

# LOW PH CONCRETES PROCESSED USING SCCO<sub>2</sub>: APPLICATIONS IN NUCLEAR WASTE STORAGE DEVICES

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## ABSTRACT

Mortar and concrete play an important role in the engineered barrier system of the near field nuclear waste repositories. In these systems, problems appear within the course of time, when the water of the rock formation takes contact with concrete, being this an alkaline ion source that causes a series of physicochemical transformations in other components of the system and diminishes the confinement capacity of radionuclides. The final objective of this work is to improve concrete characteristics of permeability, durability and resistance through carbonation process using SCCO<sub>2</sub> as a reagent. First, the reaction of calcium ions with supercritical carbon dioxide in aqueous media was studied. After a deep understanding of the carbonation reaction, several cement types were carbonated at supercritical conditions. The *in situ* precipitation of calcite between the fibers of cellulose paper is also presented.

## INTRODUCTION

The demand for precipitated calcite, the most thermodynamically stable polymorph of calcium carbonate (CaCO<sub>3</sub>), has been rapidly growing in recent years in various fields of industry: paper, rubber, plastics, paint, food, etc. Industrial applications of CaCO<sub>3</sub> are determined by the strict control of a great number of parameters, such as average particle size, particle size distribution, morphology, specific surface area or polymorphism. The carbonation reaction (eq. 1), in which the CO<sub>2</sub> is bubbled through an aqueous slurry of slaked lime or portlandite (Ca(OH)<sub>2</sub>), is the most used industrial process for calcite precipitation [1].



At typical temperatures of industrial process (between 303 and 343 K), the precipitated powder is constituted by aggregates of scalenohedral individual particles. An analysis of the literature reveals the lack of methods that allow the morphological control of calcite precipitated without the use of additives. Therefore, the development of new industrial carbonation routes for the production of calcite with different morphologies (specifically rhombohedral shapes) in the absence of expensive additives is of great interest.

The aim of the first part of this work, has been to investigate if the controlled processing of slaked lime with gas, liquid and SCCO<sub>2</sub> could be a useful tool for calcite morphological control in the carbonation process. SCCO<sub>2</sub> has been used on an industrial scale for a number of processes, most notably as a solvent for extraction and for pharmaceutical particles engineering. Promising applications in bulk low-cost materials like (a) *in situ* precipitation of rhombohedral calcite between the fibers of cellulose paper for the papermaker industry, and (b) Portland cement strength improvement by SCCO<sub>2</sub> carbonation for immobilizing radioactive waste have been widely investigated in the second part of this work.

## MATERIALS AND METHODS

### Materials

Slaked lime was obtained from Cales de Llierca S.A. (Spain). Both pure CO<sub>2</sub> and mixtures CO<sub>2</sub>:N<sub>2</sub> were supplied by Carbueros Metálicos S.A. (Spain). Cellulose cotton paper (Albet 150, pore diameter 3-5 μm) was used for the *in situ* precipitation of calcite in the paper pores. Portland cements CEM I-sulfate resistant, with and without mineral addition, supplied by Cementos Portland S.A. (Spain), were used for the carbonation testing program. The cement is constituted by *ca.* 65 % of CaO, 20% of SiO<sub>2</sub>, 4% Al<sub>2</sub>O<sub>3</sub> and minor amounts of Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, MgO, K<sub>2</sub>O and Na<sub>2</sub>O. The sample with mineral addition has 56% CEM I-SR, 35% silica fume and 9% fly ash. Cement pastes were fabricated with a ratio of water/cement=0.4 and hydrated during 7 days.

### Process

*Calcite precipitation:* calcium carbonate crystals were induced to precipitate either *via* the diffusion of gaseous CO<sub>2</sub> through an atmospheric batch reactor or *via* the addition of compressed CO<sub>2</sub> into a high-pressure closed autoclave. The experimental set-up consisted of a high pressure stainless steel stirred cylinder of 25 mL capacity. The reactor was first charged with 10 mL of slaked lime suspension of concentration 170 gL<sup>-1</sup>. Precipitation under atmospheric conditions was carried out by bubbling a mixture of CO<sub>2</sub>:N<sub>2</sub> 20:80 (% v/v) in the open vessel. Precipitation under supercritical conditions was performed by introducing CO<sub>2</sub> to the upper space of the closed vessel up to working pressure (between 5 and 20 MPa) using a syringe pump (Thar Design, SP-240). Experimental conditions were maintained for 2 h.

