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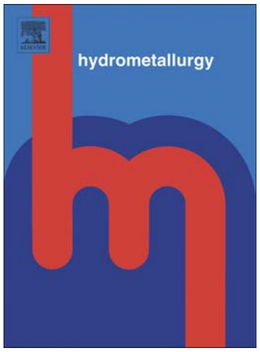

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Distinguishing between carbonate and non-carbonate precipitates from the carbonation of calcium-containing organic acid leachates

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Abstract

Two organic acids were trialled 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

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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 PCC's with small amounts of co-leached aluminium and silicon. Further work is warranted on the purification of this PCC synthesis route.

Keywords: mineral carbonation; precipitated calcium carbonate; acetic acid; succinic acid; blast furnace slag; calcium succinate.

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 colour 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 (Wypych, 2010; CCA Europe, 2012). 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, as 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 $CaCO_3$ occurs when the CO_2 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 for 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 ($CaSiO_3$). The use of succinic acid was recommended due to its greater extraction extent and favourable 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 steelworks was used as the starting material. Its chemical composition, determined by X-ray fluorescence (XRF, Panalytical PW2400), consisted mainly of CaO (41.0 wt%), SiO_2 (36.0 wt%), Al_2O_3 (11.0 wt%) and MgO (8.4 wt%). Its mineralogical composition, determined by X-ray diffraction (XRD, 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, MalvernMastersizer S), was 138.3 μm, and its geometrical specific surface area, determined by LD, was 0.47 m^2/g.

Analytical grade succinic acid ($HOOC\text{-}(CH_2)_2\text{-}COOH$) 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 minutes at 80 °C and 1000 rpm under air atmosphere in a Büchi Ecoclave reactor (1.1 liter 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 minutes, at temperatures between 60–120 °C, and applying CO_2 partial pressures between 2–50 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 hours.

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, Perkin Elmer 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 Figure 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 (~3x) than for succinic acid (~1.8x). 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 ~5 %, and in the second stage, also by ~5 %. These 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 minutes, 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; Smith and Hong-Shum, 2003; Higson, 2004).; This is contrary to the theory of Kakizawa et al. (2001), which erroneously reported a pK_a value of 3.6 for carbonic acid 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 ($pH_{1st,extr}$ = 4.4, $pH_{2nd,extr}$ = 3.7, $pH_{combined}$ = 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 Figure 2. The temperatures (T) and CO_2 partial pressures (P_{CO2}) were regulated to account for CO_2 solubility (i.e. low T with low P_{CO2}, high T with high P_{CO2}).

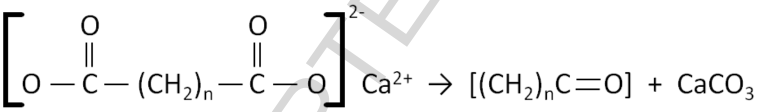
For succinic acid leachates, no precipitate was obtained at 60 °C and 2 bar, even with $NaHCO_3$ addition. At 90 °C and 6 bar, with both $NaHCO_3$ and NaOH additions, precipitates were formed, accounting for 45–54 % of the calcium content of the succinic acid leachate. Magnesium did not appreciably precipitate 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).

The precipitation extent was significantly better from acetic acid leachates (Figure 2), wherefrom 98–99 % of the calcium was precipitated. The amount of magnesium precipitation also increased substantially to 20–23 %. It is seen from Figure 2 that Al, Mg and Si precipitation is generally magnified when the higher combination of T and P was used. Given that Ca precipitation from acetic acid leachate was weakly affected by the carbonation conditions (T and P), it would thus be advisable to use the lower carbonation intensity to reduce energy demand of this processing stage and improve PCC chemical purity.

The precipitated solids were analyzed to characterize their mineralogical and morphological properties. It was discovered during the present study that the precipitates from the succinic acid leachates differed substantially from those produced from acetic acid leachates. The succinic acid leachate precipitates had a distinct XRD pattern (Figure 3a), which does not match that of any carbonate mineral phase. The acetic acid leachate precipitates have an XRD pattern that matched well with the calcite polymorph of calcium carbonate ($CaCO_3$), as shown in Figure 3b. Further analyses were performed to characterize the succinic acid leachate derived precipitates.

