

## **PAPER III**

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# Co-utilisation of CO<sub>2</sub> and Calcium Silicate-rich Slags for Precipitated Calcium Carbonate Production (Part II)

Sanni Eloneva<sup>1</sup>, Sebastian Teir<sup>1</sup>, Jaakko Savolahti<sup>1</sup>,  
Carl-Johan Fogelholm<sup>1</sup>, and Ron Zevenhoven<sup>2</sup>

<sup>1</sup> Laboratory of Energy Engineering and Environmental Protection, Helsinki University of Technology, Espoo, Finland, tel. +358 9 451 2847, fax +358 9 451 3418, sanni.eloneva@tkk.fi

<sup>2</sup> Heat Engineering Laboratory, Åbo Akademi University, Turku, Finland

**ABSTRACT:** Production of commercial calcium carbonate from calcium silicate-rich slag is an attractive concept for reducing CO<sub>2</sub> emissions. In order for this calcium carbonate to be marketable it has to be very pure, requiring separation of calcium from the slag prior to carbonation. In this study, a process concept that produces relatively pure calcium carbonate from slag is presented. It uses an aqueous solution of acetic acid to dissolve blast furnace slag, followed by removal of residues and evaporation of the acid to produce acetate, which is then dissolved in water before CO<sub>2</sub> is introduced. The alkalinity of the solution is raised by addition of sodium hydroxide, which causes calcium to precipitate as calcium carbonate. The fate of other elements released from the slag during the process was studied as well. It was found that while Si, Ti and Zr can be separated by facilitating gel formation, Al, V, Mn, Fe, and Ba require additional separation methods to produce pure calcium carbonate. The process also requires additional measures for preventing sulphuric vapour emissions. The economical feasibility of the proposed process was also investigated. The evaporation step was found to be expensive, unless the process could be integrated with a waste heat source. Recovery of the sodium acetate solution, a by-product of the carbonation step, was also considered necessary for the process to be economically feasible.

**Keywords:** mineral carbonation, blast furnace slag, acetic acid, CO<sub>2</sub> utilisation

## 1. INTRODUCTION

Carbon dioxide capture and storage (CCS) has been acknowledged as one potential method for reduction of atmospheric carbon dioxide emissions [1]. Of all CCS methods, the largest storage capacity and longest storage time is projected for mineral carbonation [2]. In mineral carbonation, CO<sub>2</sub> reacts with metal oxides in magnesium or calcium silicates

and forms stable carbonates. Steelmaking slags appear as an attempting alternative to natural calcium silicates, because they are readily available, cheap and have a high content of calcium oxide (34-52 % [3]). Due to uncertainties in the estimations of the annual amount of steelmaking slag produced globally, the theoretical CO<sub>2</sub> reduction potential of steelmaking slags varies between 60 and 170 Mt/a [4]. Although most carbonation processes suggested for

storage of CO<sub>2</sub> are relatively expensive, the commercial value of a pure calcium carbonate product could allow for a more expensive process.

In order to produce a pure calcium carbonate precipitate, calcium must first be extracted from slag. In this study, a process concept that produces relatively pure calcium carbonate by using acetic acid for leaching of calcium from blast furnace slag is presented. A mass balance study, concerning the fate of the elements released from blast furnace slag during the process, is presented as well. The economical feasibility of the process concept is also investigated.

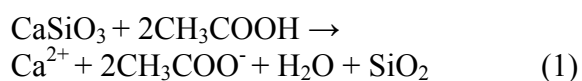
## 2. BACKGROUND

While the market price of natural calcium carbonate is about 11 €/t, the price of precipitated calcium carbonate (PCC) is roughly ten times this value [5]. PCC is used mainly as a paper filler for improving the physical quality of the paper. It consists of very pure calcium carbonate (99 % [6]) due to the production process, in which impurities are removed from the raw material (limestone, natural calcium carbonate). Although the production process involves carbonation, the total process chain produces more CO<sub>2</sub> than it consumes [4, 7]. Mineral carbonation producing calcium carbonate suitable for the PCC market could at the same time allow for reductions in atmospheric CO<sub>2</sub> emissions and produce a carbonate product with a high price. This could enable for a more expensive carbonation process.

