EuroSun 2026

MECHANICAL STABILITY EVALUATION OF SHAPED COMPOSITES FOR THERMOCHEMICAL STORAGE

Summary

This work evaluated the mechanical stability of salt-hydrate composite TCMs using different binders, hosts, and shaping methods. Mineral binders showed low stability, whereas hydraulic systems, especially sulfoaluminate cements, achieved significantly higher crush strength. Dental cements performed well but required higher binder fractions. Pelleting combined with long natural fibers further improved the stability of selected formulations. Promising candidates were identified for further development. Current work includes testing molding routes, assessing silicate binders, and investigating additional salt combinations. Future efforts will address pellet dimensions and coating strategies to optimize composite functionality.

Keywords: Thermochemical storage materials (TCM), salt-hydrate, composite, binder, mechanical stability

Field of application for the findings: Thermal energy storage

Addressed audience: researchers and academics, industrial stakeholders

1. Introduction

The importance of thermal energy storage in enabling the renewable-energy transition has been emphasized repeatedly in recent years. While sensible heat storage technologies are already well established, latent heat storage systems are now entering the market with increasing commercial success. In contrast, thermochemical energy storage remains primarily a research focus. The primary challenges arise from material-related limitations, as cycling stability, sorption capacity, and achievable power output are still critical bottlenecks and limit limit application deployment [2]. Alongside fundamental efforts to identify new reactive compounds, significant efforts are being directed toward the development of composite materials that combine well-studied, readily available constituents to enhance overall performance [1, 3].

Processing and shaping routes, together with the choice of raw materials, define the practical constraints for composite development. This work presents research on combining different binders with chloride salt-hydrates and porous host structures, with particular emphasis on evaluating their mechanical stability. Building on these findings, a logical next step is to address application-specific requirements, especially those imposed by reactor design, as different configurations demand tailored shaping strategies for thermochemical materials to ensure robust and efficient operation. This work presents preliminary results on the mechanical stability of the produced composites, through single-granule crush strength measurements for selected binders and shaping methods.

2. Materials and methods

The composites presented in this work consist of two types of active materials, a binder and additives. Highly hygroscopic salt-hydrates, such as calcium chloride ($CaCl_2$) and lithium chloride (LiCl), are used as the primary active components and are mixed in mass ratios of 7:3 and 9:1. Regionally mined clinoptilolite zeolite (clino) and the layered silicate vermiculite (verm) were used as porous host matrices. The binders are selected to enhance structural integrity while preserving sufficient porosity after curing to enable effective vapor-phase diffusion throughout the composite. Composites are prepared using three binder classes:

- mineral: attapulgite
- hydraulic (or hydraulic-type): construction cements (Portland, sulfoaluminate) and phosphate-based dental cements

- silicates: sodium and lithium waterglass

However due to space limitations only a small selection of samples using first two binder classes will be discussed in this work. Further, the additives are mainly natural hemp and birch fibers used in pelleting process for enhancing stability of cylindrical pellets. And lastly, acidic retardants were utilized in cement hydration processes.

Table 1 summarizes the sample compositions and the notation used in this work, with the mass fraction (wt.%) of each constituent indicated alongside its designation.

Tab. 1: Sample compositions and the notation used in this study are summarized here. The corresponding component ratios are provided as fractional values in wt.%. A commercial binder-free 4A zeolite from CWK is used as the reference.

Sample Name	Binder	Host	Additive	Shaping
Z4ABF (ref)				Sphere
ATT5	Attapulgite 5	Clino		Sphere
PC5	Portland 5	Clino		Sphere
PS10	Solfoaluminat 10	Clino		Sphere
PS10H	Solfoaluminat 10	Verm	Hemp	Cylinder
AC20B	Dental 20	Clino	Birch	Cylinder
AC20H	Dental 20	Clino	Hemp	Cylinder
PS30H	Solfoaluminat 30	Clino	Hemp	Cylinder

As shown in Figure 1, the samples are shaped using three distinct methods: molding into half-spheres, disc granulation to form spheres, and pelleting by pressing to produce cylindrical pellets.

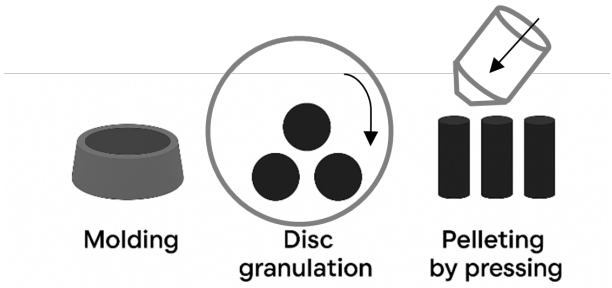


Fig. 1: Schematic representation of the shaping methods and resulting composites (from left to right): molding - half-spheres, disc granulation - spheres, pelleting by pressing - cylindrical pellets (image partly generated using Copilot).

