Enhancement of a $\text{CaO}/\text{Ca}(\text{OH})_2$ based material for thermochemical energy storage

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Abstract

The application of hydration/dehydration reactions of $\text{CaO}/\text{Ca}(\text{OH})_2$ to thermochemical energy storage systems can be facilitated by the development of Ca-based materials with improved mechanical properties when compared to the natural Ca-precursor, while maintaining good chemical activity. For this purpose, we are developing composite materials for fluidized bed or fixed bed applications synthesized using sodium silicate to bind fine $\text{CaO}/\text{Ca}(\text{OH})_2$ particles. In this work, the mechanism of decay in the mechanical properties of the resulting CaO/Ca -silicates composites over hundreds of hydration/dehydration cycles has been investigated. Based on the observed mechanism, improvements to the method of synthesis of the materials have been introduced, in order to retain the original carbonate grain volumes, which are larger than those of the equimolar quantity of the expanding $\text{Ca}(\text{OH})_2$ during hydration. A noticeable improvement in the mechanical stability of the resulting pellets was observed when the material was exposed to temperatures of around 880°C in pure CO_2 before calcination in order to avoid the decomposition of CaCO_3 during the formation of the hard Ca-silicates that provide mechanical strength to the composite. Further gains in mechanical stability

were achieved by avoiding the complete hydration of the CaO grains in the composites. These results confirm the primary role of Ca(OH)_2 anisotropic expansion as the main cause of the reduction in crushing strength of the pellets. It can be concluded that the formation of calcium silicates as binders of CaO rich grains is a promising route for the development Ca-based composite materials. However, more effort is still needed to overcome the decay in performance observed after several hundreds of cycles.

Keywords: thermochemical energy storage; composite material; calcium oxide; sodium silicate

1. Introduction

Concentrated solar power (CSP) is one of the main elements in any portfolio of renewable energies intended to decarbonize the energy system during the XXI century (IEA 2014a; IPCC 2014; IRENA 2015). Built-in energy storage technologies are undergoing intensive development because they allow CSP plants to supply power on demand (IEA 2014c). Of the different concepts for energy storage under investigation, thermochemical energy storage systems are considered by many authors as highly promising due to their high-density and potential for low-cost energy storage (see reviews by (Cot-Gores et al. 2012; Gil et al. 2010; Kuravi et al. 2013; Pardo et al. 2014b; Xu et al. 2014). In these systems, a reversible chemical reaction is used to store thermal energy in the form of chemical compounds. Depending on the properties of the thermochemical reaction, energy can be discharged at different temperatures. Currently, the major challenges of these systems are related to the stability of the material, as well as the development of effective, low cost reactor and control technology (IEA 2014b; Kuravi et al. 2013; Xu et al. 2014).

The CaO/Ca(OH)₂ hydration/dehydration reaction couple has been studied as a suitable thermochemical energy storage system by a number of authors (Azpiazu et al. 2003; Bauerle et al. 1976; Criado et al. 2014a; Ervin 1977; Kanzawa and Arai 1981; Pardo et al. 2014a; Schmidt et al. 2014). The basic conceptual design of this system is based on two steps, an initial hydration of CaO during which useful thermal heat is released at high temperatures (above 400°C). The material is then regenerated by supplying heat from the solar field to drive the dehydration of Ca(OH)₂. The high reaction enthalpy ($\Delta H^\circ_{298K} = -109$ kJ/mol), the fast reaction rates and reversibility, the appropriate temperatures required during the hydration and dehydration reactions under pure atmospheres of steam (400-550°C) for coupling with typical CSP systems based on tower technology and the low-cost material make this system an attractive thermochemical energy storage technology for CSP.

One of the main drawbacks of CaO/Ca(OH)₂ reversible systems is related to the poor mechanical properties of the material. It is well known that CaO particles obtained from the calcination of CaCO₃ from natural sources show a strong tendency to attrite (Materić et al. 2010; Scala et al. 2013) and to break during intense hydrations/dehydrations (Glasson 1958). Since CaO/Ca(OH)₂ particles or pellets will be in contact with a large flow of steam and/or air during the thermochemical reactions, a prerequisite for the development of this technology is that the material should preserve its mechanical integrity in order to minimize entrainment of the material by the gases and large pressure drop. This mechanical requirement is equally valid for fixed (Kanzawa and Arai 1981; Schaube et al. 2013; Schmidt et al. 2014) or fluidized bed reactors (Criado et al. 2014a; Ervin 1976; Pardo et al. 2014a), that are proposed for

undertaking the hydration and dehydration reactions in continuous mode. The use of very fine Ca(OH)_2 materials with improved fluid-dynamic properties by adding nanoparticles (Roßkopf et al. 2015) has also been recently proposed.

