**Coating of Ca(OH)2 / γ-Al2O3 pellets with mesoporous Al2O3 and its application in thermochemical heat storage for CSP plants**

C. M. Valverde-Pizarro1, L. Briones1, E. Sanz1, J. M. Escola1,\*, R. Sanz2,\*, J. González-Aguilar3, M. Romero3

1Department of Chemical, Energy and Mechanical Technology, 2Department of Chemical and Environmental Technology, Rey Juan Carlos University, c/ Tulipán s/n, 28933, Móstoles, Madrid (Spain)

3 High Temperature Processes Unit, IMDEA Energy, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid (Spain)

\* to whom correspondence should be addressed

e-mail: [josemaria.escola.saez@urjc.es](mailto:josemaria.escola.saez@urjc.es); raul.sanz@urjc.es

Tel: +34 91 488 70 88; +34 91 488 80 93

**Abstract**

Thermochemical heat storage using the Ca(OH)2 dehydration/hydration reaction for CSP plants requires the development of advanced materials that avoids the breakage shown by conventional CaO pellets. In this work, spherical cores made up of pelletized 60 wt. % Ca(OH)2 and 40 % γ-Al2O3 powders were coated with different mesoporous alumina coverings by means of a dip-coating route, in order to enhance its structural integrity for dehydration/hydration cycles. Three strategies of preparation were devised using as coatings alumina gels containing cetyltrimethylammonium bromide as surfactant in neutral (A2 CS) and acid pH (A4 CS) and without surfactant in neutral medium (A3 CS). In both A2 CS and A4 CS materials, denser alumina coatings were attained originating higher crushing strengths, pointing out the positive role played by the surfactant in the gel makeup. SEM images indicated that A2 presented small alumina grains (0.3 – 3 µm) highly dispersed over their surface, while over A4 CS, long sheets were appreciated. All the materials exhibited high hydration capacities after 10 cycles (> 80%, > 800 kJ/kg) at 250 ºC, but only A2 CS hold its structural integrity that was preserved even after 20 cycles without loss of its hydration capacity.

**Keywords:** Ca(OH)2 ; Heat storage; mesoporous Al2O3; γ-Al2O3; hydration capacity

1. **Introduction**

The increasing global warming is driving renewable energy in developed societies to become the main future source of energy, substituing the current model based on fossil fuels. However, renewable energy shows some disadvantages such as their intermittent feature which turn them difficult to adapt its production to the actual level of energy consumption. This fact has led towards the need of developing different storage systems to avoid the unwanted loss of the renewable energy excess during the periods of low consumer demand. Among these storage systems, chemical heat storage appears as a promising option due to its high capacity of energy storage as well as the possibility to long term operation along repeated cycles [1-3]. Chemical heat storage is based on the usage of a reversible chemical reaction which either release or store heat depending on its occurring forward/backwards [4,5]. There are many kinds of potential reactions for chemical heat storage. However, the couple CaO/Ca(OH)2 through its hydration/dehydration cycle is particularly interesting [6]:

Ca(OH)2(s) + ΔHr → CaO(s) + H2O(g)

This system presents numerous advantages such as high enthalpy of reaction (ΔHr ~ 104 kJ/mol), stability along repeated cycling, low price and fast kinetic of hydration / dehydration [7]. Additionally, this reaction takes place at medium temperatures (623 – 823 K), depending on the steam partial pressure, so at 1 bar of H2O partial pressure, the equilibrium temperature is 505 ºC [8]. This system presents high cyclability and energy density as well. Thus, 50 cycles were succesfully carried out in a fluidized bed using powdered Ca(OH)2 (4 µm, 30%) plus Al2O3 (70 %), obtaining a considerable energy density of 60 kWh m-3 [9]. This reaction was proposed long ago as particularly promising for storing the solar energy heat [10,11]. Since then, different process may be found in literature related to the application of the couple CaO/Ca(OH)2 for energy heat storage [12-18].

However, the system CaO / Ca(OH)2 shows some drawbacks. Thus, full reversibility in the dehydration step is not always found, likely due to carbonation. Therefore, higher temperature intermediate steps are suggested to deal with this problem [19,20]. If powdered CaO/Ca(OH)2 is used in the reactor, agglomeration of the fine grains is usually found along the cycling, resulting in lower heat and mass transfer rates. One way to reduce the agglomeration was the coating of the CaO/Ca(OH)2 powders with silica nanoparticles in order to hinder their coalescence [21]. On the other hand, if larger particles are used (e.g. pellets), their progressive attrition and final breakage due to the large volume change during cycling is observed, that hampers its proper operation. In this regard, it is mandatory to achieve higher mechanical and structural stability without losing optimum performance in the hydration/dehydration cycles. Thus, higher integrity of the particles was achieved by preparing calcium oxide–aluminium composites. Thus, a good hydration/dehydration performance was attained for an optimum Ca/Al molar ratio of 81/19 [22]. In this regard, enhanced structural stability of the CaO particles was also obtained by adding kaolinite to CaO-based compositions, even after 20 cycles of hydration/dehydration [23]. Additionally, core-shell composite particles formed by inner CaO plus outer hard calcium silicates showed improved mechanical and reactivity properties, holding high hydration/dehydration conversion under steam after 200 cycles [24].