Figure 4a presents the TGA and DSC curves for the succinic acid leachate precipitate. It can be seen that the decomposition pattern does not match that of calcium carbonate, which decomposes with a single loss of mass between approximately 600–750 °C (Santos et al., 2013), consisting of the decarbonation step of calcium carbonates, as described in Eq. 1. Instead, two distinct decomposition regions are seen, the first starting at 450 °C and the second beyond 670 °C. This two-step decomposition is characteristic of the thermal decomposition of dicarboxylates, including calcium succinate ($Ca(C_4H_4O_4)$), according to Eq. 2 (Patil et al., 1968):

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$



$$\left[O - \overset{\overset{O}{\|}}{C} - (CH_2)_n - \overset{\overset{O}{\|}}{C} - O\right]^{2-} Ca^{2+} \rightarrow [(CH_2)_n C{=}O] + CaCO_3 \tag{2}$$

To confirm the evidence from the TGA results, the FTIR spectrum of the succinic acid leachate precipitate was obtained, and is shown in Figure 4b. The spectrum was compared to compounds on the Spectral Database for Organic Compounds from the National Institute of Advanced Industrial Science and Technology (SDBSWeb, 2013) and the closest match found was that of magnesium succinate N-hydrate ($Mg(C_4H_4O_4)\cdot nH_2O$) (a calcium variant is not available in the database), shown in the figure in-set, with the exception of the large peak near 3400 cm^{-1}, which represents the hydrate group (Patil et al., 1968). FTIR, however, does not distinguish the cation, and as EDX analysis of the precipitate confirmed it is composed primarily of calcium, carbon and oxygen (Figure 4c), it can be confirmed that the precipitate from the succinic acid leachate is in fact calcium succinate ($Ca(C_4H_4O_4)$). The small DSC peak near 140 °C (Figure 4a) and the small bump in the FTIR spectrum around 3400 cm^{-1} suggest that the compound is only partly hydrated, possibly mono (Mathew et al., 1994).

Figure 5 presents the morphology of the carbonation precipitates. Clearly, the morphology of the calcium succinate particles (Figures 5a and 5b) is very distinct from that of calcium carbonate particles (Figures 5c and 5d). These finding are in contrast with the reported results of Baldyga et al. (2011), who report to have precipitated calcium carbonate from succinic acid leachate. However, the reported morphology of those precipitates (shown in Figure 6 (Baldyga et al., 2011)) does not appear to represent calcium carbonate. Seeing that the authors characterized their products by EDX alone, which showed calcium, carbon and oxygen contents that also make up calcium succinate, their product might possibly have been a succinate. In their prior work, Baldyga et al. (2010) do not show any characterization of the reported precipitates.

This discrepancy may also explain why Baldyga et al. (2010, 2011) were able to precipitate calcium without the addition of pH buffers. If the succinate anion precipitates with calcium, the regeneration of the acid is avoided, thus not lowering the pH, which otherwise prevents carbonate deposition. Bonfils et al. (2012) report similar findings on the use of disodium oxalate ($Na_2(C_2O_4)$) for the extraction of magnesium from serpentine. They found that carbonation of the leachate resulted in the precipitation of magnesium oxalate dihydrate ($Mg(C_2O_4)\cdot 2H_2O$), another organic acid salt, instead of the desired carbonate. This correlates well with the particularly low pK_a of 1.27 of oxalic acid (Higson, 2004). The observations of Bonfils et al. (2012) and of the present study highlight the need for accurate characterization of carbonation products, as carbonates are not the only possible product. It is thus concluded that succinic acid is not a suitable calcium extractant for producing PCC, while acetic acid is.

