

## Publication II

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## Fixation of CO<sub>2</sub> by carbonating calcium derived from blast furnace slag

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### ABSTRACT

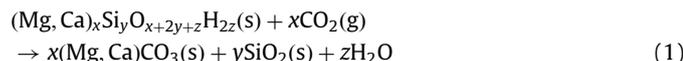
Industrial waste materials, such as steelmaking slags, appear to be potential raw materials for reducing CO<sub>2</sub> emissions by carbonation. The suitability of applying a carbonation route based on acetic acid leaching to produce carbonates from blast furnace slag is presented in this study. The effect of solution pH, temperature, and CO<sub>2</sub> pressure on the precipitation of carbonates was experimentally studied. A simple thermodynamic model was used to verify our results. The feasibility of the process was also discussed, addressing energy input requirements and the consumption of chemicals.

According to our experiments, the addition of NaOH, i.e. an increase in solution pH, is required for the adequate precipitation of calcium carbonate at temperatures of 30–70 °C and pressures of 1 or 30 bar. Preliminary process calculations showed that approximately 4.4 kg of blast furnace slag, 3.6 l of acetic acid, and 3.5 kg of NaOH would be required to bind 1 kg of CO<sub>2</sub>, resulting in 2.5 kg of 90% calcium carbonate. While the heat needed for the evaporation of the acetic acid could probably be acquired as waste heat by process integration with other processes, the electricity required for NaOH regeneration would make the process unsuitable for CO<sub>2</sub> sequestration.

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### 1. Introduction

The reduction of carbon dioxide emissions in process industries is challenging. The capture and long-term storage of carbon dioxide (CO<sub>2</sub>), also called carbon dioxide sequestration, would permit the continued use of fossil fuel combustion with reduced carbon dioxide emissions. In regions like Finland, where the geological storage of carbon dioxide is not an option because of a lack of suitable locations, mineral carbonation is a potential carbon dioxide sequestration method. In mineral carbonation CO<sub>2</sub> gas is stored by promoting magnesium or calcium oxides in silicate minerals to react with carbon dioxide and form carbonates:



Suitable silicate rocks, containing magnesium or calcium oxides, are abundant to the extent that in theory the potential for carbon dioxide storage by mineral carbonation is larger than that of other carbon dioxide storage methods. The product of mineral carbonation,

magnesium or calcium carbonate, is also thermodynamically stable under ambient conditions [1], that is, in the absence of acidification. Thus, mineral carbonation would store carbon dioxide for a very long time [2] and the post-storage monitoring of carbon dioxide stored as carbonates would not be necessary. The main problem with mineral carbonation is that in practice it requires large amounts of energy or additives to facilitate the carbonation reaction (Eq. (1)). Otherwise, the carbonation reaction would be too slow. According to a recent IPCC special report on carbon dioxide capture and storage [3], the best case studied so far is the wet carbonation process, which uses olivine as a feedstock. It is, however, quite expensive (US\$50–100/t-CO<sub>2</sub>) and carries a high energy penalty (30–50%) for the power plant where the carbon dioxide is captured.

Interest in using industrial residue materials and by-products as sources of calcium for mineral carbonation has arisen because they are readily available, cheap, and most often produced near large carbon dioxide sources. Besides that, the carbonation of these waste materials could reduce the amount of harmful substances, such as trace elements, released to the environment, as they would be trapped in inert carbonates [4]. Estimations of the annual amount of steelmaking slag produced globally range from 220 up to 420 Mt [5]. With the calcium oxide content ranging from 34% to 52% [6], this amount could potentially store about 59–171 Mt of carbon dioxide per year. Although these amounts are quite small in comparison to natural mineral

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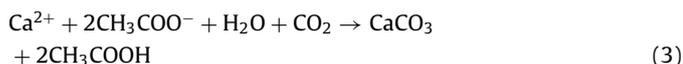
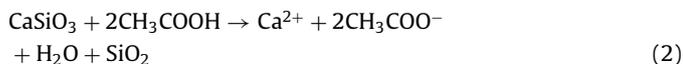
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resources, residues could provide an inexpensive means for certain emission sites to capture and store meaningful amounts of carbon dioxide. For instance, by carbonating steelmaking slag produced locally at the steel mills in Finland, the carbon dioxide emissions of an individual steel mill could in theory be reduced by 8–21% [7].

Most of the studies related to the carbonation of industrial residues concern water-based carbonation routes [8–11]. Huijgen et al. [8] reached 74% calcium conversion in 30 min by carbonating ground steel slag at 100 °C and a carbon dioxide pressure of 19 bar. Iizuka et al. [9] evaluated that the sequestration costs for a 100-MW thermal power plant would be about \$23/t-CO<sub>2</sub> for a sequestration process based on pressure change. Stolaroff et al. [10] estimated the operating costs for a simple scheme capturing carbon dioxide from ambient air to be US\$8/t-CO<sub>2</sub> sequestered. Johnson [11] found that among various waste materials, slag from stainless steel production was most effectively carbonated (at a CO<sub>2</sub> pressure of 3 bar, in 24 h). A means for carbonating waste materials by using a solution of a weak base–strong acid salt has been proposed by Yogo et al. [12]. However, the risk of leakage of ammonia from the process was found to be significant, and it was estimated that the make-up costs for leaked ammonia would be expensive [13].