In this work, we aim to enhance the structural integrity of mixed Ca(OH)2/γ-Al2O3 pellets to use them for thermochemical heat storage in concentrated solar power (CSP) plants with the hydration/dehydration cycle. To this end, several strategies were devised to cover the pellets with mesoporous alumina coatings in order to increase their integrity and long term performance in the cycling, in order to avoid its attrition and final breakage. Henceforth, the obtained results with the different coating methods are shown.

# 2. Experimental procedure

The preparation and characterization procedure of the pellets is depicted in the following section. The synthesis of the core-shell samples is simple and very little time consuming. The complete process, which includes the manufacturing and drying of the mixed Ca(OH)2/γ-Al2O3 cores, the preparation of the alumina gels, the dip-coating, drying and calcination of the pellets, can be accomplished within the same day. Besides, the gels may be stored refrigerated and used even after several days.

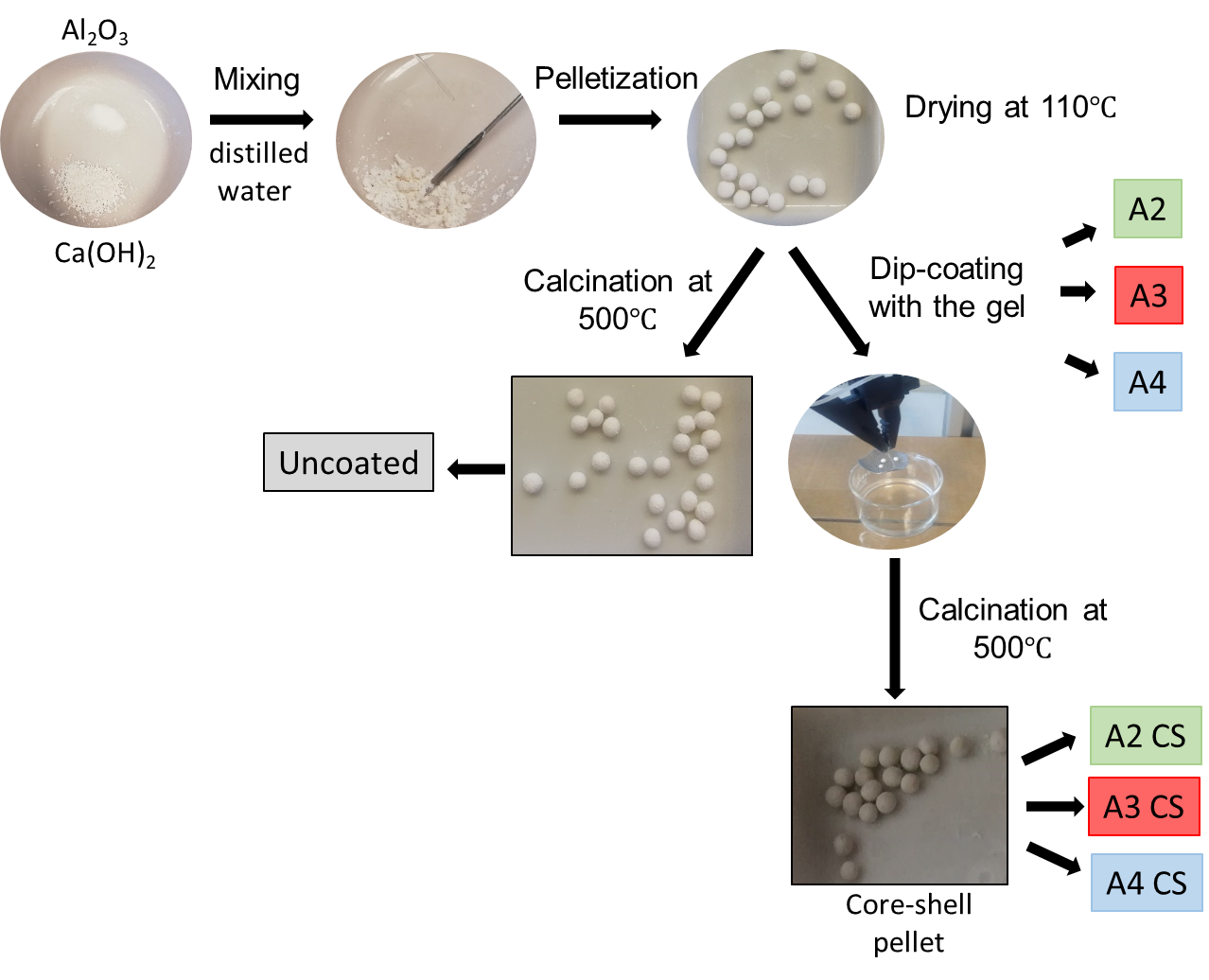
## 2.1. Materials

Commercial calcium hydroxide (ACROS Organics, 98 wt % extra pure) and acid alumina (Merck, 90%) were used as CaO precursor and binder for the preparation of CaO-based pellets, respectively. Aluminium isopropoxide (AIP) (Aldrich, 99 wt.%), hexadecyltrimethylammonium bromide (CTABr) (Aldrich, 99 wt.%), 2-propanol (Scharlau, 99 wt.%) and hydrochloric acid (Scharlau, 35 wt.% aqueous solution) were used without further purification to prepare the alumina coating gels.

