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Purification of slag-derived leachate and selective carbonation for high-quality precipitated calcium carbonate synthesis

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Abstract

Much research has been performed to synthesize precipitated calcium carbonate (PCC) from calcium extracted from blast furnace (BF) slag. A significant challenge has been obtaining a chemically pure sample with a homogeneous crystal structure and narrow particle size distribution, which can have profitable marketability (e.g. in the papermaking industry). The aim of this study was to investigate the influence of alternative and combinatory processing strategies on the chemical, morphological and mineralogical properties of BF slag-derived PCC. In a first phase, the physicochemical removal of impurities from the leachate, prior to the carbonation, was investigated, by means of temperature reduction ($20 \rightarrow 1^\circ\text{C}$) and pH elevation ($4.4 \rightarrow 8.4$); this led to selective precipitation of Al, Mg and Si. In a second phase, the operational conditions of the carbonation step were optimized, by lessening the severity of the operational conditions (90

→ 30°C and 6 → 2 bar, CO₂) and by reducing the amount of acid-neutralizing base (1.0 → 0.85 M, Na⁺/M, CH₃COO⁻) added during the carbonation process; this led to more selective calcium carbonation. Using these strategies, it was possible to synthesize chemically pure PCC (>98% Ca) with uniform morphology (scalenohedral), homogeneous mineralogy (>88% calcite) and narrow (1.09 uniformity), small (D₅₀ = 1.1 μm) particle size distribution.

Keywords: precipitated calcium carbonate; mineral carbonation; blast furnace slag; physicochemical leachate purification; process development; characterization

1. Introduction

Increased carbon dioxide emissions give rise to elevated concentrations in the atmosphere, which has a possible long-term negative effect on the global climate. The five industrial sectors with the highest carbon dioxide emissions are: (1) the power industry; (2) cement production; (3) refineries; (4) iron and steel industry and (5) petrochemical industry [1]. Currently, the potential for reuse of the emitted carbon dioxide is low. Therefore, more focus has to be placed on long-term capture and storage of emitted carbon dioxide, namely carbon capture and storage (CCS). A possible CCS route is mineral carbonation: chemically reacting carbon dioxide with calcium or magnesium containing materials, producing calcium- or magnesium carbonates [2].

In recent years, research has focused on employing waste residues from the iron and steel industry, rather than natural minerals, as source materials for the mineral carbonation, since these waste residues are inexpensive (or even have a negative price), are readily available, and are often produced near large CO₂ sources [3]. Two main types of mineral carbonation exist: direct and indirect carbonation. In the former, the source material is directly carbonated, while in the

latter, the calcium or magnesium is first extracted (e.g. using an organic lixiviant such as acetic acid or ammonium acetate) and subsequently carbonated. This results in post-carbonation precipitates with a higher purity and thus increasing the economic value, compared to direct carbonation [3]. Moreover, special attention has been given to waste materials with a high calcium content, mainly blast furnace (BF) slag and basic oxygen furnace (BOF) slag [3-7]. The choice for calcium-rich materials stems from the fact that precipitated calcium carbonate (PCC) has a larger market demand than magnesium carbonates [4].

Kakizawa et al. [8] proposed a reaction scheme (see equation (1) and (2)) to indirectly synthesize PCC from calcium present in wollastonite (CaSiO_3). Teir et al. [4] stated that, in this reaction scheme, wollastonite may be replaced by BF slag, which consists of mainly calcium silicate minerals. Subsequently, Eloneva et al. [3] experimentally synthesized non-commercial grade PCC starting from BF slag, based on the proposed reaction scheme. In a first step, the calcium was leached out from the BF slag with an acetic acid solution. Next, the leachate was separated from the post-extraction BF slag and subsequently carbonated.

During the carbonation step, an acid neutralizing agent was added to induce precipitation of calcium carbonate crystals; sodium hydroxide was selected. The PCC synthesized by Eloneva et al. [3], however, was not commercial grade; the calcium content of the post-carbonation precipitate was only between 63–89 wt%, as small amounts of aluminum, magnesium and silicon present in the initial BF slag also ended up in the post-carbonation precipitate. Furthermore,

calcite, aragonite and calcite-magnesian phases were detected in the PCC sample, making for a mineralogically and morphologically heterogeneous product.

Chiang et al. [7] attempted to optimize the extraction step by decreasing the acetic acid concentration, which led to a more selective leaching of calcium from the BF slag. However, concurrently, the overall calcium extraction extent became smaller. To balance the extent and selectivity of the calcium extraction, Chiang et al. [7] proposed a two-step leaching process. This by-passed the negative effect of high acidity on the selectivity while still maintaining a sufficient calcium extraction yield. Still, after carbonation of the leachates, the calcium concentration of the post-carbonation precipitates remained in the range of 69 – 90 wt%, and different mineralogical phases were also present. Based on these past studies, it appears that improvement of PCC purity may only be reached by removing the main impurities prior to the carbonation step, for example by selective precipitation [9].