Various proposals for improving mechanical properties of Ca-materials for use in thermochemical energy storage applications have been studied in the past. Most of the synthesis routes have consisted in the cementation or pelletization of Ca-particles using a binder or a dopant. In principle, these routes allow a higher Ca content and therefore higher energy storage densities, compared to Ca-particles supported on a porous material. The chemical and mechanical stability of Ca-based pellets obtained from CaO and Ca(OH)_2 powders doped with additives such as Al, Zn or Cu have been tested with only limited improvements to the macrostructural integrity of the materials (Fujii et al. 1994; Sakellariou et al. 2015). A recent work (Hara et al. 2013) describes a synthesis procedure for obtaining cemented materials based on the use of a clay (sepiolite) as a binder of a thermochemical energy storage material (e.g. CaO). The materials obtained following such synthesis procedures show improved mechanical properties thanks to the silicates formed after the reaction of these two components at high temperatures. Other similar materials for thermochemical energy applications have also been developed using sodium silicate ($\text{Na}_2\text{Si}_3\text{O}_7$) as binder (Bauerle et al. 1976). The main advantages of using sodium silicate for this application are its high temperature resistance, low cost and high mechanical strength when it is mixed with limestone materials, in particular when treated at high temperatures due to the formation of hard calcium silicates (McDonald et al. 2007; Taylor 1997).

In a previous work (Criado et al. 2015), we screened some synthesis conditions and evaluated composite materials rich in CaO/ Ca(OH)_2 using sodium silicate as a binder. Reactions between CaO and $\text{Na}_2\text{Si}_3\text{O}_7$ during the calcination of the material at high

temperatures were confirmed, Ca_2SiO_4 and $\text{Na}_2\text{CaSiO}_4$ being the main silicate species observed. The formation of these calcium silicate products from quantitative reactions between the binder and the CaO provided the material with a very high crushing strength (CS of over 17-18 N compared to values of 3-4 N measured for the natural calcined limestone precursor). The screening test made it possible to minimize the mass fraction of binder needed to manufacture strong pellets (molar ratios of Ca to Si, $r_{\text{Ca/Si}}$, of between 4.8 and 6.2, that will reduce the energy storage density of the resultant material by about 50%, when compared to pure CaO). The superior crushing strength values observed during the first cycles were compatible with fast reaction rates and high conversion values of around 0.6-0.7 mol H_2O absorbed per mol of total Ca. However, crushing strength values higher than 7 N could be only maintained after 100 cycles for the most suitable composite materials tested, while for certain pellets the CS decreased to values below 5 N after just 20 cycles.

The present work describes a further attempt to develop these kinds of composite materials. First, the main mechanism responsible for the decrease in the crushing strength values observed over cycling must be established and on the basis of the results the synthesis protocols can be refined and materials with a higher mechanical stability obtained.

2. Experimental section

2.1. Composite materials synthesis

As described in more detail elsewhere (Criado et al. 2015), the composite materials used in this work were synthesized as a mixture of an aqueous sodium silicate solution (reagent grade, ~10.6%w Na_2O , ~26.5%w SiO_2 and ~62.9%w H_2O from Sigma-Aldrich Co. LCC) with two different CaCO_3 as Ca-precursors, Imeco limestone (98.7%w CaCO_3) with a particle size (d_p) fraction of between 36 and 63 μm and reagent quality

co-precipitated calcium carbonate (Merck KGaA $d_{50}=14\text{ }\mu\text{m}$). Different mixtures of binder and Ca-precursors with molar Ca:Si ratios ($r_{\text{Ca/Si}}$) of between 1.5 and 9.7 were manually mixed at ambient temperature. The resultant slurries were used to form cylindrical pellets (2-3 mm long and 2 mm in diameter) that were slowly cured in an oven to release the water present in the $\text{Na}_2\text{Si}_3\text{O}_7$ solution. The curing procedure consisted of three steps in order to avoid debilitating bubble-like formations in the material due to the fast release of water: (i) heating up to 80°C ; (ii) maintenance of this temperature during 15 min and then at 110°C during 15 min and (iii) increasing the temperature to 400°C at a heating rate of $2^\circ\text{C}/\text{min}$.

In our previous work (Criado et al. 2015), and in order to ensure a fast reaction between the Ca-precursor and the sodium silicate before cycling it for hydration/dehydration, the cured pellets were subjected to a calcination reaction at 850°C in air for 10 min. In order to compare the results of the present study with the previous work, we will consider as the reference material the one obtained through the calcination step under air at 850°C . In order to explore new methods to improve the mechanical properties of such reference material, , the effect of a high initial temperature ($750\text{-}880^\circ\text{C}$) under pure CO_2 was evaluated as a new synthesis route, as will be discussed in section 3. The resulting pellet was then calcined under air at temperatures between $700\text{-}850^\circ\text{C}$ before starting the series of hydration/dehydration cycles.

2.2. Thermogravimetric analysis over cycling

After the air calcination step, the composite materials containing free CaO grains surrounded by a strong calcium silicate structure were tested for hydration/dehydration cycles under realistic operating conditions for their use in energy storage applications. For the reference cycling tests, the hydration reaction was performed under pure steam at 450°C while two different operation conditions have been evaluated for the

dehydration step: pure steam at 550°C or air at 500°C. However, and in order to study the kinetic behavior of these materials, a few tests were performed at other temperatures between 450 and 550°C as well as at different partial steam pressures, as reported below. The reaction times (t_{Hy} and t_{Dehy}) for each cycle in most tests were selected from between 0.5 and 5 min, but in some of the tests the effect of this variable was investigated by applying hydration/dehydration times as long as 400 min.

