



Hydration and carbonation reactions of calcium oxide by weathering: Kinetics and changes in the nanostructure



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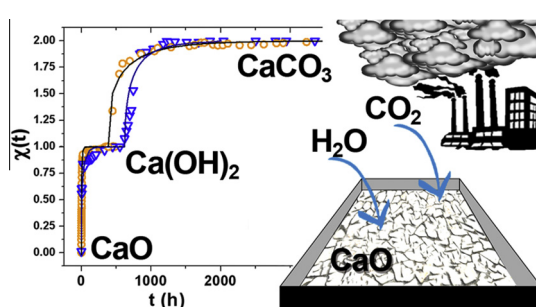
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HIGHLIGHTS

- Structure changes and mineral phases upon hydration and carbonation were revealed.
- Correlations of nanostructure with hydration and carbonation kinetics were found.
- Carbonation started after completed hydration (300–500 h depending on S_{BET}).
- Full carbonation from atmospheric CO_2 was always obtained thanks to nanostructure.
- Random Pore Model provides an empirical description of the weathering reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The weathering reactions of hydration and carbonation of nanostructured calcium oxide with atmospheric moisture and carbon dioxide have been characterized. This work is the first-to-date combined kinetic and nanostructural research on CaO oriented to two key processes for different systems, i.e. hardening of construction materials and carbon mineral sequestration. The evolution of the precipitated crystalline phases was monitored by X-ray diffraction and thermogravimetry, along with structural characterization by nitrogen physisorption, electron microscopy and small-angle scattering. Complete hydration of the samples was always found prior to the onset of carbon sequestration, which depended on the nanostructure of the samples. Hence, carbonation started after 300 h of weathering for samples with a specific surface area of $40 \text{ m}^2/\text{g}$, whereas carbonation of the samples with $20 \text{ m}^2/\text{g}$ occurred after 550 h. Full carbonation from atmospheric CO_2 (100% efficiency) was obtained in all cases. This combined research was completed by developing an empirical description of the weathering reactions in terms of a two-process Random Pore Model. Finally, this work aimed to determine the role of the nanostructure of samples based on industrial wastes as one of the most important factors for developing efficient carbon sequestration technologies.

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1. Introduction

The reactions of hydration and carbonation of calcium oxide are key steps for fundamental processes in very different systems, such as in construction materials or carbon capture and sequestration (CCS) technologies. The hardening, durability and the mechanical performance of structures based on hydrated lime mortars, cements or concrete are highly determined by these processes [1,2]. In addition, several CCS technologies [3–7] involving calcium oxide, such as flue gas separation by carbonation/calcinations loops or carbon mineral sequestration, are being deeply researched since the high concentration of CO₂ in the atmosphere is promoting climate change with a variety of hazardous consequences about society is continuously being warned [8,9].

In particular, CO₂ mineral sequestration [10–13] deserves special attention as it is by far the most durable CSS technology and, indeed, a complementary technology to already implemented carbon storage plants. Although it has been proposed as a plausible procedure to mitigate increasing carbon emissions worldwide, currently, mineral sequestration by capturing CO₂ directly from the air [14–16] (with very low energy consumption) lacks the necessary technological efficiency which would allow it to be implemented on a large scale, mainly due to the costs and kinetics of the process. To solve these obstacles, alkaline-rich mineral wastes are being proposed as sequestration agents [6,17–19] in order to decrease the costs of an industrial scale-up. Moreover, the specific (reactive) surface area has been revealed as one of the key parameters that controls the rate and the efficiency of these reactions [20–22]. Therefore, the kinetic limitations may be overcome using nanostructured sequestration agents in order to deal with reaction rates at a human scale under atmospheric conditions (1 bar, 300 K and [CO₂] ~400 ppm). Finally, the possible added-value of sequestration by-products, mainly Ca and Mg carbonates, as raw materials for subsequent processes, as construction [4,10] or paper industry [23], will promote the deployment of this technology on an industrial scale.

