



# Solvochemical carbonation of lime using ethanol: Mechanism and enhancement for direct atmospheric CO<sub>2</sub> capture



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## ABSTRACT

Carbonation of lime (CaO) using ethanol is studied for direct atmospheric CO<sub>2</sub> capture. The parameters that control the carbonation of lime using air and ethanol are determined, and operational conditions that enhance the CO<sub>2</sub> uptake are investigated. A mixture of lime and ethanol was exposed to air within a fume hood, allowing ethanol evaporation for a defined period. Results reveal that the carbonation occurs after ethanol has evaporated, when the remaining powder is exposed to the atmosphere. After contact with ethanol, the CO<sub>2</sub> uptake of lime is enhanced because the specific surface area of the powder increases. Increasing the time of exposure to the atmosphere results in an increase in the carbonation conversion (from 0.03 gCO<sub>2</sub>/gCaO for 1 day of exposure, up to 0.44 gCO<sub>2</sub>/gCaO for 60 days of exposure). Milling the solvent-lime slurry, before exposing it to the atmosphere, also enhances the carbonation yield through the effect of size reduction and mechanical activation (from 0.30 gCO<sub>2</sub>/gCaO with 5 min of pre-milling, to 0.60 gCO<sub>2</sub>/gCaO with 10 min of pre-milling). Another way to increase the carbonation yield is through the use of alkaline wastewater. Combining the wastewater with ethanol, or milling a slurry of CaO/wastewater before exposure to the atmosphere, increases the carbonation yield further to 90.2% (0.70 gCO<sub>2</sub>/gCaO) and 96.2% (0.75 gCO<sub>2</sub>/gCaO), respectively. This study reveals that ethanol/alkaline wastewater treatments, along with their different enhancement options, represent an effective viable route for sequestering CO<sub>2</sub> from the atmosphere, which could be applied to pure lime or potentially to lime-containing wastes.

## 1. Introduction

Accelerated mineral carbonation, a form of CO<sub>2</sub> capture or CO<sub>2</sub> sequestration, is a process that mimics the natural reaction of alkaline rocks with carbon dioxide from the atmosphere. In the natural process, minerals react with CO<sub>2</sub> over geological timescales. In accelerated mineral carbonation, the reaction rate is increased so that large amounts of CO<sub>2</sub> (from the atmosphere or directly from industrial emission sources) can be captured and stored permanently in CO<sub>2</sub> sinks. One category of sinks consists of solid carbonates, wherein magnesium- and/or calcium-oxides, -hydroxides and -silicates are reacted with the CO<sub>2</sub> [1]. Another category consists of deep geological formations, wherein the role of accelerated carbonation is to capture the CO<sub>2</sub>, such as in calcium looping [2], so that it can be concentrated into a high purity stream for injection.

In this study, the focus is given on the carbonation of lime (CaO) using ethanol as an accelerating solvent for the capture or sequestration of CO<sub>2</sub> from the atmosphere. Typically, carbonation of lime is

performed in an aqueous solution, at ambient to moderate temperatures [3], or dry, at elevated temperatures [4]. Some studies related to the use of ethanol for carbonation applications have been published, and point to benefits of using this solvochemical approach, as summarized hereinafter.

Seo et al. [5] precipitated calcium carbonates (calcite, aragonite and vaterite) by introducing CO<sub>2</sub> gas at a flow rate of 1 l/min in a reactor filled with ethanol (or an ethanol-water mixture) and Ca(OH)<sub>2</sub>. They observed much smaller changes in pH and electrical conductivity when using ethanol versus pure water, and concluded that the carbonation mechanism in ethanol is not as dependent on the formation of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions. Instead, they suggested that localized carbonation occurs on the surface of Ca(OH)<sub>2</sub> particles, where adsorbed water molecules aid in a two-step dissolution-precipitation mechanism. Carbonation in ethanol, and in sufficiently ethanol-rich (≥60 mol%) mixtures with water, also resulted in the formation of two additional polymorphs of calcium carbonate, namely vaterite and aragonite, not seen in experiments with pure water as the solvent.

