POLITECNICO DI TORINO Repository ISTITUZIONALE

Advancing thermochemical storage: synthesis and characterization of cement-based composite materials

Original

Advancing thermochemical storage: synthesis and characterization of cement-based composite materials / Mondello, A; Morciano, M; Lavagna, L; Pavese, M; Chiavazzo, E. - In: JOURNAL OF PHYSICS. CONFERENCE SERIES. - ISSN 1742-6588. - ELETTRONICO. - 2766:(2024), pp. 1-6. (Intervento presentato al convegno 9th European Thermal Sciences Conference (Eurotherm 2024) tenutosi a Lake Bled (SL) nel 10/06/2024 - 13/06/2024) [10.1088/1742-6596/2766/1/012218].

Availability: This version is available at: 11583/2989572 since: 2024-06-17T09:07:16Z

Publisher: IOP

Published DOI:10.1088/1742-6596/2766/1/012218

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

PAPER • OPEN ACCESS

Advancing thermochemical storage: synthesis and characterization of cement-based composite materials

To cite this article: A Mondello et al 2024 J. Phys.: Conf. Ser. 2766 012218

View the article online for updates and enhancements.

You may also like

- Piezoelectricity-based self-sensing of compressive and flexural stress in cementbased materials without admixture requirement and without poling Kairong Shi and D D L Chung
- <u>Electrical resistivity and mechanical</u> properties of cementitious composite incorporating conductive rubber fibres Wenkui Dong, Wengui Li, Guodong Long et al.
- <u>Carbon nanotubes-coated cement</u> <u>particles for cement-based sensors with</u> <u>excellent piezoresistivity</u> Jian Yuan, Dong Lu, Huiming Wu et al.



DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 130.192.232.210 on 17/06/2024 at 09:41

Advancing thermochemical storage: synthesis and characterization of cement-based composite materials

A Mondello¹, M Morciano¹, L Lavagna², M Pavese² and E Chiavazzo^{1,3}

¹ Department of Energy, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

² Department of App. Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

³ Istituto Nazionale di Ricerca Metrologica, Strada Delle Cacce 91, 10135 Torino, Italy

E-mail: eliodoro.chiavazzo@polito.it

Abstract. Thermal Energy Storage (TES) is crucial for sustainability of the energy sector, yet the development of cost-effective, robust materials remains a significant challenge. This study aims at exploring the synthesis and thermal characterization of cement-based composites for seasonal thermochemical energy storage, with the goal to harness the high energy density of hygroscopic salts while mitigating their limitations. We investigate composites with several cement matrices to improve salt-cement compatibility. Furthermore, we investigate the possible incorporation of porous low-cost compounds to enhance porosity and improve economic aspects. As far as the characterization aspects are concerned, we show experimental adsorption isotherms at different temperatures to estimate key material properties like isosteric heat and water uptake, along with the relevant figures of merit such as energy density. Our research leverages on adjustable porosity and affordability of cement as a host matrix for the 'active phase'. We studied two synthesis approaches: traditional dry impregnation and an insitu technique suitable for cements. The in-situ method, being straightforward and reproducible, permits greater control over salt content. Preliminary cost analysis positions these composites competitively in the market. Although we are still at sub-optimal stage, potential cost reduction of some less popular cement matrices suggests an opportunity for improvement.

1. Introduction

Thermochemical energy storage (TES) involves reversible physical or chemical reactions to store and release heat. Sorption TES (STES), coined by McBain in 1909[1], is typically used for lowtemperature heat storage, potentially for residential space heating. This could be achieved by capturing solar thermal energy in the range of 90 °C to 150 °C[2] with solar collectors or concentrating solar power, which then can be stored for later use during winter.

For STES, physically porous sorbent materials like zeolites and silica gel offer stability but have low energy density and capacity. Chemical sorbent materials provide higher storage capacity but are limited by deliquescence, affecting stability and performance over time. A recent promising research direction involves the development of "hygroscopic salts inside a porous matrix with open pores" (CSPM). CSPMs help mitigate deliquescence issues, improve stability over cycles, enhance mass and heat transfer through improved heat conductivity, and allow tailored properties for specific

Content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

applications[3]. They are gaining significant attention for solar-driven seasonal thermal energy storage in recent scientific literature[4].