The thermogravimetric equipment (TG) used for cyclic experiments has been described in detail in previous works (Criado et al. 2014b; 2015). The sample inside a platinum pan hangs in a quartz tube (2.5×10^{-2} m) situated in an oven that can operate at temperatures up to 1000°C. The reaction gases (H_2O , CO_2 and/or air) are introduced through the bottom of the quartz tube at a total gas flow of 7.3×10^{-6} m³/s (at standard temperature and pressure), which is equivalent to a gas velocity of 0.05 m/s at 500°C around the sample mass. This high velocity avoids the presence of external mass transfer diffusion resistances during these tests. An in-house built steam generation line coupled to the TG allows the mixtures of H_2O and air or pure steam to be introduced through a heated up pipe (by means of heating cords up to 400°C). A measured flow of liquid water from pressurized bottles is supplied to the system. A uniform and steady steam flow is achieved with this system which is aided also by filters placed along the heated pipe and a needle valve that creates a dampening effect. To avoid disturbances during the tests, the steam is continuously generated and introduced into the TG or removed from the system through a pneumatic valve.

10-15 mg of sample (one single pellet) was used when only the chemical properties of the material were studied, and around 50 mg (3-4 pellets) when the evolution of the mechanical behavior was evaluated by measuring the crushing strength (CS) of the pellets after different numbers of cycles. Reference values of 10, 40 and 200 cycles

were chosen as benchmark in order to be able to compare between different materials and testing conditions.

The chemical activity of the material over cycling was evaluated from TG measurements by estimating the hydration/dehydration molar conversion of the total Ca present in the composite (X_{Hy} and X_{Dehy}) as well as the weight fraction or the total H_2O absorption capacity (equivalent to 0.321 for pure CaO). Another useful conversion variable characteristic of the composite is $f_{CaO, exp}$, defined as the fraction of active CaO (i.e. only the “free CaO” that is able to hydrate to $Ca(OH)_2$ in the composite) thus:

$$f_{CaO, exp} = N_{Ca, active} / N_{Ca, total} \quad (2)$$

where $N_{Ca, active}$ is the mol of Ca active in the sample as CaO able to hydrate and $N_{Ca, total}$ is the total mol of Ca present in the sample.

Figure 1 represents a typical cycling test performed in the TG where the raw data recorded in the computer in the form of weight changes vs time is shown. The first decrease in sample weight is due to the release of CO_2 during the formation of calcium silicates at $880^\circ C$ in pure CO_2 . A second more pronounced weight loss is linked to the calcination of the remaining $CaCO_3$ in air at $850^\circ C$. From this point, the gas atmosphere and the temperatures are modified to allow hydration/dehydration to take place during consecutive cycles under pure steam at $450^\circ C$ and $550^\circ C$ respectively by changing the reaction temperature. Since such changes in the reaction temperature proceed smoothly (around 25 s to heat up from $450^\circ C$ to $550^\circ C$, but about 2 min for the cooling process), in all test devoted to kinetic investigations, the much faster change in reaction atmosphere has been used as the tool to move from hydration to dehydration reaction conditions. In a typical full hydration/dehydration cycle starting from a hydrated sample, when moving from hydration to dehydration, the gas mixture is changed from

pure $\text{H}_2\text{O}_{(\text{v})}$ to air and the temperature is increased from 450 to 500°C (which only takes a few seconds). Then, once the sample is completely dehydrated, the temperature is decreased and stabilized at 450°C under air before changing to pure $\text{H}_2\text{O}_{(\text{v})}$ for the hydration reaction (which is an step change compared to the time scale of the reaction cycle). This allow us to ensure that the hydration step only lasts a certain selected time, t_{Hy} . For experiment conducted under pure steam (for hydration and dehydration) only the evolution of the maximum conversion with the number of cycles is investigated, and sufficient time is allowed for full conversions in all cycles. Since these modifications to the operation conditions (gas flow rates and/or temperatures) cause small changes in the apparent weight measurements, blank tests were also performed using an empty pan to correct these disturbances. From the measured weight losses/increments (as shown in Figure 1) plots of conversion vs time or vs the number of cycles (N cycle) were obtained (see section 3) assuming that the CaO is converted to $\text{Ca}(\text{OH})_2$ during hydration.

2.3. Material characterization

In order to chemically and morphologically characterize the composite materials after different reactions and/or number of cycles, X-ray diffraction (XRD) and scanning electron microscopy (SEM) tests were performed. For the qualitative XRD tests, a Bruker D8 powder diffractometer equipped with a $\text{Cu K}\alpha$ monochromatic X-ray tube, a Göbel mirror in the incident beam, and a parallel-slit analyzer in the diffracted beam was used. A scanning step size of 0.02° with a scan step time of 1 s and a range of 5° - 60° 2θ was selected. The SEM images were taken using a Quanta FEG 650 microscope coupled to an energy-dispersive X-ray (EDX) analyzer Ametek-EDAX and an Apollo X detector. Since these samples are not electro-conductive, the materials were covered with a thin layer of iridium in order to obtain good quality SEM images.

