Production of calcium carbonate with different morphology by simultaneous CO₂ capture and mineralisation

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Highlights

- Ca conversion was below 15 wt.% in the absence of alkaline reagents.
- Ca conversion was above 80 wt.% with CO₂-absorption and mineral carbonation.
- Vaterite and aragonite particles were produced at 30 °C
- Pure aragonite prevailed at 70 °C.
- Mg concentration of 0.06 g/L did not affect the formation of pure aragonite.

Abstract

In this work, the precipitation of high-quality calcium carbonate (PCC) from synthetic Ca-rich solutions was investigated. A mixture of Ca and Mg salts were considered to reproduce the chemical composition of leachates obtained from leaching BOF slags with diluted HCl. The effect of adding NaOH and different amine-based organic solvents (PEI, MEA and AEEA) was investigated by considering an integrated process: CO₂-absorption and mineral carbonation. Ca conversion was below 15 wt.% in the absence of alkaline reagents as alkalinity is reduced when H₂CO₃ is formed under permanent introduction of CO₂. The addition of a substantial amount of NaOH (20 g/L, Ca/Na ratio of 1:1) allowed to significantly increase the Ca-conversion yield, and the morphology of calcite particles was modified from scalenohedral-rhombohedral-type to rhombohedral shape by increasing the CO₂-gas flow rate from 0.008 to 0.5 L/min. During carbonation with the addition of amine-based organic solvents, MEA and AEEA showed the highest Ca-conversion, i.e. > 80 wt.%. A combination of vaterite and aragonite particles were produced at 30 °C, while the formation of pure aragonite prevailed when the temperature was increased up to 70 °C. The effect of Mg on the formation of aragonite particles was considered negligible due to the low initial concentration, although some traces of Mg were detected in the corresponding final PCC particles.

Key words: CO₂, amines, PCC, calcium carbonate, mineral carbonation, morphology

1 Introduction

The increase in the anthropogenic carbon dioxide (CO₂) concentration in the atmosphere over the past century has originated from the combustion of fossil fuels by the transportation sector and power generation industry [1,2]. Burning oil, coal or natural gas in air to produce heat and power, releases vast amounts of CO₂ into the atmosphere [3]. About 32×10^9 tonnes of CO₂ per annum are emitted globally, which nowadays account to an accumulation of 416 ppm of CO₂ in the atmosphere (<https://www.esrl.noaa.gov>, accessed on April 2020). Due to its detrimental greenhouse effect, such accumulation of CO₂ is causing irreversible harmful effects on water and food availability, human health, ecosystem, coastlines and biodiversity [4,5]. A further increase in these figures is still expected to occur in the upcoming years [2,6]. Fossil plants (coal and gas) and heavy industry (such as cement and steel production) are the largest contributor of CO₂ emissions with 27×10^9 and 8×10^9 tonnes of total CO₂ emissions per year (globally), respectively [2].

Steelmaking is an energy-intensive process that consumes ca. 19 GJ (considered in the Blast Furnace (BF) – Basic Oxygen Furnace (BOF) processes) and emits ca. 1.9 tonne of CO₂ per tonne of crude steel [7,8]. These figures situate the steel industry among the largest contributors of CO₂ emissions. Yet, the world production of crude steel is predicted to continue to grow, and it is likely to be accompanied by an increase in the amount of CO₂ released to the atmosphere. During the production of liquid steel in a BOF, around 100 – 150 kg of slag per tonne of crude steel are produced, the exact amount depending on the hot metal quality and operational conditions [9]. Disposal and long-term storage of such waste volumes result in major costs and liabilities for the industry. However, the high Ca content of steelmaking slags makes them suitable raw materials not only to store thermal energy for further electricity generation [10,11], but also for CO₂ capture by mineral carbonation [12–20]. The extraction of Ca and/or Mg from steelmaking slags has been studied by several authors, who have considered different reagents as extractants [12,19,21–24]. Ammonium salt solutions have demonstrated a good performance to extract Ca from steel converter slags and subsequently produce precipitated calcium carbonate (PCC), with a Ca extraction efficiency that varies between 40-60 wt.%, depending on the availability of free lime (CaO) in the slag [21,23–25]. Other mineral acids, such as acetic acid

(CH₃COOH), sulfuric acid (H₂SO₄), nitric acid (HNO₃) and hydrochloric acid (HCl), to extract Ca and/or Mg from silicate minerals have also been reported [26–30]. Still, the utilisation of HCl as a leaching reagent allows the highest selectivity for Ca upon a low co-dissolution of other metals (e.g., Fe, Mn, Si). The precipitation of the extracted Ca (and Mg) can be easily performed with the aid of NaOH [30,31].