4. Conclusions

The results of this study show that when researching new leaching agents with the intent of extracting calcium from alkaline materials for subsequent production of precipitated calcium carbonate, two things are essential. First, it should be experimented if the carbonation of the leachate results in the formation of precipitates, and if to achieve this pH buffers are required, which will have an effect on processing costs and complexity. In the present study, it was found that precipitates did form when using both succinic and acetic acid leachates, but in both cases a buffering agent was required. Sodium hydroxide and sodium bicarbonate were tested, both induced the precipitation of calcium from the carbonated solution, and they were found to perform similarly, with NaOH being marginally more effective. Second, the precipitates formed must be characterized by one or more appropriate analytical technique, with XRD, TGA and/or FTIR being essential. Several works in existing literature omit extensive characterization of carbonation precipitates, under the assumption that precipitates are invariably carbonate minerals. In the present study, XRD provided the first evidence that the succinic acid leachate precipitates were not carbonates. Due to the lack of a matching compound in the available databases, further characterization by FTIR and TGA-DSC was required to identify the compound as being calcium succinate (likely mono-hydrate). SEM-EDX also pointed to discrepancies between the precipitates, but this analysis was not sufficient since chemical composition is not a unique identifier. Hence, even though the leaching performance of succinic acid was found to be superior to that of acetic acid, of the two leaching agents, only acetic acid is suitable for the production of PCC.

With acetic acid, further research and development are required for the production of marketable PCC. The results presented herein were not optimized, and greater calcium leaching extents are reportedly achieved using higher acid concentrations and lower temperatures (Teir et al., 2007). Furthermore, partial magnesium precipitation and extensive aluminium and silicon precipitation occurred during carbonation, thus contaminating the formed product. Selective precipitation by means of tuned carbonation conditions, or purification of the leachate prior to carbonation, via physical separation, selective precipitation, or with the use of sorptive materials, is necessary to improve product qualities.

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List of Figures:

Figure 1. Results of organic acid extraction (first and second step, 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 minutes.

Figure 2. Extent of Mg, Al, Si and Ca precipitation from 0.5 M succinic and acetic acid extraction leachates (expressed as percent fraction of leachates content that precipitated) after carbonation experiments at varying temperatures (60–120 °C), CO_2 partial pressures (2–40 bar) and with different additives (0.5 M $NaHCO_3$ or NaOH).

Figure 3. X-ray diffractograms of post-carbonation precipitates from succinic (a) and acetic (b) acid leachates.

Figure 4. Thermal gravimetric and differential scanning calorimetry curves of post-carbonation precipitate from succinic leachate (a); FTIR spectrum of post-carbonation precipitate from succinic leachate (inset of magnesium succinate N-hydrate obtained from SDBSWeb (2014)) (b); EDX spectrum of gold-coated post-carbonation precipitate from succinic leachate (c).

Figure 5. Morphology of post-carbonation precipitates from succinic (a, b) and acetic (c, d) acid leachates, visualized by SEM.

Figure 6. Morphology of post-carbonation precipitates from succinic acid leachate visualized by SEM by Baldyga et al. (2011). Reprinted from Chemical Engineering Research and Design, Vol. 89, No. 9, Baldyga et al., 1841–1854, Copyright 2011, with permission from Elsevier (license number 3322710276944).