2.4 Crushing strength apparatus

A SHIMPO FGE-5X dynamometer (maximum capacity 20 N, resolution 0.01 N) located in a SHIMPO MFGS-100L manual test stand was employed to measure the crushing strength of the pellets and/or their large fragments. This instrument measures the peak force (in Newtons) required to break the pellet. As pointed out in our previous work (Criado et al. 2015), only a few CS measurements can be taken on each sample during the cycling since only one pellet is extracted from the TG for CS evaluation. After the pellet and large fragments were subjected to the crushing test, the broken particle was discarded. We assumed for these CS measurements a similar standard deviation (of approximately ± 1.0 N) to that reported in our previous work.

3. Results and discussion

The main objective of the experiments carried out in this work was to explore improved synthesis routes and operating conditions needed to produce more stable composite materials containing calcium silicates (which provide the mechanical strength) while maintaining as high as possible the amount of free CaO (for the reversible hydration/dehydration reactions in thermochemical energy storage applications). To achieve this objective it was essential to identify the main cause responsible for the decay in crushing strength after only 30-40 hydration/dehydration cycles reported in a previous work (Criado et al. 2015). As mentioned in the previous work, composites produced from a mixture of CaCO_3 as Ca-precursor and $\text{Na}_2\text{Si}_3\text{O}_7$ at high molar Ca/Si ratios ($r_{\text{Ca/Si}}$) of 4.8-6.2 yielded a high fraction of active CaO (over 0.6 hydration molar conversion) and a very high crushing strength in the first hydration cycle when compared to lime obtained from the calcination of limestone. The high crushing strength was attributed to the formation of calcium silicates at temperatures between 750°C-850°C, following reactions (3) and (4) (Taylor 1997):

that can be combined to give:

It was confirmed by XRD analysis that some of the initial Ca present in the sample was consumed in the formation of these silicates (Criado et al. 2015). Despite the encouraging results, the positive effect on the crushing strength linked to the formation of the Ca-silicates gradually disappeared with the number of hydration/dehydration cycles (i.e. from an initial CS of 17-18 N to 1-2 N after about 200 cycles).

3.1. Observations on the decay of crushing strength

In order to attempt new synthesis methods and/or operating conditions to minimize the decay in crushing strength it is essential to elucidate in more detail the main mechanism for this decay. In principle, two possible regions in the pellet need to be investigated when looking for the main factor responsible for the decay in crushing strength: the small grains of CaO (molecular volume of 16.9 cm³/mol) that expand to form Ca(OH)₂ (molecular volume of 33.5 cm³/mol) during each hydration step, and the complex calcium silicate matrix surrounding the CaO/Ca(OH)₂ grains resulting from the reaction of part of the Ca-precursor with Na₂Si₃O₇.

Compositional changes in the silicate matrix due to the presence of H₂O during the hydration/dehydration tests at 450/550°C were observed by XRD. These changes are consistent with the hydration of Ca₂SiO₄ to form different hydrated silicates (Garbev et al. 2014; Mitsuda et al. 1985; Roßkopf et al. 2015; Speakman et al. 1967; Yanagisawa et al. 2006), being Ca₅(SiO₄)₂(OH)₂ the main compound identified in our samples (Criado et al. 2015). Although these hydrated silicates only represent a small fraction of the total amount of silicates present in the composite material, the formation of these

hydrates could play a role in the deterioration of the mechanical properties over cycling. Therefore, several purpose-designed tests were conducted in order to elucidate the role of the hydration mechanism in the deterioration of the crushing strength of the pellets. In the first experimental campaign, tests with extremely long hydration and dehydration times (400 min) under pure steam at atmospheric pressure (450°C during hydration and 550°C during dehydration) were performed using a typical sample of composite material ($r_{\text{Ca/Si}}$ of 4.8, initial CS of around 25 N) in order to promote the formation of a significant fraction of hydrated silicates. The samples in the form of pellets were produced by using a mixture of limestone with a particle size of 36-63 μm (60wt% referred to the total CaCO_3) and co-precipitated CaCO_3 with $\text{Na}_2\text{Si}_3\text{O}_7$. The experimental time selected was equivalent to 40 cycles in a reference test. The crushing strength of the pellets even after such long tests remained at the same value as in the initial material (i.e. CS over 25 N). Similar results were obtained when other $r_{\text{Ca/Si}}$ compositions were used. It was observed that the CS of the original pellet did not decrease after a long duration hydration test and/or an equally long period under dehydration conditions. Based on these results, as well as the confirmed reactions between the steam and the silicates framework present in the composite materials at the hydration and dehydration conditions, the formation of these hydrated phases can be ruled out as the main cause of the reduction in the crushing strength of the pellets.