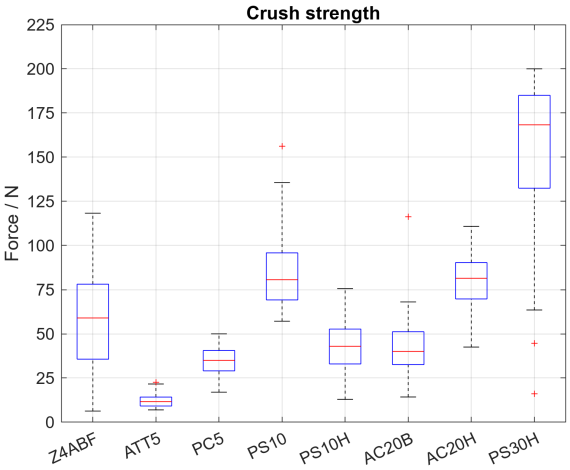
The mechanical stability tests are carried out using a self-built setup in which individual shaped samples are compressed until the onset of fracture. The maximum force (in N) recorded at the first break or collapse is defined as the crush strength (similar to the standard single pellet crush strength). Cylindrical pellets are loaded in radial orientation for cracking. Prior to testing, all samples are stored overnight at 40°C and in the controlled humidity environment of a large oven. For each series, 25 pellets were evaluated.

3. Results

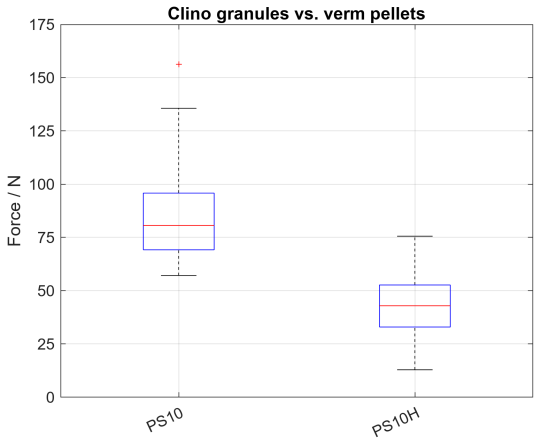
The results presented here are selected to illustrate the wide span of outcomes and to demonstrate the progressive advancement in composite development throughout the R&D process. The aim was to assess the influence of different binders and processing routes on the mechanical stability of the granules. As shown in Figure 2a, mineral binders (e.g., ATT5), which require thermal curing, exhibited low crush strength. In contrast, hydraulic binders provided higher stability; however, the exothermic hydration reaction interfered with the salt-hydrates in the Portland-cement–based samples (PC5), and increasing the binder content did not further improve their crush strength. Significantly improved mechanical performance was achieved using sulfoaluminate cements at concentrations between 10 and 30 wt.%. These formulations showed a consistent increase in crush strength with increasing binder content (e.g., PS10H $\approx$ 80 N versus PS30H $\approx$ 160 N), an effect potentially reinforced by the incorporation of fiber additives, which was only feasible for pelleted samples. To obtain comparable

mechanical stability (approximately 80 N), nearly twice the amount of dental cement was required (PS10 versus AC20H), highlighting the superior efficiency of the sulfoaluminate-based binders.

For improved clarity, two key comparisons were redrawn in Figure 2b. In addition to the processing method, the structural stability and porosity of the host material play a decisive role. Although pellets generally exhibited higher mechanical stability than granules throughout the tests, the use of the macroporous, layered host vermiculite resulted in no additional strength gain upon pelleting, as shown in Figure 2b. In contrast, granules produced with the nanoporous clinoptilolite host achieved markedly higher crush strength, reaching approximately 80 N.



(a) Statistical evaluation of selected sample sets.



(b) Influence of porous hosts and shaping method: clino granules vs. verm pellets.

Fig. 2: (a) Statistical evaluation of selected sample sets, presented as boxplots (blue) with median values indicated in red and whiskers representing the full data range. Sample compositions are listed in Table 1. Commercial 4A binderfree zeolite (CWK) on the first place as reference.(b) Exert: Disc granulated composites with the same composition show higher crush strength than the vermiculite pellets with hemp fibers.

4. Conclusion and further work

Sulfoaluminate cements and phosphate-based cements demonstrated the most promising mechanical stability when processed as pellets, particularly when combined with long natural fibers such as hemp. These formulations consistently achieved high crush strength while maintaining compatibility with the salt-hydrate composites. Ongoing work focuses on evaluating alternative shaping and molding routes and on assessing silicate binders to broaden material design strategies. Additional salt-hydrate combinations are currently under investigation and can be presented in future work. Further research will also address the influence of pellet geometry and the development of suitable coating formulations to enhance the mechanical robustness and handling properties of granules.

References

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