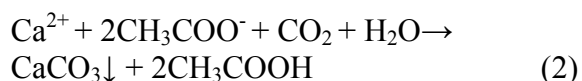
In most of the mineral carbonation processes proposed that use industrial waste materials as a raw material, carbonation is done in one step [8]. Therefore, the carbonated product contains also most of the impurities and other compounds found in the raw material. However, by extracting calcium from the slag before carbonation,

purer calcium carbonate could probably be produced.

Kakizawa et al. [9] proposed the use of acetic acid for the extraction of calcium from natural calcium silicates (such as wollastonite) prior to carbonation. In this process, carbonation is divided into two process steps: In the first process step, wollastonite is dissolved in acetic acid (1), after which silica is separated from the formed calcium acetate solution.



In the second step (2), CO<sub>2</sub> is introduced to the calcium acetate solution producing calcium carbonate precipitate and acetic acid, which is recycled back to the first process step.



Since only limited experimental data was found on this proposed process, we have investigated the possibility to use acetic acid for extraction of calcium from steelmaking slags prior carbonation. Part I of this paper was presented at ECOS'2005 [7].

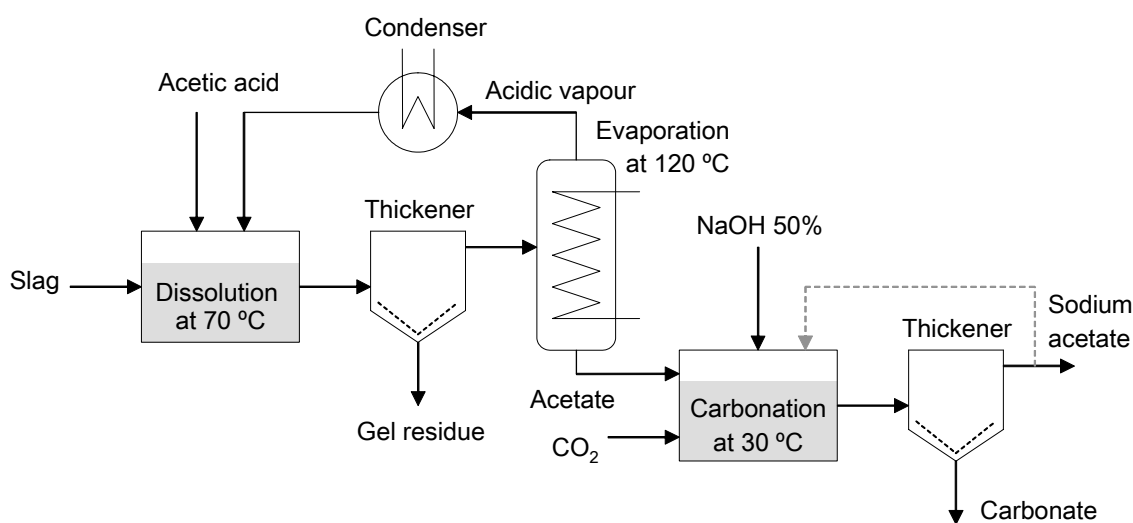
## 3. IMPROVED PROCESS CONCEPT

Dissolution of steelmaking slags in acetic acid was studied by thermodynamic equilibrium calculations and laboratory-scale batch experiments [10]. According to thermodynamic equilibrium calculations (using Outokumpu's HSC 5.1 software), all compounds (except for Ti) in blast furnace slag (one type of steelmaking slag) should dissolve in aqueous solution of acetic acid at 30-70 °C, and a large part of the dissolved metals should form acetates. Laboratory-scale batch experiments (at 50 °C) showed that various steelmaking slags indeed dissolved rapidly in acetic acid. While calcium was efficiently leached from all of

the slags used, the best extraction efficiency was reached with blast furnace slag (~100 %). However, a surplus of acetic acid was required for a feasible calcium extraction, leaving the formed solution acidic. Since other elements, besides calcium, were dissolved as well, measures for the removal of these compounds prior to carbonation are required. Silica was found to form gel at a solution temperature of 70 °C, allowing it to be removed by filtration. More detailed results have been published elsewhere [10].

