Chemically Active Silica Aerogel−Wollastonite Composites for CO₂ Fixation by Carbonation Reactions

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Carbonation reaction from the dissolution of minerals, mainly silicates, is an option for long-term storage of CO₂, offering capacity exceeding that of other strategies, and certain advantages such as the formation of insoluble and inert products. This study presents the results of carbonation reactions utilizing silica aerogel−wollastonite composites. The procedure for synthesis of the precursor powders with wollastonite stoicheiometry, as well as the compositional and textural features of the resulting composites, was examined first. The kinetic and efficiency of carbonation reactions in aerogel−wollastonite composites were also determined. X-ray diffraction quantitative analysis and thermogravimetric analysis were used to determine the proportions in percent of the resulting carbonate phases. The conversion reaction reaches values above 81% in composites with CaO content of up to 40% by weight, after 40 min of reaction time. The conclusion is that these aerogels, offering a very high specific surface area, are attractive potential materials for CO₂ sequestration and as a supporting material for fast carbonation reactions.

Introduction

The increasing influence of anthropogenic CO₂ emissions on climate change and associated environmental effects are stimulating the search of technologies for CO₂ sequestration as an alternative for emission reduction. The main strategies currently under study involve long-term storage in geological reservoirs, both terrestrial and oceanic,[1] as well as the conversion of CO₂ into solid materials that are more thermodynamically stable.[2−5]

Permanent disposal based on carbonation reactions, a procedure also known as mineral sequestration,[6] is one of the most promising ways currently being studied for CO₂ sequestration. This process is similar to a natural mechanism known as *rock weathering*[7] that has regulated the atmospheric CO₂ over geological time. In natural systems carbonation takes place through the dissolution of minerals, mainly silicates, thus forming the corresponding carbonates and a solid byproduct, namely amorphous silica.

The design of materials for long-term CO₂ sequestration based on carbonation reactions first requires the formation of thermodynamically stable carbonates. Thus, most processes currently under research focus on metal oxide-bearing materials containing divalent cations, usually alkaline-earth metals or ferrous iron. Wollastonite, $CaSiO_3$, olivine, Mg_2SiO_4, and multioxide silicates, such as serpentine $Mg_3Si_2O_5(OH)_4$[7−9] or glauconite clays[1] incorporating iron and magnesium, are usually employed for this purpose. Silicates containing only alkali metals (such as sodium and potassium) are usually discounted because the corresponding carbonates are very soluble in water.

However, although carbonation is in theory a promising way for sequestering significant amounts of CO₂, the main challenges at the present moment are the development of economically viable processes.[10] Mineral carbonation starting from natural silicates is a slow process that must be kinetically enhanced to make this procedure useful for practical purposes. In aqueous systems, the divalent cation dissolution from the precursor silicates seems to be the main rate-limiting step, and most research efforts have been devoted to finding ways to speed-up the cation extraction from the precursor materials.[11,12]

Several strategies are being used to achieve this goal. Among others, these include the use of microemulsions and/or layered mineral phases, previously activated to make these materials more reactive.[13] In addition to the use of natural silicates, considerable effort is being devoted to the design and synthesis of new products and processes that can improve the reaction rates and optimize the efficacy of CO₂ sequestration.[14]

Given the above considerations, our work is focused on the analysis of aerogels with high specific surface area as the supporting material for fast carbonation reactions. Aerogels are nanoporous materials made by a sol−gel process[15] followed by drying at supercritical conditions.[16−18] They present very fine porosity and are very dense when they are produced with the assistance of ultrasound during preparation of the wet gel.[19,20] Also, aerogels can be moulded to any shape, size, and chemical functionality.[21] These properties make aerogels attractive materials for use in the adsorption, capture, and sequestration of pollutant gases. For the particular purpose of CO₂ fixation, the addition of an active divalent cation silicate, such as wollastonite, is necessary to promote the CO₂ speciation and its subsequent capture via carbonation reactions in a solid stable phase. Synthetic wollastonite powders have been incorporated into

