

# **Shortlisting of Composite CaO-Based Structured Bodies Suitable For Thermochemical Heat Storage With The CaO/Ca(OH)<sub>2</sub> Reaction Scheme**

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Table S1

## Composite CaCO<sub>3</sub>/kaolinite pellets

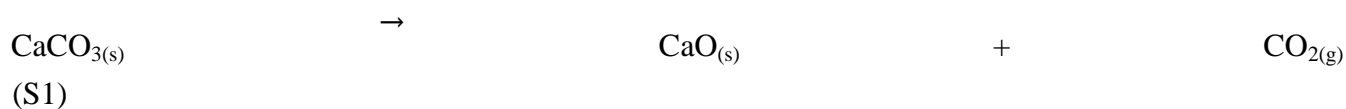
Emphasizing on the mechanical properties of composite CaO/kaolinite pellets, preliminary evaluation experiments were carried out on pellets with kaolinite content of 10 and 25 wt %. For the preparation of composite pellets, Natural89 ( $\geq 89$  wt % CaCO<sub>3</sub>) and Natural98 ( $\geq 98.7$  wt % CaCO<sub>3</sub>) were employed as Ca-precursors, with Natural89 powder being used after calcination at 900°C for 2 h under air followed by storage at ambient atmosphere, therefore generating Ca(OH)<sub>2</sub>. The manufacturing process included Ca-precursor and kaolinite mixing via the solid mixing technique (following the rest of steps as described in detail in the manuscript) and stabilization of the final pellets via calcination at 900 °C for 4 h. In Natural89 derived materials, XRD analysis on milled pellets right after their calcination revealed the formation of the ternary Ca/Al/Si phase regardless of kaolinite content applied. However, examining the mechanical properties of the fresh calcined pellets, it was found that formulations with 10 wt % of kaolinite exhibited low mechanical strength values (between 2 and 7 N), whereas pellets with higher kaolinite content proved to be less susceptible to breakage with CS values of 16-19 N. Such CS measurements were carried out on multiple pellets (around 10 per sample) and values presented here correspond to the range noted. When Natural98 was employed as Ca-precursor, the composition was similar to the one identified in Natural89 materials including CaO, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> and SiO<sub>2</sub> peaks. Regarding mechanical stability, Natural98\_kaolinite25 pellets presented higher resistance to breakage with CS values of 22-30 N.

**Table S1.** List of materials examined: Composition and mechanical properties of fresh pellets

Material	T <sub>calcination</sub> / °C	Composition	CS <sub>fresh</sub> / N
Natural89_kaolinite10	900	CaO, Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> , SiO <sub>2</sub>	2-7
Natural89_kaolinite25	900	CaO, Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> , SiO <sub>2</sub>	16-19
Natural98_kaolinite25	900	CaO, Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> , SiO <sub>2</sub>	22-30

## Estimation of free CaO content in composite materials

The estimation of free CaO content after calcination was based on the reasoning/assumption that during calcination and apart from the solid state reaction of the two precursors (eq. 3 in the manuscript), two side reactions take place, including the decarbonation of  $\text{CaCO}_3$  resulting to CaO (eq. S1) and the dehydration of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  resulting to  $\text{Al}_2\text{SiO}_7$  (eq. S2). The decarbonation reaction could be considered as competitive. From the literature, though, it is known that decarbonation can initiate from  $650\text{ }^\circ\text{C}$ <sup>1</sup>. Moreover, according to XRD analysis performed on  $\text{CaCO}_3$ /kaolinite samples calcined at various temperatures between 750 and  $1000\text{ }^\circ\text{C}$  (not here presented),  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  formation is favored at  $T > 800\text{ }^\circ\text{C}$ . Thus, composite  $\text{CaO}/\text{Ca}_2\text{Al}_2\text{SiO}_7$  materials production would not be inhibited. The purity of Ca-precursor was crucial and it was assumed that the impurities contained in  $\text{CaCO}_3$  grades were completely inert during both gehlenite formation and cyclic reactions. Considering the weight ratio of the two precursors, the stoichiometric formation of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  and the side products according to eq. 3 (in the manuscript), free CaO was calculated as the difference between the total CaO employed and the CaO consumed for  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  formation.