*Calcite precipitation into porous cellulose paper:* a similar set-up and procedure as the one explained for calcite precipitation was used for the preliminary experiments on the impregnation of cellulose cotton paper with calcite. The paper was first added to the reactor together with 2 mL of Ca(OH)<sub>2</sub> suspension and the systems was equilibrated for 0.5 h under stirring in order to impregnate the cellulose with the slaked lime. Then, SCCO<sub>2</sub> was infused at 20 MPa and 318 K. 2-h batch runs were performed.

*Cement carbonation:* experiments were carried out in a high pressure apparatus with continuous CO<sub>2</sub> flow. Liquefied CO<sub>2</sub> was compressed to 20 MPa by means of a membrane pump (Lewa EK-M-210). Cement sample was introduced in a 10 mL tubular reactor placed into an air oven heated to 318 K. The system pressure was controlled with a back pressure regulator (Tescom 26-1761). After system stabilization, the experimental conditions were maintained for 2 h at low flow rate of CO<sub>2</sub>.

### Characterization

Samples composition was analyzed by X-ray diffraction (XRD) with a Rigaku Rotaflex RU200 B instrument. Micrographs were recorded in a scanning (SEM, Hitachi S-570) electron microscope. The specific pore volume (P<sub>v</sub>) distribution of cements was determined by low-temperature N<sub>2</sub> adsorption, using an ASAP 2000 Micromeritics INC.

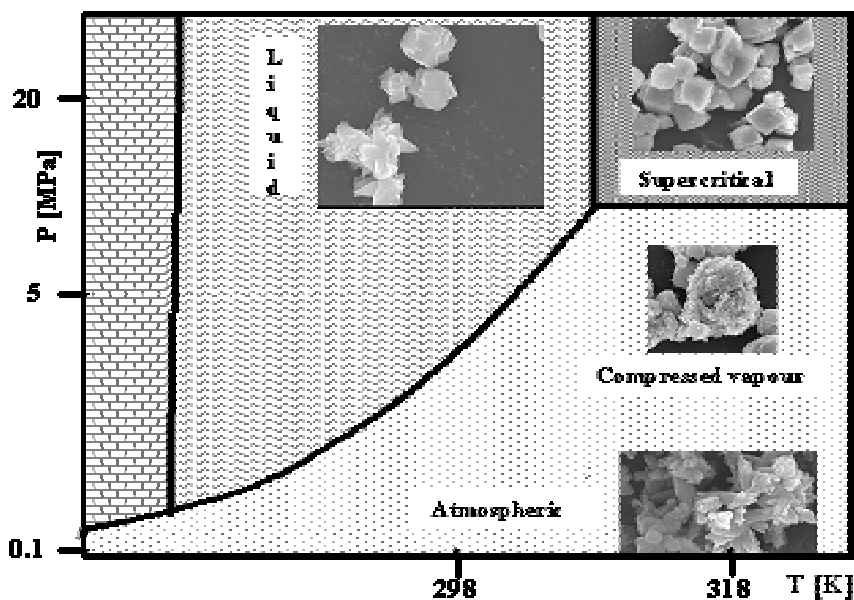
## RESULTS AND DISCUSSION

### Calcium precipitation

Powdered CaCO<sub>3</sub> was obtained by a precipitation processes from high concentrated Ca(OH)<sub>2</sub> suspensions, emulating the industrial carbonation process [1]. XRD analysis identified calcite as the CaCO<sub>3</sub> polymorph precipitated under all the operating conditions [2]. In the three-phase system, solid-gas-liquid Ca(OH)<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O, both the supersaturation and the ratio between the concentration of calcium and carbonate species ( $[Ca^{2+}]/[CO_3^{2-}]$ ) play an important role in determining the growth morphology of calcite crystals. Primary factors affecting the  $[Ca^{2+}]/[CO_3^{2-}]$  ratio in the crystallizing media are: i) the concentration of soluble

$\text{Ca}^{2+}$  which is controlled by the rate of dissolution of  $\text{Ca}(\text{OH})_2$ , and ii) the rate of  $\text{CO}_2$  dissolution and mass transfer into water to form available  $\text{CO}_3^{2-}$ . In experiments performed in this work, morphologic changes were induced by varying the  $\text{CO}_2$  concentration and, therefore, the ratio  $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$  in the bulk solution.