We have previously investigated the possibility of using acetic acid as a calcium-dissolving agent in the carbonation of steelmaking slags [14]. This process is similar to the process proposed by Kakizawa et al. [15], in which calcium is extracted from a calcium silicate, such as wollastonite, by using an aqueous solution of acetic acid (Eq. (2)). After the extraction the residue is removed and carbon dioxide is introduced into the calcium acetate-containing solution and calcium carbonate precipitates (Eq. (3)):



The main advantage of these kinds of indirect, multi-step processes, compared to direct, one-step carbonation processes, is that they allow pure calcium carbonate to be produced, because silica and other impurities can be removed before the calcium carbonate is precipitated. Pure calcium carbonate could probably be marketed at a high price, for example precipitated calcium carbonate (PCC) (>100€/t [16]), which is a filler and coating material (used in e.g. office paper [17]). This would allow a more expensive carbonation process to be used.

We found that calcium was more rapidly and efficiently extracted from the steelmaking slags tested than from wollastonite in aqueous solutions of acetic acid [14]. However, other elements (such as magnesium, aluminium, silica, and iron) from steelmaking slags dissolve as well. Removing these species requires more separation steps. The dissolved silicon was found to be easy to separate by filtration if the dissolution was carried out at 70–80 °C.

In this paper the possibility of precipitating calcium carbonate from aqueous solutions of calcium acetate derived from blast furnace slag is investigated. The dependency of solution pH on precipitation by adding sodium hydroxide is experimentally studied, as are raising temperature and CO<sub>2</sub> pressure. A simple thermodynamic model was used to verify the results. Finally, the feasibility of the process is discussed, addressing energy input requirements and the consumption of chemicals.

## 2. Methodology

### 2.1. Test facilities and materials

All the precipitation experiments performed under atmospheric pressure conditions, as well as all solution preparations, were carried out using the same experimental set-up (see Fig. 1). This test rig contained a glass reactor in which solutions were stirred by a magnetic stirrer. The glass reactor was surrounded by an open water bath, which was heated using a separate, temperature-controlled water bath connected to the open water bath. To avoid evaporation losses, the reactor was equipped with a condenser cooled with tap water. The pH and temperature of the solution were measured using electrodes ( $\pm 0.1$  °C,  $\pm 0.1$  pH), allowing data to be monitored and logged in real time. The pH electrode was calibrated before each test series. Nitrogen and carbon dioxide gas bottles were connected through a flow rate controller, allowing carbon dioxide or nitrogen to be bubbled through the solutions.

Two experiments were also performed at elevated pressures using a batch reactor with a volume of 250 ml and a maximum allowed total pressure of 40 bar. The reactor was heated using a temperature-controlled, closed water bath connected to the copper coil surrounding the reactor (Fig. 2). The reactor temperature was measured with a PT100-type electrode, while the total pressure of the reactor was monitored with a mechanical pressure meter. The reactor was connected to a nitrogen bottle and a carbon dioxide bottle supplying pressurised gas. The reactor was also equipped with a safety valve and a ventilation valve (for gas purge). The pressure in the reactor was kept constant by keeping the gas inlet valves open (other valves closed) at the set-point pressure.

The granulated blast furnace slag used in the experiments was provided by the Ruukki steel plant in Raahe. The structure of the slag was analysed by X-ray diffraction (XRD) using a Philips X'Pert PW3040 and the composition of the slag was analysed by X-ray fluorescence spectroscopy (XRF) using a Philips PW2404 at an external laboratory. Before being analysed by XRF, the samples were ground to a particle size <10 μm and pressed into a briquette. The XRF data were analysed by the service provider

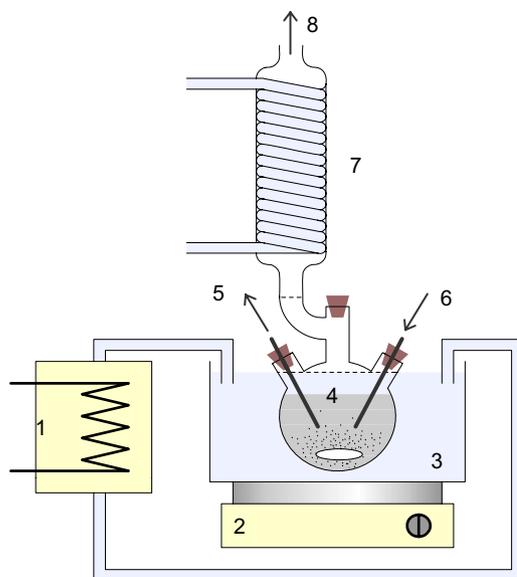
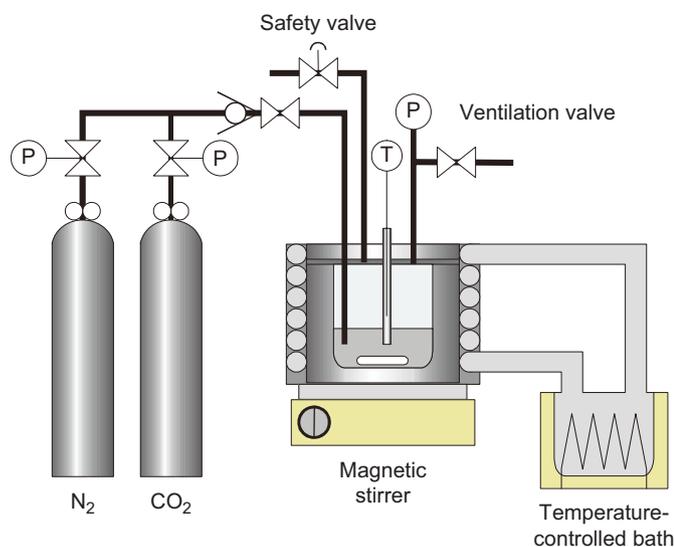


