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STUDY OF ETTRINGITE-RICH CEMENTITIOUS MATRICES FOR THERMOCHEMICAL ENERGY STORAGE: FROM LABORATORY CHARACTERIZATION TO A LARGE-SCALE APPLICATION

Summary

In the context of the global transition toward renewable energy, efficient heat storage systems are essential for overcoming the intermittency of sources such as solar power and provide the required grid flexibility. Thermochemical energy storage materials offer a promising solution to this challenge, with ettringite emerging as a leading candidate because of its low production cost, low operating temperature (< 100 °C), and high theoretical energy density. However, the initial integration of ettringite-rich cementitious materials at the system level yielded an energy density of 104 kWh/m³, which is lower than the storage capacity observed for the powder form of the material. Scaling up research from laboratory to system scale requires appropriate material processing that is both cost-effective in terms of raw materials and manufacturing time. To address this discrepancy, this study proposes a novel manufacturing process for a cementitious formulation named "C80P20" using a one-step granulating plate technique. This approach aims to facilitate industrial scalability and maximize energy density at the grain-bed level.

Keywords: Ettringite, Cement paste granules, Wet granulation, Physicochemical structure, Thermochemical heat storage, Cyclability
Field of application for the findings: Thermal Energy Storage
Addressed audience: Researchers

1. Introduction

Solar energy and wind are an accessible and environmentally friendly energy sources, but their intermittent nature is a significant impediment to its widespread deployment, as there is often a mismatch between supply and demand. Energy transition is therefore accompanied by the development of energy storage, like heat storage, to overcome the intermittency of these clean energies. It can ensure thermal comfort and the reliability of the energy supply for residential heating and domestic hot water throughout the year, regardless of seasonal constraints, which are currently provided by fossil fuels (Ayaz et al., 2021).

Thermochemical energy storage (TCES) materials have attracted considerable interest because of their high energy storage density, negligible heat losses over long periods, and potential for long-term (e.g., seasonal) storage (Solé et al., 2015). Despite their theoretical promise and attractive advantages, TCES technologies are still in the early stages of development and face several critical shortcomings that hinder their widespread commercialization, such as the lack of reactor-scale experimentation (Galazutdinova et al., 2024).

In this context, ettringite has emerged as a promising thermochemical material with a high energy density (547 kWh/m³ on pure salts). Ettringite can be synthesized from cement, making it an economical material compared to its competitors. It is a chemically stable alternative to phase-change materials for low-temperature applications (below 100 °C). The implementation of ettringite as a storage material faces heat and mass transfer problems related to the geometry of the material. This resulted in a decrease in energy density, from 262 kWh/m³ to 104 kWh/m³ (Chen et al., 2021).

2. Objectives

These limitations highlight the critical need for an ettringite-rich cementitious material capable of addressing durability, kinetic, and structural integrity issues, particularly in a thermochemical reactor. The development of such a material requires controlling its porous network to achieve high permeability for efficient heat and mass transfer with adequate mechanical resistance (Ndiaye et al., 2020).

Consequently, for successful system-level integration, the evaluation criteria must extend beyond material-specific properties such as the hydration energy density. This study broadens the analysis to include macroscale parameters such as the material bed architecture (bulk density, porosity, and specific surface area), technoeconomic characteristics (manufacturing process and material geometry), and dynamic performance (reaction kinetics and mass transfer limitations). The objective of this work is twofold: first, to maximize the ettringite density (in kg/m³) of a composite bed derived from an ettringite-rich cementitious mixture "C80P20"; second, to study its thermochemical potential with a view to integration into a thermal storage system.

To this end, a new manufacturing process has been proposed to produce material granules from the C80P20 cementitious mix. Compared with crushed hardened cement paste, wet granulation produces dense, spherical particles with a higher ettringite density. This study also suggests a new method to calculate the ettringite content of ettringite-rich cement pastes using thermogravimetry analysis. However, following thermochemical cycle analyses of 1.2 mm grains, the ettringite content within the materials has little effect on their ability to release stored heat. This observation leads to the hypothesis of a predominant hydration reaction of ettringite on the surface of the grains.

3. Methodology

In this study, eleven materials were manufactured: two materials by crushing a hardened cement paste (CHCP) (Chen et al., 2021) and nine according to a wet granulation process (WG), with different water/cement (W/C) ratios controlled by the addition of a superadsorbent.