Aqueous-soluble amine-based organic solvents for CO₂ absorption enable highly efficient removal of CO₂ from flue gases in a process better known as amine scrubbing for CO₂ capture [32]. The amine is regenerated by stripping with water vapour at temperatures between 100-120 °C, and the water is condensed from the vapour, leaving pure CO₂ for further compression at high pressures [32–35]. The amine CO₂-scrubbing process, however, is limited by the high energy input requirements of the regeneration step. Notice that the storage and safe disposal of the captured CO₂ must meet the necessary requirement to ensure a low impact in the environment. Thus, mineral carbonation represents a promising technology that allows to sequester CO₂ in a stable mineral carbonate. Hence, the integration of the mineral carbonation with the CO₂-absorption process substitutes the regeneration stripping process required in the conventional amine-scrubbing technology for CO₂ capturing. The utilisation of monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP), have already been studied as solvents to capture CO₂ and subsequently produce PCC by considering liquids solutions enriched with Ca²⁺ or Mg²⁺ ions [36–39]. The integration of CO₂ absorbed in MEA with alkaline Ca-bearing solids has also been reported [40]. The study has demonstrated that carbon mineralisation can be much higher with CaO (conversion up to 80 wt.%) due to its ease of dissolution, rather than with CaSiO₃ (conversion up to 36 wt.%), but the method requires a concentration of 50 wt.% of MEA, long period of contacting time (> 1 h) and temperatures > 30 °C.

The effect of different organic solvents on the production of different crystalline polymorphs (aragonite, vaterite, calcite), as well as on the quality of the final product (e.g., co-precipitation of other metals, particle size distribution), however, has not yet been systematically investigated.

The present study aimed to precipitate high-quality PCC from synthetic Ca-rich solutions, which were reproduced based on the leach liquor obtained from leaching BOF slag with 0.5-0.7 mol/L HCl, liquid-

to-solid ratio of 1, at 45 °C, and 10 min of continuous agitation (reference chemical composition of the leach liquor: Ca = 10-11 g/L; Mg ~ 60 g/L; Mn < 1g/L; Fe < 1 g/L; Si < 0.05 g/L; pH = 10-11). Due to the low concentration of Mn, Fe and Si, only Ca and Mg were considered as case-study elements. Firstly, the effect of different CO₂-gas flow rates (Q_{CO_2}) and temperatures was studied in absence of alkaline reagents. Secondly, the effect of the pH on the production of high-quality PCC was studied by considering the addition of NaOH at 30 °C, but with different Q_{CO_2} . Thirdly, mineral carbonation and amine-based absorption processes were analysed as an integrated process. The addition of different amine-based organic solvents, i.e. polyethylenimine (PEI), ethanolamine (MEA), aminoethylethanolamine (AEEA), at different Q_{CO_2} and temperatures, was evaluated. The corresponding PCC products were analysed in terms of elemental composition, mineralogy, morphology and particle size distribution.

2 Materials and methods

Synthetic solutions were prepared by considering a Ca concentration of 10 ± 0.2 g/L (added as CaCl₂·2H₂O, 99.5% Chem-Lab), and Mg concentration of 0.06 ± 0.02 g/L (added as MgO in experiments with and without NaOH, and as MgCl₂·6H₂O in experiments with amine-based organic solvents, both two compounds were acquired from Sigma-Aldrich). Milli-Q water (18.2 MΩ cm) was used to prepare the solutions. Carbonation experiments were carried out in a 200 mL beaker (100 mL synthetic solution) with continuous agitation. The agitation was performed by a magnetic stirrer (4 cm long, 7.5 mm diameter, 6 g). CO₂ gas (99.9925%, Air Liquid) was introduced continuously at defined Q_{CO_2} (0.008-0.5 L/min), which was controlled with a flow meter.

Carbonation experiments with direct injection of CO₂, and no addition of alkaline reagents, were performed by considering a Q_{CO_2} of 0.1 and 0.5 L/min, and a temperature range between 30-70 °C. The selection of the temperatures was done randomly to evaluate the effect of this variable on the formation of PCC particles at temperatures below 100 °C. The selection of the CO₂ gas flow rate was done based on the work of Santos et al. [41]. Carbonation experiments with addition of NaOH (99.25%, Fisher