The focus of the present work is on the indirect carbonation of calcium originating from BF slag, with the goal to synthesize marketable PCC intended for use as filler in paper products. For this application, the carbonate has to be chemically pure (~98 wt% calcium), should have a homogeneous mineralogical structure, a small average particle size and a narrow size distribution [10]. The approach was to investigate the influence of alternative and combinatory processing strategies on the chemical, morphological and mineralogical properties of BF slag-derived PCC, in view of generating a high-quality product. The research focus was divided in three stages:

- (a) the separation of the leachate and the post-extraction BF slag, targeting the removal of (nearly) all suspended particles (mainly silica) and residual BF slag prior to the carbonation;

- (b) investigation towards the physico-chemical removal of the most prevalent impurities, i.e. silicon, aluminum and magnesium, prior to the carbonation; and
- (c) optimization of the carbonation conditions to precipitate PCC with a sufficiently high calcium content, homogeneous crystal structure, small average particle size and narrow size distribution.

To finalize the present study, an optimized process set-up is suggested and experimentally tested.

2. *Materials and methods*

2.1. *Materials*

Ground granulated BF slag was obtained from a Belgian industrial steelworks. For the different experiments, the BF slag was manually milled with mortar and pestle. The resulting material had a D_{50} value of 2.1 mm and a uniformity coefficient (U) of 12 ($U = D_{60}/D_{10}$); these values were determined via classic sieving classification. Wavelength dispersive X-ray fluorescence (WDXRF, Panalytical PW2400) was used to determine the chemical composition. The slag was composed of following oxides: CaO (41.2 wt%), SiO₂ (35.3 wt%), Al₂O₃ (10.1 wt%), MgO (7.0 wt%); metallic components were Ti (0.8 wt%), Fe (0.4 wt%) and Mn (0.3 wt%). X-ray Diffraction (XRD, Philips PW1830) showed the slag to be largely amorphous; amorphicity is caused by the granulation process whereby the slag is rapidly cooled, preventing crystallization.

BF slag was chosen over BOF slag because of the following advantages: (i) higher production output (0.25 – 0.30 tonne BF slag per tonne crude iron); (ii) a more consistent mineralogical and chemical composition; and (iii) a higher aluminum content (10-14 wt% Al₂O₃) [7]. The last characteristic is important with respect to the feasibility of the two-way valorization of

ironmaking slag, as proposed by Chiang et al. [7]. In the proposed process, in addition to producing PCC, the post-extraction ironmaking slag is upgraded to a marketable zeolitic material in order to help off-set the costs of CCS. To enable zeolite synthesis, however, the calcium extraction from the slag must be very extensive; therefore it was also a focus of the present work to maximize calcium extraction from BF slag.

The lixiviant used was analytical grade acetic acid (CH_3COOH), the pH adjusting base used was analytical grade sodium hydroxide (NaOH), the carbon dioxide used was industrial grade (99.5 %), and water used was ultrapure ($>18.1 \text{ M}\Omega\cdot\text{cm}$).

2.2. Experimental methodology

The experimental procedure commenced by selectively extracting calcium from the BF slag in a two-step leaching process with acetic acid. The two-step method was used to avoid the detrimental effect of high acidity on the extraction selectivity while still attaining a sufficient extraction yield. In each step, 731 ml of a 2.0 mol/l acetic acid solution was mixed with the 100 g BF slag solids in a Büchi Ecoclave reactor (internal volume = 1.1 liter, electrically heated, cooled with water in a cooling mantle, mixed with a turbine impeller, baffled). The slurry was mixed at 30 °C for 60 min at 1000 rpm. After the second extraction step, both leachates were blended together. These leaching conditions were based on the work of Chiang et al. [7]. In select experiments, to establish the necessary steps to separate the post-extraction BF slag residue and the acetic acid leachate, a one step-leaching action was instead performed (731 ml acetic acid, 2.0 mol/l in combination with 50 g BF slag).

The next stage in the experimental process was to separate the leachate solution from the post-extraction residual solids (including the bulk of the suspended silica particles). Separation

consisted of centrifugation and/or filtration (depending on the experimental goal, as discussed in the results section). Centrifugation was performed using a Heraeus Labofuge 400 centrifuge, operated at 4000 RCF (relative centrifugal force) for 10 min; the leachate was collected as the supernatant. Filtration was performed using Whatman No. 2 filter paper (pore size = 8.0 μm) or Millipore MF membrane filters (pore size = 0.45 μm).