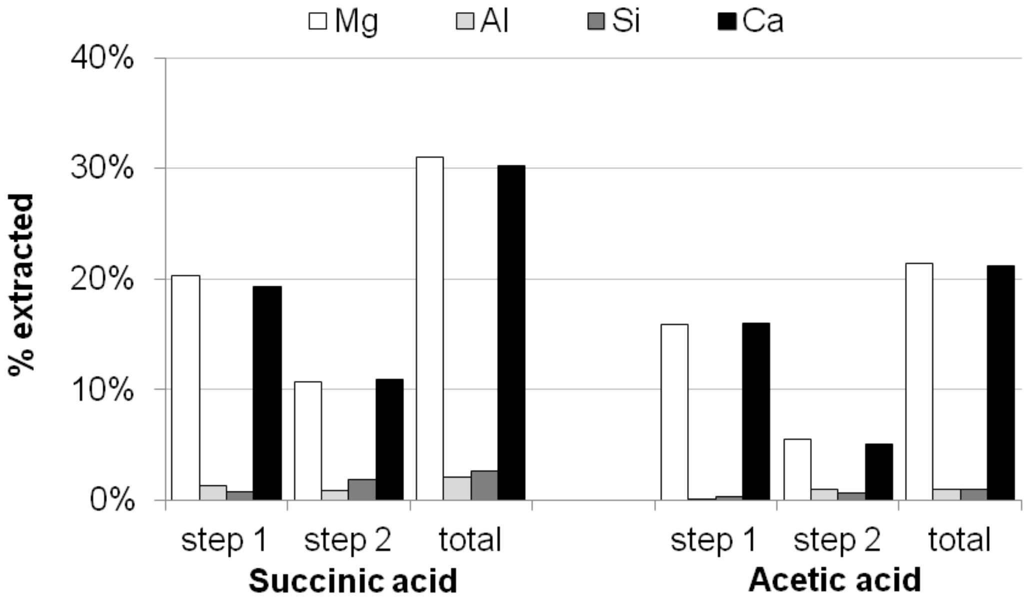
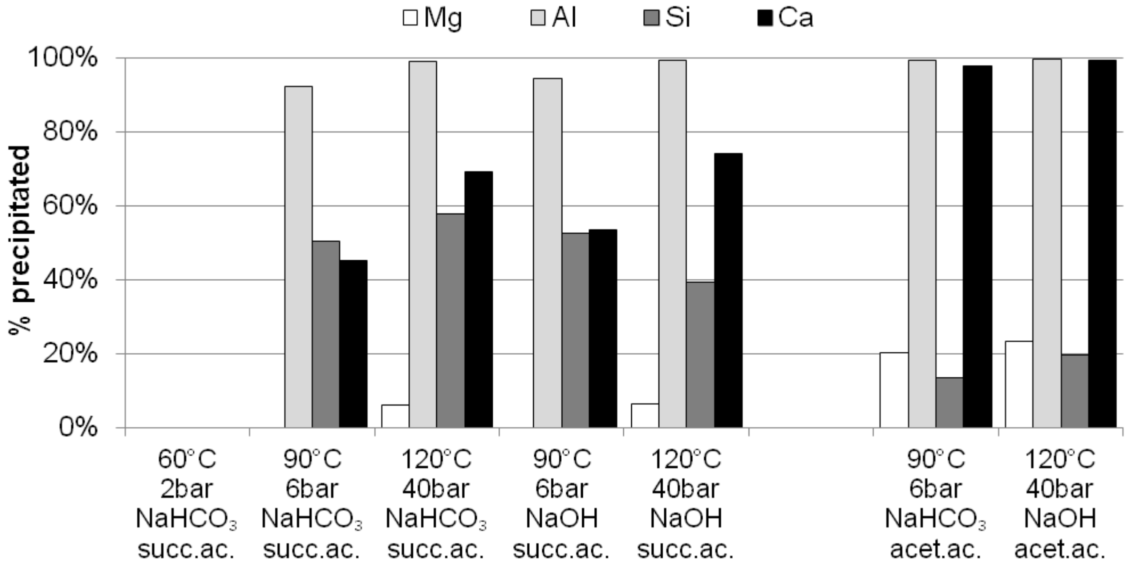

□ Mg
□ Al
■ Si
■ Ca
40%
30%
20%
10%
0%
% extracted
step 1
step 2
total
Succinic acid
step 1
step 2
total
Acetic acid

Figure 1



Mg
Al
Si
Ca
100%
80%
60%
40%
20%
0%
% precipitated
60°C 2bar NaHCO3 succ.ac.
90°C 6bar NaHCO3 succ.ac.
120°C 40bar NaHCO3 succ.ac.
90°C 6bar NaOH succ.ac.
120°C 40bar NaOH succ.ac.
90°C 6bar NaHCO3 acet.ac.
120°C 40bar NaOH acet.ac.