In particular, an example for Natural98 is provided and the following procedure was followed:

- It is assumed that all impurities remain inert during calcination/hydration/carbonation.
- 1g of Natural98 limestone (98.7 % purity) renders 0.553 g of CaO through calcination (eq. S1), with 1.3% of impurities remaining inert. ( $\text{MW}_{\text{CaO}}=56.08\text{ g/mol}$ ,  $\text{MW}_{\text{CaCO}_3} = 100.09\text{ g/mol}$ )  
Thus, in 75% wt of Natural98 limestone 0.415 g of CaO (74% wt due to impurities) are contained.

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<sup>1</sup> Halikia, I.; Zoumpoulakis, L.; Christodoulou, E.; Prattis, D. *The European Journal of Mineral Processing and Environmental Protection* **2001**, 1, 2, 89-102

- The dehydration of 25% wt of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  (eq. S2) renders 0.215 g of  $\text{Al}_2\text{SiO}_7$  (MW  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 = 258.16 \text{ g/mol}$ , MW  $\text{Al}_2\text{Si}_2\text{O}_7 = 222.13 \text{ g/mol}$ )
- Therefore, the reaction of 0.215 g of  $\text{Al}_2\text{SiO}_7$  requires 0.109 g of CaO (eq. 3 in the manuscript) for gehlenite formation.
- Concluding, free CaO is equal to  $0.415 - 0.109 = 0.306 \text{ g}$  of CaO, corresponding to 49% of the total amount of material produced (including  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  and  $\text{SiO}_2$ ).

Similarly, free CaO content can be estimated for Natural89 as 45% of final material.

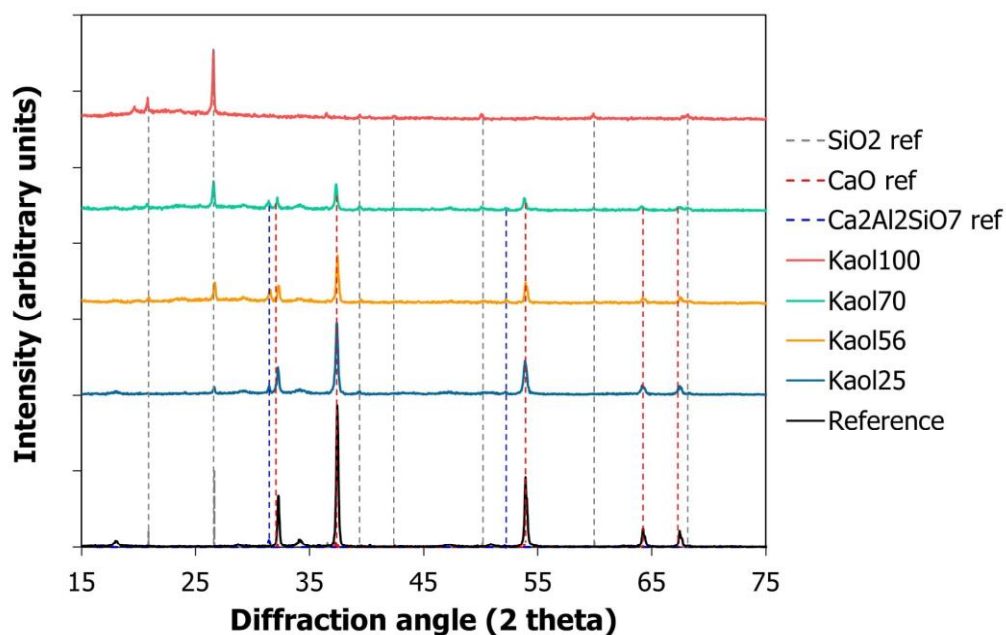
## **XRD patterns of composite CaCO<sub>3</sub>/kaolinite pellets**

Figures S1, S2 and S3 present the results from the XRD analysis performed on the composite materials studied in the current work in their fresh form (i.e. after calcination). In these comparative diagrams, the reference diffraction peaks of the three main crystal phases –CaO, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> and SiO<sub>2</sub>– are depicted with dotted lines. Evidently, the main crystal phase identified in all composite materials is CaO, assigned to the [200] crystallographic plane (2theta=37.36 degrees). The addition of kaolinite resulted in the formation of a mixed Ca/Al/Si phase corresponding to gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>). The main peak of the ternary Ca/Al/Si phase (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) characterized the [211] crystallographic plane (2theta=31.42 degrees) and it was profound in almost all CaCO<sub>3</sub>/kaolinite composite materials. Also, SiO<sub>2</sub> phase is evident in all materials, mainly the one assigned to the [011] crystallographic plane (2theta=26.64 degrees).

