



Technical note

Distinguishing between carbonate and non-carbonate precipitates from the carbonation of calcium-containing organic acid leachates

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ABSTRACT

Two organic acids were trialed for the extraction of calcium from steelmaking blast furnace slag for the purpose of precipitated calcium carbonate (PCC) production: succinic and acetic acids. While the leaching performance of succinic acid was superior, carbonation of its leachate did not result in the production of PCC, but rather the precipitation of calcium succinate, and only after the use of pH buffering agents (sodium hydroxide or bicarbonate). In contrast, carbonation of the acetic acid leachate resulted in the production of PCC, also with the aid of buffering agents. This discrepancy highlights the need for a combination of chemical, mineralogical and morphological analytical techniques for the accurate characterization of carbonation precipitates for future publications in this field. Additional effects observed in this study were the low atom-efficiency of the acids for calcium leaching, at ~20–30% of the stoichiometric value, the low extraction selectivity but high carbonation selectivity between calcium and magnesium, and the contamination of the formed PCCs with small amounts of co-leached aluminum and silicon. Further work is warranted on the purification of this PCC synthesis route.

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1. Introduction

The production of precipitated calcium carbonate (PCC) from natural and waste-derived alkaline materials has been a major focus of research due to the numerous commercial uses for this material such as: filler, pigment and color stabilizer in papers, paints, polymers and pharmaceuticals applications; pH buffer and neutralizer in environmental and water treatment applications; and as a component of foodstuffs, fertilizers and animal feed (CCA Europe, 2012; Wypych, 2010). An ideal calcium leaching agent should have high extraction efficiency, and less affinity for the alkaline earth elements than the carbonate ion to allow the precipitation of carbonates upon pH-swing (Santos et al., 2014). Kakizawa et al. (2001) proposed acetic acid for the extraction of calcium from silicate minerals, stating that this acid is stronger than silicic acid and weaker than carbonic acid. They theorized that both the extraction and the crystallization reactions could occur spontaneously when acetic acid is used. However, precipitation extent was limited at 20% as re-dissolution of CaCO₃ occurs when the CO₂ partial pressure is exceedingly high.

Eloneva et al. (2008) was able to achieve higher precipitation extent (up to 74%) with the aid of NaOH as an acid neutralization agent to precipitate calcium carbonate crystals from blast furnace slag (BFS).

Baldyga et al. (2010, 2011) compared three different organic acids, adipic, acetic and succinic, for the leaching of calcium from the natural mineral wollastonite (CaSiO₃). The use of succinic acid was recommended due to its greater extraction extent and favorable kinetics. Also reported was that significant carbonation-induced precipitation of calcium from succinic acid leachate could be achieved in the absence of pH buffers; precipitation yield was 90%, compared to only 30% in the case of the acetic acid leachate.

The initial aim of the present study was to confirm if succinic acid also performs better than acetic acid in the case of PCC synthesis using BFS as the calcium source. In the course of the study, upon extensive characterization of the precipitates, discrepancies were found between the materials formed from the different leachates. These findings have not been reported in existing literature and present some important insights to the field. The focus of this technical note is the reporting of these discrepancies and the description of techniques for the accurate characterization of carbonation precipitates.

2. Materials and methods

Granulated blast furnace slag (GBFS) from a steelwork was used as the starting material. Its chemical composition, determined by X-ray fluorescence (XRF, Panalytical PW2400), consisted mainly of CaO (41.0 wt.%), SiO₂ (36.0 wt.%), Al₂O₃ (11.0 wt.%) and MgO (8.4 wt.%). Its mineralogical composition, determined by X-ray diffraction (XRD,

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Philips PW1830), was found to be mainly amorphous. Preference was given to the use of actual slag rather than synthetic materials, as in prior work (Bodor et al., 2013) we have observed discrepancies in the reactivity of mineral phases present in the slags relative to those same phases synthetically produced, which may be attributable to solid solution effects and differences in cooling path. To increase specific surface area of GBFS, beneficial to extraction, the slag was run through a Retsch ZM100 centrifugal mill (1400 rpm, 500 μm sieve mesh). The mean particle diameter ($D[4,3]$) of the resulting material, determined by wet laser diffraction (LD, Malvern Mastersizer S), was 138.3 μm , and its geometrical specific surface area, determined by LD, was 0.47 m^2/g .