Fig. 1. Experimental set-up used for experiments performed at atmospheric gas pressures: (1) Temperature-controlled bath; (2) magnetic stirrer; (3) external bath; (4) glass reactor; (5) sample extraction, pH, and temperature electrodes; (6) gas flow in; (7) tap water-cooled condenser; (8) gas out.



**Fig. 2.** Experimental set-up used for experiments performed at a total gas pressure of 30 bar.

using an internal fundamental parameter-based quantification method. The error analysis of the XRF method was reported by the service provider. Acetic acid (99.8 wt%) and an aqueous solution of sodium hydroxide (49.0–51.0 wt%) were obtained from Merck. The carbon content was determined by total carbon (TC) analysis using a Leybold–Heraeus CSA2003.

## 2.2. Experimental methods

Prior to the precipitation experiments, 50 g of blast furnace slag was dissolved in 1 l of aqueous solution of acetic acid (20 vol%) at 70 °C, with 1 l N<sub>2</sub>/min ( $\pm 0.2$  l/min) bubbling through the solution. After 2 h, the solution was filtered to remove slag residue and precipitated silica gel. This was done four times in order to produce enough solution for the precipitation experiments. Dissolution conditions were chosen on the basis of our previous work [14] to yield a solution containing a high concentration of calcium and low concentrations of other elements. Since a surplus of acetic acid was used (10 mol of acetic acid/mol of calcium in the slag), the formed solution was acidic (pH ~4). In a process route proposed by Kakizawa et al. [15], calcium carbonate is precipitated from a solution of calcium acetate (Eq. (3)). Calcium acetate is a weakly basic salt. Therefore, the excess acid was evaporated from the solutions at 150–160 °C overnight. The resulting solid acetate salt precipitates were weighed and analysed by XRD, XRF, and TC.

In the first precipitation experiment series, the effect of solution pH on the precipitation of calcium carbonate was tested. First, 10 g of the solid acetate salt that had been produced was dissolved in 200 ml of distilled water. Nitrogen (1 l/min) was bubbled through the solution until the solution temperature stabilised at 30 °C. The solution was stirred at 600–700 rpm. When the nitrogen flow was switched off, a carbon dioxide gas flow (1 l/min) was switched on. After 20 min, when the pH and temperature of the solution had stabilised, a specific amount (0, 2, 5, or 20 ml) of a sodium hydroxide solution (50 wt%) was introduced into the solution. The pH of the solution was allowed to stabilise for 2 h and 15 min, after which the carbon dioxide flow was switched off and the solution was filtered using a Whatman 50 filter paper (3- $\mu$ m pore size). The filtered precipitate was washed using distilled water to remove any water-soluble compounds (e.g. sodium hydroxide, sodium carbonate, calcium acetate). The

precipitate was then dried at ~120 °C overnight, after which it was analysed using XRD, TC, and XRF.

The effect of an elevated solution temperature (50 or 70 °C) on calcium carbonate precipitation was tested in the second precipitation experiment series both with and without the addition of sodium hydroxide.

Kakizawa et al. [15] achieved the best precipitation efficiency at a carbon dioxide pressure of 30 bar. Therefore, we performed two additional precipitation experiments at 30 bar ( $\pm 1$  bar). Because of equipment restrictions, 10 g of solid acetate salt was dissolved in only 100 ml of distilled water. Sodium hydroxide (5 ml, 50 wt%) was added to the first pressurised experiment, while the second was performed without. The solution was stirred with a magnetic stirrer at 1000 rpm. When the temperature of the solution had stabilised at 50 °C, the reactor was pressurised to 30 bar using pure carbon dioxide. After 2 h, the pressure was lowered to 1 bar and the solution was filtered using a Supor 0.45- $\mu$ m membrane.

## 3. Results

### 3.1. Carbonation experiments

XRD and XRF analyses of the blast furnace slag showed that it consisted mostly of calcium oxide, silicon dioxide, magnesium oxide, and aluminium oxide in amorphous phases (Table 1). Solid acetate salts produced from the slag contained calcium acetate hydrates but also magnesium acetate, according to the XRD analyses. The XRF analyses confirmed that the calcium contents were quite high (27–28% CaO), although the magnesium content was also significant (7% MgO) (Table 2). These solids are henceforth referred to as “calcium acetates” and solutions prepared from them as “solutions of calcium acetate”.

The precipitation of calcium carbonate from a solution of calcium acetate, as well as enhancement of the precipitation by increasing the pH with the addition of NaOH, was first tested at atmospheric pressure and 30 °C. The pH of the solutions increased immediately by 2–7 pH units (from a solution pH of ~5.9) after the addition of 8–76 g of NaOH/l, after which the pH started to decrease, indicating that a reaction was occurring (Fig. 3). A small decrease in pH (~0.5 pH units) also occurred for the solution to which no sodium hydroxide was added directly after the carbon dioxide flow was switched on (from an original solution pH of ~6.5).