## 2.2. Preparation of the cores

Figure 1 depicts the preparation process of encapsulated CaO-based pellets. A mixture of commercial Ca(OH)2 and γ-Al2O3 in a 60/40 weight ratio was grounded in a mortar to ensure an initial homogenous mixing and later forming a fine and thick paste by pouring distilled water drop by drop. This material was conformed into spherical granules that were arranged in three sets according to their mean diameter into small (between 2.2 and 2.8 mm), medium (2.8 - 3.5 mm) and large (3.5 - 4 mm).

γ-Al2O3 was used as binder in order to ensure structural integrity of pellets. A 60/40-w/w makeup was selected as trade-off between higher mechanical strength and larger CaO dispersion into inert γ-Al2O3. The latest mitigates CaO sintering, which leads to a steady loss in capacity e.g. in carbonation reactions, so a critical CaO particle size was observed, being necessary to be below this value for achieving high performance [25-27].



**Figure 1.** Scheme of the preparation procedure of the core-shell samples.

## 2.3. Pellet coating

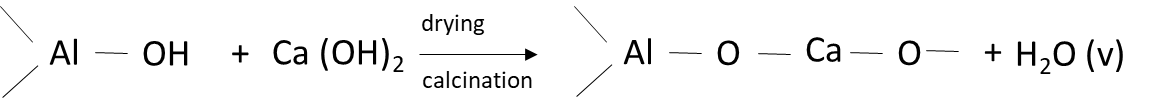
Mesoporous alumina coatings were prepared according to the sol-gel procedure reported by Aguado *et al.* [28, 29]. Three alumina gels were synthesized and denoted as A2, A3 and A4. A2 gel was prepared as follows. Firstly, two solutions were obtained: solution A containing 2-propanol and AIP and solution B containing the CTABr surfactant, hydrochloric acid and distilled water. Both solutions were stirred at room temperature until complete dissolution and then mixed together and kept under stirring at room temperature for 4 h. The molar composition of this A2 gel was 1 AIP: 0.3 CTABr: 0.05 HCl: 22 H2O: 17 2-propanol. A2 and A3 gels were synthesized according to the same procedure, except for the presence of cetyltrimethylammonium bromide surfactant in the makeup of A2 gel, being absent in the A3 gel. Both A2 and A3 gels showed virtually neutral pH (~ 7 – 7.5). Additionally, a third gel named A4 was obtained following a similar method to that of A2 gel but with higher hydrogen chloride content (ratio of 0.6). This originated a drop of the pH of A4 gel to around 4. These three different gel compositions were chosen to check the effect of the presence/absence of surfactant as well as the pH of the synthesis gel of mesoporous γ-Al2O3 upon the covering degree of the mixed Ca(OH)2/γ-Al2O3 particles.

Ca(OH)2/γ-Al2O3 pellets were impregnated by the gel by dip-coating. Here several granules were immersed into the gel for 2 seconds and slowly removed and put into a crucible. Then they were heated at 2 ºC/min from ambient up to 80 ºC and kept at this temperature for 2 h to remove the 2-propanol and later calcined at 500 ºC for 3 h under stagnant air to harden the alumina shell. This procedure was hold identical for all the obtained core-shell samples

The physicochemical properties of the alumina coatings were modified by changing the alumina gel makeup. Thus, A3 gel was also obtained without adding the CTABr surfactant to the synthesis mixture, holding the same molar ratios of the remaining reagents to those of A2 gel. In addition, A4 gel was prepared maintaining the same makeup of A2 gel except for increasing the ratio of HCl up to 0.6. The final core-shell pellets were called as A2 CS, A3 CS and A4 CS, respectively.

Some of the pellets were not coated with any alumina covering, being denoted as “uncoated”.

The degree of coating obtained depended on the type of used gel and the size of the pellet. Thus, for A2 and A4 CS pellets, the share of coating varied within 2 – 8 wt %, decreasing with the growing pellet size while for A3 CS pellets, it was fairly lower (0.8 – 3 wt%). This fact is indicative that the presence of the surfactant in the gel makeup is decisive for achieving meaningful shares of coating. In this regard, it is likely that the surfactant surrounds the alumina particles of the gel, furnishing them with a positively charged surface, which facilitates their interaction and subsequent adherence over the negatively charged surface of the Ca(OH)2 particles of the pellet [30]. The formation of the coatings is meant to be based on sol-gel chemistry, wherein the condensation reaction outlined as follows