To further confirm whether cycling hydration/dehydration conditions could have an effect on the crushing strength of the silicates forming the composite, a stoichiometric sample ($r_{\text{Ca/Si}}=1.5$ i.e. to achieve the complete conversion of Ca into calcium silicates and a CS>30 N for the fresh sample) was synthesized and subjected to 40 cycles of hydration/dehydration under pure steam (by cycling again between 450°C and 550°C). Again, the CS of the material was unaffected by the cycling hydration test. The

experiments with these stoichiometric samples allowed us to study the textural characteristics of these silicates without the interference of CaO porous materials, which represent the greater part of the final pellets that have a higher $r_{\text{Ca/Si}}$. For this purpose, some samples were extracted at different stages of these tests so that they could be examined by SEM, as shown in Figure 2. As can be seen, although some textural changes are visible in the sample after 40 cycles (Figures 2a and b compared to Figures 2c and d), it is clear that the silicate layer maintains a very rich network of pores and bridging formations, which seems to explain the high reactivity (in terms of hydration/dehydration rates when CaO is present in the pellet). Since a large pore network is still maintained for the pellets without any free CaO and a similar structure is observed before and after cycling, it can be concluded that the decay in the crushing strength of the composite materials can only be due to the consecutive growth/shrinkage cycles of the small CaO/Ca(OH)₂ grains embedded in these Ca-silicate structures when free CaO is available.

3.2. New strategies to improve the mechanical stability

It is conjectured that the growth of Ca(OH)₂ grains during hydration produces an increasing number of fractures on the hard Ca silicate framework. A logical consequence of this mechanism is that any method to introduce into the composite larger empty volumes per CaO grain, without compromising the overall strength of the pellet, must have a positive effect on the mechanical stability of the pellet as the grains of CaO will have more room to grow into Ca(OH)₂ grains. In order to test this approach as a possible route to enhance the mechanical performance of the pellet over cycling, two strategies were explored:

- Promoting the formation of the calcium silicate framework in conditions such that each grain of CaO has a larger volume in which to grow as Ca(OH)₂. In

other words, creating the necessary conditions such that the regions with free CaO inside the silicate network have a larger volume than the volume occupied by the fully converted Ca(OH)_2 .

- Carrying out hydration/dehydration cycles in conditions where the conversion of the free CaO grains to Ca(OH)_2 is incomplete. In other words, ensuring that the pore and grain volume associated with each CaO grain is never completely filled by Ca(OH)_2 .

Both strategies should lead to fewer mechanical tensions inside the pellet when it is subjected to a hydration cycle if the growth of Ca(OH)_2 is the main mechanism responsible for the loss in crushing strength over cycling.

3.2.1. Synthesis under CO_2 at high temperature

The first strategy can be implemented and tested by exploiting the fact that the precursors of the CaO grains in the pellets are themselves small grains of CaCO_3 (Criado et al. 2015). Even if the original CaCO_3 grains were nonporous, these grains would have a higher volume ($36.9 \text{ cm}^3/\text{mol}$) than the equivalent nonporous grain of Ca(OH)_2 ($33.5 \text{ cm}^3/\text{mol}$). Therefore a simple way to achieve the objective set above is to allow the formation of the calcium silicate framework while avoiding the decomposition of the original CaCO_3 grains. In order to achieve this, an initial heating stage of the composites under pure CO_2 at high temperatures was investigated as a suitable way to facilitate the formation of the silicate structures (see Figure 3) without calcining the CaCO_3 (the equilibrium temperature for the calcination of CaCO_3 in pure CO_2 being about 900°C (Barin 1989)).

As shown in Figure 3, the cured mixture of CaCO_3 and $\text{Na}_2\text{Si}_3\text{O}_7$ is heated up to the 750-880°C range under CO_2 . These temperatures are high enough to ensure the formation of calcium and sodium silicates following reactions (6) to (9):

XRD analysis of the resulting composite after this thermal treatment confirmed the formation of the products of reactions (6-9), as can be seen in Figures 4a and b for a stoichiometric sample and a typical composite with a $r_{\text{Ca/Si}}=4.8$, respectively. This treatment under CO_2 also modifies the nature of the silicates compared to the reference material (see equation (5)), due to the formation of carbonated phases (i.e. $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ and $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$). However, as indicated in Figure 3, there is a final step for the synthesis of the CaO rich pellet where the pellet is calcined in air at temperatures between 700-850°C so that the remaining CaCO_3 grains will decompose into free CaO suitable for subsequent cycling hydration/dehydration reactions (see Figure 4c). After this calcination step the carbonated silicates will also decompose, mainly into Ca_2SiO_4 and $\text{Na}_2\text{CaSiO}_4$. No major changes were observed when comparing this new treatment with a single calcination step under air following reaction (5). The XRD analyses shown in Figure 4 have provided the qualitative information of the major compounds present in these samples, allowing us to propose the basic mechanism for the reactions between CaO and $\text{Na}_2\text{Si}_3\text{O}_7$ shown in Figure 3. More detailed discussion on other minor Ca-Si-Na compounds/crystalline phases linked to smaller signals in the XRD plots, are beyond the scope of this work. Further SEM images of a stoichiometric sample (Figure 5) after the two synthesis steps evaluated, indicate that the silicates formed under these new

protocols retain a rich porous network despite the high temperatures used in their formation, as CO_2 gas is evolved (reactions (6) and (7)).