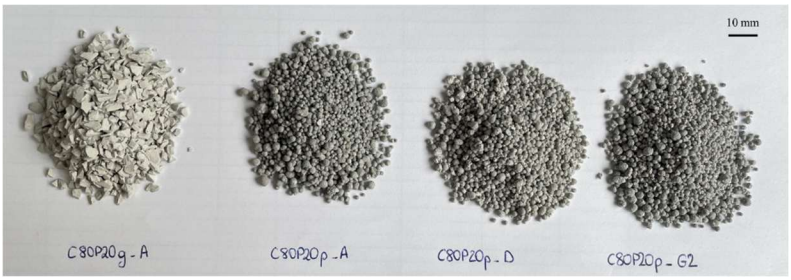

Figure 1: Picture of the 4 formulations selected for the next stage of the study (1-3.15 mm diameter granulometry)

The samples were first aged for seven days in a temperature-controlled laboratory at 20 °C. Bulk density, mercury intrusion porosimetry (MIP), specific surface area and scanning electron microscopy (SEM) analyses were performed on grains with a diameter of 1–3.15 mm. The grains were ground to a fineness of less than 125 µm to prepare samples for thermogravimetric analysis (TGA) and X-ray diffraction (XRD).

The initial chemical analyses of the eleven materials allow for a preliminary understanding and selection of promising materials for thermochemical analysis. Figure 1 shows the four materials selected according to initial analysis. Materials C80P20p-A and C80P20g-A serve as references for both manufacturing processes (CHCP and WG). Materials C80P20p-D and C80P20p-G2 represent promising candidates for thermochemical storage, characterized by a W/C ratio greater than 0.6 with a single-step manufacturing process. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) coupled with a humidity control system were used to characterize a thermochemical loading/unloading cycle of the four C80P20 selected materials on 1.2 mm diameter grain shape. To conclude on the advantages of using ettringite in a cementitious matrix, a cycling test was carried out in a climate chamber. The C80P20p-G2 granules underwent 50 loading/unloading cycles, with thermochemical analysis performed at different cycling intervals.

4. Results and discussion

The bulk density of the packed bed material enables the calculation of the ettringite density (kg/m³), which is a more relevant unit for scaling up heat storage technology. On the basis of the results of the ettringite density and BET specific surface area, two formulations, C80P20p-D and C80P20p-G2, manufactured on the granulation plate, appear to be the most promising candidates for thermal storage applications. C80P20p-G2 has the highest ettringite volumetric content of 745 $kg_{ettringite}/m^3_{bulk\ mat}$. C80P20p-D and C80P20p-G2 have the highest BET specific surface area of 14.4 and 14.1 m^2/g, respectively. This analysis suggests that the surface condition of these materials is promising for promoting heat and mass transfer during the hydration reaction and therefore potentially increasing the final heat released by the material. The results of TGA/DSC cycles on 1.2 mm diameter granules showed that the storage capacities of the grains depend on the amount of ettringite, but the hydration energies of the four materials tested are similar, as if their internal composition had no impact on the hydration kinetics.

Material C80P20g-A has the highest hydration heat energy at 601.3 J/g, followed by material C80P20p-D at 540 J/g. Materials C80P20p-G2 and C80P20p-A are slightly lower at 480 J/g and 501 J/g, respectively. By using the bulk density of each material, it is possible to estimate its energy density. Although the volumetric estimation identifies C80P20p-A as having the highest energy density of 146 kWh/m³, the results across all four materials are uniform, with a standard deviation of 8.4 kWh/m³. The results of hydration energies over 50 cycles indicate that the energy density of the material remains constant over 50 cycles, maintaining on average at 530 J/g, or 148 kWh/m³ for the C80P20p-G2 granules.

5. Conclusion

A major finding of this work is the validation of the one-step granulation technique as a method with high industrial manufacturing viability. Compared with the multistage CHCP method, the WG process significantly reduces manufacturing time and complexity while enhancing safety. The material results of this study, such as the content of ettringite, porosity, specific surface area, differ. However, these discrepancies do not impact the hydration kinetics of the grains or their associated thermochemical properties. These findings support the hypothesis of limiting hydration at the grain surface, which is covered with ettringite according to SEM images. Since the reactivity is concentrated at the grain interface, the material is particularly vulnerable to surface degradation. A cyclability study revealed that the active layer is thermochemically stable over 50 dehydration/hydration cycles and exhibits low susceptibility to carbonation.

6. References

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