This study aims to synthesize and investigate novel composite materials for seasonal lowtemperature sorption heat storage, focusing on affordability and widespread availability of raw materials. The objective is to develop commercially appealing sorbent materials, even with lower energy density values. Cement is explored as a potential host matrix for various salt hydrates due to its cost-effectiveness, global ubiquity, and controllable porosity. Sepiolite is introduced as a second porous phase. The study covers the characterization of pure cement paste properties, synthesis, and analysis of cement-based composite materials. Additionally, potential water sorption heat storage applications in space heating and a preliminary economic analysis will be evaluated.

2. Materials and methods

Three types of cement have been employed in this work: Portland cement (PC) and calcium-sulfoaluminate (CSA) cement from Italcementi (Ultracem 52.5 R and Ali Pre Green, respectively), and calcium-aluminate cement (CAC) branded Ciment Fondu® from Imerys Aluminates. Sepiolite was purchased from Lampa Accessories, and MgSO₄ (in the form of the eptahydrate MgSO₄·7H₂O) as active salt for TES was supplied by Merck.

Equipment included a Radwag laboratory scale PS 510/C/1 balance (1 mg resolution), a Preciva digital caliper (0.01 mm resolution), a National Instruments acquisition system with LabVIEW 2017 software, a Thunder Scientific 2500 climatic chamber (with RH uncertainties between 0.2%rh and 2%rh and 0.4 °C air temperature uncertainty), and a Sartorious MA-150 scale (1 mg resolution).

Cement samples were prepared conventionally by mixing defined amounts of deionized water and dry cement powder, following the water to cement weight ratio (w/c ratio), a critical parameter in cement production influencing sample porosity. Sepiolite was added to the cement powder in weight ratios of up to 70%.

The procedure for preparing salt-loaded samples involves blending proper amounts of water, dry cement powder, and sepiolite to form a homogeneous slurry. This slurry is then poured into metallic molds with four equal compartments (each measuring $80 \times 20 \times 20$ mm, with a volume of 32 cm^3) to produce four specimens with consistent mixes and curing conditions. Following methodologies from previous studies[5], two types of salt loading are conducted:

- a) Standard method ("two-steps" or "dry impregnation"): Samples are initially prepared with deionized water and then infiltrated with a saturated MgSO₄ solution.
- b) Innovative method[5] ("one-step" or "*in situ*"): Samples are prepared by directly incorporating the saturated solution into the slurry. This method enhances reproducibility, salt dispersion in the matrix and stability over time.

Subsequently, both sample types undergo same treatment that consists of removing the water by a heat treatment at 140 °C. Mass and volume of all the samples were obtained using the Radwag balance and the digital caliper, and then the geometrical density was calculated by their ratio.

A preliminary calorimetric analysis was performed following Lavagna et al.'s procedure[5]. Dehydrated samples, obtained by oven drying, were placed in a well-insulated vessel (figure 1) with liquid water on top. A sharp rod pierced a polyethylene film separating the compartments, allowing immediate contact between water and samples. Temperature changes were monitored using K-type thermocouples and an acquisition system. The vessel, 3D printed in ABS and waterproof, held around 35 g of composite (figure 1) and excess water (0.7 ratio). The temperature difference (ΔT) estimated composite energy density, considering masses (M_i) and specific heat capacities ($c_{p,i}$) of water, pure cement and MgSO₄·7H₂O. The energy density equation

$$E = \Delta T \sum_{i} M_{i} c_{p,i} \tag{1}$$

is only valid under adiabatic conditions neglecting thermal losses to the environment, which the authors determined that could be done safely.



Figure 1. On the left, a schematic representation of the experimental setup (actual dimension in mm). On the right, pellets of composite samples.

3. Results and discussion

PC				CAC				CSA				CAC 85.0% - PC 15.0%			
Label	Sep (%)	w/c	In Situ	Label	Sep (%)	w/c	In Situ	Label	Sep (%)	w/c	In Situ	Label	Sep (%)	w/c	In Situ
1	-	1.0	Х	7	-	1.5	Х	11	-	1.0	Х	14	70	1.5	\checkmark
2	-	1.5	х	8	70	1.5	\checkmark	12	70	1.5	Х				
3	30	1.0	Х	9*	70 (H ₂ O)	2.2	\checkmark	13	70	1.5	\checkmark				
4	30	1.5	х	10*	70 (MgSO ₄)	2.2	\checkmark					CA	C 77.5%	- PC 2	22.5%
5	70	1.0	Х									Label	Sep (%)	w/c	In Situ
6	70	1.5	Х									15	70	1.5	

Table 1. List of composite synthetized with their composition and salt-loading procedure used.