Crushing strength measurements of the composites obtained following the new protocol yielded values beyond the measuring limit of our apparatus (30 N) revealing that these composites had formed an extremely hard silicate framework around the remaining grains of unreacted CaCO_3 . More importantly, the resulting silicates after calcination should retain the volume originally occupied by the CaCO_3 grain (that acts as a template during the first high temperature heat treatment) resulting in an excess of void volume due to the smaller molecular volume of CaO compared to that of CaCO_3 (16.9 and 36.9 cm^3/mol respectively). This void volume should, in theory, allow the Ca(OH)_2 grains to grow with less influence on the silicates layer.

Several tests were performed in order to study the effect of the heating temperature under pure CO_2 and air on the chemical and mechanical properties of the pellets (Table 1). Temperatures between 700-880°C were studied for the two steps under CO_2 and air. Also, sufficiently long times for each temperature tested were selected to ensure the complete calcination of all species (this is confirmed when a constant weight measurement is achieved on the thermogram as shown during the calcination step in Figure 1). As can be seen in Table 1, for the temperatures studied, no significant differences were observed in the chemical properties of the samples tested, X_{Hy} values being at least 0.5 at cycle 10 in all the tests. Longer tests of up to 40 cycles confirmed that the chemical activity remained stable over cycling (same X_{Hy} values as reported in Table 1 for cycle 10). TG studies confirmed the high reaction rates for different hydration and dehydration operation conditions. Complete conversion of the active $\text{CaO}/\text{Ca(OH)}_2$ present in these samples was achieved within less than 2 min for the reference operation conditions (see Figure 6). These reaction rate results for the new

materials were compared with a kinetic model developed for CaO from the calcination of natural CaCO_3 (Criado et al. 2014b), and summarized in equations (10) and (11) for hydration and dehydration respectively.

$$X_{\text{Hy}} = 1 - (1 - t/\tau_{\text{Hy}})^3 \quad (10a)$$

$$\tau_{\text{Hy}} = 1 / [(1/dp) \cdot 3.5 \cdot 10^{-4} \exp(59.4 \cdot 10^3 / (R \cdot (T + 273))) \cdot (v_{\text{H}_2\text{O}} - v_{\text{eq}})] \quad (10b)$$

$$X_{\text{Dehy}} = (1 - t/\tau_{\text{Dehy}})^3 \quad (11a)$$

$$\tau_{\text{Dehy}} = 1 / [(1/dp) \cdot 7.3 \cdot 10^4 \exp(-60.8 \cdot 10^3 / (R \cdot (T + 273))) \cdot (v_{\text{eq}} - v_{\text{H}_2\text{O}})] \quad (11b)$$

where t is the time (s), τ_i the complete conversion time (s), dp the average particle size (μm), R the universal gas constant (J/mol K), T the temperature ($^\circ\text{C}$), $v_{\text{H}_2\text{O}}$ the steam volume fraction and v_{eq} the equilibrium volume fraction, which can be estimated by means of equation (12) (Barin 1989):

$$v_{\text{eq}} = (2.3 \cdot 10^8 / P_{\text{Tot}}) \cdot \exp(-11607/T) \quad (12)$$

P_{Tot} being the total pressure (kPa).

In order to apply this model to the pellets, we have considered two extreme cases for defining the effective particle size in equations (10b) and (11b). Either it can be assumed that the composite behaves as a mass of individual grains of $\text{CaO}/\text{Ca}(\text{OH})_2$ (with a dp of 36-63 μm) following the kinetic model of equations (10) and (11). This is equivalent to assuming that the highly porous Ca-silicate matrix in the pellets does not introduce any relevant resistance to the progress of reactions. Under these conditions considerably faster reaction rates can be expected, as shown in Figure 6. Alternatively, it can be assumed that the pellet is a single reacting large particle with an equivalent diameter of 1400 μm (calculated from the volume of a sphere with the same volume as the cylindrical pellet). In this case lower reaction rates can be expected. The results of

Figure 6 indicate that the reactivity of these composite materials can be modelled using a kinetic model close to a shrinking core model at pellet scale. This is possible thanks to the high porosity of the silicate layer that allows the rapid diffusion of steam towards the $\text{CaO}/\text{Ca}(\text{OH})_2$ grains, as shown in Figures 2 and 5.

Finally, the tests were directed towards investigating the evolution of the crushing strength of the new materials with the number of cycles. As can be seen in Table 1, a significant improvement was detected for the samples calcined at higher temperatures, with CS values beyond the measuring limit of our apparatus. Further tests of up to 40 cycles were carried out on these materials. Although a drop in the CS values to around 18 N was observed, this represents a considerable advance on the CS measured compared to the reference materials (when only a calcination step under air is included in the synthesis route) with the same $r_{\text{Ca}/\text{Si}}$. Other composite samples with even higher $r_{\text{Ca}/\text{Si}}$ (up to 9.7) and lower initial crushing strengths were synthesized in order to study the positive effect of the new synthesis route. In the case of these samples, similar crushing strengths were measured for the cured and cycled material after 10 cycles, confirming the positive effect of the new synthesis route. However, after a longer number of cycles lower crushing strength were observed ($\text{CS} < 2$ N up to 100 for a $r_{\text{Ca}/\text{Si}} = 9.7$ vs a $\text{CS} < 2$ N after only 20 cycles measured for a reference material with the same $r_{\text{Ca}/\text{Si}}$). These results confirm that the new synthesis route translated into a very substantial improvement of the crushing strength values for the first cycles of hydration/dehydration, although a clear decrease in the CS measurements was detected for a longer number of cycles.