Precipitation of calcium carbonate from a solution of acetic acid and dissolved blast furnace slag was studied by laboratory-scale batch experiments [11, 12]. It was found that the acidity of the solution prevented precipitation of carbonates. While addition of sodium hydroxide raised the solution pH

resulting in formation of precipitate containing carbonates, a considerable amount of sodium hydroxide was required. Adding an extra step into the process enabled to decrease the sodium hydroxide requirements. In this step, the solution containing acid and dissolved slag was evaporated. Evaporation caused the compounds in the solution to precipitate as a solid acetate powder, which was dissolved in water. Pure CO<sub>2</sub> (at 1 atm) was then introduced to the acetate solution for precipitation of calcium carbonate. This enabled the production of relatively pure (80-90 %) calcium carbonate using significantly less sodium hydroxide. More detailed results are reported elsewhere [11, 12].



**Figure 1:** Process concept for producing calcium carbonate from blast furnace slag

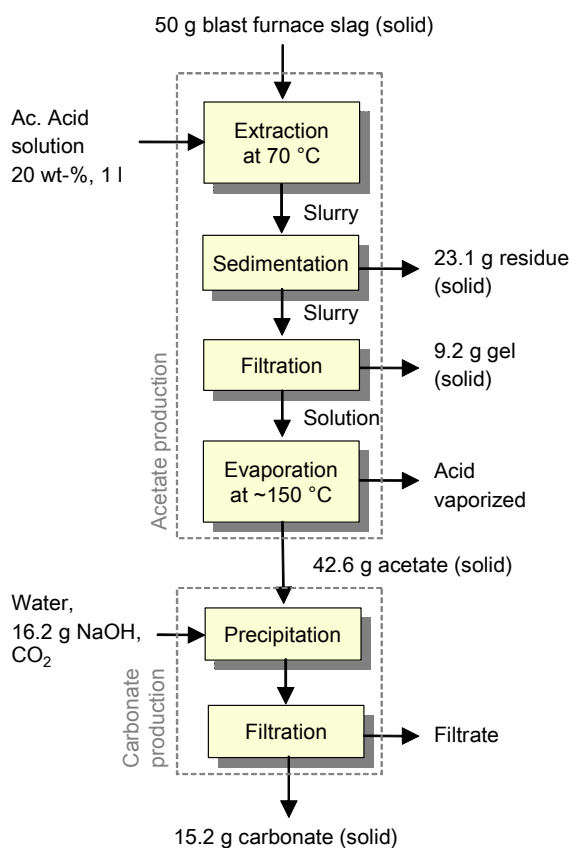
Based on these experimental studies, it seems that in order to produce pure calcium carbonate from blast furnace slag, a multi-step process is required (Figure 1): At first, blast furnace slag is dissolved in an acetic acid solution at about 70 °C, followed by sedimentation for removal of the solid slag residue, and filtration for removal of the formed gel. The filtered solution is then evaporated at high temperature producing

acetate and volatile acetic acid, which can be condensed and send back to the extraction reactor. The produced acetate is dissolved in water and CO<sub>2</sub> is introduced into the solution. Finally, sodium hydroxide is added for raising the alkalinity of the solution, causing calcium carbonate to precipitate. The precipitated calcium carbonate is removed by filtration and

washed for removal of any water-soluble compounds (such as sodium acetate).

#### 4. ELEMENTAL MASS BALANCES

In order to study the behaviour of other elements in the slag at various process stages, one set of batch experiments, representing the carbonation process in development, were performed. This allowed for calculation of the elemental mass balances of the process (Figure 2).



**Figure 2:** Mass balance set-up of the procedure for producing calcium carbonate from blast furnace slag (quantities are scaled to match an input of 50 g slag).

50 g of blast furnace slag was dissolved for 2 h in one litre of a 20-wt % acetic acid solution at 70 °C. The residual slurry was separated by sedimentation and decanting the solution. The decanted solution contained a gel, which was separated by