During the experiments performed at 30 °C, 1–21 g of precipitate was formed per litre of calcium acetate solution (10 g Ca/l) using 0–76 g of NaOH/l (Fig. 4). The solution pH had a clear effect on the precipitation: the yield increased as the amount of NaOH (and thus the solution pH) was increased up to about

**Table 1**  
Composition of blast furnace slag as determined by XRF analysis

| Element                        | Composition (wt%) <sup>a</sup> |
|--------------------------------|--------------------------------|
| CaO                            | 40.6 ( $\pm 0.1$ )             |
| SiO <sub>2</sub>               | 34.1 ( $\pm 0.8$ )             |
| MgO                            | 10.7 ( $\pm 0.4$ )             |
| Al <sub>2</sub> O <sub>3</sub> | 9.4 ( $\pm 0.3$ )              |
| S                              | 1.7 ( $\pm 0.1$ )              |
| TiO <sub>2</sub>               | 1.7 ( $\pm 0.1$ )              |
| Fe <sub>2</sub> O <sub>3</sub> | 0.90 ( $\pm 0.03$ )            |
| K <sub>2</sub> O               | 0.6 ( $\pm 0.1$ )              |
| MnO                            | 0.5 ( $\pm 0.05$ )             |

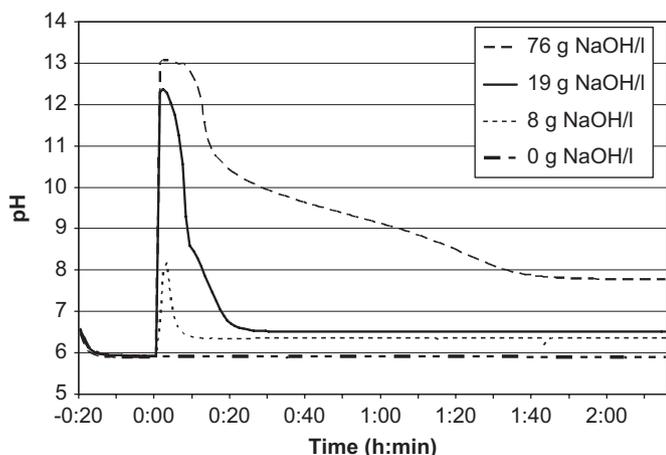
<sup>a</sup> Only elements present at >0.1 wt% are shown.

**Table 2**  
Details of preparations and compositions<sup>a</sup> (according to XRF and TC analyses) of acetates derived from blast furnace slag

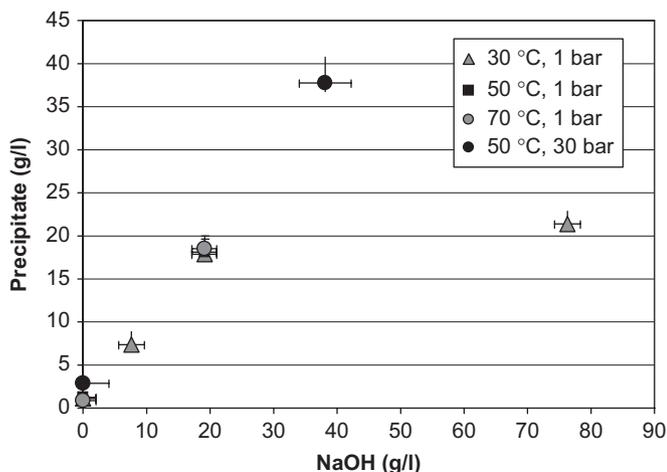
| Prepared acetate batch <sup>b</sup> | Blast furnace slag (g) | Acetic acid (l, 20 vol%) | Acetate formed (g/l) ( $\pm 0.1$ ) | CaO (%) ( $\pm 0.1$ ) | C (%) ( $\pm 0.3$ ) | MgO (%) ( $\pm 0.4$ ) | Al <sub>2</sub> O <sub>3</sub> (%) ( $\pm 0.1$ ) | Na <sub>2</sub> O (%) ( $\pm 0.05$ ) | SiO <sub>2</sub> (%) ( $\pm 0.1$ ) | Mn (%) ( $\pm 0.05$ ) | Fe (%) ( $\pm 0.01$ ) | K <sub>2</sub> O (%) (0.02) |
|-------------------------------------|------------------------|--------------------------|------------------------------------|-----------------------|---------------------|-----------------------|--|--------------------------------------|------------------------------------|-----------------------|-----------------------|-----------------------------|
| A                                   | 2*50                   | 2*1                      | 42.9                               | 27.3                  | 27.4                | 7.0                   | 2.0  | 0.24                                 | 0.8                                | 0.27                  | 0.19                  | 0.26                        |
| B                                   | 2*50                   | 2*1                      | 38.4                               | 27.8                  | 25.4                | 7.1                   | 2.0  | 0.25                                 | 0.7                                | 0.26                  | 0.18                  | 0.26                        |

<sup>a</sup> Only components available in at least another one of the acetates in concentrations of  $> 0.19\%$  are listed.

<sup>b</sup> Batch A was used for precipitation experiments at atmospheric pressure and batch B for pressurised experiments.



