simple mixer, having an outer blade tip diameter of 7 cm. All experiments were carried under atmospheric pressure. During the experiments, the reaction vessel was submerged in a thermostatic water bath (MGW Lauda C-20) at a constant temperature of 23 °C. Fig. 1 presents the laboratory setup. A VWR pH electrode (SJ 113, 662–1382), and a 1.5 mm K-type thermocouple measured the pH and temperature of the experiment, respectively, for both reaction and washing stages.

For each experiment, the desired solvent was first poured into the reactor, followed by mixing until the temperature and pH were stabilized. Then, the weighed slag was poured into the same reactor and mixed for 20, 5, or 1.25 min. The extracted solution mixture was then vacuum filtered with 2.7 μm pore size filter paper (Whatman 1450–110). A ~10 mL liquid sample was taken from the Ca-rich solution to analyze the composition and concentrations of the dissolved elements. The filtered residual slag cake was dried in an oven for 15 h at 120 °C. The residual slag cake was weighed before and after drying for total mass loss before and after extraction.

2.3. Extractive grinding method

All the wet extractive grinding experiments were performed in an AR−MINI ball mill made by Kerasil (Nurmijärvi, Finland). The mill was
equipped with a ceramic jar with a rubber seal. Due to the closed system, the pH was measured only before and after each experiment. It was impossible to measure the continuous temperature profile because of the closed nature of the system. At the end of the experiments, samples were taken for elemental analysis.

A total number of 255 ceramic balls of diameter 13.5 mm were used, ~4.6 g each, with density $\rho_b = 3.6 \text{ g/cm}^3$. The inner dimensions of the mill jar were $120 \times 120 \text{ mm}$ (diameter $\times$ length), volume $1357 \text{ cm}^3$. These dimensions result in a critical rotational speed of 130 rpm. The actual rotational speed used was 90 rpm, 70% of the critical value, as suggested by [23].

The apparent density, $\rho_a$, and porosity, $\varepsilon_s$, 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 $\rho_s$ was therefore determined to be $1.55/(1-0.46) = 2.87 \text{ g/cm}^3$. Different milling parameters are presented in Table 1.

Based on [23], if the value of $U$ approaches 100%, this would suggest that the mill is overloaded with powder, and ball impacts would then be damped by particles between the grinding media. However, based on the values in the Table 1, $U$ values of 1.5–6.2% suggests that impacts should not be damped excessively by suspended particles, and there was enough abrasion on slag particles with grinding balls.

Slag (15, 30, and 60 g) was mixed with 500 ml of solvent and loaded into the jar. After 20, 10, or 1.25 min of extractive grinding, the ball mill was stopped, and the slurry was vacuum filtered with 2.7 µm filter paper. The rest of the procedure was similar to the previous set-up for the mechanical mixing. Due to the closed nature of the system, temperature and pH was measured at the start and end of experiments. A typical flow diagram of our system is illustrated in Fig. 2.

### Table 1

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

### Table 2

The chemical compositions of original steel converter slags 0–250 µm, analyzed using ICP-OES.