Figure 2

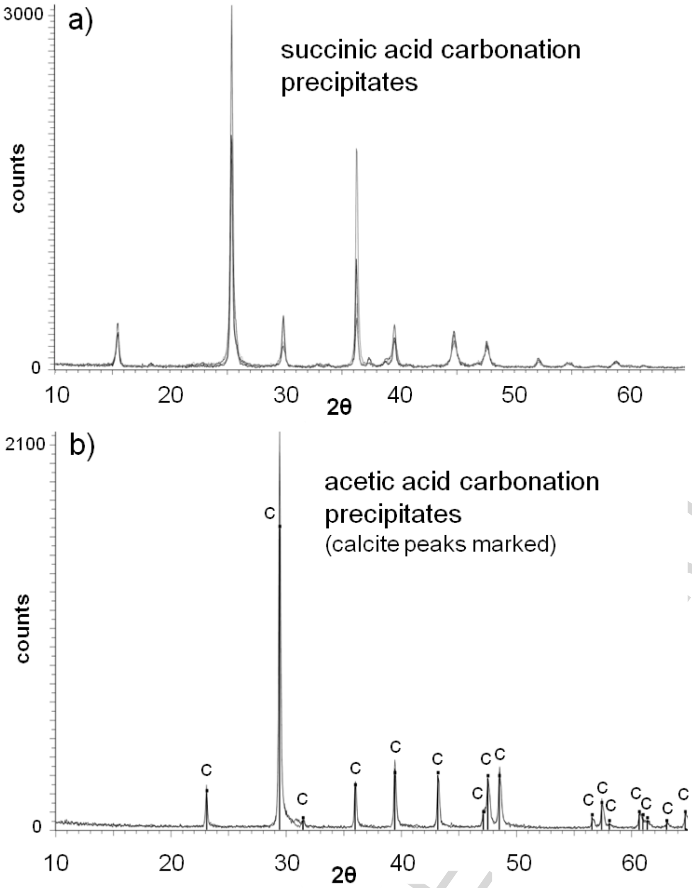

a)
succinic acid carbonation precipitates
3000
0
counts
10
20
30
40
50
60
2θ
b)
acetic acid carbonation precipitates
(calcite peaks marked)
2100
0
counts
c
10
20
30
40
50
60
2θ