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TEOS
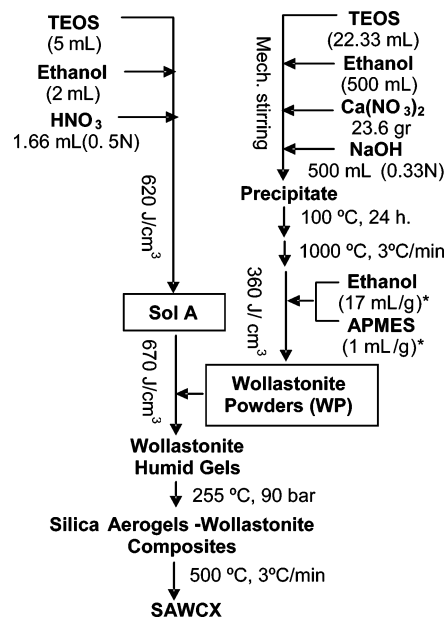(5 mL)

Ethanol
(2 mL)

HNO$_3$
1.66 mL(0.5N)

TEOS
(22.33 mL)

Ethanol
(500 mL)

Ca(NO$_3$)$_2$
23.6 gr

NaOH
500 mL (0.33N)

Mech. stirring

Precipitate

100 °C, 24 h.

1000 °C, 3°C/min

620 J/cm^3

360 J/cm^3

Ethanol
(17 mL/g)*

APMES
(1 mL/g)*

Sol A

670 J/cm^3

Wollastonite
Powders (WP)

Wollastonite
Humid Gels

255 °C, 90 bar

Silica Aerogels -Wollastonite
Composites

500 °C, 3°C/min

SAWCX

Figure 1. Flowchart showing the routes for synthesis of the studied materials. (*) Ethanol and APMES volumes indicated were used for 1 g of precipitate powder. The different values of energy density submitted by ultrasound are described in J/cm^3 at the various different steps in the whole process. A device delivering to the system 0.6 W·cm^{-3} of ultrasound power was employed.

silica aerogels by a sol–gel process, and silica aerogel–wollastonite composites with different concentrations of powders were prepared. The efficacy of these materials in the capture of CO$_2$ has been investigated.

Experimental Section

Processing and Experimental Methods. Powders with wollastonite stoicheiometry were prepared by controlled hydrolysis and polycondensation of the appropriate amounts of tetraethoxysilane (TEOS) and tetrahydrated calcium nitrate Ca(NO$_3$)$_2$·4H$_2$O. These reagents were dissolved in an ethanol solution, and then NaOH was added until powder precipitation took place. The powder was extracted by centrifugation, washed (several times) in distilled water and ethanol, and finally dried at 100 °C. Once dried, the powder was heat-treated in air at 1000 °C for 2 h; the heating rate was 3 °C/min. Prior to their inclusion into the gel, the powder surface was chemically modified with 3-aminopropyltrimethoxysilane (APMES) in order to facilitate and stabilize a colloidal dispersion into the host matrix. The mixture APMES/powders was diluted in ethanol with the assistance of ultrasound. A device delivering to the system 0.6 W·cm^{-3} of ultrasound power was employed[15.] The total energy dissipated in this step was 360 J·cm^{-3}. The slurry was added under ultrasonic agitation (670 J·cm^{-3}) to a sol previously elaborated by hydrolysis and polycondensation of TEOS, which resulted in a gelling time short enough to avoid decantation of the powders. This treatment, together with the control of gelling time, ensured the homogeneous distribution of the powder throughout the gel. Finally, the gel was placed in an autoclave to obtain the aerogel by supercritical extraction with ethanol. This procedure for the synthesis of the precursor powders, as well as the aerogel–wollastonite composites, is presented in Figure 1.

Three samples were studied: wollastonite powders heat-treated at 1000 °C (WP), and two silica aerogel–wollastonite composites prepared by adding 2.4 and 10 g of WP to the sol A as described in the synthesis flowchart. These mixtures give

Table 1. Characteristics of the Samples

sample	chemical composition		textural characteristics	
	CaO, %	SiO$_2$, %	specific surface area (m^2/g)	porous volume (cm^3/g)
WP	43	55	0.92	0.002
SAWC26	26	68	319.0	0.611
SAWC40	40	55	93.7	0.262
SiO$_2$-aerogel	-	97	1055.2	2.18

rise to composites containing 26 and 40 wt % of CaO, which were further heat-treated at 500 °C; from now on in the text, these are referred to as SAWCX with X being the CaO wt %. The composition of the most CaO-rich composite is close to the stoicheiometry of pure wollastonite.