| Case Method | SLR/time | Ca (mg/g) | Fe (mg/g) | Si (mg/g) | V (mg/g) | Mn (mg/g) | Mg (mg/g) | Al (mg/g) | Cr (mg/g) |
|-------------|----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|
| MM/30/20    |          | 360       | 148       | 32.5      | 17.3     | 15.0      | 9.6       | 6.9       | 1.9       |
| MM/30/05    |          | 363       | 137       | 33.0      | 16.9     | 14.8      | 9.2       | 6.9       | 1.9       |
| MM/30/1.25  |          | 352       | 146       | 22.4      | 16.9     | 14.8      | 9.1       | 6.9       | 1.9       |
| MM/60/20    |          | 345       | 150       | 31.8      | 17.0     | 14.9      | 9.0       | 6.8       | 1.9       |
| MM/60/05    |          | 323       | 142       | 31.6      | 16.5     | 14.4      | 8.8       | 6.8       | 1.9       |
| MM/60/1.25  |          | 364       | 140       | 32.2      | 17.0     | 14.9      | 9.1       | 7.1       | 1.9       |
| MM/120/20   |          | 306       | 133       | 25.5      | 12.1     | 10.7      | 6.9       | 4.8       | 1.3       |
| MM/120/05   |          | 357       | 139       | 22.1      | 17.0     | 14.6      | 8.8       | 7.1       | 1.9       |
| MM/120/1.25 |          | 421       | 205       | 33.1      | 17.2     | 14.9      | 8.5       | 7.0       | 1.9       |
| EG/30/20    |          | 431       | 193       | 33.7      | 17.8     | 15.3      | 8.9       | 7.3       | 2.0       |
| EG/30/05    |          | 405       | 186       | 32.8      | 16.9     | 14.6      | 8.2       | 6.9       | 1.9       |
| EG/30/1.25  |          | 417       | 197       | 30.4      | 16.7     | 14.0      | 8.1       | 6.8       | 1.8       |
| EG/60/20    |          | 392       | 188       | 22.5      | 16.9     | 14.6      | 8.2       | 6.9       | 1.9       |
| EG/60/05    |          | 426       | 178       | 30.5      | 16.5     | 14.0      | 8.2       | 6.8       | 1.8       |
| EG/60/1.25  |          | 419       | 170       | 31.1      | 16.3     | 13.7      | 8.1       | 6.5       | 1.8       |
| EG/120/20   |          | 397       | 178       | 31.4      | 16.1     | 14.1      | 7.8       | 6.8       | 1.8       |
| EG/120/05   |          | 399       | 180       | 31.5      | 17.1     | 14.1      | 7.9       | 6.6       | 1.8       |
| EG/120/1.25 |          | 398       | 183       | 31.6      | 16.7     | 13.9      | 7.8       | 6.6       | 1.8       |
| Average     |          | 381.9     | 166.2     | 31.7      | 16.6     | 14.3      | 8.5       | 6.8       | 1.8       |
| Standard deviation |          | 35.9      | 23.3      | 1.8       | 1.2      | 1.0       | 0.6       | 0.5       | 0.1       |
solution was also analyzed after extraction using ICP-OES. The analysis of the mineralogical phase of the powdered original slag and the residual slag was performed using an X-ray diffractometer (XRD, Smartlab, Rigaku, Japan) with the operating parameters of Cu Kα radiation (λ = 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 was performed for analyzing morphological phase and elemental composition in the slag samples before and after by using scanning electric 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 sputter coater (LECIA EM ACE600), along with a thin layer (~4 nm) of titanium/iridium before observation. Fourier transform infrared spectroscopy (FTIR) was performed on original and residual slag to identify different compounds and functional groups present in the slag particles. 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. The main objective of these analyses was to have more information on what phenomena takes place during the extraction, and also try to have support for observations from different methods’ viewpoint.

2.5. Analysis of the slag

All the experiments were performed using slag from the basic oxygen steelmaking converter (BOF) in a steel manufacturing plant (SSAB, Rahe Works, Finland). The slag was first extracted from a large barrel into a glass bottle and mixed thoroughly to keep the slag powder composition uniform throughout the batch. Two samples were then taken from the same slag bottle at the same time, one for analysis and another one for performing experiments. After composition analysis, extraction results were calculated based on the average of all 18 analysis

Fig. 3. Extraction pattern of calcium (1st row) and dissolution of vanadium, silicon, and magnesium (2nd, 3rd, and 4th rows).
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The composition of the solid slag sample was analyzed using inductively coupled plasma-atomic adsorption spectroscopy (ICP-OES) at the Chemical Technology Department at Aalto University. The complete analysis of the slag sample is shown in Table 2. The steel size fraction used in this study was original slag with a particle size distribution between 0 and 250 µm and it was not sieved for different size fractions for this study. The same 0-250-µm slag was used for both traditional mechanical mixing (MM) and extractive grinding (EG).

As can be seen, there is a significant deviation in the concentration of elements. This is a very important observation since if only one sample is analyzed for the slag, it will result in a very poor confidence in the results. This is mainly because ICP-OES uses only a ~0.2 g sample of slag for analysis, while these experiments used 15 to 60 g of slag. An analyzed sample would then represent only from 0.2/15 = 1.3 to 0.2/60 = 0.3% of the actual slag used in the experiments.