between the hydroxyl moities of the alumina sol and those placed on the Ca(OH)2 particles surface is occurring during the drying and calcination steps, releasing water in the process [31]. This surface coating is made up of calcium aluminates of amorphous nature since far higher temperatures are required to attain crystalline phases (T > 1200 ºC) [32]. This point was checked by preparing gels of similar composition of the coating and according to the same recipe. Their XRD patterns (data not shown) confirmed the absence of crystalline calcium aluminates. At any rate, a hard alumina coating was attained over the Ca(OH)2 particles, as inferred from the crushing force of the core-shell pellets. These crushing strength values were obtained from 15 samples of every core-shell pellets, calculating their respective mean and standard deviation. The uncoated pellets and those coated with the A3 gel showed the lower crushing strength at every size, being placed within the 7 – 12 N range. In contrast, the core-shell particles prepared with A2 and A4 gels displayed higher crushing strengths, being inferior to 20 N for sizes below 2.8 mm and above 20 N for sizes between 2.8 – 4 mm. This is in keeping with the higher share of coating when using both A2 and A4 gels and it bears out the success of this strategy of incorporating the surfactant in the synthesis makeup of the alumina gels to enhance the mechanical stability of the pellets. In light of these results, for further studies in this work, pellets with a size within the range 2.8 – 3.5 mm were chosen.

Finally, the starting Ca(OH)2/Al2O3 cores without any coating were also studied as reference materials and denoted as “uncoated”.

## 2.4. Characterisation of coated pellets

Crushing strength under compression of the pellets was measured in a Chatillon MT Ametek dynamometer. Fifteen pellets of each batch and category were crushed to calculate mean force as well as standard deviation.

Coating morphology was determined by scanning electron microscopy (SEM) by means of a Hitachi TM-1000 apparatus equipped with an energy-disperse X-ray spectroscopy (EDX) detector.

Coating textural properties were characterised by nitrogen adsorption/desorption isotherms at 77 K in a Micromeritics Tristar 3000 instrument. Powders remaining from the gel excess in the crucible after the calcination of the coated pellets were also collected and subjected to the analysis. Prior to the analyses, the samples were outgassed in two degasification steps under nitrogen at 90 ºC for 30 min and 200 ºC for 480 min. Specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) method within relative pressures between 0.05 and 0.17, while the pore size distributions were obtained by using the Barrett-Joyner-Halenda (BJH) equation applied to the desorption branch of the isotherm [33,34].

Crystalline phases formed in the samples were determined by X-ray diffraction (XRD) in a Philips X’PERT MPD diffractometer using Cu-Kα radiation to check their crystallinity. XRD patterns were collected between 5 and 90º using a step size of 0.1 and a counting time of 2 s. To monitor the evolution of the materials, samples were characterised by XRD as made, after one dehydration/hydration cycle, and after five consecutive cycles. Besides, mean crystal size of each phase was calculated by means of the Scherrer equation [35].

Dehydration/hydration tests were conducted in a Netzch TG 209F3 Tarsus thermomicrobalance coupled with a water vapour generator. Dehydration was carried out at 600 ºC in argon flow (20 mL/min) and hydration at 250 ºC under a 0.96 g/h steam flow in argon. Synthesised materials were subjected to 5, 10 or 20 consecutive cycles. Hydration capacity was calculated as the ratio between the relative mass increase undergone by the CaO contained in the samples in the hydration stage and that of pure CaO powder (obtained by calcination at 500 ºC of commercial Ca(OH)2) under the same test conditions.

(1)

Thus it is assumed that CaO powder can be considered as reference and provides the maximum capacity (100%), and hydration capacity is uniquely due to CaO hydration. Additionally, the energies potentially released for each sample were calculated according to their CaO content and hydration yield, considering the enthalpy of the exothermic reaction as 104 kJ/mol or 1854.6 kJ/kg.

# 3. Results and discussion

## 3.1. Characterization of the core-shell particles

It is noteworthy that the visual inspection of the fifteen A2 CS and A4 CS pellets before entering the hydration/dehydration cycles did show neither apparent fractures nor breakage. In contrast, A3 CS pellets usually displayed surface fractures and some of them were broken. Figure 2 illustrates the SEM micrographs of the obtained core-shell particles. With A2 CS, the occurrence of uniformly distributed alumina grains over its surface is appreciated. These grains show a size of roughly 0.3 – 3 µm and they do not cover completely the pellet surface, leaving spaces among the A2 alumina particles. Additionally, the presence of fine grains of Ca(OH)2 is also observed below the alumina coatings, and they contain a significant amount of macropores. This is a positive finding considering that the occurrence of pores below 200 nm in CaO is highly required for attaining high hydration activity [36]. A3 CS pellets present remarkable fractures and their surface exhibits the presence of alumina grains of close size (0.3 – 3 µm) to those of A2 CS.