**Fig. 3.** Inline pH recordings of the precipitation experiments at 30 °C and atmospheric pressure (CO<sub>2</sub> flow switched on at -0:20 and NaOH added at 0:00).



**Fig. 4.** Amount of precipitate formed in relation to amount of NaOH used. (Calcium concentration 10 g/l in solutions of calcium acetate used in experiments performed at 1 bar and 20 g/l at 30 bar.)

19 g of NaOH/l (pH ~12), after which the increase in yield was insignificant. At higher solution temperatures (50 and 70 °C), the precipitated amounts were similar to those at a solution temperature of 30 °C (Fig. 4), indicating that the solution temperature does not have any effect on the yield. The precipitated amounts were greater at a higher pressure (30 bar, 50 °C), but the initial calcium concentration of the calcium acetate solution (20 g Ca/l) was also higher than that for the solution used in the atmospheric experiments (10 g Ca/l). If the initial calcium concentration of the solution used at 30 bar had been 10 g/l, the yield from the experiments at 30 bar would only have been half of the reported values (Fig. 4) and would have fitted the trend of the yield from the atmospheric experiments.

**Table 3**

Phases in the precipitates formed without any NaOH addition identified by XRD

| Temperature (°C) | Pressure (bar) | Phases identified (in descending apparent order of magnitude)   |
|------------------|----------------|---|
| 30               | 1              | Amorphous crystal structure, traces of quartz (SiO <sub>2</sub> ) and bohmite (Al <sub>2</sub> O <sub>3</sub> · H <sub>2</sub> O) |
| 50               | 1              | Amorphous crystal structure, traces of quartz (SiO <sub>2</sub> ) and aluminium oxide hydroxide (AlO(OH))                         |
| 70               | 1              | Amorphous crystal structure, traces of quartz (SiO <sub>2</sub> ) and calcite (CaCO <sub>3</sub> )                                |
| 50               | 30             | Amorphous crystal structure   |

According to the XRD analyses (Table 3), the precipitates formed without the addition of any sodium hydroxide were mainly amorphous, containing traces of quartz, as well as aluminium oxide hydroxide, bohmite, or calcite. Even if the precipitates had been pure calcium carbonate, calcium conversion from the calcium acetate solution could have been 6% at maximum. While the calcium conversion at a pressure of 30 bar would agree with the results of Kakizawa et al. [15], it is quite unlikely that the precipitate was pure calcium carbonate, because of its amorphous structure. Evidently, the precipitation of calcium carbonate is inadequate at these conditions without the addition of sodium hydroxide, i.e. raising the pH of the solution.

All the precipitates formed by adding sodium hydroxide contained calcium carbonates (Table 4). Carbon dioxide was bound as calcite and aragonite, but also as calcite magnesium, which contains a small fraction of magnesium. Silicon oxide was also found in the precipitate formed with 8 g (NaOH)/l (calcium acetate solution). The XRF analyses revealed that the precipitates also contained small amounts of other elements, such as silicon, sodium, aluminium, iron, and manganese (Table 4). By assuming that all calcium oxide was bound as calcium carbonate, the calcium carbonate content of the precipitates was calculated to be ~63–89 wt% ( $\pm 1\%$  unit). The purity of commercially available PCC is typically about 99% [18], indicating that calcium carbonate produced by this method without additional purification is not suitable for use as PCC.

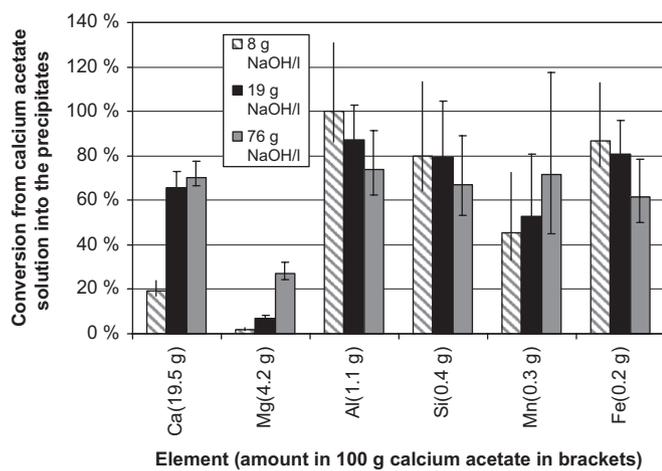
The percentages of the elements transferred from the solution of calcium acetate into the formed precipitates were calculated by using the results from the XRF analyses (Fig. 5). Calcium conversion was calculated to be 19–74% with 8–76 g of NaOH/l. A clear increase in conversion occurred when the amount of sodium hydroxide was increased from 8 to 19 g/l of calcium acetate solution.