3. Results and discussion

In this section, the results for the extraction efficiency of Ca and the degree of dissolution of V, Si, and Mg, are presented and compared with extractive grinding (EG) and traditional mechanical mixing (MM). Then, the powder characterization analysis using XRD, SEM-EDS, FTIR methods are presented. Finally, opportunities for utilizing PCC produced as a make-up chemical in the Ca-looping CO2-capture process, for improving the CO2 capture potential are discussed.

3.1. Extraction efficiency and degree of dissolution

\[ X_i = \frac{c_i V}{m_S y_0} \]  

In Eq. (5), \( c_i \) is the concentration of species \( i \) in the solution (g/L), \( V \) is the volume of the solvent (L), and \( y_0 \) is the initial mass fraction of the element \( i \) in the slag of mass \( m_S \) (g) used in the experiment. Fig. 3
illustrates the total extraction efficiency of Ca, V, Si, and Mg after 1.25, 5, and 20 min, with 2 mol/L concentrations of NH₄Cl.

In the previous paper [9], SLR = 30 g/L and M = 2 mol/L, and at 20 min residence time, gave a 63% Ca yield. In this study, under these same conditions, Ca yield has reached 73%, see Figs. 4 and 5. This is probably due to only one sample being used for the initial slag in our previous work. It can be seen clearly that, after the first 1.25 min, 30 g/L, the Ca yield is almost the same for both MM and EG methods, but then the reaction stops for MM. For EG, Ca continues to dissolve and reaches a much higher level as quickly as the first 5 min processing. For SLR = 60 g/L and 120 g/L, Ca yield significantly drops, showing clear stoichiometric limitations. This phenomenon occurs due to the saturation of the NH₄Cl solvent with Ca ions from the slag, and there not being enough H₃O⁺ ions present in the solution that could enhance CaO dissolution further. These results are of the utmost importance for this study as they explain the extent to which the SLRs can be increased or decreased with respect to varying residence time.

The dissolution of V shows a similar trend with Ca (Fig. 3, second row). With EG, and 30 g/L, 100% more V is dissolved in comparison with MM after 20 min residence time. By increasing the SLR, the dissolved fraction decreases, showing clear stoichiometric limitations. For example, when the amount of slag is quadrupled, the dissolution degree drops ~75%. Silicon (Fig. 3, third row) presents different behavior from all other components. There seems to be no significant difference between EG and MM, except at the smallest residence time and lowest SLR. Again, a clear stoichiometric limitation can be observed for both EG and MM. It also seems that only the surface silica is dissolved, which could result from the contact time not having a significant effect on the Si; it remains constant with decreasing reaction time. For Mg (bottom row), Fig. 3 shows that EG separates more Mg for 30 and 60 g/L. The stoichiometric limitation is not as clear as with other elements.

Due to the closed nature of the EG ball mill system, it was impossible to measure the online pH. Therefore, only end values for all results are presented here. In order to understand whether EG has really enhanced dissolution and not just removed material by grinding, the end pH values and Ca yields are plotted for both MM and EG in Figs. 4 and 5, respectively.

As can be seen in Figs. 4 and 5, the EG results fit quite well on a single curve, but there is much more deviation in the mechanical mixing tests. Here, the role of Ca on pH is only considered, which is, of course, not able to explain the full correlation.

3.2. XRD characterization of original and residual slags

This section discusses the detailed physical characterization of the solid slag before and after the extraction process. Please see, part “2.4 Characterization techniques” above and [28] for the details of the method description. XRD was used to detect the compositions of the solid slag before and after the extraction. However, XRD phase analysis of the slag was difficult due to the amorphous nature or high content of impurities and a variety of indistinguishable elements in the steel converter slag. In addition to the original slag, residual slags from two experiments with 60 g/L and 20 min residence time, MM/60/20 and EG/60/20 were analyzed (Fig. 6).