Rhombohedral morphology will be favored by enhancing the concentration of  $\text{CO}_3^{2-}$  species in the mother solution, which will reduce the ratio of  $\text{Ca}^{2+}$  excess. The first action to decrease  $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$  ratio was to enhance  $\text{CO}_2$  dissolution in water, accomplished by raising the working pressure. A reference series of 2-h runs was performed using dense vapor, liquid and supercritical  $\text{CO}_2$ . In the three experiments, pure rhombohedral calcite was precipitated, with a mean crystal size of 4-5  $\mu\text{m}$ , although marked differences on the crystals morphology were observed (Fig. 1). At 318 K and  $\text{CO}_2$  pressure of 5 MPa (compressed vapour) the microscopic examination of the precipitated crystals revealed agglomerated rhombohedral calcite. A further pressure increase to 20 MPa and dropping the temperature to 298 K (liquid) produced rhombohedral calcite with sharp steps. Finally, at 20 MPa and 318 K (supercritical) particles of rhombohedral calcite with smooth surfaces were observed. The smaller medium particle size was encountered for the system precipitated under supercritical conditions.

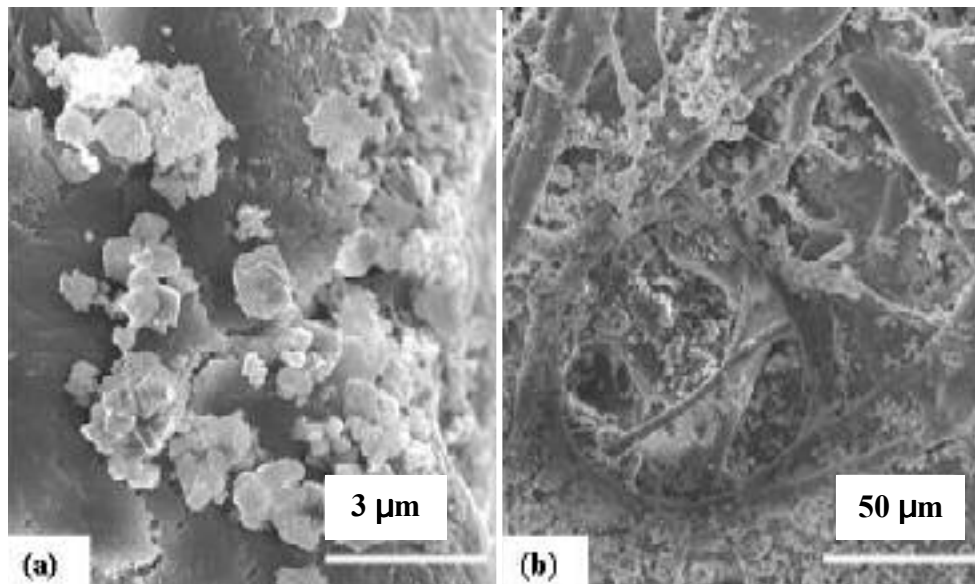


**Figure 1.** Morphology of the precipitated particles at different  $\text{CO}_2$  experimental conditions: atmospheric, compressed vapour, liquid and supercritical.

In general, the currently utilized manufacturing processes of precipitated calcium carbonate are slow, with low carbonation efficiencies. Scalenohedral forms are usually obtained and agglomeration can not be avoided without the use of additives. This work showed the possibility of precipitate rhombohedral calcite with a low degree of agglomeration by using  $\text{SCCO}_2$  as a reagent. The use of high pressure  $\text{CO}_2$  is also desirable for increasing reaction rate and carbonation efficiency. The use of dispersed rhombohedral calcite can be also relevant in higher added value applications ranging from cosmetics to biomaterials. The analysis of calcite precipitation under  $\text{SCCO}_2$  conditions was also performed with the aim of extending the application to the formation of composite materials containing fine crystals of  $\text{CaCO}_3$ . Examples are the *in situ* precipitation of rhombohedral calcite between the fibers of cellulose paper or inside the pores of alkaline Portland cement.