Chemical) were performed at 30 °C by considering a concentration of 7, 10 and 20 g/L. The experiments were carried out in the same beaker with the same synthetic solution and agitation speed, but with Q_{CO_2} between 0.008-0.5 L/min. Carbonation experiments with the addition of 5 vol.% of amine-based organic solvents were performed at different temperatures (30-70 °C), and with Q_{CO_2} of 0.02 and 0.1 L/min. The amines considered in this research were: Polyethylenimine (PEI, molecular weight ca. 800 g/mole, branched, Sigma Aldrich), ethanolamine (MEA, 99%, Acros Organics, 61 g/mole), and aminoethylethanolamine (AEEA, 98%, Merck, 104 g/mole), which were directly added to the synthetic solution. PEI was previously prepared at 50 wt.% by dissolving it in milli-Q water at room temperature. The pH of the solution was measured continuously in every experiment, which lasted 35 min. The slurries after carbonation were filtered using filter paper (pore size 0.45 µm) and diluted with 2 vol.% HNO₃ for Inductively Couple Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis for Ca and Mg. The corresponding amount of Ca in solution, α % (in wt.%), was calculated according to equation 1:

$$\alpha \% = \left[\frac{\text{Amount of metal in solution after carbonation}}{\text{Initial amount of metal before carbonation}} \right] \times 100 \quad (1)$$

The level of Ca conversion (in wt.%) was calculated according to equation 2:

$$Ca \text{ conversion} = 100 - \alpha \% \quad (2)$$

The obtained PCC was dried and studied by X-ray powder diffraction (XRD, Bruker D2 Phaser). The powder morphology was investigated by scanning electron microscopy (SEM, Philips XL30). The particle size of the samples was measured by laser particle size analysis (Malvern Mastersizer 3000). The concentration of Mg in the final PCC was obtained by total digestion of the produced PCC with 3 vol.% HNO₃ followed by ICP-OES (PerkinElmer Optima 8300) analysis.

3 Results and discussion

3.1 Influence of gas flow rate and temperature – no alkaline reagents

The influence of different gas flow rates was evaluated by considering synthetic solutions prepared with 4 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 9 mg of MgO . The initial pH of the solution was around 10-11 due to the buffer effect of MgO in contact with water. The level of Ca conversion at different Q_{CO_2} and temperature is presented in Figure 1. The highest conversion, i.e. 11-13 wt.%, was achieved in the first 10 min of experiments at 30 °C. Initially, CO_2 -gas reacts with water to form carbonic acid (H_2CO_3). Due to the low stability, H_2CO_3 chemically decomposes into $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ at $\text{pK}_{\text{a}1} = 6.35$ and $\text{pK}_{\text{a}2} = 10.2$, respectively (at 25 °C). Higher temperatures than that of 30 °C did not enhance the Ca conversion due to the reduction of CO_2 's solubility in water with the increase of the temperature [42]. The pH of the solution was reduced from an initial value of 11 to a value ca. 5 in the first 5 min of carbonation. Hence, the formed CaCO_3 started readily being dissolved under acidic conditions, i.e. $\text{pH} < 6$ [23]. Therefore, in order to enhance the Ca conversion from the solution, a pH-value > 7 must prevail.

Figure 1: Influence of the CO₂-gas flow rate and temperature in the pH and Ca conversion during carbonation (no addition of alkaline reagents).

3.2 Carbonation with addition of NaOH

The addition of NaOH was evaluated in a similar synthetic solution than the one described in section 3.1. Mineral carbonation and the production of high-quality PCC was studied under strong alkaline conditions, therefore NaOH was added to the synthetic solution. The influence of different NaOH concentration on pH and Ca conversion, at 30 °C, is presented in Figure 2 and 3, respectively. As it was described in section 3.1, in the absence of a strong base, the continuous addition of CO₂ into the synthetic solution caused a fast reduction of the pH's solution. However, as it was expected, the pH of the solution increased from 10 to 12 as soon as NaOH was added. It must be noticed that CO₂ started to be introduced into the reactor simultaneously with the addition of NaOH within the first 2-3 min of starting the experiments. Thereafter, the pH started to decrease as the carbonation reaction proceeds (Figure 2). The carbonation reaction reached the equilibrium when the pH of the solution was

approximately 6. The carbonation rate, i.e. rate at which the solution's pH was reduced, was significantly influenced by the Q_{CO_2} . As it was observed, a quick reduction of the pH was observed when the Q_{CO_2} was increased.

Figure 2: Influence of different NaOH concentration on the pH during carbonation at 30 °C: Initial Ca/Na ratios before precipitation: 1:1 with 20 g/L NaOH, 2:1 with 10 g/L NaOH, 3:1 with 7 g/L NaOH.