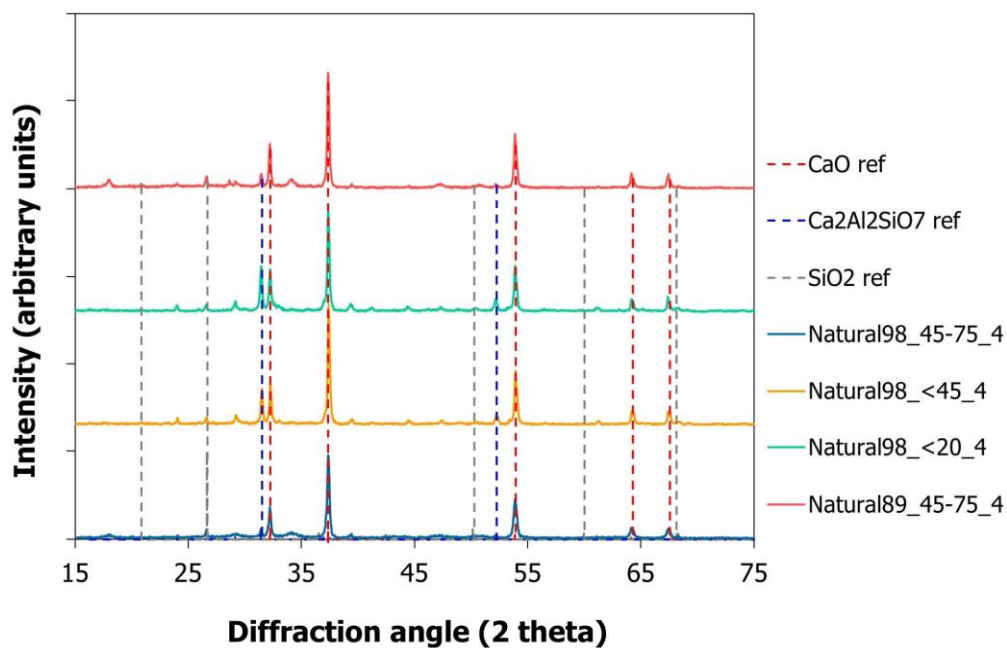
Regarding Figure S1, notably, increasing kaolinite amount in the composite materials did not affect the intensity of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> peaks. However, it resulted in SiO<sub>2</sub> peaks with higher intensity in material Kaol70 than in the rest of compositions. Given that pure kaolinite formulations (denoted as Kaol100) consisted of almost single-phase SiO<sub>2</sub> peaks, such a decrease in their intensity in composite materials is natural considering the addition/increase in CaO content employed. Therefore, gradually lower amounts of kaolinite were employed for Kaol70 to Kaol25 leading to SiO<sub>2</sub> peaks with lower intensity.

In relation to samples presented in Figure S2, as it is also stated in the main manuscript, employing CaCO<sub>3</sub> precursors with different particle size affected Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> peaks. In particular, in Natural98 derived materials with smaller CaCO<sub>3</sub> particle sizes, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> peak became more intense and narrower, resulting to different crystallite sizes (as shown in Table 5 in the manuscript). Natural89 derived sample presented similar behaviour with the corresponding Natural98derived one.