Figure 3

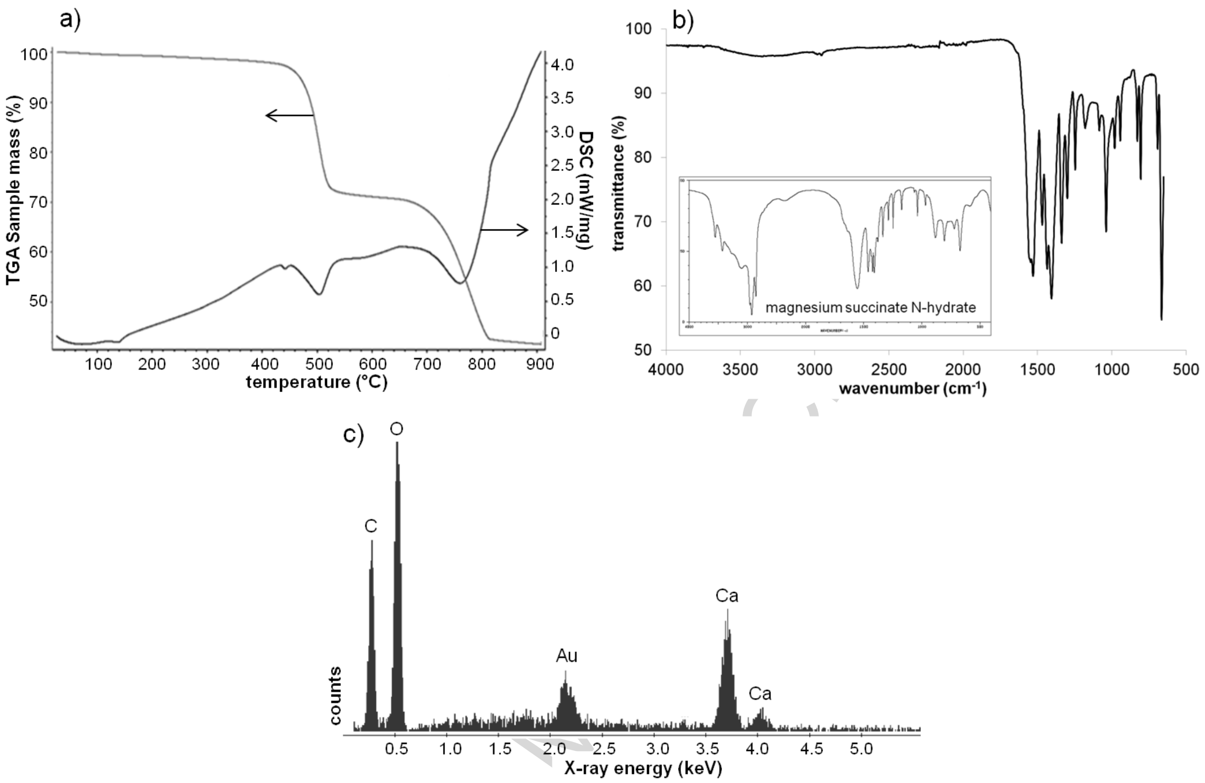
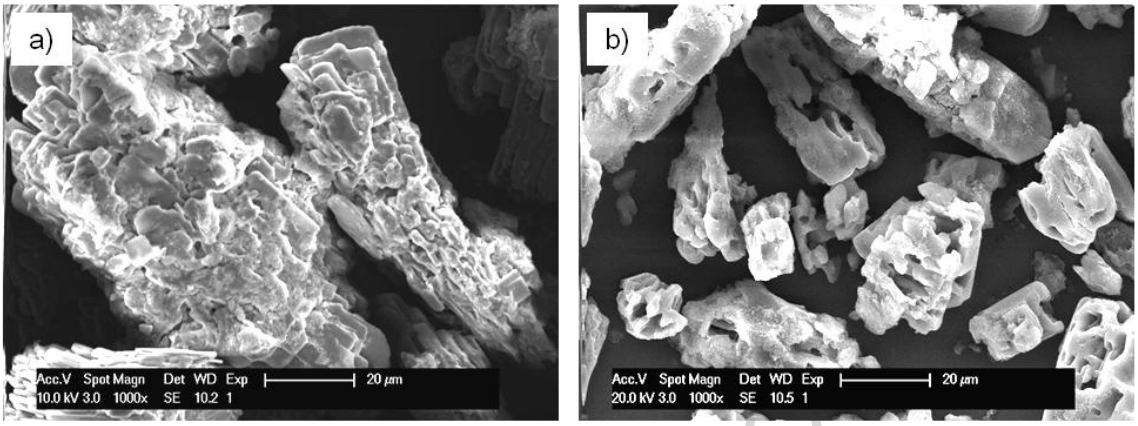
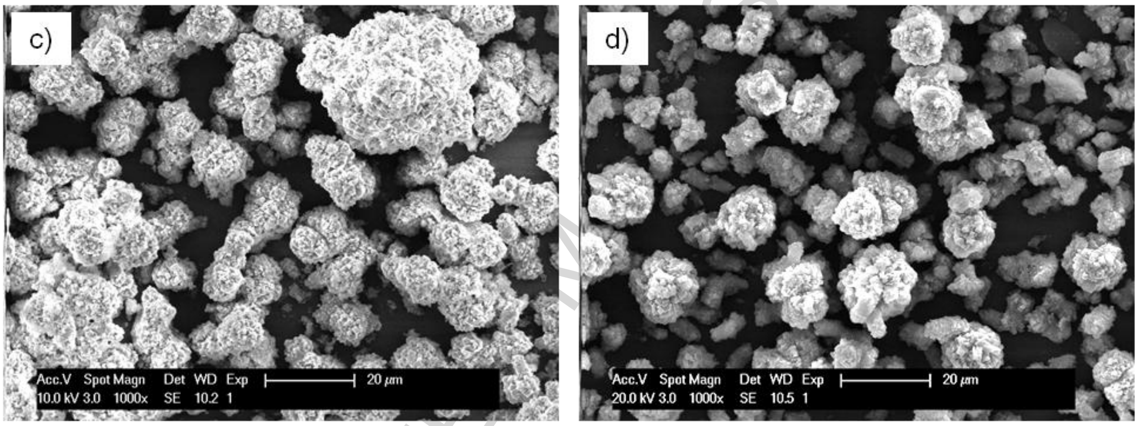