**Figure 2.** SEM images of the core-shell pellets after calcination at 500 ºC.

The considerable fracturing shown over A3 CS may be ascribed to the absence of the surfactant in the synthesis medium, which resulted in decreased adhesion and a lower degree of coating as aforementioned. Additionally, it is also likely that the surfactant abated the surface tension over the Ca(OH)2/γ-Al2O3 pellets during the coating process, originating less strain and thereby, preventing the formation of fractures. For the case of A4 CS, the presence of fractures is scarce and similar to A2 CS. However, its surface looks different from those of A2 and A3 CS pellets. Thus, it is largely covered by sheet-like alumina pieces with a size of roughly 20 – 50 µm. In addition, some disperse alumina grains of larger size (5 – 10 µm) to those previously observed over both A2 and A3 CS are also appreciated. Consequently, the lower pH of the A4 gel favours the condensation of the alumina sol over the surface of Ca(OH)2/γ-Al2O3 pellets, leading mostly towards long alumina sheets instead of small uniformly dispersed grains.

Another key issue is to ascertain the porosity of the gels, since the occurrence of pores in the alumina coatings is mandatory to facilitate the diffusion of water throughout the pellet in their subsequent application for thermochemical heat storage. In this regard, Figure 3 illustrates the nitrogen adsorption-desorption isotherms at 77 K and BJH pore size distribution of calcined gels. These isotherms were attained of the calcined gels following the same drying and calcination procedure but without coating the pellets. The three calcined gels display a type IV isotherm according to the IUPAC classification [34], featured by the occurrence of a steep jump in adsorption at intermediate/high relative pressures indicative of the presence of mesopores in the material [37-42]. This jump is placed at p/p0 > 0.8 for A2 and A3 gels, while for A4 is situated at lower p/p0 (0.6 – 0.8). This fact points out that the pore size distribution for A2 and A3 gels are displaced at larger pore sizes (5 – 100 nm) than for A4 gels (3 - 20 nm), being also narrower for the latter. Thereby, this pore size distribution is centered at 20, 25 and 8 nm for A2, A3 and A4 gels, respectively. Additionally, A2 and A3 calcined gels show the presence of larger mesopores/ macropores than for A4 calcined gel, wherein intraparticular mesopores are mainly present. Regarding the textural properties of the calcined gels, their BET surface areas and pore volumes are above 250 m2 g-1 and 0.6 cm3 g-1 for all of them, which is quite remarkable and it bears out their high porosity.

****

**Figure 3.** N2 adsorption-desorption isotherms at 77 K and pore size distributions of the alumina coating powders

## 3.2. Hydration / Dehydration experiments

The A2, A3 and A4-coated pellets were initially subjected to 10 successive hydration/dehydration cycles to test their performance for thermochemical heat storage. Dehydration was carried out at 600 ºC under flowing Ar. This temperature allow for release adsorbed CO2, which is easily uptake by Ca(OH)2 from atmospheric air and forming CaCO3 [43], and prevent the formation of calcium aluminates by reaction of the Ca(OH)2 and γ-Al2O3 of the core, which would lead inevitably to a progressive loss in hydration capacity [44]. Hydration was performed at 250 ºC under a humid Ar stream containing 0.96 g/h of water. These conditions were chosen as a first approximation to those existing in a hypothetical concentrated solar power (CSP) plant wherein dehydration would be caused by solar concentrators. Figure 4 illustrates the hydration capacity along ten successive cycles of the four pellets chosen in this research. All of them show a similar behaviour, since its hydration capacity increases with the cycling, reaching a steady value roughly in cycle 3 - 4 which is hold in subsequent cycles. This final stable value differs among the core-shell materials, being the highest for the uncoated material (97%, 956.5 kJ/kg), followed by A2 and A3 CS pellets (~ 90 - 92%, 887.4 - 907.2 kJ/kg) and at certain distance, A4 CS material (84%, 828.3 kJ/kg).



**Figure 4.** Hydration capacity of the uncoated and core-shell pellets in ten-cycle experiments. (Dehydration at 600 ºC and hydration at 250 ºC)**.**

These high values point out the high performance of all the core-shell materials. In addition, the observed order in hydration capacity may be ascribed to the enhanced accessibility for water over A2 and A3 CS pellets, caused by the presence of dispersed alumina grains over their surface, leaving spaces for water diffusion. In contrast, for A4 CS, the presence of a denser sheet-like alumina coating blocks to some extent the access to water, diminishing the total hydration capacity. On the other hand, the lower hydration capacities observed during the first cycles are ascribed to the occurrence of CaCO3 in the samples, which is not fully removed until several dehydration/hydration steps take place (~ 3).



**Figure 5.** XRD patterns of the A2 CS sample: (top) as made; (center) after one dehydration/hydration cycle; and (bottom) after five dehydration/hydration cycles.

This fact can be easily appreciated in Figure 5 that exhibits the XRD patterns of the A2 CS material as made, after 1 cycle and after 5 cycles. The as prepared A2 CS pellet shows the existence of, not only Ca(OH)2 and CaO, but a considerable amount of CaCO3 as well. After one cycle, the reflections of the CaCO3 decreased slightly and, after 5 cycles, they virtually disappeared, being only present those of Ca(OH)2 and CaO. Interestingly, no reflections pertaining to crystalline calcium aluminates were observed in the XRD patterns which confirms the suitability of the chosen temperature for carrying out the dehydration of the core-shell pellets. These XRD patterns also indicate some sintering of the Ca(OH)2 particles, since the application of the Scherrer law showed an increase in the crystal size from 14 nm (1 cycle) to 59 nm (5 cycles).