The experiments for monitoring the fixation of CO$_2$ were carried out in a reactor under agitation. This device consists of a plastic container isolated from the external atmosphere by means of a hermetic stopper, which is pierced and through which a pH electrode is inserted to monitor the variation of this parameter. The container is connected to a CO$_2$ tank through two valves for the entry and exit of CO$_2$.

The samples (0.5 g) were ground and dispersed in distilled water (25 mL) and then submitted to gas flow under atmospheric pressure and temperature. The experiments consist of the injection of successive doses of CO$_2$ during 40 min, and the reactor is then left at rest overnight before checking the degree of carbonation of the wollastonite materials. After the samples were placed in the reactor and when the pH of the solution reached 10.5, they were submitted to CO$_2$ flux. The pH was monitored during the experiment. After 15 min, its value decreases monotonically down to 6.3–6.5. This value then remains stable until the experiment is completed. A pH microsensor (10 μm tip Unisense) was employed to monitor the onset of the composite dissolution process from the inner part of the aerogel body during the carbonation experiments.

Prior to testing the capacity of the silicate hosted in the aerogel matrix to sequester CO$_2$ gas, several techniques were used for the characterization of the powders. The compositional and textural features of the samples (see Table 1) were determined by X-ray fluorescence (Bruker S4 Pioneer model) and the Brunauer-Emmet-Teller (BET) method (Sorptomatic 1990, CE instruments), respectively.

X-ray diffraction (XRD) experiments were performed on a Bruker diffractometer (D8 Advance) with graphite monochromator and Cu K$_\alpha$ radiation. The intensities were measured in a 2θ range (5–50°) with a step of 0.2° and a counting time of 1 s per step. Quantitative phase analysis (QPA) of the crystallization products was done following the Rietveld method.[22] This analysis was applied to characterize both the composition of synthetic wollastonite powders and the relative amount (wt %) of carbonate phases obtained from carbonation reactions. The Fullprof program was employed in all calculations.[23] For the particular purpose of QPA, the structural model was kept unchanged during refinements, so only instrumental and profile parameters were refined: (i.e., diffractometer zero, background, scale, cell dimensions). A pseudo-Voigt function was employed to model the profile intensities. The average size of crystallite domains was determined by the Scherrer method from the reflection broadening, based on the analysis of the Lorentzian part of this pseudo-Voigt function.

Results and Discussion

Figure 2 illustrates the sequence of phase transformation by temperature during the preparation and synthesis of the powders.

Table 2. Analysis of the Samples at the End of Carbonation Reaction

| sample	reaction time (min)	QPA. Rietveld method (wt %)[b]			thermogravimetric analysis: AWL/MTWL[c] (wt %)
		calcite	wollastonite 1T	wollastonite 2M	
WP	25	32.40 (3)	3.82 (2)	63.78 (2)	9/24.3
WP	40	51.16 (3)	1.12 (2)	47.71 (2)	13/24.3
SAWC40	40	81.06 (3)	1.83 (2)	17.10 (2)	20/24
SAWC40[a]	40	81.00 (3)	2.15 (2)	16.86 (2)	20/24
SAWC26	25	100	−	−	−

[a] Corresponds to repeated experimental runs. [b] E.d.s. is in parenthesis. [c] Actual weight loss/maximum theoretical weight loss.
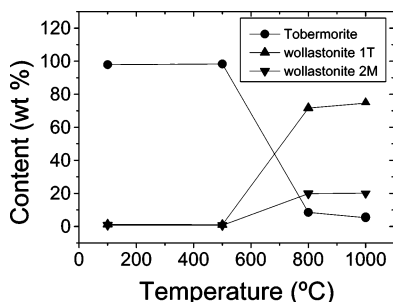
Figure 2. Temperature phase transformation pathways of synthesized powders resulting from Rietveld refinements.
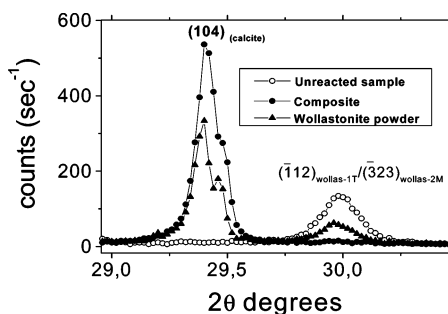
Figure 3. Raw XRD spectra showing the intensity differences in the (104) calcite reflections as a result of the different efficiency in carbonation reaction of composite relative to WP.