A substantial amount of other major ( $> 0.1$  wt%) elements (Mg, Si, Al, and Fe) in the calcium acetate ended up in the precipitates as well (Fig. 5). The conversion of manganese, like the conversion of magnesium, increased when the amount of added sodium hydroxide was increased. While the conversion of aluminium, iron, and silicon decreased somewhat as the amount of added sodium hydroxide was increased, the conversion was still high ( $> 60\%$ ) even when using 76 g of NaOH/l. The conversion of magnesium was the poorest (2–27%), but depended strongly on

**Table 4**

Phases and compositions of the precipitates formed with NaOH addition as identified by XRD, XRF, and TC

| NaOH (g/l) | Temperature and pressure (°C, bar) | Phases identified (in descending apparent order of magnitude)                                      | CaO (%) ( $\pm 0.7$ ) | C (%) ( $\pm 0.3$ ) | MgO (%) ( $\pm 0.1$ ) | Al <sub>2</sub> O <sub>3</sub> (%) ( $\pm 0.3$ ) | Na <sub>2</sub> O (%) ( $\pm 0.2$ ) | SiO <sub>2</sub> (%) ( $\pm 0.1$ ) | Mn (%) ( $\pm 0.1$ ) | Fe (%) ( $\pm 0.3$ ) |
|------------|------------------------------------|--|-----------------------|---------------------|-----------------------|--|-------------------------------------|------------------------------------|----------------------|----------------------|
| 8          | 30, 1                              | Calcium carbonate (CaCO <sub>3</sub> ), silicon oxide (SiO <sub>2</sub> )                          | 35.2                  | 10                  | 0.9                   | 13.8   | 0.33                                | 4.4                                | 0.8                  | 1.05                 |
| 19         | 30, 1                              | Calcite (CaCO <sub>3</sub> )   | 50.1                  | 11.1                | 1.3                   | 5.0  | 0.49                                | 1.81                               | 0.39                 | 0.40                 |
| 19         | 50, 1                              | Calcium carbonate (CaCO <sub>3</sub> ), calcite magnesium ((0.129 Mg, 0.871 Ca)(CO <sub>3</sub> )) | 47.3                  | 10.2                | 2.6                   | 5.4  | 0.26                                | 1.99                               | 0.44                 | 0.50                 |
| 19         | 70, 1                              | Calcite (CaCO <sub>3</sub> ), aragonite (CaCO <sub>3</sub> )                                       | 49.5                  | 10.2                | 1.5                   | 5.3  | 0.19                                | 1.93                               | 0.43                 | 0.48                 |
| 76         | 30, 1                              | Calcite (CaCO <sub>3</sub> ), calcite magnesium ((0.06 Mg, 0.94 Ca)(CO <sub>3</sub> ))             | 45.0                  | 10.5                | 4.5                   | 3.5  | 2.8                                 | 1.28                               | 0.44                 | 0.26                 |
| 19         | 50, 30                             | Calcite magnesium ((0.06 Mg, 0.94 Ca)(CO <sub>3</sub> )), calcium carbonate (CaCO <sub>3</sub> )   | 45.4                  | 11.4                | 3.0                   | 4.4  | 2.4                                 | 1.51                               | 0.46                 | 0.39                 |

**Fig. 5.** Elements transferred from the calcium acetate solution to the precipitate at 30 °C and atmospheric pressure.

the amount of sodium hydroxide added. Evidently, in order to produce pure calcium carbonate from blast furnace slag, the calcium acetate solution produced should be virtually free of other elements, although small concentrations of magnesium can be allowed.

Assuming that all the carbon in these precipitates was bound as carbonates (as indicated by XRD, Table 4), the calcium acetate solution would have consumed 3–8 g of CO<sub>2</sub>/l. This is 25–77% ( $\pm 5\%$  units) of the maximum carbon dioxide binding ability of the calcium acetate solution according to its calcium concentration. Similarly, at a pressure of 30 bar, 72% of the maximum CO<sub>2</sub> binding ability of the calcium acetate solution was used.

### 3.2. Thermodynamic calculations

Thermodynamic equilibrium calculations were carried out to investigate the precipitation of calcium carbonate from the calcium acetate solution. The solution equilibrium was calculated using Outokumpu HSC 5.11, which is a computer program based on the minimisation of the Gibbs free energy. The program calculates multi-phase chemical reaction equilibrium for ideal solutions, and should therefore give an indication of the maximum precipitation yield of calcium carbonate from the calcium acetate solution.

The thermodynamic calculations performed showed that the addition of sodium hydroxide should have a clearly more pronounced effect on the calcium carbonate conversion than temperature, pressure, and calcium concentration (Fig. 6). Calculating the equilibrium composition for a system representing the experimental conditions used (1 bar, 30 °C, ~10 g Ca/l) shows

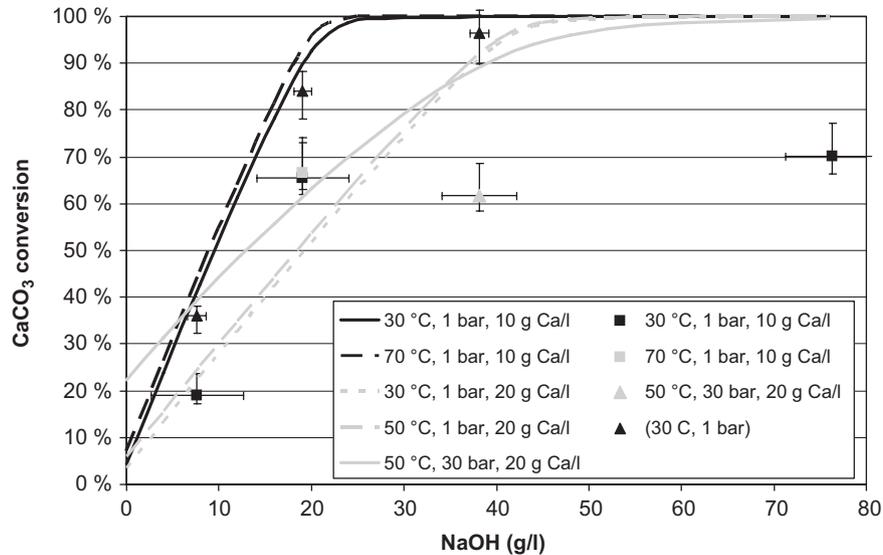
that increasing the amount of the sodium hydroxide used to 8 or 28 g NaOH/l raises the conversion to 43% or 100%, respectively. The gap between the experimentally found conversions and thermodynamically calculated conversions was 21–30% units for the cases where sodium hydroxide was used.