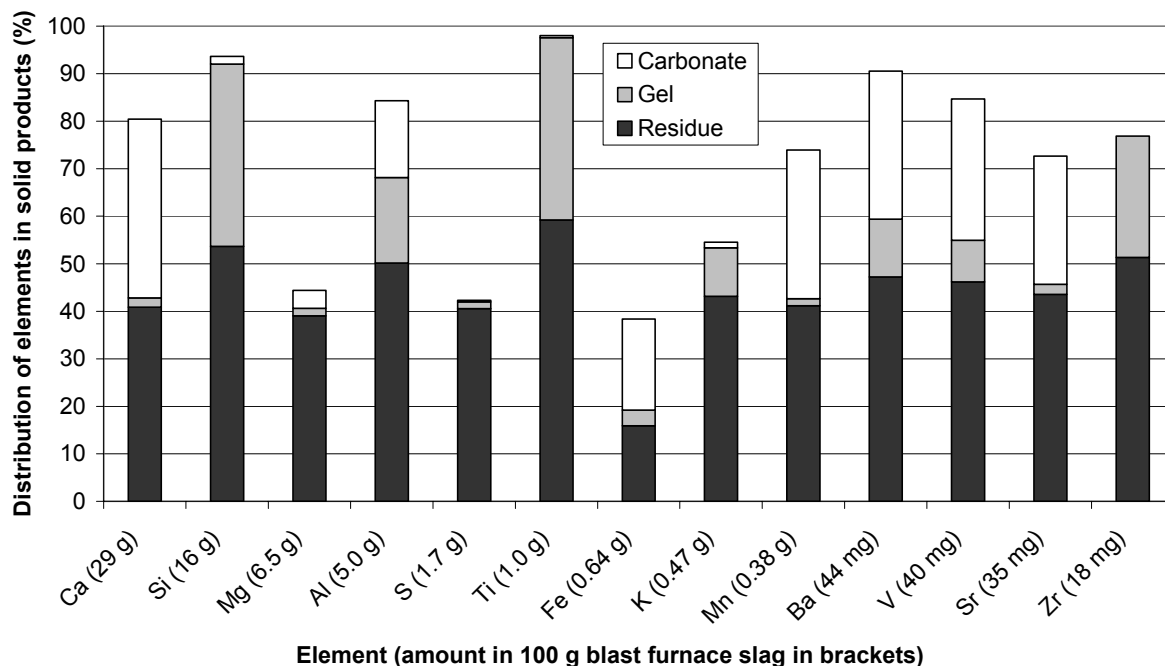
filtration. Both the gel and residue were washed and dried. The filtered solution was evaporated at 150 °C, which caused a solid acetate to precipitate. The acetate was recovered (42.6 g), of which 10 g was mixed with water and carbonated with one litre CO<sub>2</sub>/min. 5 ml NaOH solution (50 wt-%) was added, causing carbonate to precipitate. These results were scaled to match an input of 42.6 g acetate. After 135 min, the slurry was filtered, washed and dried. All solids were analysed using X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF). The XRD analyses confirmed that the carbonated solids consisted mostly of calcium carbonate as calcite.

Elemental mass balances were set up for the outgoing and incoming solid streams based upon the XRF data. Additional mass balances were set up separately for the two sub-processes (acetate preparation and calcite precipitation), in order to get more detailed information about the enrichment or depletion of elements in outgoing solid streams.

The results from the elemental mass balance for the whole process are shown in Figure 3. It can be seen that none of the elements reach a mass balance closure of 100 %. This is probably due to loss of elements with the evaporated acid and the filtrate from the carbonated slurry, as these streams were not analysed for trace elements. Most significant are the losses of Mg, S and Fe, for which the mass balance closure is less than 50 %. For Al, Si, Ca, Ti, V and Br more than 80 % of the input is accounted for in the outgoing solid streams. As seen in Figure 3, for about half of the elements a considerable percentage of the input ends up in the carbonate. These elements are Al (16 %), Ca (38 %), V (30 %), Mn (31 %), Fe (19 %), Sr (27 %) and Ba (31 %). Very little or none of Si, S, K, Ti and Zr end up in the carbonate, with considerable amounts of Al (18 %), Si (38 %), Ti (38 %) and Zr (26 %) found in the gel collected after filtration. With the exception of Fe, 40 % or more of each

element are retained in the slag residue. This was expected, since the amount of acid used allowed only for partial dissolution of the blast furnace slag. We have previously shown that with higher acid/solid ratio it is possible to achieve a complete dissolution of

the blast furnace slag [10]. On average, for the acid and solid amounts used as mentioned, 44 % of elements exit the process during sedimentation as residue, 12.5 % during filtration as gel and 15 % end up in the carbonate.



**Figure 3:** Elemental mass balance of the total process. Fractions indicate the amount of each element in the solid (by-) product of the process.