Analytical grade succinic acid ($\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$) and acetic acid (CH_3COOH) were used for the calcium extraction stage. The extraction was done in two steps, to moderate acidity and thus improve leaching selectivity (Chiang et al., 2014). In each step, 731 ml of fresh 0.5 M acid solution was mixed with the solids (100 g milled GBFS in the first step, and the residual solids from the first step in the second step) for 60 min at 80 °C and 1000 rpm under air atmosphere in a Büchi Ecoclave reactor (1.1 l internal volume, equipped with turbine impeller mixer, electrically heated and water cooled). The slurry was vacuum filtered (Whatman No. 2 filter paper) to separate the leachate solution from the residual solids.

The leachates from the first and second extraction steps were combined and split into two equal fractions. Each fraction was subjected to carbonation in the Ecoclave reactor for 60 min, at temperatures between 60 and 120 °C, and applying CO_2 partial pressures between 2 and 50 bar. For some experiments, analytical grade sodium bicarbonate (NaHCO_3) or sodium hydroxide (NaOH) were included, in equimolar amounts to the organic acid concentration used in the extraction stage for each leachate, to buffer the pH and induce precipitation. Precipitates were vacuum filtered, washed thoroughly with DI water to remove soluble organic compounds, and dried at 105 °C for 24 h.

The extraction leachates and post-carbonation filtered solutions were analyzed for pH and for aqueous concentrations of Al, Ca, Mg and Si by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Electron X Series). The mineralogical, chemical and morphological properties of the post-carbonation precipitates were characterized by XRD, XRF, thermal gravimetric analysis with differential scanning calorimetry (TGA–DSC, TA Instruments Q500), Fourier transform infrared spectroscopy (FTIR, PerkinElmer Frontier), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX, Philips XL30 FEG).

3. Results and discussion

A comparison is made between the extraction efficiency of acetic and succinic acid, using 0.5 M concentrations in each of two extraction steps. This concentration results in a 2:1 calcium-to-acid molar ratio at each extraction step, or 1:1 in total. The purpose of using this concentration is assessing how close to stoichiometric the extraction extent is. The results of aluminium, calcium, magnesium and silicon extraction from milled GBFS are presented in Fig. 1. The leaching of aluminium and silicon is better contained with acetic acid, though the leaching extent with succinic acid is also rather low (maximum 2.7% silicon extraction). Both Ca and Mg are extracted in equivalent amounts fraction-wise, so there is no selectivity between these two alkaline components, although substantially more calcium is extracted since BFS is richer in CaO than in MgO (41.0 wt.% versus 8.4 wt.%, respectively). Leaching of Ca and Mg is substantially greater in the first step than in the second step, but the difference is larger in the case of acetic acid ($\sim 3\times$) than for succinic acid ($\sim 1.8\times$). Also, the dicarboxylic succinic acid proves to be more effective in extracting the alkaline components, reaching 30–31% total extraction extent compared to 21% for the monocarboxylic acetic acid. The leaching extent of succinic acid surpasses that of acetic acid both in the first stage, by $\sim 5\%$, and in the second stage, also by $\sim 5\%$. These