Based on the XRD patterns (Fig. 6), the mineralogical phase containing calcium, silicon or iron in the steel slag and the residual slags...
mainly consisted of portlandite Ca(OH)$_2$, magnetite Fe$_3$O$_4$, quartz SiO$_2$, dicalcium silicate 2CaO•SiO$_2$, and mayenite Ca$_2$Al$_4$O$_7$. A strong peak related to quartz is noticeable on the diffraction pattern of EG/60/20. Distinct 2CaO•SiO$_2$ peaks are also observed at regular intervals on the patterns of residual slags, revealing that they were unaffected by the NH$_4$Cl solvent, which agrees with the Si dissolution results discussed in the previous section. It also supports our earlier observations that NH$_4$Cl acts as a selective solvent towards CaO-bearing species (portlandite) and leaves behind silicates and Fe-bearing phases in the residual slag. However, the XRD patterns of the residual slags also contain some level of CaO-bearing phases. This suggests that the used solvent extracted its maximum possible amount of CaO and became saturated with CaO, although some CaO was still left behind in the residual slag [24-27]. In addition to these observations, the X-ray patterns also indicate an amorphous nature of the residual slags. In summation, the X-ray diffraction method confirms that the main constituent of the original slag is portlandite CaO-bearing species, which is transformed to mainly SiO$_2$-bearing species in the solid residue after the extraction.

3.3. SEM characterization of original and residual slags

The morphological and elemental characterization of the slag particles before and after CaO extraction are studied using a scanning electron microscope (SEM)-Energy-dispersive X-ray spectroscopy (EDS), as shown in Fig. 7. Please see [28] for the details of the method description.

Here, the steel slag is analyzed for the visual appearance and surface structure. It was observed that the morphology of the slag particles undergoes a noticeable change during the extraction. Before the extraction of CaO, the particles have distinct edges and filled bulky shape, there are no visible pores present on the surface of the original slag particles. In other words, the particles possess a filled surface and structure. Fig. 7 shows the morphological change of the residual slag after the extraction. Here, we used residual slag, test EG/60/20, for microscopic imaging after drying at 120 °C. After extraction, there are finer particles attached to the surface of the larger particles, small particles are agglomerated and small holes appear on the surface of the particles due to the removal of CaO, and the structure becomes highly porous. In our future work, the chemical composition of these new formed structures will be analyzed in detail. Based on SEM-EDS, the Si content of the original slag was 3.9% which was increased to 15.5% in the residual slag. The Ca contents of the original and residual slag were 37.9% and 23.5%, respectively. This corresponds to extraction efficiency of 1–0.235/0.379 = 38%, being slightly less to values obtained from liquid side analysis, Fig 3, top row, middle. These results again confirm the selectivity of the extraction process for Ca-species while leaving the Si-species. Meanwhile, other trace elements are also reduced after extraction, and Fe phases tend to appear on the particle surface (e. g. 16.8% in the residual slag), which is consistent with the XRD analysis.

3.4. FTIR analysis of original and residual slags

FTIR-ATR spectra were recorded over a range of 4000–500 cm$^{-1}$, as shown in Fig. 8. This spectrum can be divided into two groups, 4000–1500 cm$^{-1}$ and 1500–500 cm$^{-1}$, the functional group region, and the fingerprint region, respectively.

The original slag reveals no major functional groups present in the functional group region, although some weak functional group are present. The residual slag exhibits a peak at 2973 cm$^{-1}$, which corresponds to amine salts, NH$_4$Cl here. There are weak peaks that occur in the original slag at 2051, 2192, 3777, 2383 cm$^{-1}$ which represents the presence of periclase, MgO. In the residual slag, a small peak occurring at 1627 cm$^{-1}$ corresponds to a portlandite, Ca(OH)$_2$, band region. As an opposite to this, in the original sample, Ca seems not to be attached to hydroxide ion. The wide band from 1400 cm$^{-1}$ to 1500 cm$^{-1}$ as well as the smaller band at 864 cm$^{-1}$, correspond to amorphous CaCO$_3$ (calcite) present in both the original and residual slags, similar content was previously reported for steel slag [29,30]. In addition, the fingerprint regions reveal clear peaks at 1021 cm$^{-1}$, which is due to the SiO$_2$-bearing species being present in the residual slag. Other small bands also occur at 1130 cm$^{-1}$, (Si-O-Si, cage siloxane) and 1025 cm$^{-1}$ (Si-O-Si, branching siloxane), 871–873 cm$^{-1}$ (CaCO$_3$/SiO) [19, 32–33]. The bands at 942 cm$^{-1}$ can be attributed to silica or stretching vibrations of Al–O and Si–O for amorphous aluminosilicates. These results from the FTIR analysis are well in line with the rest of findings from ICP, XRD and SEM-EDS analyses.