The thermodynamic calculations predicted a calcium conversion of 4% at atmospheric pressure and 22% at 30 bar when no sodium hydroxide was used, but the experiments performed under similar conditions did not result in any detectable amount of precipitated carbonate. Although XRD did not detect any carbonate phases, it is possible that amorphous carbonate was formed. This possibility could not be tested for, because in both cases the yield was too small for XRF or TC analysis.

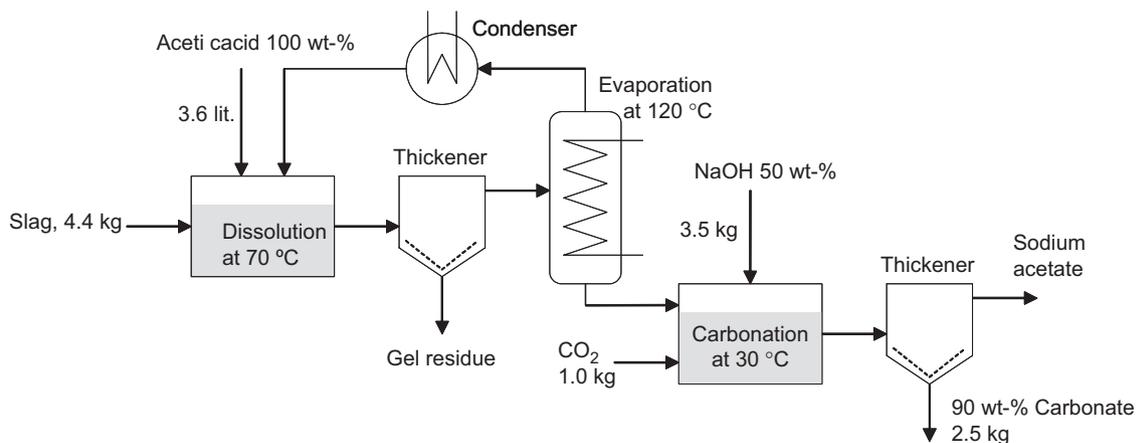
The thermodynamic calculations were based on a pure calcium acetate solution, while the experiments were performed with calcium acetate produced from blast furnace slag that also contained various other elements. Therefore, part of the difference between the results of the modelling and experiments can be explained by the precipitation of other compounds (containing elements such as magnesium, iron, silica, and aluminium), which were not included in the model. This was verified by a series of experiments (30 °C, 1 bar, 10 g Ca/l) with chemical purity calcium acetate (94 wt%, manufactured by Riedel-de Haën), which reduced the gap between the experimental and modelling results to ~5% units. Since the pH of the calcium acetate solutions had clearly stabilised before the experiments were finished, it seems unlikely that a longer reaction time would have improved precipitation, indicating that the precipitation of calcium carbonate in these conditions is equilibrium-controlled.

### 3.3. Preliminary process calculations

Experimental results indicated that ~19 g NaOH/l of calcium acetate solution (10 g Ca/l) was close to the point where precipitation reaches its limit (at 30 °C, 1 bar), and thermodynamic equilibrium calculations showed that the point was ~28 g NaOH/l. With the latter amount of NaOH, about 20 g of 90% pure calcium carbonate should precipitate per litre of calcium acetate solution produced from blast furnace slag, binding ~8 g CO<sub>2</sub>. This means that in order to bind 1 kg of carbon dioxide, 126 l of prepared calcium acetate solution is needed with 3.5 kg of NaOH, producing ~2.5 kg of 90% pure CaCO<sub>3</sub>. We have previously demonstrated [14] that complete dissolution of the blast furnace slag is possible with a high acid-to-solid ratio (~6 l of acetic acid/kg of blast furnace slag). Therefore, production of this calcium acetate solution would consume approximately 4.4 kg of the slag and 26 l of acetic acid (100 wt%). While the evaporation and condensation of the acetic acid used for dissolving the slag facilitates the relatively easy recycling of a large part of the acid (~22.5 l), this requires energy, the generation of which may produce carbon dioxide emissions.



**Fig. 6.** Calcium carbonate conversion from a solution of calcium acetate under various conditions based on thermodynamic calculations compared to the results from the experiments with blast furnace slag derived calcium acetate solution. The "triangle"-shaped marker (30 °C, 1 bar) represents results from the experiments with chemical purity calcium acetate (94 wt%).



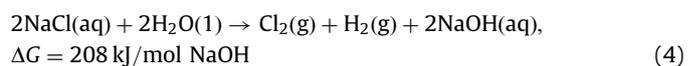
**Fig. 7.** A process scheme for binding 1 kg of carbon dioxide by carbonating acetate produced from blast furnace slag.