Figure 6 displays the snapshots taken of the core-shell materials after the 10 cycles. Both the uncoated and the A3 CS pellets broke into several chunks, so they lost completely their respective structural integrity, and are of no use for a future application in a fixed bed reactor. In contrast, A4 CS improved this result and it broke just in one side while A2 CS showed only surface fractures and remained intact, despite the considerable volume change occurring during the hydration / dehydration cycle (~ 95%).



**Figure 6.** Snapshots of the uncoated and core-shell pellets after ten-cycle experiments.

Figure 7 illustrates the SEM images of these core-shell materials after the ten cycles. The uncoated pellet lost its spherical shape and was fragmented into several chunks. In contrast, A2 CS exhibits some surface fractures, but it holds its spherical shape. Additionally, the presence of small alumina grains is appreciated although unlike the starting material before the cycling, some coalescence of the alumina grains is observed over its surface. Interestingly, the alumina grains are not detached after the ten cycles remaining stuck on the pellet surface which bears out the stability of the covering regardless of the presence/absence of water in the reacting atmosphere. In addition, the inner structure of A2 CS is rather porous and the whole appearance of the A2 CS particle may be regarded as a sponge-like one.



**Figure 7.** SEM images of the core-shell pellets after ten dehydration/hydration cycles.

In contrast, A4 CS showed in one side the formation of big holes which detached some of the alumina sheets originally formed. This fact indicates that the occurrence of long alumina sheets on A4 CS surface hampered to a certain extent the diffusion of the formed gases outside the pellet. Thereby, the high strain created inside the A4 core-shell particle led finally to a partial separation of the alumina sheets in one side of A4 CS after the cycling. In this regard, A2 CS material, which includes highly dispersed alumina grains on its surface instead of alumina sheets, represents a more interesting option for thermochemical heat storage since it facilitates the diffusion of water outside the pellet, alleviating the generated strain.

Considering the promising results obtained with A2 CS, it was tested for 20 cycles as well and the attained results are shown in Figure 8.



**Figure 8.** Hydration results of A2 CS in a twenty-cycle experiment (dehydration at 600 ºC and hydration at 250 ºC). (A) Weight variation and cyclability; (B) comparison of cycles 1, 10 and 20; and (C) hydration capacity.

It can be appreciated that A2 CS pellets hold essentially the same hydration capacity after 20 cycles to that after 10 cycles, which bears out its high performance. Interestingly, their respective hydration curves (see Figure 8.B) virtually coincide which bears out the high reproducibility of the procedure of the core-shell pellets preparation. In addition, it is also indicating that despite the growth of CaO particles by sintering along the cycling, this phenomenon did not affect the hydration kinetics. This averts the possibility of formation of an outer passivation layer that hampers water diffusion, at least in the range of crystal sizes at stake in this work, as it was shown to occur in carbonation [26].

Figure 9 illustrates the SEM images of A2 CS after 20 cycles and it maintained its spherical shape with some surface fracturing. In addition, the presence of small alumina grains highly dispersed over the A2 CS surface is clearly distinguished, which are hold along the repeated cycling. It must be said that the crushing strength of the pellets decreased meaningfully after the repeated cycling (< 10 N), since the continuous expansion/contraction caused by the hydration/dehydration cycles modifies largely the final pellet volume. However, the small alumina grains of the coating, that are highly dispersed throughout the pellet surface, act as a sort of tiny stitches, holding together the Ca(OH)2 particles and preserving its spherical shape. One final point to check was the assessment of A2 CS under more realistic temperature conditions during the cycling. In this regard, it is desirable that during operation, the dehydration temperature was as low as possible while on the contrary, the hydration temperature was as high as possible, in order to diminish the temperature gap between both stages. Thereby, an additional cycling experiment was carried out comprising 5 dehydration/hydration steps wherein the first dehydration step was performed at 600º C and the following ones at 550 ºC. On the other hand, all the hydration stages were done at 420 ºC using the same mass flow of steam as previously. In this experiment, from the third cycle on, the hydration capacity was hold steady in a remarkable 84% (828.3 kJ/kg). This bears out that A2 CS worked out very well under close conditions to those expected for a true thermochemical heat storage process based on the couple CaO/Ca(OH)2. On the other hand, the hydration of the A2 CS pellets led towards a roughly 16 - 17 wt. % rise, which is acceptable in normal operation in fixed bed reactors. Therefore, A2 CS is a promising core-shell material for thermochemical heat storage in CSP plants and proves the feasibility of this approach to increase the structural integrity of the CaO pellets.