3.2.2. Incomplete hydration of the CaO grains

A final attempt to improve the long term mechanical stability of the pellets was made by avoiding the complete hydration of the CaO grains embedded in the pellet. Since all of

our investigations so far suggest that the growth of CaO grains over consecutive hydration/dehydration cycles is the main reason for the deterioration of the crushing strength of our composite materials, positive effects ought to follow from this uncompleted conversion strategy. Based on the kinetic behaviors shown in Figure 6, two different hydration times were selected: 0.5 and 1 min in order to be able to abort hydration at a sufficiently relevant value of CaO conversion. Tests of up to 40 cycles again provide encouraging results: CS values above 30 N were measured at cycle 40 for a typical material with $r_{\text{Ca/Si}}=4.8$ while X_{Hy} values of around 0.3 and 0.4 were maintained for hydration times of 0.5 and 1 min respectively. Comparison of these results with the ones previously reported, confirms that short reaction times are a suitable strategy for reducing the rapid decrease in the crushing strength of these materials over cycling.

Figure 7 also shows this positive effect on the crushing strength for longer numbers of cycles when the two strategies studied in this work are combined. As mentioned above, the reference composite material experienced a rapid drop in the CS values (see the open symbols in Figure 7). In the case of the composite material synthesized in this work CS values above 28 N (4 times higher when compared to the reference material) can be maintained over 100 cycles when $t_{\text{Hy}}=1$ min under the same operation conditions. A penalty on the maximum conversion to Ca(OH)_2 is paid with this approach, as only modest hydration molar conversions of around 0.4 at cycle 100 are obtained. A certain trend towards an increase in these conversions can be observed, with X_{Hy} close to the maximum $f_{\text{CaO,exp}}$ of the material. This can be explained in terms of the activation behavior of CaO/Ca(OH)_2 grains during the consecutive hydration/dehydration cycles, resulting in higher reaction rates at grain level as the number of cycles increases. This tendency towards higher conversions again raises the problem of decay in crushing

strength. The mechanical stresses within the pellet must intensify at higher hydration conversions and lower CS values will be reached if the CaO grains are allowed to fully convert to Ca(OH)_2 . In view of these results, lower reaction times should be considered for longer numbers of cycles in order to achieve a compromise between high crushing strength and a suitable chemical activity (i.e. $X_{\text{Hy}} \approx 0.4$). SEM images (Figure 8) of the material tested in Figure 7 confirm the positive effect of the partial hydration reported. After 40 cycles of incomplete hydration, the grains of CaO/Ca(OH)_2 largely maintain their integrity, with a continuous silicate layer between them (despite the presence of a few cracks when compared to the fresh material). On the other hand, when the material is allowed to achieve maximum conversion and CS has fallen to lower values (i.e. $N_{\text{cycle}} > 200$) their general morphology is more homogeneous, with the grains of CaO/Ca(OH)_2 completely broken up and it being impossible to visually distinguish them from the silicate layer.

In summary, only a relative degree of success was achieved by combining the two strategies investigated in this work. To the best of our knowledge, no CaO rich material has been described before in large particulate form that is capable of withstanding more than 100 cycles of intense hydration/dehydration under pure steam and sustaining CS values higher than 28 N. The idea of using the original grains of CaCO_3 precursors as templates to create volume for the growth of CaO grains seems a very promising route. The partial conversion of the material to limit the growth of Ca(OH)_2 crystals also contributes to an improvement of the results. However the benefits introduced by this last approach are achieved at the expense of important design parameters in the energy storage system (i.e. a reduced energy storage density as the conversion to Ca(OH)_2 decreases) as well as the need to envisage strategies to control the maximum conversion achieved by the solids in future works focused on the reactor and process development

at large scale. Reactor design and operation must take this into account to find the necessary compromises. In addition, the search for other types of composite material, using alternative binders to sodium silicate, should continue. The strategies analyzed in this work to improve their performance might also prove to be effective for other similar composite materials.

Conclusions

The mechanical and chemical behavior over cycling of new $\text{CaO}/\text{Ca}(\text{OH})_2$ composite materials for thermochemical energy storage applications has been investigated in this work. Reference materials containing $\text{CaO}/\text{Ca}(\text{OH})_2$ grains inside a Ca-silicate matrix show high initial crushing strength, CS, but display a sharp decay in crushing strength after only 20 cycles. The investigation of similar materials with different initial quantities of Ca and Si precursors confirmed that the observed decay was linked to the successive growth/shrinkage cycles of the small $\text{CaO}/\text{Ca}(\text{OH})_2$ grains embedded in the Ca-silicate structures and not to changes linked to the hydration of the silicates. The anisotropic growth of $\text{Ca}(\text{OH})_2$ grains must generate internal forces acting on the hard silicate layer in which they are embedded. In light of this, two different routes to minimize the drop in CS values were evaluated. These routes led to significant improvements in the crushing strength of the composite materials. The first route involved the introduction of a first heating step under pure CO_2 to allow the formation of the Ca silicates at high temperature without calcining the CaCO_3 grains used as Ca-precursor. After a subsequent calcination of the remaining CaCO_3 material in air, it was demonstrated that the grains of CaO had available a larger volume in which to grow as $\text{Ca}(\text{OH})_2$. Fast hydration/dehydration reaction rates were measured, consistent with the extensive pore network of the silicate layer in the composite. In relation to the mechanical properties, the materials showed improved CS values compared to reference