The production of sodium hydroxide is also energy-intensive. Therefore, the energy requirements of this process route (see Fig. 7) were assessed to determine the net reduction of carbon dioxide emissions.

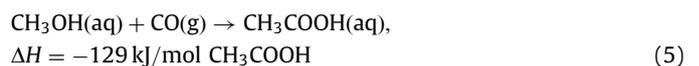
The heat requirements of different parts of the process were calculated from reaction enthalpies using Outokumpu's HSC 5.1 software. Process conditions (such as temperatures, pressures, solution concentrations, etc.) were chosen on the grounds of the experimental results. The heating of the raw materials (up to 70 °C) and dissolution of blast furnace slag (calculations were based on wollastonite, which resembles blast furnace slag) in acetic acid (50 wt%), require 1 MJ of heat/kg of slag. With a stronger acetic acid solution, the heat requirement is reduced (~9 kJ/kg of slag with a 100 wt% acetic acid solution). The evaporation temperature for the excess acid was set to 120 °C, i.e. slightly above the boiling point of pure acetic acid (118 °C). Assuming that the released vapour consists of steam and acetic acid gas, the heat requirement of the evaporation step would be 1–2 MJ/l of acetic acid solution evaporated, depending on the concentration of the acetic acid. Since neither temperature nor pressure was found to have any significant effect on the carbonation process, the carbonation could be carried out at

30 °C and a carbon dioxide pressure of 1 bar (i.e. no need for reactor pressurisation). The precipitation of calcium carbonate would produce 2 MJ of heat/kg of carbon dioxide stored.

While the evaporated acetic acid solution could be condensed and sent back to the dissolution reactor, the acetic acid bound as calcium acetate, as well as the sodium hydroxide used, would need to be purchased or regenerated. Sodium hydroxide is produced via the chloralkali process, which involves the electrolysis of an aqueous solution of sodium chloride. The amount of electricity needed for electrolysis can be calculated as the change in Gibbs free energy for the electrolysis reaction:



This shows that approximately 5.2 MJ of electricity would be required to produce 1 kg of sodium hydroxide (at room temperature). The most common acetic acid manufacturing process is methanol carbonylation, in which methanol reacts with carbon monoxide:



This route for the manufacture of unrecoverable acetic acid should actually produce 2.15 MJ of heat (at 25 °C)/kg of acetic acid produced, but requires methanol and carbon monoxide as source materials.

The carbon dioxide emission factor for coal is 94.6 g/MJ [19] and CO<sub>2</sub> emissions from a coal-fired power plant are roughly 800 kg/MWh [20]. Therefore, carbon dioxide emissions from the heat and electricity generation would be from 6 to 13 times the amount of carbon dioxide stored by the carbonation step (with 100 and 50 wt% acetic acid solutions, respectively). The temperature required for the evaporation step is quite low, and it is very likely that the required heat could be acquired by process integration using waste heat from the steelmaking plant itself. However, although hydrogen and chlorine gas are both co-products of sodium hydroxide production, the electricity requirements of electrolysis make the process described above unsuitable for carbon dioxide storage, unless the sodium hydroxide can either be replaced by a cheaper alkaline (waste) stream or recycled.

The conventional PCC production chain produces approximately 0.22 kg of carbon dioxide/kg of calcium carbonate produced [21]. If the impurities in the calcium carbonate produced from blast furnace slag could be removed and the precipitate could be sold as PCC, the replacement of conventionally produced PCC would reduce the carbon dioxide emissions somewhat. However, these savings are small in comparison with the carbon dioxide generated from sodium hydroxide production.

#### 4. Conclusions

According to our experiments, the precipitation of calcium carbonate from an aqueous solution of blast furnace slag-derived calcium acetate at temperatures of 30–70 °C and pressures of 1 or 30 bar is insignificant. The addition of sodium hydroxide, i.e. increasing the solution pH, resulted in the formation of calcium carbonates (calcite, aragonite, calcite magnesium) even at atmospheric pressure and 30 °C. Clearly, making the solution pH higher by the addition of NaOH is required for efficient carbonation. The calcium carbonate content of the precipitates was calculated to be ~60–90%. Substantial amounts of magnesium, silicon, aluminium, and iron originating from the blast furnace slag also ended up in the calcium carbonate precipitate. The calcium acetate solution should therefore be free of these elements, in order to produce calcium carbonate suitable for use as PCC (i.e. 99% purity) from blast furnace slag.

Preliminary process calculations showed that approximately 4.4 kg of blast furnace slag, 3.6 l of acetic acid (100 wt%), and 3.5 kg of sodium hydroxide would be required to bind 1 kg of carbon dioxide, resulting in 2.5 kg of 90% calcium carbonate.

The sodium hydroxide regeneration, as well as the energy requirement of acetic acid evaporation, would very probably produce more carbon dioxide than would be bound by the carbonation step. The heat needed for the acetic acid evaporation needs to be acquired as waste heat by process integration with other processes. However, electricity would still be required to regenerate NaOH electrochemically. Possible ways of precipitating calcium carbonate of higher purity from steelmaking slags, as well as of replacing acetic acid with another solvent, are currently being investigated.

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