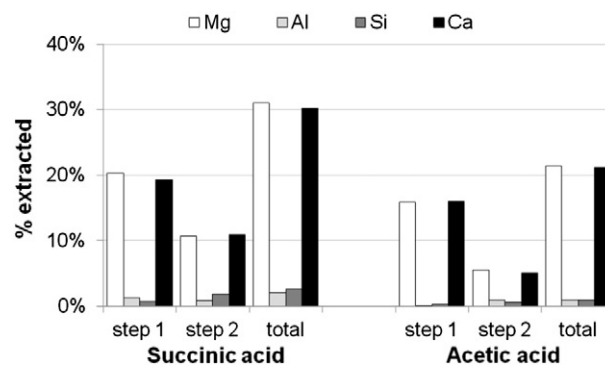


Fig. 1. Results of organic acid extraction (first and second steps, and total) of Mg, Al, Si and Ca from milled GBFS using 0.5 M succinic acid (left) or 0.5 M acetic acid (right) at 80 °C for 60 min.

results are in agreement with the findings of Baldyga et al. (2010, 2011) for the leaching of calcium from wollastonite.

The leachates from the extraction stage were subjected to carbonation treatment with the intent of producing precipitated calcium carbonate (PCC). In the tests performed, besides using leachates produced using the two different organic acids (succinic and acetic acids), three additional parameters were varied for investigation: temperature, CO_2 partial pressure and pH buffering additive.

The first test conducted used the same carbonation conditions that Baldyga et al. (2011) used to precipitate the most quantity of calcium from succinic acid leachate, namely: 80 °C, 50 bar CO_2 , 60 min, and no additive. These conditions, however, did not result in the precipitation of solids in the present study. The same observation is reported by Eloneva et al. (2008) for the precipitation of calcium from calcium acetate solution, wherein only upon addition of NaOH to regulate the pH closer to 12 (from an original value of 6.5) significant precipitation occurred. Spontaneous carbonate mineral formation does not occur due to the fact that the acid dissociation constants of acetic and succinic acids ($pK_a = 4.7$ and $pK_{a1} = 4.2$, respectively) do not fall in-between those of carbonic acid and silicic acids (6.3 and 9.8, respectively) (Domenico and Schwartz, 1998; Higson, 2004; Smith and Hong-Shum, 2003). This is contrary to the theory of Kakizawa et al. (2001), who reported a pK_a value of 3.6 for carbonic acid (which is the theoretical, but not the effective value in the presence of dissolved carbon dioxide) to inaccurately state that acetic acid fell in between the inorganic acids. Baldyga et al. (2011) may have obtained precipitation because the leaching of calcium from wollastonite was near completion in that study. In this case, since the acid was added in 1:1 acid to calcium molar ratio, it was largely consumed, and thus the pH of the leachate (not reported) was likely less acidic than in the present experiment ($\text{pH}_{1\text{st,extr}} = 4.4$, $\text{pH}_{2\text{nd,extr}} = 3.7$, $\text{pH}_{\text{combined}} = 4.0$).

To induce precipitation, all other experiments performed in the present study used NaOH or NaHCO_3 (which besides acting as a buffer, is also reported to increase the concentration of carbonic ions in solution (Chen et al., 2006)) as pH neutralizing additives. Results of magnesium, aluminium, silicon and calcium precipitation from the extraction leachates after carbonation are presented in Fig. 2. The temperatures (T) and CO_2 partial pressures (P_{CO_2}) were regulated to account for CO_2 solubility (i.e. low T with low P_{CO_2} , high T with high P_{CO_2}).

For succinic acid leachates, no precipitate was obtained at 60 °C and 2 bar, even with NaHCO_3 addition. At 90 °C and 6 bar, with both NaHCO_3 and NaOH additions, precipitates were formed, accounting for 45–54% of the calcium content of the succinic acid leachate. Magnesium did not appreciably precipitate under these conditions, but large fractions of aqueous Al and Si did precipitate. At 120 °C and 40 bar, with both pH buffers, further precipitation occurred, accounting for 69–74% of the calcium and 6% of the magnesium contents of the succinic acid leachate (this amount of Mg is equivalent to <2 wt.% of the amount of calcium precipitated).

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