In a final processing stage, the leachate solution was carbonated. Carbonation of the leachate was performed at different reaction intensities (30 – 90 °C and 2 – 6 bar CO_2) for 60 min at 1000 rpm in the Büchi Ecoclave reactor. To promote precipitation of calcium carbonate and neutralize the regenerated acetic acid, sodium hydroxide was added, in amounts varying from 1.4 to 2.0 mol/l; the latter is equimolar with respect to the acetic acid used in the extraction step. The carbonation precipitates were collected via filtration using Whatman, No. 2 filter paper, thoroughly washed with distilled water and dried for 24 h at 105 °C.

In specific experiments to improve purity, an extra step was added to the experimental procedure, focusing on the removal of soluble impurities. This extra step was fitted between the solid/liquid separation stage and the carbonation stage. First, the temperature of the leachate was lowered (to between 0 and 20 °C) by placing the leachate in a refrigerator. Once cooled, the leachate was filtered with Millipore MF membrane filters to remove precipitates. In additional experiments, the pH of the leachate was increased by sodium hydroxide addition (0.50 – 1.25 mol/l), followed by filtration with Millipore MF membrane filters to remove precipitates. After these steps, the purified leachates from were carbonated as previously described.

2.3. Analytical methods

The mineralogical composition of the different precipitates was determined by Rietveld refinement of XRD data using TOPAS Academic 4.1 (Coelho Software). To determine the chemical composition of the different precipitates, the solids were dissolved in nitric acid (65 wt%). Subsequently, the Al, Ca, Fe, Mg, Mn, Si and Ti contents were determined via Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Electron X Series). The concentrations of Fe, Mn and Ti were neglected due to their limited occurrence, and the sum of Al, Ca, Mg and Si contents was then normalized to 100% for ease of purity comparison. The aqueous concentrations of Al, Ca, Mg and Si in the leachates and in the post-carbonation liquid medium were also determined via ICP-MS measurements. The morphology of the solid materials was visualized by Scanning Electron Microscopy (SEM, Philips XL30 FEG). The average particle size diameter and size distribution of the solids were measured via wet Laser Diffraction Analysis (LDA, Malvern Mastersizer 3000).

2.4. Geochemical modelling

Geochemical modelling of aqueous equilibria was performed using Visual MINTEQ (ver. 3.1, KTH). The activity coefficients were calculated using the Specific Ion Interaction Theory model (SIT), valid for the ionic strengths < 4 M, as modelled here (0.8891 – 1.4922 M).

3. Results and discussion

This research was divided in three phases. In the first phase, the post-extraction solid/liquid separation was optimized. In the second phase, soluble impurities were removed from the leachate. In the third phase, the carbonation process was optimized. These three phases are

presented in the next sections. In a final section, the overall optimized process is discussed and the optimized product presented.

In order to illustrate the attained improvements of the present work, a reference PCC sample was also synthesized using the same conditions of Chiang et al. [7]. The XRD diagram of the reference PCC sample is shown in Figure 1 and the quantitative results of the XRD Rietveld refinement are shown in Table. The PCC sample consisted predominantly of the calcite mineral (67.2 wt%). However, different undesired mineral phases were detected, and the chemical purity of the post-carbonation precipitate was low: 77.5 wt% Ca. As a result of the combination of low chemical and mineralogical purity, the morphology of the PCC sample was influenced, with a very limited amount of homogeneous calcite crystals forming, as visualized by SEM (Figure 2).

Figure 1: XRD diagram of the reference PCC sample.

Table 1: Mineralogical composition (wt% of crystalline fraction) of the reference PCC sample, determined by XRD Rietveld refinement; < indicates that the presence of the specific mineral is less than the estimated quantification accuracy of ± 2.0 wt%.

Mineral phase	Mineral formula	Wt(%)
Aragonite	CaCO_3	2.0
Calcite	CaCO_3	67.2
Magnesian calcite	$\text{Ca}_{1-0.85}\text{Mg}_{0-0.15}\text{CO}_3$	4.8
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	4.1
Huntite	$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$	2.1
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	3.6
Magnesite	MgCO_3	2.3
Monohydrocalcite	$\text{CaCO}_3 \cdot \text{H}_2\text{O}$	<
Nesquehonite	$\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$	5.4
Vaterite	CaCO_3	5.8

Figure 2: SEM picture of the reference PCC sample.

3.1. Post-extraction solid/liquid separation

In preliminary experiments, filter clogging due to silica deposits were observed when attempting to separate the extraction leachate from the residual solids by direct filtration. Silica is a by-product of acid leaching of BF slag, whereby the alkaline components from the silicate (Ca and Mg) go into solution leaving behind amorphous colloidal silica. To improve the separation, centrifugation was adopted. This allowed for removal of the residual BF slag together with a bulk

amount of the silica (75 %) prior to filtration; there was, however, still a large amount of silica suspended in the supernatant: 780 mg/l. Carbonation of this supernatant under standard conditions resulted in precipitate with silicon concentration of 14 wt%; too high for commercial use of PCC as filler material. Therefore subsequent purification by filtration remained necessary.