As it is depicted in Figure 3, the Ca conversion increased just as the concentration of NaOH was increased, independently of the gas flow rate. Contrary to the system without addition of an alkaline reagent, the addition of NaOH allowed a more efficient saturation of the solution with HCO_3^- ions, due to the formation of $NaHCO_3$ at high pH, which is highly soluble (solubility of 96 g/L at 20 °C). The carbonation reaction caused the pH to decrease. Thus, the Ca conversion resulted the highest (90 wt.%) with 20 g/L of NaOH, i.e; Ca/Na ratio before precipitation of 1:1.

Figure 3: Influence of different NaOH concentration on Ca conversion at 30 °C. Initial Ca/Na ratios before precipitation: 1:1 with 20 g/L NaOH, 2:1 with 10 g/L NaOH, 3:1 with 7 g/L NaOH.

The mineralogical composition of the PCC products obtained with the addition of 20 g/L NaOH were analysed by XRD. With low gas flow rates, i.e. 0.008 L/min, the solid product resulted in a mixture of portlandite ($Ca(OH)_2$), aragonite ($CaCO_3$) and calcite ($CaCO_3$) (Figure 4). Pure calcite was obtained with $Q_{CO_2} \geq 0.02$ L/min.

Figure 4: XRD pattern of the solid product obtained after carbonation with addition of 20 g/L of NaOH (Ca/Na ratio before precipitation of 1:1) at 30 °C.

Although XRD analysis did not detect the presence of Mg mineral phases, such as MgO, Mg(OH)₂, in the samples of final PCC products (due to the low concentration), it was detected by chemical analysis after total dissolution of the solid products in HNO₃. A relatively high concentration of Mg was identified in the PCC formed with low gas flow rate (Figure 5). As it was observed in Figure 2, the carbonation rate is diminished when Q_{CO_2} is also reduced. With low gas flow rate, the solution was not saturated with CO₂, but it was saturated with NaOH instead. Due to the high pH of the solution, Mg remains thermodynamically stable as Mg(OH)₂ [43]. Furthermore, Mg²⁺ ions can substitute Ca²⁺ ions site in the calcite lattice, thus suppressing the nucleation and growth of calcite particles [44,45]. The relatively high co-precipitation of Mg observed with $Q_{CO_2} = 0.008$ L/min could explain the formation of aragonite. according to the observations reported by Santos et al. [41].

Figure 5: Effect of the Q_{CO_2} on the Mg precipitation (in mg of Mg per gram of PCC) after carbonation with addition of 20 g/L NaOH (Ca/Na ratio before precipitation of 1:1).

The morphology and particle size distribution of the formed PCC after carbonation with 20 g/L NaOH, and different gas flow rates, are shown in Figure 6 and 7, respectively. At low gas flow rate, i.e. $Q_{CO_2} < 0.02$ L/min, the particles resulted in a scalenohedral/rhombohedral-type shape, which formation was favoured by the prevalence of Ca^{2+} over CO_3^{2-} ions, i.e. non-stoichiometric condition with Ca^{2+}/CO_3^{2-} ratio > 1 , at high pH-conditions (pH ~ 12) [46]. Rhombohedral particles were easily distinguishable at gas flow rates > 0.1 L/min. Aragonite particles were characterised by needle-shape appearance when viewed in SEM, while calcite particles were often identified by rhombohedral crystal shapes [45,47,48]. The morphology transition from aragonite to calcite particles can be explained by the gradual decrease of the solution's pH. Thus, according to these results, it is believed that aragonite particles were formed at pH values slightly lower than 12, while calcite particles could be formed at pH values lower than 11 [49].

The size of the particles was $< 3 \mu m$ (d_{90}), with the smallest particles formed at high Q_{CO_2} (Figure 7). The accumulation of HCO_3^- and CO_3^{2-} ions by increasing the Q_{CO_2} led to a fast carbonation rate, as it was shown in Figure 2. Thus, the nucleation rate was enhanced with high Q_{CO_2} , which promotes the formation of PCC particles with rhombohedral shape [50]. A bimodal distribution was observed in that sample produced with $Q_{CO_2} = 0.1$ L/min due to the break-up of aggregates during the analytical

procedure used to obtain the granulometric profile. The particle size distribution of these samples was measured by a Malvern Mastersizer 3000 with MS14 sample dispersion unit.

Figure 6: SEM images of PCC formed after carbonation with addition of 20 g/L NaOH (Ca/Na ratio before precipitation of 1:1). CO₂-gas flow rate at (a) 0.008 L/min, (b) 0.02 L/min, (c) 0.1 L/min, and (d) 0.5 L/min.