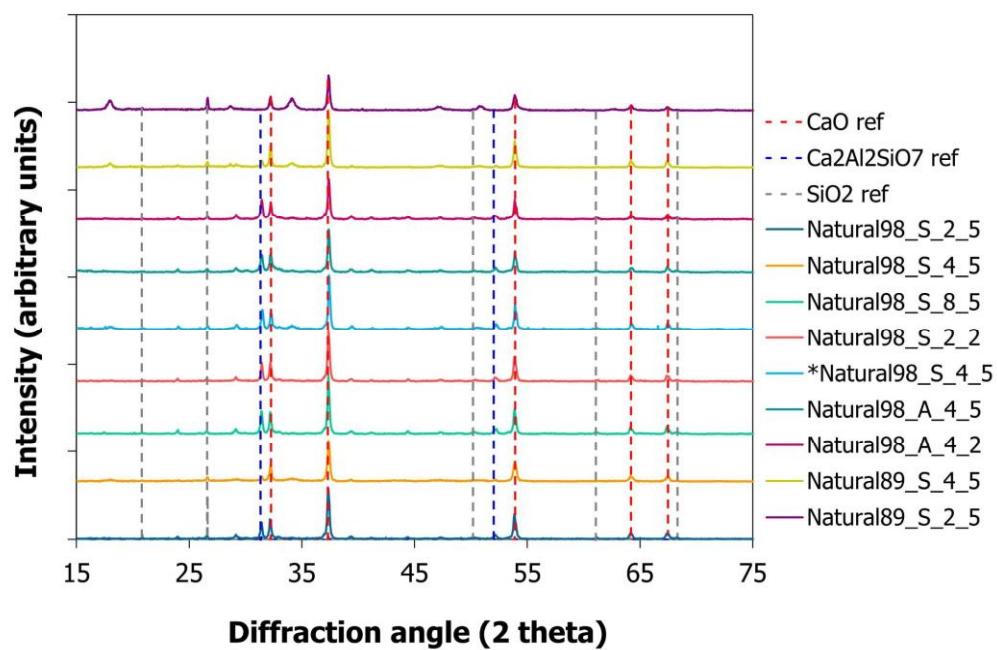
As depicted in Figure S3 and also stated in the main manuscript, the application of different conditions during preparation of the Natural98-derived composite materials did not affect notably the morphology of the crystal phases peaks. On the other hand, in the case of Natural89-derived samples, it is clear that calcining the material for 2 h resulted in no formation of the ternary Ca/Al/Si phase, while there were clear Ca(OH)<sub>2</sub> peaks at 18, 34, 47 and 51 degrees.



**Figure S1.** XRD analysis for Reference and clay composite materials (JCPDS Card Numbers used: CaO: 00-048-1467;  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ : 00-035-0755;  $\text{SiO}_2$ : 00-085-0695)



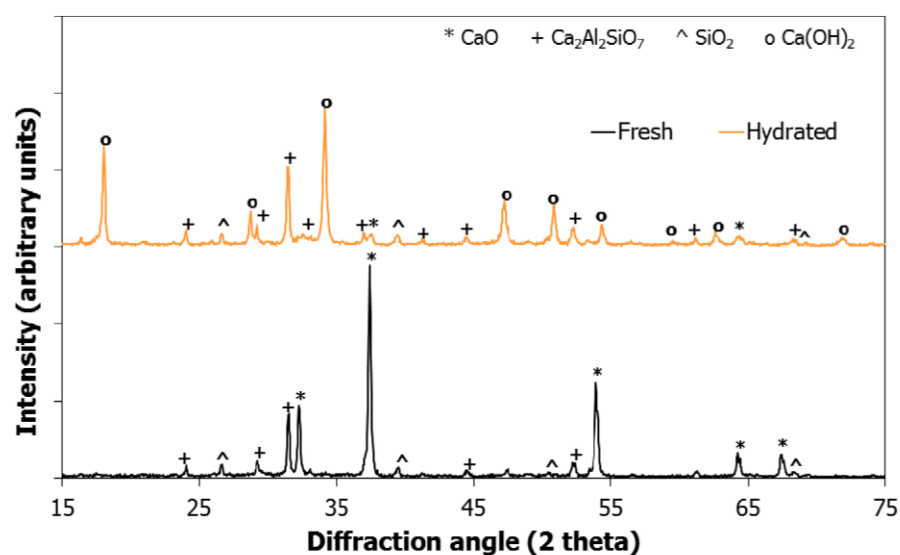
**Figure S2.** XRD analysis for composite CaO/kaolinite (75/25 %wt) materials with different Caprecursors (JCPDS Card Numbers used: CaO: 00-048-1467;  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ : 00-035-0755;  $\text{SiO}_2$ : 00-0850695)



**Figure S3.** XRD analysis for composite CaO/kaolinite (75/25 % wt) materials prepared under different conditions (JCPDS Card Numbers: CaO: 00-048-1467; Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>: 00-035-0755; SiO<sub>2</sub>: 00-085-0695)

## Inertness of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ towards hydration reaction

Considering the difficulty to obtain pure  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , another approach was followed in order to define the participation of the ternary Ca/Al/Si phase in the hydration reaction. To this respect, multiple composite pellets of Natural98 derived material were subjected to hydration according to the protocol described in the main document and the particles were obtained at their hydrated form. XRD analysis was conducted on these pellets in powder form (right after hydration). According to results obtained (Figure S4), only  $\text{Ca}(\text{OH})_2$  peaks were identified, thereby proving that the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phase is not subjected to hydration under the conditions applied in the present study.