Filtration experiments indicated that the pore size of the employed filter had a small effect on the Si concentration in the filtrate: 615 mg Si/l (pore size: 8.0 μm) and 515 mg Si/l (pore size 0.45 μm). However, there was a significant effect on the purity of the post-carbonation precipitate. The elemental silicon content in the precipitates from these filtrates were, respectively, 5 and 1 wt%. Therefore the optimal post-extraction solid/liquid separation process consists of centrifugation followed by supernatant microfiltration.

3.2. Post-centrifugation removal of colloids and soluble impurities

Removing the main soluble impurities, i.e. silica, magnesium and aluminum, from the leachate prior to carbonation is a possible route to obtain sufficiently chemically pure PCC. In a first investigation route, the effect of the leachate temperature on the silica solubility was experimentally determined. Experiments in pure water indicate that there is a proportional relationship between these two parameters [11]; i.e. silica solubility decreases with a decrease in solution temperature. However, in the current process set-up, the leachate contained large amounts of metal-acetates (e.g. calcium acetate); hence the exact influence of temperature on the silica solubility was unknown. In the performed experiments, the temperature of the centrifuged leachate was varied between 1 °C and ambient temperature (20 °C). After cooling, the precipitated silica was filtered out by membrane microfiltration. The silica removal efficiency was determined by sampling the leachate and measuring the silica concentration prior the

temperature variation and after the filtration. The calculated removal efficiencies are shown in Figure 3 as a function of temperature. By cooling the leachate down to 1 °C, a silica removal efficiency of nearly 60 % was attained.

At 1 °C, the silica concentration in the filtered leachate was 263 mg/l. However, in pure water at 1 °C the solubility is ± 50 mg/l [11]. The explanation for this discrepancy is twofold. First, primary silica particles have an average diameter of ± 5 nm [12], while the membrane pore size was 450 nm. Secondly, the presence of other ions may have influenced the silica solubility.

Figure 3: SiO₂ removal yield (%) after cooling and microfiltration of the leachate with respect to temperature (diamond symbols). Additionally, the concentrations after filtration are shown (square symbols); Si concentration before cooling = 530 mg/l.

In addition to silica, the leachate contained relatively high amounts of magnesium and aluminum, respectively around 2,000 and 1,000 mg/l. According to the reaction mechanism proposed by Kakizawa et al. [8], both metals were bound to acetate ions. Both metal-acetates have high water

solubility. However, by adding sodium hydroxide to the centrifuged leachate, the metals may form hydroxides according to the following reaction mechanism:

In contrast to the metal-acetates, magnesium and aluminum hydroxides have a very low solubility, respectively 14 and 1 mg/l in pure water at 20 °C. After the sodium hydroxide addition, these hydroxides precipitated out of solution and were removed via microfiltration. The removal efficiency was calculated per adjusted pH value in order to assess the effect of a pH increase; the initial pH was 4.4 and the results are shown in Figure 4. A pH adjustment to 8.4 (addition of 1.25 mol NaOH/l) entailed a magnesium and aluminum removal extent of 64 and 92 %, respectively. The removal efficiency of magnesium and aluminum may even be further increased by the addition of more sodium hydroxide.

Figure 4: Removal of soluble impurities after sodium hydroxide addition expressed in percentages as a function of pH alteration of the leachate; initial unaltered pH was 4.40.

Geochemical modelling helps explain the pH-dependent precipitation of aluminum and magnesium. Figure 5 shows that the saturation index of several aluminum species surpass zero (saturation) when the pH increases due to NaOH addition. The species responsible for the aluminum removal in the present study appears to be amorphous $\text{Al}(\text{OH})_3$, as this species' saturation index surpasses saturation from pH 6.34 onwards, when aluminum precipitation was found to occur (Figure 4).

Figure 5: Saturation index, determined by geochemical modelling, of possible solids species forming during pH adjustment of the leachate ($T = 20^\circ\text{C}$); initial leachate conditions: $\text{Ca}^{2+} = 0.5 \text{ mol/l}$; $\text{Mg}^{2+} = 0.0823 \text{ mol/l}$; $\text{Al}^{3+} = 0.037 \text{ mol/l}$; $\text{CH}_3\text{COO}^- = 2 \text{ mol/l}$. No phases were allowed to precipitate in the model.