Figure 7: Particle size distribution (in vol.%) of PCC particles formed after carbonation with addition of 20 g/L NaOH (Ca/Na ratio before precipitation of 1:1), and different CO₂-gas flow rate (in L/min).

It must be noticed that the application of NaOH at an industrial level for mineral carbonation can be limited by its high consumption. In the present investigation, the highest Ca conversion was achieved

with a NaOH concentration of 20 g/L, which represents a Ca/Na-ratio of 1:1. In view of these results, ca. 830 kg of NaOH will be necessary to produce 1 tonne of CaCO₃ (Ca conversion of 90 wt.%), which will result in an estimated cost around 330-420 USD. This cost implies that NaOH must be used in small volumes and/or low concentration, while regeneration and recycling could be essential. Although the formation of thermally stable Na₂CO₃ was not detected in the final PCC products, the recyclability of aqueous NaOH can be significantly reduced when Na₂CO₃ is formed [51].

3.3 Carbonation with addition of organic solvents

The organic solvents PEI, MEA and AEEA were studied separately by considering a concentration of 5 vol.% in the temperature range between 30-70 °C. Two different Q_{CO_2} were considered: 0.1 and 0.02 L/min. With the exception of PEI, MEA and AEEA were directly added to the synthetic solution. PEI was first prepared at 50 wt.% in Milli-Q water before mineral carbonation due to the high viscosity at room temperature (200 – 500 cP). The effect of organic solvents was evaluated in a synthetic solution prepared with 4 g of CaCl₂·2H₂O and 46 mg of MgCl₂·6H₂O. The initial pH of the solution was around 11 due to the buffer effect of the organic solvents. Notice that in this stage, MgCl₂·6H₂O was used to ensure a complete miscibility of the phases before starting the carbonation.

As it can be seen in Figure 8, at the beginning of the carbonation process, i.e. between 0-5 min, a significant reduction of the solution's pH was observed. It is believed that in this period of time CO_{2(aq)} molecules were absorbed in the organic solvent by forming either zwitterion (chemical reaction 1) or carbamate (chemical reaction 2). The reaction mechanism between CO₂ molecules and the amine-based solvents has been studied by several researchers [52–55]. However, the formation of zwitterion and/or carbamate have been considered as intermediates in the present investigation.

Both products easily undergo deprotonation by the amine, according to chemical reactions 3 and 4

It has been reported that carbamates are produced in the pH-range between 9-11 [53], which in this investigation would correspond to the pH-range registered at the beginning of the carbonation process. The continued introduction of CO₂ gas into the reactor, however, led to the decomposition of both zwitterion and/or carbamate due to the hydration of CO₂ molecules, which finally resulted in the liberation of HCO₃⁻ ions, as is described by chemical reactions 5 and 6.

Presumably, the decomposition of zwitterion/carbamate was initiated after 5 min of carbonation, when the pH was < 8.5 (Figure 8). At this period of time, Ca started to react with HCO₃⁻ ions to first form Ca(HCO₃)₂ (chemical reactions 7 and 8), which rapidly decomposed into CaCO₃ and H₂O (chemical reaction 9).

About 10 wt.% of Ca was converted after 5 min carbonation. Hence, the reduction of the pH-value observed between 5-15 min of carbonation was caused by the protonation/deprotonation of carbamate, which simultaneously led to the formation of PCC solid particles. The reaction reached equilibrium between 10-20 min at pH 7.0 (± 0.5), when the majority of Ca has reacted. Still, the equilibrium was slightly faster with AEEA compared to MEA.

Figure 8: Effect of the temperature on the change of the pH and Ca-conversion (in wt.%) during carbonation with different amine-based organic solvents (5 vol.%, $Q_{CO_2} = 0.1$ L/min).

3.3.1 Effect of the temperature

The increase of the temperature allowed to enhance the rate at which the pH was reduced during carbonation, i.e. the carbonation rate (Figure 8). According to the desorption mechanism used in the CO_2 -amine scrubbing process [32], the decomposition of zwitterion/carbamate is enhanced by increasing the temperature, which also contributes to a swift release of HCO_3^- ions. This can be confirmed by the conversion yield of Ca by increasing the temperature. Carbonation with MEA and AEEA allowed a Ca conversion > 60 wt.% after 15 min, which was further enhanced at high temperatures (90-95 wt.% at 60-70 °C). Meanwhile, the Ca conversion obtained with PEI reached up to 67 wt.% only at 70 °C. It must be noticed that MEA molecules contain primary amine groups, and AEEA has both primary and secondary amine groups in its structure [56], whereas PEI molecules are highly branched structures that not only contain primary and secondary amines groups, but also tertiary amine groups in the ratio of 1:2:1 [57]. The formation of zwitterion/carbamate is described by the reaction of CO_2 with primary and secondary amine groups only [58,59]. However, the reaction of CO_2 with tertiary amine groups is described by the base-catalytic effect on the hydration of CO_2 molecules