When the two sub-processes were examined, more detailed information about the behaviour of elements was observed. For example, for Mg the mass balance closure from start to evaporation state was nearly 100 %, but the mass balance closure from evaporation to filtration is about 6 %. This shows that 6 % of the extracted magnesium precipitated during the carbonation process and the rest remained in solution. Also K, as well as V, Mn, Sr and Ba to a lesser extent exhibit similar behaviour as Mg. The mass balance of S (as well as the observed odour during extraction and evaporation) indicates that most of the extracted sulphur was probably lost as sulphuric vapours. None of the zirconium reaches the second sub-process. The deficit in mass balance for Fe is probably due to the use of a magnetic stirrer: upon removal of the magnetic bar

from the solution, part of the magnetic iron released from slag was lost.

The mass balance analysis shows that most of the extracted Mg, K, Ca, V, Mn, Fe, Sr, and Ba ended up in the intermediate acetate product, while most of the extracted Si, Ti, and Zr ended up in the gel. The elements in the acetate precipitated during the carbonation stage as follows: more than 80 % of Al, Si, Ti and Fe; 80 – 20 % of S, Ca, V, Mn, Sr and Ba; less than 20 % of Mg and K. The results show that for obtaining a pure calcium carbonate product it is important that the acetate contains mostly calcium acetate, although small concentrations of magnesium and potassium can be allowed. While Si, Ti and Zr can be separated by facilitating gel formation, Al, V, Mn, Fe, and Ba require additional separation methods. Since very little sulphur

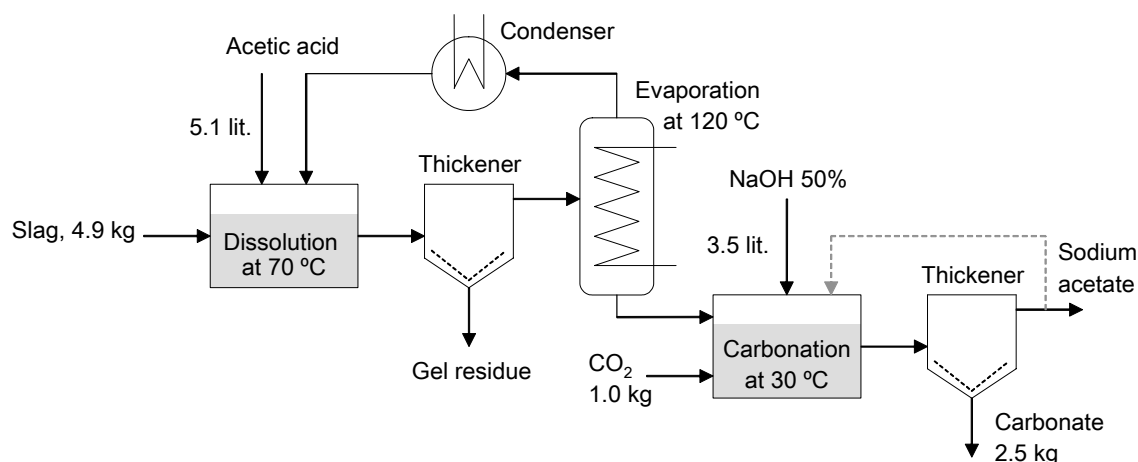
was captured in any of the solid products, the process requires additional measures for preventing sulphuric vapour emissions due to dissolution of sulphur. Instead of adding separation steps to the process, it may be more feasible to use another solvent, which would extract calcium more selectively from blast furnace slag.

## 5. ECONOMICAL ANALYSIS

There is a clear need for technology that is able to reduce CO<sub>2</sub> emissions while being also inexpensive. Therefore, preliminary calculations were performed based on the results from the batch experiments to investigate the economical feasibility of the proposed process.

The carbonated solid from the batch experiment described in Section 4 contained

55 wt-% carbonate according to total carbon and XRD analyses. This means that about 8.0 kg of blast furnace slag, 32 l pure acetic acid and 3.4 l aqueous sodium hydroxide solution (50 wt-%) would be needed to bind 1 kg of CO<sub>2</sub>. However, as it was pointed out earlier, complete dissolution of the slag is possible with higher acetic acid/solid ratio. Therefore, it can be assumed that if an adequate amount of acetic acid (6 l per kilogram of blast furnace slag [10]) is used, the blast furnace slag can be completely dissolved, forming gel and acetate in same relation to the described batch experiment. Assuming that the formed acetate is converted into carbonate with the same conversion as in the batch experiment, only 4.9 kg of blast furnace slag and 29 l pure acetic acid would be required to bind 1 kg of CO<sub>2</sub> (Figure 4). This would produce 2.5 kg of 89 % calcium carbonate.