This work focused on the kinetics of the weathering processes of nanostructured calcium oxide samples obtained from a calcium-rich by-product of the acetylene industry [16]. Acetylene produced via calcium carbide generates an aqueous suspension of calcium hydroxide that is very efficient for carbon sequestration by weathering, as it is able to capture up to 30% of the total CO₂ emissions of the synthesis process of the acetylene itself. The weathering of calcium oxide implies moisture adsorption and hydration, yielding calcium hydroxide, and carbonation, which involves CO₂ fixation, to produce calcium carbonate and release water. The net reaction can be represented by:



Hydration and carbonation reactions may proceed by two different regimes: a first regime involving rapid chemical reaction and a second regime slowed down because of the formation of an impervious by-product layer [5,24–26]. This passivating layer can lead to pore closure, preventing the exposure of unreacted CaO to gases for further reaction, and therefore, the kinetics of the second regime became governed by the diffusion of ions through it. Nevertheless, it was found that this retardant phenomenon can be minimized in microstructured samples [21,27]. Moreover, the catalytic effect of water in the carbonation reaction is well known [20,28,29], so the presence of liquid-like adsorbed water from atmospheric moisture allows Ca²⁺ and OH⁻ ions to be formed as a consequence of the solubility of the minerals and the subsequent precipitation of new minerals.

A simple method for researching the kinetics of the weathering reactions consists of accurately registering weight changes in

samples exposed to atmospheric gases [30,31]. Based on these experiments, Aono proposed an exponential form for gas–solid kinetics under controlled atmospheres where the sample mass depends on time, $M \propto (1 - e^{-t/\tau})$. The characteristic kinetic constant τ has been found to depend not only on the gas concentration, but also on the nanostructure of the sample [20,24,32,33]. In particular, for chemically identical samples the difference between the reaction kinetics and efficiency can be explained in terms of differences in pore geometry or specific surface area.

But the nanostructure is a dynamic characteristic upon weathering [28,34,35]. To describe this phenomenon, different kinetic models have been proposed [36,37], for example the Random Pore Model [38] (RPM), which has been considered in different systems, such as gas–solid carbonation kinetics of air pollution control residues [39] or carbonation–calcination cycles on calcium oxide [5,40]. The parameters of the RPM model are obtained as a function of the internal pore structure (porosity, pore distribution, specific surface area, etc.) of the pristine sample.

This work aimed to reveal the relationships between the kinetics and nanostructure of calcium oxide upon hydration and carbonation by weathering. Changes in the nanostructure (specific surface area, pore volume and particle size), morphology and crystalline phases were also analyzed. In addition, structural experimental data were considered for jointly modeling both reactions based on the RPM. Additionally, this work intended to provide valuable information in order to enhance the viability of CO₂ mineral sequestration technologies.

2. Materials and methods

2.1. Synthesis of highly reactive powders

The calcium-rich slurry (waste) from the acetylene industry was kindly supplied by AIR LIQUIDE España SA. X-ray fluorescence and X-ray diffraction analyses revealed a composition of portlandite (calcium hydroxide, Ca(OH)₂) above 95 wt.%. Reported structural analyses showed a high specific surface area (47.5 m²/g) and the presence of submicrometric grains formed by bundles of sticks smaller than 200 nm. This material was fully characterized and successfully tested as carbon sequestration agent by weathering [16]. The calcium-rich slurry was heat-treated in order to obtain nanostructured calcium oxide, CaO. Heat treatments involved $t_h = 600$ °C for 1 h (above the dehydroxylation temperature of portlandite [41]) or $t_h = 800$ °C for 1 h, to obtain samples with different nanostructures due to incipient sintering [22,42]. The samples will be referred as CaO600 and CaO800, respectively. A minimum of 15 samples was considered for each treatment to ensure reproducibility and for statistics. 300 °C, 500 °C and 1000 °C and 0 h, 0.5 h and 4 h were considered to check consistency, but no significant differences were observed regarding the subject of this work. All the obtained samples consisted of a fine white powder.

2.2. Weathering experiments

Immediately after heat treatment, two batches of the CaO were taken from the furnace and exposed to air, and one of them was placed on a precision balance. Special care was taken to equalize the fineness and compactness of the powder. The weathering reactions were researched by monitoring the weight of the first batch as a function of time for weathering intervals up to 4000 h, whereas control samples were taken from the second batch to investigate changes in the structure or composition. Room conditions were kept constant at 25 °C and 50% relative humidity by an air conditioning system. Non-reactive porous silica was

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