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Adanez et al. [6], Li et al. [7], and Arpin and Yusup [8] have used ethanol as a pre-treatment for enhancing the reactivity of lime in gas/solid reaction systems. Li et al. [7] mention the use of CaO modified with ethanol/water for increasing the CO<sub>2</sub> capture conversion in looping carbonation/calcination cycles within a twin fixed-bed reactor system. Adanez et al. [6] studied desulphurization of flue gas using CaO, and showed that CaO modified with ethanol/water solution could enhance the SO<sub>2</sub> removal. According to Arpin et al. [8], ethanol/water hydration enhances CO<sub>2</sub> capture performance of CaO sorbent and prolongs its performance over multiple cycles performed in a thermogravimetric analyzer (TGA). It has been highlighted in all three studies that CO<sub>2</sub> and SO<sub>2</sub> capture capacity of CaO modified with ethanol/water solution is enhanced because of the decrease of mean particle size and improvement of the porous structure. It has been shown by Li et al. [7] that ethanol molecules enhance H<sub>2</sub>O molecule affinity to CaO and penetrability in CaO during the hydration reaction, leading to the expansion of the CaO pores.

Additionally, many authors [9–15] have studied alcohol dispersions of Ca(OH)<sub>2</sub> nanoparticles (also called nanolimes) used in the conservation of cultural heritage or for consolidation of carbonate rocks in building protection applications. According to those studies, the mixture ethanol/nanolime can lead to the pseudomorphic replacement of calcium hydroxide by calcium ethoxides Ca(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. The replacement mechanism is an interface-coupled dissolution-precipitation, and results in amorphous calcium alkoxides. They have shown that in an aqueous environment, CO<sub>2</sub> from the atmosphere reacts faster with calcium alkoxide than with calcium hydroxide. The replacement thus results in an increase in the carbonation rate and improves the carbonation yield. The extent to which the hydroxides are turned into alkoxides depends on the reactivity of the Ca(OH)<sub>2</sub> (determined by the specific surface area of the nanoparticles and lattice defects) and the time of exposure to the alcohol. It has been highlighted that two different reaction routes turn the calcium alkoxide into calcium carbonate, with the first being considered to have faster kinetics: (i) CO<sub>2</sub> insertion into the Ca–O bond of the calcium-alkoxide, and (ii) hydrolysis into Ca(OH)<sub>2</sub> followed by carbonation [13].

Among the studies published in literature, apart from the case of nanolimes, no work has been performed on CO<sub>2</sub> capture performance of an ethanol/CaO mixture simply exposed to CO<sub>2</sub> from the atmosphere for the purpose of developing viable solutions for climate change mitigation. This work attempts to provide more insight into the mechanisms of carbonation of lime using ethanol by investigating the parameters that control the carbonation process, and finding conditions that could enhance the CO<sub>2</sub> uptake yield and kinetics. For this purpose, the effects of exposure time, pre-milling, and addition of alkaline wastewater have been studied. Various material characterization methods have been utilized to highlight how ethanol modifies CaO particles. Finally, possible industrial applications of this process are proposed and discussed.

## 2. Materials and methods

Calcium oxide (CaO, Acros Organics) with purity of > 97% (heavy metals: max. 100 ppm, iron: max. 1000 ppm, nitrate: max. 500 ppm, and sulphate: max. 1000 ppm), Basic Oxygen Furnace (BOF) slag (0.2 < D < 0.7 mm) provided by a steelmaking plant, and ethanol with purity of 99% (VWR Chemicals) were used for the experiments. MilliQ water (18.2 MΩ cm) and alkaline wastewater (pH = 11.69) from the same steelmaking plant (water used to clean the off-gasses in the deduster) were mixed with ethanol in selected experiments to study the effect of water or wastewater addition on CO<sub>2</sub> uptake. Table 1 shows the composition of the alkaline wastewater.