This graph is based on data resulting from the Rietveld analysis of four X-ray diffraction patterns obtained in a high-temperature chamber (Anton Paar HTK1200) at 100 °C, 500 °C, 800 °C, and 1000 °C. At the two lower temperatures (100 °C and 500 °C), a major amorphous component was differentiated, although a broad crystalline phase is also present. This was identified as tobermorite, $Ca_5Si_6O_6(OH)_2$ (Pattern Diffraction File, PDF, no. 01-089-6458). At the higher temperatures (800 °C and 1000 °C) both the amorphous and the hydrated silicates disappear. At these temperatures, a mixture of both polytypes of wollastonite, triclinic (1T) and monoclinic (2M) wollastonite, gives the final products (PDF no. 01-072-2284 and 01-072-2297, respectively).

The synthesized powders were further tested for CO_2 fixation both alone and hosted in the aerogel matrix. Figure 3 shows the raw XRD spectra for the unreacted sample, together with that resulting from the 40 min carbonation reaction applied to both wollastonite powders (WP) and composites (SAWC40). The extent of carbonation reaction resulting in $CaCO_3$ (as calcite, PDF no. 00-005-0586) was determined in both materials by QPA following the above procedure. The results from the QPA indicating the amount of wollastonite transformed into calcite, for several reacting times, in both powders (WP) and composites (SAWCX), are summarized in Table 2.

After the first dose was applied, the amount of resulting carbonate was additionally determined by thermogravimetric analysis (TGA) in air (Setaram Setsys 16/18). Thus, Figure 4 shows the weight loss of the sample SWAC40. A peak can be
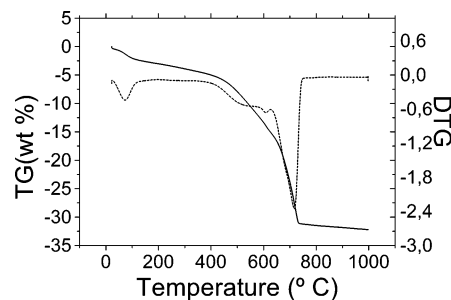
Figure 4. TGA and DTG curves of the composite SAWC40.

observed in the differential curves (TGA and DTG) between 535 °C and 750 °C related to the decomposition of the carbonate, according to a previous analysis of a pure carbonate.

From the detailed analysis of these data, the efficiency of the conversion reaction that takes place inside the reactor can be evaluated. In this reaction 1 mol of wollastonite is converted into 1 mol of calcite according to

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad (1)$$

Taking into account the composition of sample SAWC40, the maximum theoretical weight loss (MTWL) caused by CO_2 release would be about 24%, if all the wollastonite reacted to form calcite. The actual weight loss (AWL) is approximately 20%. This result is presented together with those obtained from the rest of the samples in Table 2, all of them being equivalent to the wollastonite/calcite transformation values determined by XRD.

Two important conclusions, at least, can be drawn from these results. First, the performance of the composites in CO_2 capture is better than that of the powders. This demonstrates that the dispersion of wollastonite powders in the aerogel matrix greatly enhances the kinetic of silicate dissolution; second, the efficiency of the carbonation process observed in the SAWC40 sample is much higher than that reported by various authors working on samples made of natural wollastonite,[7−9] this conversion rate being about 33% faster than that obtained with other natural silicates.[3] Moreover, the reactor setup has the advantage of simplicity because it does not require any special experimental conditions in contrast to the previously reported processes involving careful control of the solution chemistry as well as high pressure and high temperature conditions.[9,13]