The removal mechanism of magnesium could be attributed to spinel (MgAl_2O_4) precipitation, which reaches saturation above pH 6.34. Some works have reported precipitation of spinel in aqueous solution (e.g. Alvar et al. [13]), but it is unclear if its formation is limited to well-controlled chemical conditions (which are used in recent works to promote high surface area and nano-crystallite sizes). Packter et al. [14] studied the co-precipitation of aluminum and magnesium hydroxides in simple solutions buffered by sodium hydroxide at low temperatures,

and found that above pH ~7.6 spinel precursors in the form of $\text{Mg}_x(\text{H}_2\text{O})_n(\text{OH})_{2x-4}[\text{Al}_2(\text{OH})_{10}]$ (where $x = 2, 4$ or 6) appeared. Brucite ($\text{Mg}(\text{OH})_2$) precipitation is another possibility, as it has the next highest saturation index; however, since its saturation index is still considerably negative (undersaturated) even at pH 8.43, there would have to be additional effects to account for its partial precipitation.

In addition to aluminum and magnesium, a significant amount of silicon was also removed at higher pH values. Silicon was present in the leachate primarily as suspended colloidal silica. After the addition of sodium hydroxide, the pH rose and the aluminum and magnesium precipitated as hydroxides, forming voluminous flocs that entrained the suspended silica particles.

A small undesired side-effect of the sodium hydroxide addition was that small amounts of calcium were also removed from the leachate, however not in such an amount that the technique affected the subsequent PCC production yield significantly. The calcium removal is small compared to magnesium and aluminum due to its hydroxide form having substantially larger solubility.

Sodium hydroxide was chosen as pH increasing agent because further on in the carbonation step its presence was needed as acetic acid neutralizer to induce calcium carbonate precipitation [3]. Thus, in this extended process set-up the sodium hydroxide is only added earlier on in the process. Therefore, overall no additional chemicals were used in comparison with the research of Chiang et al. [7].

After carbonation of the most purified leachate (pH = 8.4), the calcium content in the precipitate was 96.6 wt%, a significant increase compared to the reference sample. The purification of the

leachate had also a distinct positive effect on the mineralogical composition of the post-carbonation precipitate; more extended purification entailed a larger calcite fraction, while aragonite and vaterite phases were no longer present (see Table 2).

Table 2: Mineralogical composition (wt% of crystalline fraction) of the carbonation precipitates after addition of varying amounts of sodium hydroxide to the leachate, determined by XRD Rietveld refinement; < indicates that the presence of the specific mineral is less than the estimated quantification accuracy of ± 2.0 wt%. The XRD diagrams are given in Figure SC 1 in the supplementary material.

Mineral phase	pH leachate prior to carbonation					
	4.7	5.0	5.5	6.3	7.4	8.4
Aragonite	20.1	5.5	<	<	<	<
Calcite	57.8	68.5	77.7	69.6	74.3	78.0
Magnesian calcite	4.0	5.3	4.1	8.7	11.4	7.4
Dolomite	2.7	4.1	3.0	3.7	2.0	<
Huntite	<	<	2.3	2.4	2.3	<
Hydromagnesite	2.0	2.1	3.8	2.8	2.3	<
Magnesite	<	<	<	<	<	<
Monohydrocalcite	<	<	<	<	<	<
Nesquehonite	<	4.1	2.5	3.5	2.8	3.4
Vaterite	7.3	5.1	<	4.0	<	<

The attained morphological improvements were clearly visible via electron microscopy. SEM images of the post-carbonation precipitates synthesized under standard conditions are presented in the Figure 2, while SEM images from the post-carbonation precipitate originating from the purified leachate are shown in FigureA. In the SEM images of the former, the particles were very heterogeneously sized and many impurity particles were visible; while in the latter, the calcite particles were uniform and little impurities were present. This uniform particle size was a direct consequence of the removal of the impurities from the leachates prior to carbonation, and can be quantitatively visualized in the LDA size distributions of the different post-carbonation precipitates (Figures SC 2, 3, 4 and 5 in the supplementary material).

This novel separation/purification method opens new perspectives for the application of slag-derived leachates for the production of PCC as the main impurities, i.e. magnesium, aluminum and silicon, were removed in large amounts from the leachate prior to carbonation, resulting in a PCC sample with a high purity (96.6 wt% Ca).

3.3. Optimization of carbonation parameters

In a next phase, the carbonation step was further optimized in order to: (1) prevent the undesired co-precipitation of magnesium; (2) synthesize PCC with homogeneous calcite crystals. Chiang et al. [7] chose to add an acid neutralizing additive (sodium hydroxide or sodium bicarbonate) in equimolar amounts relative to the acetic acid amount used in the extraction step. However, an increased basicity induces the formation of magnesium carbonate [15]. Thus, the undesired co-precipitation of magnesium carbonate may be prevented by adding a sub-equimolar amount of base prior to carbonation. The leachates used here were obtained using the standard method of Chiang et al. [7]; i.e. not yet implementing the additional purification techniques described in sections 3.1 and 3.2.