[60]. Thus, during the carbonation with PEI, the formation of zwitterion/carbamate is disrupted at a certain level by the formation and subsequent decomposition of carbonic acid (H_2CO_3), according to chemical reactions 10-12. Hence, during carbonation with PEI, the CO_2 -absorption rate becomes slower than with MEA/AEEA, which make it less efficient for mineral carbonation. However, as it has been reported, PEI can allow a high CO_2 absorption when it is loaded on a wide variety of support materials [61–68].

The XRD analysis of the final PCC formed after carbonation with PEI, MEA and AEEA is presented in Figure 9. The precipitates formed after carbonation with PEI are composed of a mixture of different $CaCO_3$ polymorphs, i.e. calcite, aragonite, vaterite. It is reported that PEI of high molecular weight (> 700 g/mole) allows to stabilise the formation of vaterite/aragonite at $20^\circ C$ [69]. The PEI considered in this investigation had a molecular weight of ca. 800 g/mole, and at $40^\circ C$ it was possible to observe the stabilisation of both above-mentioned polymorphs (PCC was also formed at $30^\circ C$, but it could not be separated from the solution due to the high viscosity). The stabilisation of calcite with PEI was only observed when carbonation was performed at high temperatures, i.e. $70^\circ C$. The PCC formed with MEA and AEEA is composed of a mixture of aragonite and vaterite when carbonation was performed at $30^\circ C$. However, at temperatures higher than $30^\circ C$, the formation of aragonite predominated. Several authors have reported the formation of vaterite and calcite at low temperatures ($< 50^\circ C$), while at high temperatures ($> 50^\circ C$) aragonite and calcite became the dominant phases [19,70–75]. In particular, the formation of vaterite particles could be attributed to the adsorption of positive solvent molecular ions, e.g., RNH_3^+ , $R_2NH_2^+$, to the negatively charge [00-1] plane of vaterite, which is commonly composed of CO_3^{2-} and Ca^{2+} ions in a hexagonal orientation and is unable to expose (001) faces [76,77]. Nevertheless, calcite was less predominant than vaterite and/or aragonite in the final PCC formed with MEA and AEEA at $70^\circ C$.

Figure 9: XRD pattern of the PCC formed after carbonation, at different temperatures, with addition of different amine-based organic solvents (5 vol.%, $Q_{CO_2} = 0.1$ L/min). A: aragonite, V: vaterite, C: calcite.

3.3.2 Effect of low CO_2 -gas flow rate

The carbonation process with PEI was not considered in this part of the study, due to the relatively low Ca-conversion obtained with $Q_{CO_2} = 0.1$ L/min (up to 67 wt.%), which was not improved by reducing the Q_{CO_2} . Nevertheless, the Ca-conversion yield was very high (> 80 wt.%) when MEA and AEEA were considered. Still, it is believed that the formation of zwitterion/carbamate can be significantly reduced when less CO_2 is introduced into the aqueous solution, i.e. low Q_{CO_2} . This also limits the presence of H^+ , HCO_3^- and CO_3^{2-} ions, reducing the solution's supersaturation. In fact, as it is described in Figure 10, the solution's pH was reduced slowly when CO_2 was introduced into the reactor at a gas flow rate of 0.02 L/min. The slow pH reduction demonstrated that the protonation reaction of the zwitterion/carbamate was restricted by the low Q_{CO_2} , resulting in a reduction of the Ca-conversion rate. Thus, at 30 °C, about 70 wt.% of Ca was converted into $CaCO_3$, but it was further enhanced up to more than 90 wt.% by increasing the temperature. Still, high Ca-conversions were achieved only after 30 min of carbonation with $Q_{CO_2} = 0.02$ L/min. As already was described in section 3.3.1, the decomposition of zwitterion/carbamate is improved at high temperatures, which can explain the increase in the Ca-conversion rate. It must be noticed that at temperatures > 30 °C, AEEA allowed a faster reduction of

the solution's pH than MEA. It is believed that due to the ability of AEEA to form carbamates much more rapidly than MEA [78], AEEA allowed to obtain higher Ca-conversion yields than MEA, particularly at high temperatures.

Figure 10: Effect of the temperature on the change of the pH and Ca-conversion (in wt.%) during carbonation with $Q_{CO_2} = 0.02$ L/min and different amine-based organic solvents (5 vol.%).