A basic setup was used (Fig. 1), which consisted of a ceramic bowl with a powder sample of 3 g that is mixed with 20 ml of liquid (liquid-solid ratio (L/S) of 7 l/kg) and put inside a fume hood (CO<sub>2</sub> 500 ppm +/- 20, 675 m<sup>3</sup>/h) to allow solvent evaporation for a determined

**Table 1**  
Composition of the alkaline wastewater.

	Values	Unit
OH <sup>-</sup>	234	mg/l
CO <sub>3</sub> <sup>2-</sup>	47.0	mg/l
HCO <sub>3</sub> <sup>-</sup>	0.0	mg/l
F <sup>-</sup>	3.6	mg/l
Ca <sup>2+</sup>	360	mg/l
Mg <sup>2+</sup>	0.0	mg/l
K <sup>+</sup>	88.5	mg/l
Fe <sup>+3</sup>	7.1	mg/l
Suspended solids	40.1	mg/l

duration. Other L/S ratios were also tested to find an optimal value. At completion of the experiment, the (dry) powder sample is stored in airtight plastic bag to prevent further carbonation, and is then characterized by the methods described next. It is important to note that, though not tested in this study, the evaporated ethanol would need to be recovered from the gas phase (e.g. by condensation) and re-used to make the process sustainable given the large volumes of ethanol used per gram of sequestered CO<sub>2</sub>.

To investigate the effect of pre-milling on CO<sub>2</sub> uptake, a second series of samples is prepared: 3 g of powder together with 5 ml of solvent are put in a polypropylene grinding jar packed with an ordered array of cylindrical sintered corundum grinding elements. This jar is put in a McCrone Micronising Mill (Glen Creston) for a defined duration. The ground powder is washed from the jar with 15 ml of the same solvent, and then treated as previously described.

A thermo-gravimetric analyzer (TGA) of type STA 409PC (Netzsch) is used to determine the CO<sub>2</sub> uptake mass per gram of sample. The sample is heated from 25 °C to 900 °C under an inert nitrogen atmosphere with a heating rate of 10 °C/min. The weight loss measured between 25 °C and 550 °C corresponds to the mass of H<sub>2</sub>O (loss of the superficial water at T < 100 °C, then loss of the structural water up to 550 °C) [1–4]. The weight loss measured between 550 °C and 900 °C corresponds to the mass of CO<sub>2</sub> that is taken up by the sample during carbonation [1–4]. The CO<sub>2</sub> uptake (gram of CO<sub>2</sub> per gram of CaO) is determined according to Eq. (1). The carbonation yield is determined as the ratio between the actual CO<sub>2</sub> uptake to the maximum CO<sub>2</sub> uptake, calculated according to the stoichiometric conversion of CaO to CaCO<sub>3</sub>, which equals 0.78 gCO<sub>2</sub>/gCaO.

$$\text{CO}_2 \text{ uptake (gCO}_2\text{/gCaO)} = (\Delta m_{550^\circ\text{C} - 900^\circ\text{C}}) / (m_{900^\circ\text{C}}) \quad (1)$$

A D2 Phaser (Bruker) is used to perform X-Ray Powder Diffraction (XRD) analysis on the powder. After obtaining the diffraction pattern, the peaks are qualitatively analyzed by the software EVA (Bruker) for identification of crystalline phases, and a semi-quantitative Rietveld refinement analysis is performed with TOPAS Academic V5 (Coelho Software) to determine the mass fraction of each identified crystalline phase.

A Mastersizer 3000 (Malvern) is used to perform wet (in ethanol) laser diffraction on the samples in order to determine the particle size distribution. The cumulative particle size diameters Dv(10), Dv(50) and Dv(90) are calculated from the volume-based distribution; the average of five measurements is presented in this paper, with a deviation lower than 0.6%.

In order to study the chemical effect of ethanol on lime, FT-IR analysis has been performed with a FT-IR Spectrometer Spectrum 100 (PerkinElmer), and NMR (<sup>13</sup>C NMR) measurements have been performed on an Avance III 500 MHz spectrometer (Bruker) equipped with a 4 mm H/X/Y magnetic angle spinning (MAS) probe.

A NOVA 2200e (Quantachrome Instruments) nitrogen adsorption analyzer, with software package NovaWin, is used to determine the specific surface area of the particles, applying BET theory. An XL30 FEG (Philips) scanning electronic microscope (SEM) is used to visually study

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