A first set of experiments was performed in which the amount of added sodium hydroxide was stepwise decreased from 2.0 to 1.4 mol/l; addition of smaller amounts resulted no longer in the precipitation of calcium carbonate as determined by XRD measurements. The relation between the precipitation extent of Al, Ca, Mg and Si and the amount of sodium hydroxide added prior to carbonation is shown in Figure 6. The chemical and mineralogical composition of the different precipitates is shown, respectively, in Figure 7 and Table 3.

Figure 6: Precipitation extent of Mg, Al, Si and Ca from the leachate after carbonation.

Figure 7: Composition of post-carbonation precipitates expressed in weight percentage per element, normalized to 100% total; results determined via ICP-MS.

Table 3: Mineralogical composition (wt% of crystalline fraction) of the carbonation precipitates after addition of varying amounts of sodium hydroxide to the leachate, determined by XRD Rietveld refinement; < indicates that the presence of the specific mineral is less than the estimated quantification accuracy of ± 2.0 wt%. The XRD diagrams are given in Figure SC 6 in the supplementary material.

Mineral phase	NaOH added (mols per liter leachate)						
	1.4	1.5	1.6	1.7	1.8	1.9	2.0
Aragonite	28.5	26.7	23.4	22.0	14.2	<	<
Calcite	32.7	48.0	47.6	59.6	65.9	70.5	70.6
Magnesian Calcite	6.7	2.1	12.8	<	5.4	7.3	7.5
Dolomite	2.7	4.6	<	2.4	<	4.0	4.2
Huntite	2.7	2.1	<	<	<	2.2	2.2
Hydromagnesite	4.8	3.1	3.4	3.1	2.9	3.4	3.6
Magnesite	4.8	<	<	<	2.7	<	<
Monohydrocalcite	<	<	<	<	<	<	<
Nesquehonite	8.6	4.6	5.7	4.4	2.6	3.9	3.4
Vaterite	4.6	5.7	3.0	4.0	2.8	3.2	2.9

The precipitation of magnesium from the leachate was significantly prevented by adding a sub-equimolar amount of sodium hydroxide. The magnesium concentration in the carbonation precipitate was 9.7 wt% at equimolar amounts, while at a sub-equimolar amount the concentration ranged between 2.3 and 3.2 wt%.

Geochemical modelling (Figure 8) shows that at high sodium hydroxide concentrations, calcium-magnesium carbonates (huntite and dolomite; magnesian calcite was not modelled) are susceptible to precipitation, and the saturation index of magnesite also approaches the precipitation point. At sodium hydroxide concentrations below 1.7 mol/l, only calcium carbonates have non-negative values of saturation index (calcite was allowed to precipitate in the model, therefore its saturation index is maxed at zero). The model also shows that even at the lowest sodium hydroxide concentration, 1.4 mol/l, calcium carbonate is favored to precipitating, which was observed experimentally (Figure 7). However, at this pH level (5.41, calculated from

charge balancing), the model predicts that calcium precipitation is partial, which is also in agreement with the lower precipitation extent measured experimentally (53%, Figure 7).

Figure 8: Saturation index, determined by geochemical modelling, of select carbonate species potentially forming during carbonation of the leachate (90°C, 6 bar CO₂); initial leachate conditions: Ca²⁺ = 0.5 mol/l; Mg²⁺ = 0.0823 mol/l; Al³⁺ = 0.037 mol/l; CH₃COO⁻ 2 mol/l. The calcite phase was allowed to precipitate in the model, hence its saturation index is maxed at a value of zero (i.e. precipitation point).

Precipitation of aluminum was only slightly influenced by the added amount of sodium hydroxide; between 89.5 – 92.3 % of aluminum present in the leachate precipitated during carbonation. Based on the results presented in Figure 4, it may be concluded that the aluminum precipitated as hydroxides as a direct consequence of the increase in hydroxyl ion concentration (see reaction (4)), rather than due to the carbonation conditions. These results highlight the need for the purification techniques of section 3.2, to avoid the presence of aluminum in the PCC, as shown in Figure 7.

Increasing the amount of sodium hydroxide prior to carbonation enhanced the precipitation of calcium from the leachate; a maximum was attained at 1.8 mol/l sodium hydroxide. This is

desirable as it improves the overall PCC yield and purity (as seen in Figure 7, the PCC purity improves as the ratio of calcium to impurities increases). Further increasing the base concentration had no additional positive effect; rather, it promoted undesirable magnesium precipitation. The highest PCC purity (79.9 wt% Ca) occurred at a base concentration of 1.7 mol/l, as this combined high calcium precipitation with low magnesium precipitation (the two main components of the leachate).

Varying the amount of added sodium hydroxide prior to carbonation had not only an effect on the chemical composition of the post-carbonation precipitates, but also on the distribution of the mineralogical phases, as shown in Table 3. Decreasing the added amount of sodium hydroxide prior to carbonation promoted the growth of a larger aragonite crystal fraction. This increase at lower sodium hydroxide concentration is explainable by the research of Kitamura et al. [16]. These researchers stated that aragonite formation is favored at lower calcium hydroxide concentrations. By adding less sodium hydroxide prior to carbonation, the resulting calcium hydroxide concentration in the leachate was lower (see reaction (5)).