### Applications in the papermaking industry

In the specific case of the paper industry,  $\text{CaCO}_3$  has been increasingly used as filler, since *ca.* 80% of the world paper production has been converted to an alkaline papermaking process.  $\text{CaCO}_3$  improves some paper properties such as opacity, printing characteristics, luster and whiteness. In this process, particle shape and particle size distribution are two of the most important filler properties. For instance, paper filled with rhombohedral calcite is more easily processed than paper filled with scalenohedral calcite. Additionally, a narrow crystal size distribution is always preferred. In the actual industrial process,  $\text{CaCO}_3$  particles are added to the papermaking pulp suspended in water. Recently, several improved methods for the production of filler-containing paper pulp appear in which the filler is precipitated *in situ*. Among them, the Fiber Loading<sup>TM</sup> [3] process showed that fiber loading with calcium carbonate can be accomplished by an *in situ* reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{CO}_2$  in pressurized reactors (0.3-1 MPa) previously filled with paper pulp. In the present work, the precipitation process by infusion of  $\text{SCCO}_2$  was applied to the formation of calcite inside of the pores of cellulose paper. Under these experimental conditions, observation of the SEM micrographs indicated that the rhombohedral shape of calcite was precipitated (Fig. 2a). Particles bound to the cellulose fibers are evidenced very deep inside the pores (Fig. 2b).



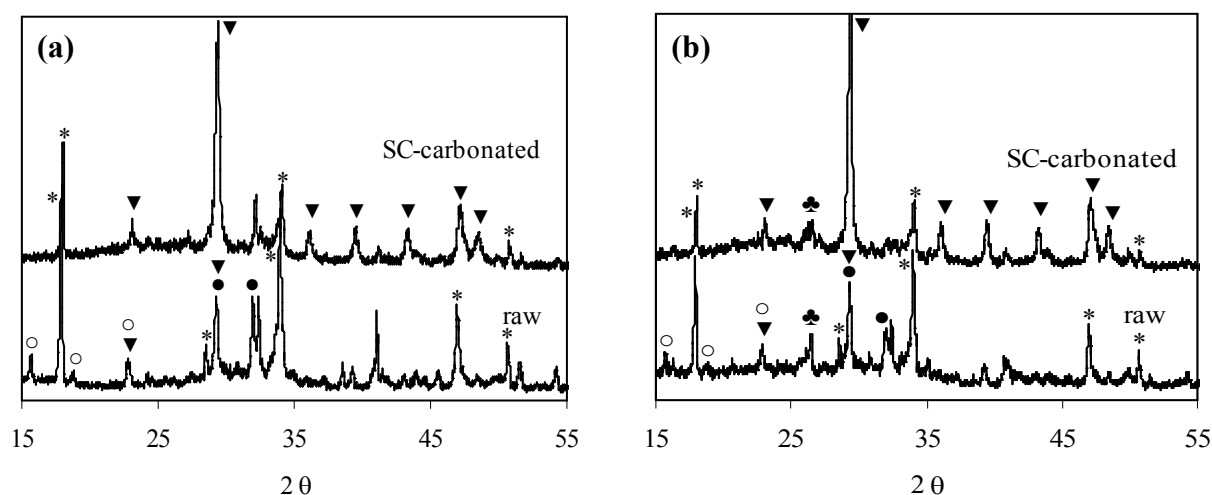
**Figure 2.** Hollow cellulose fibers impregnated with calcite *in situ* precipitated using  $\text{SCCO}_2$

### Applications in nuclear waste storage systems

Concrete is used in radioactive containment structures as a barrier, liner and encasement of containers. Recent improvements in concrete mechanical properties and compactness have been achieved by means of the optimization of the granular packing and the adjustment of pozzolans and other admixtures. Hence, this material has been suggested as a candidate for its use in deep geological repositories of nuclear wastes, in a potentially humid environment. However, leaching processes take place when concrete is in contact with groundwaters, leading to chemical and physical transformations of the concrete due to this interaction [4]. Carbonation of concrete consists in the chemical reaction between the  $\text{CO}_2$  present in the air and the calcium contained in the cement pore solution, in equilibrium with the hydration products. One of the main consequences of carbonation phenomenon is the

modification of the pH in the pore solution from a standard value between 12.5 - 13.5 for Portland cements, to a value below 9 in the carbonated zones. Many designs for radioactive waste confinement, particularly in deep geological underground disposal, envisage the presence of cementitious materials in conjunction with clay (bentonite) barriers [5]. In realistic conditions, relevant to high level radioactive waste repositories, confinement durability is limited by concrete interaction with clays, host-rock and groundwater. The evolution of the microstructure of cementitious materials in contact with groundwaters will vary depending on the type of cement used to produce concrete. The use of carbonated cements with a pH similar to that of the bentonite pores (7 to 9) will not cause instability in the clay. The final objective of this on-going work is to improve the physical properties of concrete porosity, permeability, mechanical strength and leachability through carbonation process using  $\text{SCCO}_2$  as a reagent [6,7].