The analysis of the factors influencing the carbonation reaction in the studied material is also of particular interest. The high efficiency obtained can be related to the high rate of wollastonite dissolution followed by the fast release of Ca^{2+} ions to the solution. This speed of reaction produces a rapid increase of the solution pH,[24] which is dependent on the specific surface area of the silicate.[25] This dissolution process can be considered a consequence of the synergetic association of two main factors. First the nanometric size of the wollastonite crystals, which in turn increases the reactive surface and, second, the homogeneous space distribution of crystals provided by the
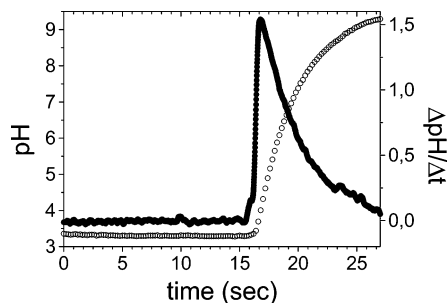
Figure 5. Time lag for the onset of the wollastonite dissolution as measured by pH-microsensors with a spatial resolution of 20 μm. representing pH(t) (open circles) and ΔpH(t)/Δt (black circles).

aerogel support, which is useful in avoiding the production of retarding films.

Figure 5 shows the time evolution of the pH as measured by a microsensor placed in the inner part of the aerogel body. As can be seen, the induction time for the onset of wollastonite dissolution, marked by a sharp increase of pH, is only a few seconds. As the wollastonite dissolution continues, the pH of the solution is furtherly stabilized at 10.5, as result of the production of monomers from the release of silicic acid.[24] When the solution is submitted to CO_2 flux, a sharp decrease of the pH follows and it progressively tends toward a stable value of 6.3 until the silicate is fully consumed. The above process rapidly induces the first and second deprotonations of the carbonic acid (HCO_3^- and CO_3^{2-}) and consequently speeds up the carbonation reaction that is kinetically controlled by the concentration of CO_3^{2-} specie in the solution.

As can be seen (Figure 6), the width of the needles that form the synthesized wollastonite particles are of a few tenths of nanometers. This aspect was carefully examined in two ways. First, pore distribution from Hg porosimetry (inset in Figure 6) indicates a sharp peak between 6 and 10 nm radii. According to the micrograph in Figure 6, this peak accounts for the irregular surface resulting from the acicular texture that can be observed. The second part of the curve formed by maximum centered at
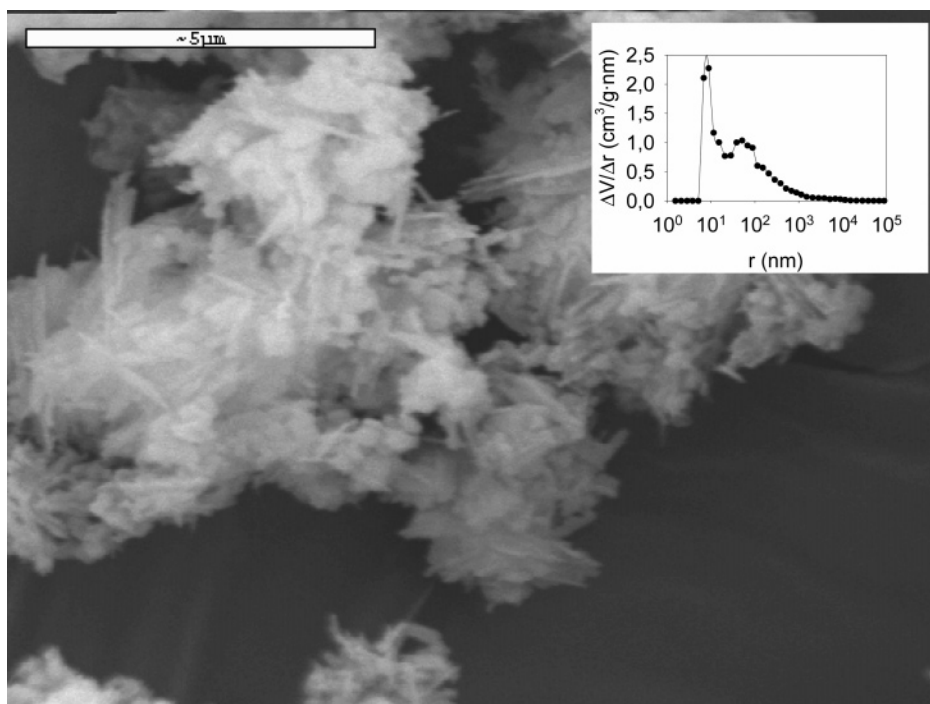
~60 nm followed of a long tail corresponds to a hierarchical distribution of aggregates from ~400 nm size to few tenths of micrometers. The long tail of this distribution accounts for pores between agglomerates. Second, the average crystallite size was calculated from the reflection broadening in the XRD spectra by using the Scherrer equation. The results from this analysis give average sizes values of 61 and 40 nm, respectively, for the triclinic and monoclinic wollastonite polytypes.