The mineralogical analysis of the PCC particles formed after carbonation with $Q_{CO_2} = 0.02$ L/min is presented in Figure 11. The PCC formed with MEA and AEEA at 30 °C was composed of a mixture of aragonite and vaterite. However, at 70 °C, the formation of aragonite predominated. Some traces of vaterite were also identified in the PCC obtained at 70 °C with MEA. A similar behaviour was observed in the PCC's obtained at high Q_{CO_2} (Figure 9).

Figure 11: XRD pattern of the PCC formed after carbonation, at two different temperatures, with $Q_{CO_2} = 0.02$ L/min and different amine-based organic solvents (5 vol.%). A: aragonite, V: vaterite, C: calcite.

3.3.3 Particle size and morphology

The morphology of PCC particles formed with high gas flow rate, i.e. $Q_{CO_2} = 0.1$ L/min is depicted in Figure 12. Needle-shaped particles were identified by SEM in those PCC particles formed at 70 °C with MEA and AEEA, which confirmed the formation of aragonite particles. The particles formed at 70 °C with PEI showed a mixture of needle and rhombohedral shape, which confirmed the formation of aragonite and calcite. Nonetheless, at 30 °C, particles did not show distinct morphology, but they were identified as clusters of spherical particles, which is typical of vaterite crystal growth [47]. In addition, PCC particles formed at 30 °C were smaller than the particles formed at 70 °C, shown by the particle size distribution in Figure 13. This was caused by the reduction of the nucleation rate when the temperature was increased. Vaterite particles are predominantly formed with a slow nucleation rate [79]. Thus, aragonite particles resulted from the subsequent nucleation of metastable vaterite crystals [41,80,81].

Figure 12: SEM images of PCC formed after carbonation, at 30 and 70 °C, with addition of (a) PEI (at 40 °C), (b) MEA and (c) AEEA. CO₂-gas flow rate 0.1 L/min.

Figure 13: Particle size distribution of PCC particles formed after carbonation with addition of 5 vol.% of PEI, MEA and AEEA, at different temperature, and with $Q_{\text{CO}_2} = 0.1 \text{ L/min}$.

During carbonation with low gas flow rate, i.e. $Q_{\text{CO}_2} = 0.02 \text{ L/min}$, at 30 °C, the effect of gas flow rate on particle size was only observed during carbonation with AEEA, but not with MEA, although the morphology was slightly different at the same temperature (Figure 14 and 15). PCC particles formed with MEA were identified as mixture of needle and rhombohedral shapes. With AEEA, however, particles had a rhombohedral shape (Figure 14). During carbonation with low gas flow rate, but at temperatures $> 30 \text{ }^\circ\text{C}$, particles started showing very well-defined needle-shape (Figure 14). This was caused by the insufficient supply of CO_2 due to a limited solubility at high temperatures. This leads to low supersaturation of the solution with HCO_3^- and CO_3^{2-} ions, promoting a slow nucleation rate [50]. Nevertheless, as it can be seen in Figure 15, at a temperature of 70 °C, when the gas flow rate was

increased from 0.02 until 0.1 L/min, slightly bigger particles were formed either with MEA or AEEA, presumably due to a fast protonation of zwitterion/carbamate at high temperatures.

Figure 14: SEM images of PCC formed after carbonation, at 30 and 70 °C, with addition of (a) MEA and (b) AEEA, and $Q_{\text{CO}_2} = 0.02$ L/min.

Figure 15: Effect of the gas flow rate (Q_{CO_2}) on the particle size distribution of PCC particles formed during carbonation with addition of 5 vol.% of MEA and AEEA, at 30 and 70 °C.

3.3.4 Effect of Mg on PCC production

It has been reported that the presence of Mg^{2+} ions can influence the synthesis of PCC particles, in particular the formation of aragonite when the Mg^{2+} concentration is high [41,45,82]. Mg concentration in the final PCC formed after carbonation is an important parameter for certain industrial applications such as paper coating or polymer filler. During carbonation with amine-based organic solvents, besides Ca precipitation and independently from the effect of the temperature, more than 95 wt.% of Mg co-precipitated simultaneously with Ca. Although it has been reported that that Mg^{2+} ions can substitutes Ca^{2+} ions site in the lattice of vaterite particles [83], it is most likely that Mg^{2+} stabilizes aragonite by absorbing on the calcite microcrystal surface, thus promoting the formation of aragonite [44,45]. PCC particles exhibited different morphologies between 30 and 70 °C, with aragonite crystals being formed at high temperatures (Figure 12 and 13). Still, the effect of Mg on the morphology and on the formation of aragonite particles was less significant due to the low initial concentration, i.e. 0.06 g/L.