**Figure 9.** SEM micrographs of the A2 CS sample after 20 dehydration/hydration cycles.

**4. Conclusions**

Core-shell mesoporous alumina – [Ca(OH)2/γ-Al2O3] pellets were prepared following a dip coating method using three different alumina gels (A2, A3 and A4) differing in the presence / absence of cetyltrimethylammonium bromide surfactant as well as in their pH. The presence of the surfactant in the gel makeup resulted in harder core-shell pellets with higher shares of coatings and less fracturing (A2 CS and A4 CS), likely by the decrease in surface tension originated by the surfactant during the covering. Additionally, the pH of the surfactant containing alumina gels also affected the nature of the coating, leading towards uniformly disperse alumina grains between 0.3 and 3 µm at pH ~ 7 – 8 while at pH ~ 4, it gave rise to longer alumina sheets. All the core-shell pellets showed high hydration capacity after 10 cycles (> 80%, > 800 kJ/kg) although only A2 CS pellets holds its spherical shape with a sponge-like appearance despite the distinct volume change occurring during the cycling. This was also observed after 20 cycles, wherein both its hydration capacity and spherical shape was preserved with only some slight fracturing in its surface. Therefore, A2 core-shell materials showed enhanced structural integrity and are promising materials for thermochemical heat storage in CSP plants.

**5. Acknowledgments**

The authors wish to thank Comunidad de Madrid and European Structural Funds for their financial support to ALCCONES project (S2013/MAE-2985) and ACES2030-CM project (S2018/EMT-4319). C. M. Valverde-Pizarro thanks Comunidad de Madrid for the funding through the grant PEJD-2017-PRE/AMB-4390.

**6. Nomenclature**

In this section, the main acronyms and symbols used in this paper are explained. These are the following ones:

**A2**: Alumina gel containing the surfactant CTABr in its makeup and with neutral pH

**A3**: Alumina gel without the surfactant CTABr in its makeup and with neutral pH

**A4**: Alumina gel containing the surfactant CTABr in its makeup and with acid pH

**A2 CS**: pellets made up of a core of a physical mixture of Ca(OH)2 and γ-Al2O3 (60/40 w/w) with a surface shell of mesoporous alumina formed from A2 gel.

**A3 CS**: pellets made up of a core of a physical mixture of Ca(OH)2 and γ-Al2O3 (60/40 w/w) with a surface shell of mesoporous alumina formed from A3 gel.

**A4 CS**: pellets made up of a core of a physical mixture of Ca(OH)2 and γ-Al2O3 (60/40 w/w) with a surface shell of mesoporous alumina formed from A4 gel.

**AIP**: Aluminium isopropoxide

**BET**: Brunauer-Emmett-Teller method for determining surface area of solids

**BJH**: Barrett-Joyner-Halenda method for determining mesopore size of solids

**CSP**: Concentrated solar power

**CS**: Core Shell

**CTAB**r: hexadecyltrimethylammonium bromide

**IUPAC**: International Union of Pure and Applied Chemistry

**p/p0**: relative pressure (quotient between the adsorbate pressure in the cell containing the solid and the saturation vapor pressure of the adsorbate at the operating temperature)