materials in the first hundred cycles. Further gains in crushing strength (i.e. for longer number of cycles) were observed when this new synthesis route was combined with an incomplete conversion of CaO to Ca(OH)₂. In this case, crushing strength values of above 28 N were retained during 100 cycles when incomplete conversion was maintained (i.e. X_{Hy} around 0.4) in each cycle. Higher conversions of CaO to Ca(OH)₂ again led to materials with lower crushing strength after more than 200 cycles. These results indicate that a suitable compromise between two conflicting tendencies must be found during operation of these materials in energy storage systems: high CS values for a very long number of cycles are only achievable with modest hydration conversions ($X_{Hy}<0.4$). A primary objective for future works in this field is to increase these chemical activities while maintaining the same level of CS of the pellets developed in this work.

Acknowledgements

The financial support provided by the European Commission under the 7th Framework Program (StoRRe Project GA 282677) is acknowledged. Y.A. Criado thanks the Government of the Principality of Asturias for a Ph.D. fellowship (Severo Ochoa Program). Help from Dr. A. Borrego in the microscopic analysis of the samples is also acknowledged.

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Figure 1. Typical weight changes vs time measured in the TG for a repeated number of hydration/dehydration cycles (under pure steam at 450°C and 550°C respectively) except in the two high temperature periods at the beginning of the thermogram: pure CO₂ at 880°C is used during the first period of silicates formation and air at 850°C during the calcination.

Figure 2. SEM images of a stoichiometric sample of co-precipitated CaCO_3 and $\text{Na}_2\text{Si}_3\text{O}_7$ after **a)** curing, **b)** calcination under air at 850°C , **c)** and **d)** 40 cycles of hydration/dehydration under pure steam at $450^\circ\text{C}/550^\circ\text{C}$.

Figure 3. Mechanism proposed for the formation of different compounds and porous structures after a two high-temperature steps: initial silicates formation under pure CO_2 and then calcination in air.

Figure 4. XRD results for a stoichiometric composite material (a) and a typical material with $r_{\text{Ca/Si}}=4.8$ (b and c). Plots a) and b) correspond to samples after 20 min under CO_2 at 880°C and c) followed by calcination under air at 850°C during 20 min. Please take into account that the effect over the background is caused by the low crystallinity of some of the samples. JCPDS Card Numbers used: CaO 01-070-5490, CaCO_3 01-071-3699, Ca_2SiO_4 01-070-0388, $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$ 01-074-0371, $\text{Na}_2\text{CaSiO}_4$ 00-024-1069 and $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ 00-028-1059.

Figure 5. SEM images of a stoichiometric sample of co-precipitated CaCO_3 and $\text{Na}_2\text{Si}_3\text{O}_7$ after **a)** heat treatment under CO_2 at 880°C and then **b)** calcination under air at 850°C .

Figure 6. a) Hydration and **b)** dehydration molar conversion (X_{Hy} and X_{Dehy}) vs time (s) at different temperatures and steam volume fractions (v_{H_2O}) for a composite sample of $r_{Ca/Si}=4.8$ ($f_{CaO, exp}=0.53$) prepared following the procedure described in Figure 3. Dotted lines plotted for each experimental conditions using equations (10) and (11).

Figure 7. Contrast between the chemical (as hydration molar conversion, X_{Hy}) and mechanical behavior (as crushing strength, CS) of the reference material (open symbols) and a material synthesized following the route described on Figure 3 and $t_{Hy}=1$ min (grey symbols). The $f_{CaO, exp}$ values from equation (2) are included as dotted lines.

Figure 8. SEM images of a material synthesized following the route described on Figure 3 and $t_{Hy}=1$ min. **a)** Fresh, **b)** after 40 cycles and **c)** after >200 cycles. Ca-grains indicated by the areas inside the dotted lines.

Table 1. Chemical and mechanical evaluation of a composite sample prepared following the procedure described on Figure 3 at different temperatures and cycled for hydration/dehydration under pure steam (450°C/550°C).

Sample	Temperature (°C)		CS (N)		X _{Hy} at Cycle 10 (t _{Hy} =5 min)
	CO ₂	Air	Cured	Cycle 10*	
CaCO ₃ 36-63 µm (60%w) + Co-precipitated r _{Ca/Si} = 4.8	750	750	25	11	0.54
	880	700		24.3	0.50
		750		30	0.51
		850		30	0.50

*Reference material: CS=17 N at cycle 10