In Figure 16 the effect of the temperature on Mg precipitation after carbonation with different amine-based organic solvents is depicted. In comparison to MEA and AEEA, a non-negligible effect of the temperature on the Mg precipitation was only observed on the PCC formed after carbonation with PEI. The highest Mg concentration, ca. 4 mg Mg/g PCC, was observed in the temperature range between 30-40 °C. Mg^{2+} ions from the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ precipitated as $\text{Mg}(\text{OH})_2$ due to the high pH of the solution. However, it is believed that $\text{Mg}(\text{OH})_2$ is less soluble in PEI than in MEA and AEEA, due to the difference in the bulk solution viscosity [84]. Although, solvents were added with the same volumetric concentration, i.e. 5 vol.%, their molecular weight were different, which could also lead to difference in the bulk solution viscosity. The increase in temperature could reduce the viscosity of the solution with PEI, enhancing the diffusion of ions within the solution. This could explain the reduction of Mg precipitation at temperatures above 40 °C. Slightly less Mg tended to precipitate with PEI when the temperature was increased. It is presumed that, due to the high molecular weight of PEI, Mg^{2+} ions slow down the nucleation rate of calcite as the temperature was raised, which resulted in the growth of calcite. This was confirmed by the XRD analysis on the PCC formed after carbonation with PEI at 70 °C (Figure 9 and 12). Conversely, temperature changes did not significantly affect the precipitation of Mg during carbonation with MEA nor AEEA, resulting in an average of about 2.2 (± 0.3) mg Mg/g PCC. Although, the precipitation of Mg could not be avoided completely, the final PCC resulted with a purity of 99.9%. Notice that these experiments were performed with a constant concentration of amine-based organic solvents of 5.1 wt.% (based on the dilution in Milli-Q water), which is significantly lower compared to traditional CO_2 capture processes that use about 20-30 wt.% [33,34]. This resulted in a consumption of 2 g of solvent/g PCC. Yet, it is believed that the solvent consumption can be further reduced by enhancing the mass transfer at the gas-liquid interface and the kinetics of the carbonation reaction, for instance, by using a continuous tubular reactor [85].

Figure 16: Effect of the temperature on the Mg precipitation (in mg of Mg per gram of PCC produced) after carbonation ($Q_{\text{CO}_2} = 0.1$ L/min) with different amine-based organic solvents (5 vol. %).

4. Conclusions

In this work, the effect of different CO₂-gas flow rates and temperatures was investigated to produce high-quality PCC with different morphologies and particle sizes. The effect of adding NaOH and different amine-based organic solvents (PEI, MEA and AEEA) was investigated by considering an integrated process of CO₂-absorption and mineral carbonation. Ca conversion was below 15 wt.% in the absence of alkaline reagents as alkalinity is reduced when H₂CO₃ is formed under a constant gas flow rate. The addition of a substantial amount of NaOH (20 g/L) allowed to significantly increase the Ca-conversion yield, and the morphology of calcite particles was modified from scalenohedral-rhombohedral- to rhombohedral shape by increasing the CO₂-gas flow rate from 0.008 until 0.5 L/min. However, this approach would demand ca. 830 kg of NaOH per tonne of CaCO₃, which will result in an estimated cost around 330-420 USD. During carbonation with addition of amine-based organic solvents, the addition of PEI limited the Ca-conversion up to 67 wt.%, whereas with the addition of MEA and AEEA showed the highest Ca-conversion, i.e. > 80 wt.%. A combination of vaterite and aragonite particles were produced at 30 °C, while the formation of pure aragonite prevailed when the temperature was increased up to 70 °C. It was noticed that only with the addition of AEEA, the particle size could be modified from large to small aggregates by increasing the CO₂-gas flow rate. The size of PCC particles formed during carbonation with addition of MEA did not show a significant difference by changing the CO₂-gas flow rate nor by changing the temperature. The effect of Mg on the formation of aragonite particles was considered negligible due to the low initial concentration, although some traces of Mg were detected in the corresponding final PCC aggregates formed after carbonation. The final PCC resulted with a 99.9% of purity using 5 vol.% of solvent, which resulted in a consumption of 2 g of solvent/g PCC.

Finally, it must be noticed that similar carbonation results can be expected from real BOF slags leachates, as long as leaching conditions (acid concentration, liquid-to-solid ratio, residence time and temperature) allow to maximise the dissolution yield of Ca with the lowest dissolution of other elements.

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