The SEM micrograph of the SAWC40 aerogel-wollastonite composite (Figure 7) shows the homogeneous dispersion of the wollastonite particles in the silica matrix. The BET analysis of the samples, Table 1, confirms as well that this method permits the production of composites that retain their properties of high porosity and specific surface area. Unlike the synthetic wollastonite powders alone or the natural wollastonite sample, these properties of the composites ensure the complete dissolution of wollastonite grains during the carbonation reaction. This avoids the formation of a film of precipitate that could slow down or completely inhibit the process.[1,21] Finally, other notable advantages of these aerogels are the ease with which they can be manipulated and their chemical functionality. The synthesis of a composite with this stoicheiometric composition (SAWC40) acts as a true reservoir of Ca (II) ions, presenting a concentration close to that of the natural samples, for which the proportion of CaO is approximately 44%, and close also to that of synthetic powders (WP). The composite SAWC40, however despite having a lower CaO content, gives a better performance due to its porosity and high specific surface area. In this way, without any special experimental condition, a very short time of carbonation is required, ~40 min, that represents a yield of 0.43 kg of CO_2/kg of $CaSiO_3 \cdot$h.

In the present state of this research, the analysis of the carbonation reaction is being performed at a laboratory scale, where high purity chemicals are used, and consequently a direct extrapolation based on the laboratory costs to a large scale experiment is unlikely. At the moment, this results in a noncompetitive material regarding the average cost of the
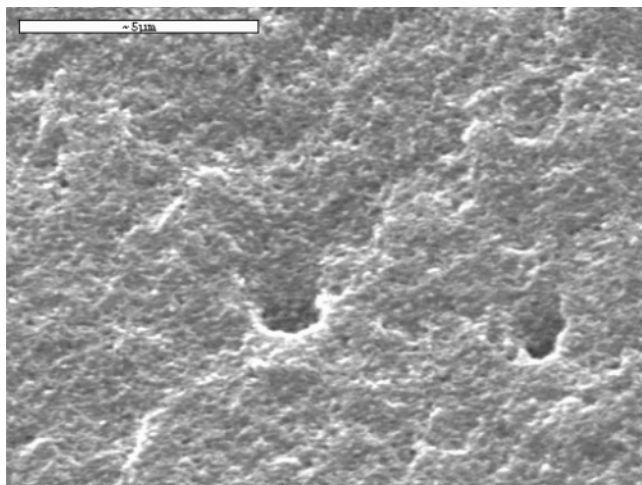

Figure 6. SEM image of wollastonite powders (WP) where their acicular texture can be observed. The inset corresponds to the pore size distribution from Hg porosimetry.

Figure 7. SEM image of SAWC40 aerogel−wollastonite composite. Homogeneous distribution of wollastonite can be observed throughout the aerogel.

reported industrial CO_2 fixation by the carbonation process. Nevertheless a rough estimation of the cost[26] based on the processing of industrial material and energy consumption suggests that the final cost of large scale CO_2 capture will be nearly in the same order of most of carbonation processes from activated materials. It must be a goal of the future to test initial materials that reduce costs.

Conclusion

In summary, the synthesis of silica aerogel−wollastonite composites permits large amounts of CaO to be hosted. This processing allows the composite to maintain the textural characteristics of aerogel that are found to be very efficient in the process of sequestration to eliminate CO_2. The intrinsic properties of these aerogel composites accelerate the carbonation kinetics under normal conditions of pressure and temperature, in comparison to their natural counterpart. With no special experimental condition required, only a very short time (40 min) is necessary for carbonation. Moreover, a high rate of wollastonite → calcite conversion has been observed in comparison with the times and rates obtained in natural samples. The conversion reaction, referring to the mineral phase hosted in the aerogel matrix, attains values above 81% in composites with CaO content of up to 40% by weight. As a result, these aerogels with very high specific surface area prove to be attractive materials for CO_2 sequestration and as a supporting material for fast carbonation reactions. We consider this methodology economically viable on the basis of reduction in price of the starting materials.

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