**SEM**: Scanning Electron Microscopy

**XRD**: X-ray diffraction

# 7. References

1. A. Gil A, M. Medrano, I. Martorell, A. Lázaro, P. Dolado, B. Zalba, L. F. Cabeza. Renew. Sust. Energ. Rev. 14 (2010) 31 – 55.
2. M. Medrano, A. Gil, I. Martorell, X. Potau, L. F. Cabeza. Renew. Sust. Energ. Rev. 14 (2010) 56 – 72.
3. D. Aydin, S. P. Casey, S. Raffat. Renew. Sust. Energ. Rev. 41 (2015) 356 – 367.
4. P. Pardo, A. Deydier, Z. Anxionnaz-Minvielle, S. Rougé, M. Cabassud, P. Cognet. Renew. Sust. Energ. Rev. 32 (2014) 591 – 610.
5. T. Yan, R. Z. Wang, T. X. Li, L. W. Wang, I. T. Fred. Renew. Sustain. Energ. Rev. 43 (2015) 13 – 31.
6. P. E. Halstead, A. E. Moore. J. Chem. Soc. (1957) 3873 – 3875.
7. Y. A. Criado, M. Alonso, J. C. Abanades. Ind. Eng. Chem. Res. 53 (2014) 12594 – 12601.
8. F. Schaube, L. Koch, A. Wörner, H. Müller-Steinhagen. Thermochim. Acta 538 (2012) 9 – 20.
9. P. Pardo, Z. Anxionnaz-Minvielle, S. Rougé, P. Cognet, M. Cabassud. Solar Energy 107 (2014) 605 – 616.
10. G. Ervin G. J. Solid State Chem. 22 (1977) 51 – 61.
11. M. S. Murthy, P. Raghavendrachar, S. V. Sriram. Solar Energy 36(1) (1986) 53 – 62.
12. Y. A. Criado, M. Alonso, J. C. Abanades, Z. Anxionnaz-Minvielle. Appl. Them. Eng. 73 (2014) 1087 – 1094.
13. I. Fujii, M. Ishino, S. Akiyama, M. S. Murthy, K. S. Rajanandan. Solar Energy 53(4) (1994)329 – 341.
14. M. Linder, C. Roβkopf, M. Schmidt, A. Wörner. Energ. Procedia 49 (2014) 888 – 897.
15. F. Schaube, A. Wörner, R. Tamme. J. Sol. Energy Eng. 133(3) (2011) 031006-1-7.
16. F. Schaube, A. Kohzer, J. Schütz, A. Wörner, H. Müller-Steinhagen. Chem. Eng. Res. Des. 91(5) (2013)856 – 864.
17. F. Schaube, I. Utz, A. Wörner, H. Müller-Steinhagen. Chem. Eng. Res. Des. 91(5) (2013) 865 – 873.
18. Y. A. Criado, A. Huille, S. Rougé, J. C. Abanades. Chem. Eng. J. 313 (2017)1194 – 1205.
19. M. N. Azpiazu, J. M. Morquillas, A. Vazquez. Appl. Therm. Eng. 23 (2003) 733 – 741.
20. J. Yan, C. Y. Zhao, B. Q. Xia, T. Wang. Energy 186 (2019) 115837.
21. C. Roβkopf, S. Afflerbach, M. Schmidt, B. Görtz, T. Kowald, M. Lender, R. Trettin. Energy Convers. Manage. 97 (2015)94 – 102.
22. K. G. Sakellariou, G. Karagiannakis, Y. A. Criado, A. G. Konstandopoulos. Solar Energy 122 (2015) 215 – 230.
23. K. G. Sakellariou, N. I. Tsongidis, G. Karagiannakis, A. G. Konstandopulos. Energy Fuels 31 (2017)6548 – 6559.
24. Y. A. Criado, M. Alonso, J. C. Abanades. Ind. Eng. Chem. Res. 54 (2015) 9314 – 9327.
25. B. Feng, W. Liu, X. Li, H. An. Energy Fuels 20 (2006**)** 2417 – 2420.
26. H. Sun, J. Wang, X. Liu, B. Shen,C. M. A. Parlett, G. O. Adwek, E. J. Anthony, P. T. Williams, C. Wu. J. Mater. Chem. A 7 (2019)9977 – 9987.
27. J. Sun, Y. Guo, Y. Yang, W. Li, Y. Zhou, J. Zhang, W. Liu, C. Zhao. Fuel 256 (2019)116009
28. J. Aguado, J. M. Escola, M. C. Castro, B. Paredes. Microporous Mesoporous Mater. 83(1-3) (2005)181 – 192.
29. J. Aguado, J. M. Escola, M. C. Castro. Microporous Mesoporous Mater. 128 (2010) 48 – 55.
30. J. T. Muth, J. A. Lewis. Langmuir 33(27) (2017)6869 – 6877.
31. R. E. Przekop, P. Marciniak, B. Sztorch, A. Czapik, M. Stodolny, A. Martyla. J. Aust. Ceram. Soc. 54(4) (2018)679 – 690.
32. J. Livage. Stud. Surf. Sci. Catal. 85 (1994) 1 – 42.
33. M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K. S. W. Sing. Pure Appl. Chem. 87(9) (2015) 1051 – 1069.
34. K. A. Cychosz, R. Guillet-Nicolas, J. García-Martínez, M. Thommes, Chem. Soc. Rev. 46 (2017) 389 - 414.
35. P. E. J. Saloga, A. F. Thünemann, Langmuir 35 (2019) 12469 - 12482.
36. J. Zhang, S. Zhang, M. Zhang, Z. Wang, G. Qian, J. Liu, X. Gong. Chin. J. Chem. Eng., doi.org/10.1016/j.cjche.2019.02.024.
37. J. García-Martínez, C. Xiao, K. A. Cychosz, K. Li, W. Wan, X. Zou, M. Thommes, ChemCatChem 6 (2014) 3110 - 3115.
38. J. Čejka, N. Žilková, J. Rathouský, A. Zukal. Phys. Chem. Chem. Phys. 3(22) (2001) 5076 – 5081.
39. F. Vaudry, S. Khodabandeh, M. E. Davis. Chem. Mater. 8 (1996)1451 – 1464.
40. S. A. Bagshaw, T. J. Pinnavaia. Angew. Chem. Int. Ed. 35(10) (1996)1102 – 1105.
41. S. Cabrera, J. E. Haskouri, J. Alamo, A. Beltrán, D. Beltrán, S. Mendioroz, M. D. Marcos, P. Amores. Adv. Mater. (1999) 379 – 381.
42. V. González Peña, I. Díaz, C. Márquez-Álvarez, E. Sastre, J. Pérez-Pariente. Microporous Mesoporous Mater. 44 (2001) 203 – 210.
43. H. Hattori. Chem. Rev. 95 (1995) 537 – 558.
44. R. Ianoş. Ceramics Inter. 44(17) (2018) 21908 – 21913.