3.5. Potential of the combined SLAG2PCC and CA-looping CO$_2$-capture

The principle of combining X2PCC in the Ca-looping CO$_2$ capture process is presented in Fig. 9a and b. It is assumed that both annual iron-
and steel-making slags, 600 Mt in total, would be utilized as raw materials. In this study, a moderate, but experimentally validated Ca yield of 53% is assumed in the X2PCC process. As it is shown in this paper, the extraction rate was found to be higher 70% with our new technology, but still needs data about how much of this can be carbonated. Using a confirmed value (53%) already takes the carbonation step into account. Values for the Ca-looping process were based on [31,32]. We have confirmed that the CaO purge fraction is \( f_p = 0.02 \), taken from the CaO entering to the carbonator. The CO2-capture efficiency in the carbonator was assumed to be 0.96. From these variables, the average conversion of CaO to CaCO3 equals \( X_a = 0.221 \).

It is assumed that all 284 Mt of PCC produced from iron- and steel-making slags is used as make-up chemical, upper right arrow in Fig 9a. The regenerated and used sorbent amounts in Fig 9b refer to the annually recycled amount that has passed through the process in one year. In practice, the process needs to be started using fossil-based limestone powder, but this is then gradually replaced by the circular PCC. Based on Fig. 9a and b, instead of using PCC obtained by carbonation as the final mineral storage for CO2, a considerably higher CO2-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 CO2 emissions. Of course, we still then need to have a safe storage method available for CO2 or a CCU application that could accept the amount of CO2 captured. Certainly, this means that we need to continue using limestone from virgin resources in the iron and steel industry, and no circular economy solution for closing the Ca-loop in steel and iron industry is obtained for this part. One could think that the iron and steel industry is only borrowing the limestone, and its final use is as a CO2 sorbent. For these purposes, CaCO3 from our X2PCC has the advantage of having small particle size (10–20 \( \mu \)m) and large surface area without the need of energy-intensive grinding. This concept, however, needs to be further analyzed in further detail and this will be studied in ongoing and future work.

4. Conclusions

In this paper, the main focus was on the CaO recovery from steel-making slags using the X2PCC process in which CaO is selectively dissolved from slag powder, clean Ca solution filtered, and finally, by bubbling CO2 into the solution, dissolved Ca precipitated as CaCO3/PCC. Usually, PCC has many applications in several industries, such as in paper, board, paint, and plastic production. In this paper, the focus is on the further improvements on the wet extractive grinding process, wherein grinding of the slag is combined with the Ca extraction step. This was already found to be superior to mechanical mixing in our previous paper [10]. In this study, a brief detailed analysis was carried out to better understand its potential and mechanisms. The effect of the processing time (1.25–20 min), and the effect of solvent-slag stoichiometry, by varying the slag-to-solvent ratio (30–120 g/L) were studied. The potential of using PCC as a sorbent for Ca-looping CO2-capture process was also discussed.

It was found that the Ca-yield and dissolution rate increase significantly by the EG process, i.e. the yield increased from 35 to over 70%, in comparison with normal mechanical mixing. The rate of dissolution also increased significantly. SEM-EDS and XRD analyses of original slag confirmed that original slag contains portlandite, and when these Ca-bearing species are extracted out, the structure of the particles becomes highly porous. It was found that the total quantity of calcium significantly varies in the slag. Using only one solid sample is not enough. It was found that maximum extraction efficiency, 73% could be obtained with extractive grinding and the lowest slag-to-solvent ratio of 30 g/L.

If the PCC, produced from both iron and steelmaking slags, is used as mineral carbonation storage for CO2, we can bind 125 Mt of CO2 (using all 600 Mt of annually produced slag), i.e., 0.3% of annual global CO2 emissions (37 Gt in 2018). However, if we use the PCC produced in Ca-looping CO2-capture as a make-up sorbent, we are able to bind 1500 Mt of CO2, i.e., ~4% of global annual emissions or over 60% of the iron- and steel-making CO2 emissions. In our future work, the feasibility of this process concept will be studied in detail to understand its industrial potential.

Author contribution statement

Muhammad Owais carried out the experiment. Muhammad Owais wrote the manuscript with support from Prof. Mika Järvinen. Muhammad Owais also 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.

Declaration of Competing Interest

None.

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