a)
TGA Sample mass (%)
100
90
80
70
60
50
DSC (mW/mg)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
100
200
300
400
500
600
700
800
900
temperature (°C)
b)
transmittance (%)
100
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
500
wavenumber (cm-1)
magnesium succinate N-hydrate
c)
C
O
Au
Ca
Ca
counts
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
X-ray energy (keV)

Figure 4



90 °C, 6 bar, CO_2, $NaHCO_3$, succinic acid

120 °C, 40 bar, CO_2, $NaHCO_3$, succinic acid



90 °C, 6 bar, CO_2, NaOH, acetic acid

120 °C, 40 bar, CO_2, $NaHCO_3$, acetic acid

Figure 5

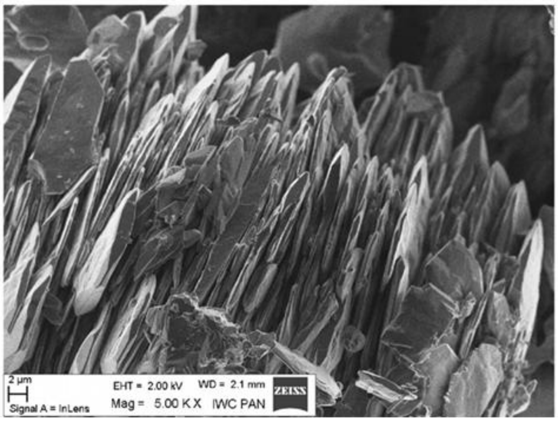
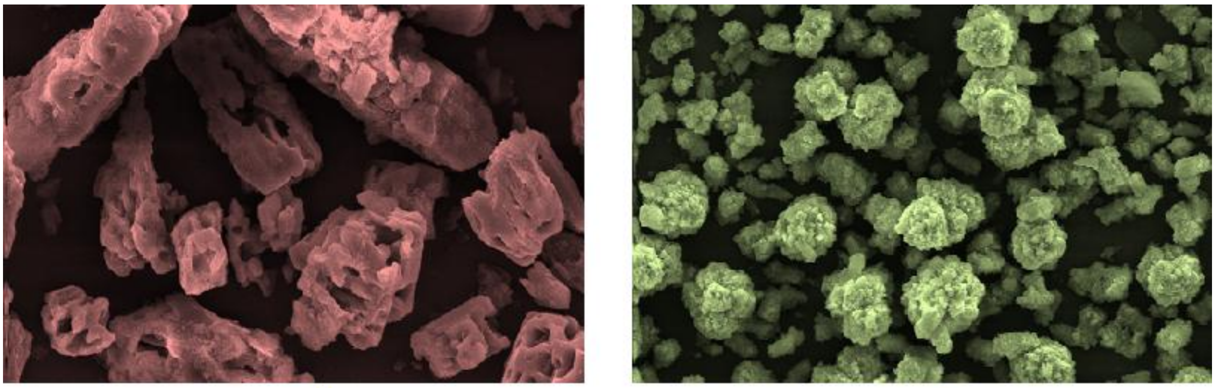


Figure 6



succinic acid leachate $\xrightarrow{CO_2}$ calcium succinate

acetic acid leachate $\xrightarrow{CO_2}$ calcium carbonate

Graphical abstract

Highlights

- Blast furnace slag was leached with succinic and acetic acids to extract calcium.
- The addition of pH buffers was required to induce precipitation upon carbonation.
- Carbonation of succinic acid leachate resulted in undesirable calcium succinate.
- Carbonation of acetic acid leachate resulted in desirable calcium carbonate.
- Determination of precipitate properties requires accurate characterization.