The presence of aragonite (22.0 wt%, rod shaped particles) is visible in the SEM images of the post-carbonation precipitate after addition of 1.7 mol/l NaOH, shown in Figure 10B.

Furthermore, the particle size remained heterogeneously distributed and relatively large amounts of impurities were still present, similar to the reference sample (Figure 2).

Hu and Deng [17] stated that the formation of aragonite is favored over calcite at higher temperatures; in the range of 60 – 70 °C. To prevent the growth of aragonite crystal, the reaction temperature should be beneath this threshold. To confirm this theory, carbonation experiments

were performed at varying temperatures: 30, 60 and 90 °C. For these experiments, the standard leachate preparation method of Chiang et al. [7] was used. The mineralogical and chemical compositions of the three resulting post-carbonation precipitates are given, respectively, in Table 4 and Figure 9.

Table 4: Mineralogical composition (wt% of crystalline fraction) of the carbonation precipitates after carbonation at different temperatures and carbon dioxide partial pressures, determined by XRD Rietveld refinement; < indicates that the presence of the specific mineral is less than the estimated quantification accuracy of ± 2.0 wt%. The XRD diagrams are given in Figure SC 7 in the supplementary material.

Mineral phase	Operating conditions		
	30 °C – 2 bar CO ₂	60 °C – 3.5 bar CO ₂	90 °C – 6 bar CO ₂
Aragonite	<	3.9	8.7
Calcite	80.1	68.7	68.3
Magnesian Calcite	6.3	4.1	5.1
Dolomite	<	3.4	2.3
Huntite	<	3.6	2.8
Hydromagnesite	<	3.4	2.3
Magnesite	<	<	<
Monohydrocalcite	<	<	<
Nesquehonite	4.2	2.8	4.8
Vaterite	2.2	5.8	<

Figure 9: Composition of post-carbonation precipitates expressed in weight percentage per element, normalized to 100% total; results determined via ICP-MS.

Decreasing the reaction temperature successfully prevented the formation of aragonite crystals in the post-carbonation precipitate (Table 4). An additional effect was that the chemical purity of the carbonation precipitate improved (Figure 9); from 69 wt% calcium at 90 °C to 77 wt% at 30 °C. At the lower temperature, the post-carbonation precipitate had a more homogeneous crystal structure. The XRD Rietveld refinement confirmed only the presence of a calcite (80.1 wt%), magnesian calcite (6.3 wt%), nesquehonite (4.2 wt%) and vaterite (2.2 wt%). SEM images of the post-carbonation precipitate confirm the presence of the large calcite fraction; see FigureC. Furthermore, these SEM images illustrate that the particle size of the precipitate is more uniform than one synthesized under the reference conditions (Figure 2).

The decrease in reaction temperature had no visible effect on the magnesian calcite fraction. The expectation was that the fraction of magnesian calcite would be lower as the severity of the reaction decreased, as this would be less optimal for magnesium carbonate formation [15]. Seemingly, the formation rate of magnesian calcite is not related to the needed conditions for

magnesium carbonate formation. This can be related to the fact that magnesium calcite consists of calcite mineral with magnesium substitution in the calcite crystal lattice; therefore calcite promoting conditions also promote magnesian calcite formation.

In general, the obtained results indicate possibilities for cost savings, as a chemically purer and more homogeneous precipitate was obtained with a decreased reaction severity. Based on our recent work on carbonation in open reactors (i.e. <1 atm CO_2), PCC synthesis can be accomplished in even less severe conditions, especially in the presence of sonication [19] or nickel catalyst [20]. Also, carbonation is an exothermic reaction, so in an insulated continuous reactor (e.g. plug flow tubular reactor [21]), if needed, it is possible to contain or recycle reaction heat to sustain the temperature requirements.

Figure 10: SEM images of select post-carbonation precipitates obtained: (A) after carbonation of the leachate purified by addition of 1.25 mol NaOH/l leachate prior to a filtration; (B) after carbonation of the leachate by adding 1.7 mol NaOH/l leachate as acid neutralizing additive; (C) after carbonation under reduced severity, 30 °C and 2 bar CO₂ partial pressure.

3.4. Optimized process experiments

Using optimal separation, purification and carbonation methods, the different improvements described in the previous sections were combined in a novel slag-to-PCC synthesis process set-up, illustrated in Figure 11.

Figure 11: Envisioned slag-to-PCC synthesis process.