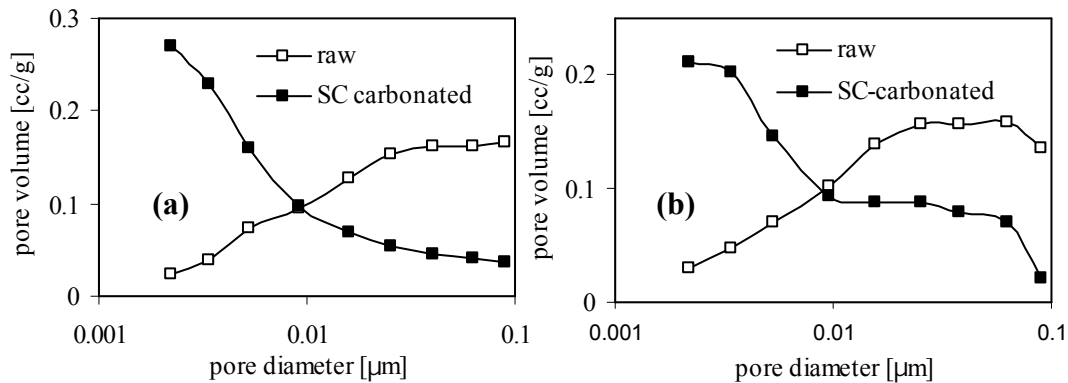
Carbonation leads to a progressive decalcification of the hydrated cement paste. This decalcification occurs when the calcium concentration decreases in the pore water because of the calcium consumption induced by the carbonation reaction (eq. 1). In atmospheric carbonation,  $\text{Ca}(\text{OH})_2$  is first dissolved, followed by calcium silicate hydrates (CSH) and ettringite or other calcium aluminosilicate hydrates. However, the mechanisms of carbonation process are different in function of the type of concrete [8]. The first non-expected result of this research was the observation of a different behavior when using  $\text{SCCO}_2$  as a reagent for cement carbonation: ettringite was the first totally carbonated species, while  $\text{Ca}(\text{OH})_2$  was still present in the media (Fig. 3).



**Figure 3.** XRD-patterns of raw and SC-carbonated (a) CEM I-SR, and (b) CEM I-SR with mineral addition ( $\text{Ca}(\text{OH})_2$ : \*; CSH gel: ●; ettringite: ○; calcite: ▼; mineral addition: ♣).

The carbonation starts from the cement surface and penetrates slowly into the interior of the grains. The rate-controlling step is the diffusion of the  $\text{CO}_2$  into the grain. When calcium carbonate precipitated into pores, the diffusivity of the matrix decreased. Moreover, the molar volume of  $\text{CaCO}_3$  is larger than that of  $\text{Ca}(\text{OH})_2$ , resulting in the closure and/or blockage of pores. Hence, the rate of carbonation reaction declines and thus, further carbonation in cement paste progresses slowly. Therefore, although the supercritical method reduces the necessary time for cement carbonation, the 2-h run applied in this work was not long enough to induce total carbonation of the samples. The BET method was used to calculate the pore volume distribution from the measured adsorption isotherms of the raw and

carbonated samples. Data indicate that the SC-carbonated samples had a significant larger part of the porosity attributed to pores with small pore radii. This effect is expected to reduce the sample permeability (Fig. 4).



**Figure 4.** BET adsorption pore volume plots ( $dV/d\log D$ ) for raw and supercritical carbonated (a) CEM I-SR, and (b) CEM I-SR with mineral addition.

## CONCLUSION

In general, the currently utilized manufacturing processes of precipitated calcium carbonate are slow, with low carbonation efficiencies. This work showed the possibility of precipitate rhombohedral calcite with a low degree of agglomeration by using  $\text{SCCO}_2$  as a reagent. Given logistical considerations, quality needs and filler cost determine the choice of filler composition and morphology for each application. Preliminary results showed also the possibility of rhombohedral calcite precipitation within the pores of a fibrous material. The final objective of this work is to improve concrete characteristics of durability and resistance through carbonation process using  $\text{SCCO}_2$  as a reagent.

## ACKNOWLEDGES

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