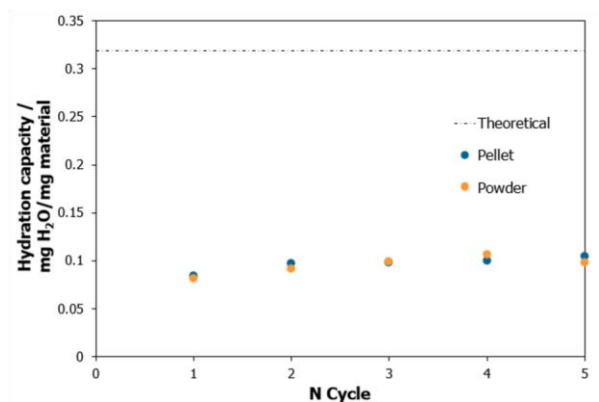


**Figure S4.** XRD analysis of fresh and hydrated Natural98 derived pellets

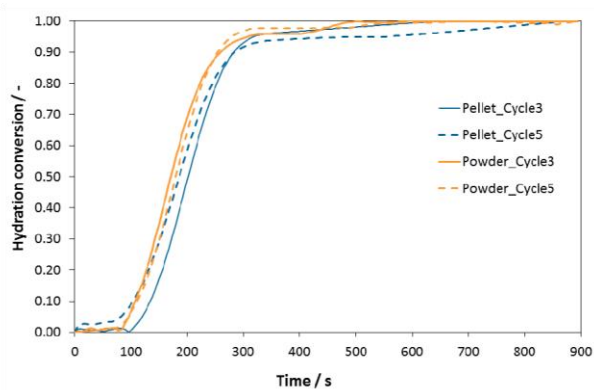


## Hydration capacity and rate of composite pellet and powder

On an effort to determine if the structured shape of the composite materials examined in this study affects the hydration capacity and reaction rate of the materials, preliminary experiments were conducted on a composition in pellet and powder form. The material studied derived from Natural98  $\text{CaCO}_3$  particles with a size  $<45\ \mu\text{m}$  combined with 25 wt % of kaolinite and was calcined at  $900\ ^\circ\text{C}$  for 4 h with  $5\ ^\circ\text{C}\cdot\text{min}^{-1}$ . A 5-cycle experiment was performed both in pellet and powder form (amount equal to 1 milled formulation). The evaluation protocol applied in this experiment included hydration at  $450^\circ\text{C}$  for 15min and dehydration at  $550\ ^\circ\text{C}$  for 20 min, while the atmosphere applied in both reactions was 75 vol % of steam ( $P_{\text{total}}=1\ \text{bar}$ ). Figure S5 shows the hydration capacity measured for both samples on the basis of total fresh material mass (after calcination), as well as the hydration rate noted for these samples for cycles No. 3 and 5. As it can be seen in Figure S5a, the hydration capacity noted for these samples was similar and around 30% w.r.t. the maximum theoretical value. These capacities are slightly lower than the one presented for Natural98\_ $<45$  pellet in Table 6 of the manuscript corresponding to a hydration efficiency of 40%, which is justified by the lower steam concentration applied in this preliminary examination. Moreover, the analysis of both measurements in Figure S5b showed that the reaction rates between the pellet and powder samples were very close. In particular, for the composite pellet, hydration reaction at cycle 3 began by  $t=50\ \text{s}$ , while for the powder it began at about  $80\ \text{s}$ . However, they became identical by  $t=170\ \text{s}$  during the fast part of the reaction and were completed by  $t=600\ \text{s}$ . In cycle 5, hydration reaction started at the same time for both samples, but hydration conversion was achieved slightly faster for the composite powder reaching its maximum value at  $t=500\ \text{s}$ . Therefore, the structured shape of the composite materials did not have any notable effect on materials hydration performance.



a.



b.

**Figure S5.** a. Hydration performance of composite pellet and powder in the course of 5 hydration/dehydration cycles, b. Hydration conversion of composite pellet and powder with time