In a first step, the calcium is selectively extracted from the BF slag with acetic acid. Subsequently, the post-extraction solid residue is separated from the calcium acetate-containing leachate. The optimal solid/liquid separation step comprises of centrifugation followed by membrane microfiltration; the former aims at the removal of the suspended silica, to eliminate filter clogging, and the bulk of the residual slag, while the latter consists of a polishing action. In

the optimized process, the centrifuged supernatant is cooled down to 1 °C prior to microfiltration, in order to decrease the solubility of silica and precipitate it out of solution.

To subsequently synthesize PCC, additional sodium hydroxide must be added during carbonation, to neutralize the reconstituted acetic acid. However, in contrast to previous practices, a sub-equimolar amount (1.7 mol, NaOH/l) of sodium hydroxide, with respect to the acetic acid employed in the leaching step (2.0 mol, CH₃COOH/l), is added. Furthermore, sodium hydroxide is added prior to the cooling step. In this manner, the main soluble impurities, i.e. aluminum and magnesium, are transformed from soluble acetates to poorly soluble hydroxides; the latter precipitate out of solution and are subsequently removed by microfiltration. The voluminous hydroxide flocs that form entrain much of the suspended small silica particles that remain after centrifugation.

As a consequence of this train of purification steps, a leachate with a very high purity is obtained, minimizing the co-precipitation of impurities together with the PCC in the next and final step: carbonation. This approach is successful in decreasing the co-precipitation of magnesium with the PCC, thus increasing the product purity. Furthermore, this carbonation can be performed at a lower severity (30°C and 2 bar, CO₂), favoring the formation of calcite and preventing the formation of aragonite; this results in a post-carbonation precipitate with a homogeneous mineralogical content and morphology, as presented next.

The calcium content of the hereby obtained post-carbonation precipitate was 98.1 wt% (see Figure 12); this is sufficiently high to be applicable as filler material in paper [10], and can truly be referred to as PCC. The main impurity present in this precipitate was magnesium (1.5 wt%), which from a toxicity perspective is passive and therefore not worrisome. The aluminum

concentration was close to zero (0.1 wt%), while no silicon was detected (<0.1 wt%). Even higher purity, if required, may be obtained by more precisely optimizing the amount of sodium hydroxide added prior to the separation of the leachate.

Figure 12: Composition of the optimized carbonation precipitate expressed in weight percentage per element, normalized to 100% total; results determined via ICP-MS.

The mineralogical composition of the optimized precipitate was determined via quantitative XRD measurement; the results are given in Table 5, while the XRD diagram is presented in Figure 13. The calcite fraction of the post-carbonation precipitate was large, 88 wt%. Furthermore, small amounts of nesquehonite and magnesian calcite were present, both around 3 wt%. Mineral phases present below 2 wt%, which summed to 5.8 wt%, are at the quantification limit of the technique, so their presence is uncertain and may be overestimated. It can thus be concluded that a product with a very uniform crystalline mineral composition was synthesized.

Table 5: Mineralogical composition (wt% of crystalline fraction) of the carbonation precipitates obtained with the optimized process set-up, determined by XRD Rietveld refinement; < indicates that the presence of the specific mineral is less than the estimated quantification accuracy of ± 2.0 wt%.

Mineral phase	wt%
Aragonite	<
Calcite	88.2
Magnesian Calcite	2.8
Dolomite	<
Huntite	<
Hydromagnesite	<
Magnesite	<
Monohydrocalcite	<
Nesquehonite	3.2
Vaterite	<

Figure 13: XRD diagram of the post-carbonation precipitate synthesized with the optimized process.

A graphical representation of the particle size distribution of the obtained precipitate is shown in Figure 14. The precipitate met the desired qualities of a small average particle size and a narrow size distribution, as stated by Tavakkoli et al. [18] and Gill [10]. Further optimization of the particle size and size distribution may be attained by adjusting the carbonation conditions further.

Figure 14: Particle size distribution of the optimized carbonation precipitate, determined by wet laser diffraction analysis; overlapping lines represent measurement replicates.

4. *Conclusions*

The present work has investigated the possibility to produce precipitated calcium carbonate (PCC) with a high chemical purity, homogeneous mineralogical structure and narrow particle size distribution by reacting carbon dioxide with calcium extracted from blast furnace (BF) slag. To achieve this goal, a previously proposed three-step process was optimized and extended with additional novel purification steps, focusing on the removal of fine colloidal particles and soluble impurities. For the first time, it was possible to synthesize papermaking grade PCC from calcium present in BF slag.

The envisioned process opens a new pathway for PCC preparation, whereby an industrial residue is used in place of natural resources, which is attractive from a sustainability perspective due to the waste valorization being combined with non-renewable resource preservation. Still, further research and process development is needed to maximize the economic potential of the proposed process. The main hurdle with the current set-up is the high amount of liquid waste after the carbonation; more research towards lixiviant regeneration is warranted. The main opportunity

that was not addressed in this work is the upgrading of the post-extraction slag residue, and of other produced solid residues, to valuable products.

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