**Figure 4:** Process concept including mass flow rates.

While part of the acetic acid would be bound in the acetate after reacting with blast furnace slag, producing additional water (see Equation 1), most of it would have to be evaporated to dry out the acetate. Although in the described batch experiment the used acetic acid solution contained excessive amount of water (79 wt-%), 50 wt-% acetic acid solution is more likely to be used in reality, requiring smaller amount of solution to be evaporated. Outokumpu's

HSC 5.1 software was used for calculating the heat requirement for evaporation of the acetic acid solution. This program calculates the enthalpy difference between given input and output streams. In the proposed process concept, dissolution of blast furnace slag occurs at solution temperature of 70 °C, thus the input temperature of the acetic acid solution (50 wt-%) was set to 70 °C. Evaporation temperature was set to 120 °C, which is slightly above the boiling point of

pure acetic acid (118 °C). It was assumed that the released vapour consists of steam and acetic acid gas. According to these calculations, the heat requirement of the evaporation step of the proposed process is 27 kWh per kg of CO<sub>2</sub> stored as carbonate. The consumer price of hard coal in heat production has been about 14 €/MWh in the inland areas of Finland [13], thus the evaporation step would cost 390 €/t CO<sub>2</sub>. This expensive, considering that the current price of CO<sub>2</sub> in European CO<sub>2</sub> emission market is much lower (~3.9 €/t CO<sub>2</sub>, January 2007). It might, however, be possible to integrate this proposed process to the CO<sub>2</sub> emission source that has suitable waste heat available for the evaporation of the acetic acid solution.

While the evaporated acetic acid solution could be condensed and send back to the dissolution reactor, acetic acid bound in acetate, as well as the used sodium hydroxide, would possibly be more difficult to recycle, since it is likely that they would be in a form of sodium acetate solution. Unless these were recycled, 3.5 l sodium hydroxide solution (50 wt-%) and about 5 litre pure acetic acid solution would be consumed per each CO<sub>2</sub> kilogram carbonated. The current price of a 50 wt-% aqueous sodium hydroxide solution is about \$170-\$200 per ton (~130-150 €/t), and the price of pure acetic acid \$0.47-\$0.53 per pound (~0.79-0.89 €/kg) [14], thus sodium hydroxide requirements would cost 350-410 €/t CO<sub>2</sub> and acetic acid 4200-4700 €/t CO<sub>2</sub>. Therefore, the sodium acetate solution must be recovered for reuse, in order for the proposed process to be economically feasible. One option might be to replace sodium hydroxide with alkaline waste solutions from other industrial processes. Pure sodium acetate is also a relatively strong base, thus it might be possible to use it instead of sodium hydroxide. However, this has not yet been investigated.

The current market price of commercial blast furnace slag is about 10 €/t [15]. Assuming that produced precipitate could be

sold as precipitated calcium carbonate (PCC) (~100 €/t), the costs of the evaporation and recovery should not exceed 200 €/t CO<sub>2</sub> in order for the process to be compatible under the current price of CO<sub>2</sub>. However, the price may rise quickly, if stricter greenhouse gas emission reductions are set up as the climate change is seen more threatening.

## 6. CONCLUSIONS

A process concept for producing calcium carbonate from blast furnace slag was presented and verified by experiments.

It was found that the intermediate acetate product should contain mostly calcium acetate to allow for precipitation of pure calcium carbonate. While Si, Ti and Zr can be separated by facilitating gel formation during the dissolution of blast furnace slag, additional separation methods for the removal of Al, V, Mn, Fe and Ba, as well as measures for preventing sulphuric vapour emissions, are still needed.

Preliminary calculations showed that the heat requirements for evaporation of the acetic acid is large, but could be covered for using low-grade waste heat (120 °C) from other industrial processes. The requirements of sodium hydroxide and acetic acid were also found to be expensive, requiring recovery of the produced sodium acetate solution. However, if the produced precipitate could be sold as precipitated calcium carbonate for more than 100 €/t CaCO<sub>3</sub>, process costs up to 200 €/t CO<sub>2</sub> could be allowed, which is significantly more than current CO<sub>2</sub> storage processes. Therefore, more research is required to investigate the recovery and reuse of chemicals demanded by the process. However, the possibility to use other solvents should also be investigated.

## ACKNOWLEDGEMENTS



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