Fifteen different types of samples were prepared for this work by exploring various combinations between type of cement, salt-loading procedure, w/c ratio and sepiolite %, as shown in table 1.

We performed the preliminary calorimetric analysis on 8 representative samples. For each composite material, different samples were tested to have a larger set of data, except for composite 6.

Label	m_s (g)	$ ho_s$ (g/cm ³)	T_i (°C)	<i>T_f</i> (°C)	E_d (MJ/m ³)	$ar{E_d}$ (MJ/m ³)
4	3.74 3.04	1.07 1.07	21.90 20.50	26.60 25.00	65.01 74.53	69.77
5	4.23 4.47	1.15 1.15	22.00 21.90	27.50 27.50	71.73 70.19	70.96
6	3.56	1.06	21.60	27.70	85.92	85.92
8	2.68 2.58 2.02 2.90	1.12 1.12 1.12 1.12	20.40 16.90 21.60 19.40	25.20 22.20 25.30 25.30	92.58 116.75 92.98 105.85	102.04
12	3.12 2.98 2.07	1.01 1.01 1.01	20.00 20.50 21.10	23.80 24.90 24.40	57.34 69.13 72.79	66.42
13	2.70 2.74 2.67 2.47 2.51 2.24	1.04 1.04 1.04 1.04 1.04 1.04	16.20 21.00 21.60 18.30 19.60 20.30	21.10 26.80 28.80 24.30 26.30 25.70	85.37 99.31 127.22 113.16 125.10 111.82	110.33
14	1.41 2.62	1.06 1.06	22.20 22.70	24.90 28.00	89.72 98.78	94.25
15	1.61 2.64	1.04 1.04	22.50 23.50	25.40 28.00	84.47 84.56	84.52

Table 2. Label, total mass of the sample (m_s) , geometrical density (ρ_s) , initial (T_i) and final (T_f) reference temperatures, energy density (E_d) and mean energy density (\overline{E}_d) of 22 samples from 8 different composite materials.

According to the data in Table 2, considering 80 MJ/m³ as an arbitrary acceptable threshold, most samples meet this requirement, indicating promising potential. Composites 4, 5, and 12 fall below this threshold and are deemed non-promising, while composites 8, 13, 14, and 15 show potential for further development. Composite 6, although meeting the energy density threshold, is excluded because already studied by Cangelmi[6] obtaining favourable results.

Regarding the two different salt-loading procedures, very indicative is the comparison between composite 12 and composite 13; in fact, they share the same composition in terms of type of cement, w/c ratio and sepiolite %, with the only difference in the salt-loading procedure, but the difference between their mean energy density value is near the 50% in favour of the one synthetized with the "*in situ*" procedure. In light of this, we can consider the "*in situ*" procedure as the better option to obtain composite with higher energy density.





A more precise method[7] was then applied to accurately estimate the energy density of select composites at real world operational boundary condition. Two isotherms, depicted in Figure 2 at 30°C and 50°C, were generated by fitting experimental water uptake values obtained through sample weighing after reaching equilibrium at constant temperature and RH levels (0%, 10%, 30%, 50%, 70%, and 90%) in the climatic chamber. Then, by employing the Polanyi potential theory[7], isotherms at different temperatures were predicted for the studied composites. This enabled the derivation of corresponding isosteric curves in the Clapeyron chart, as shown in Figure 2, allowing the determination of cycled heat and subsequently, energy density.

	Units	Composite						
		8	13	14	15			
$\bar{E}_{d (\text{preliminary})}$	(MJ/m ³)	102.0	110.3	94.25	84.52			
Ed (Salustro et al.[7])	(MJ/m ³)	95.1	83.9	85.23	84.65			
ΔE_d	%	7.1	27.3	10.05	0.16			

Table 3. Mean energy density (\overline{E}_d) obtained by preliminary analysis, energy density values (E_d) calculated by Salustro et al.[7] and the percentage difference (ΔE_d) between them.

In table 4 are shown the values of energy density estimated by the preliminary calorimetric analysis, the values obtained by Salustro et al.[7] for the same composites by the method described before and the percentage difference between this two. We can notice that the discrepancy between the values is generally under the 10%, excluding the composite 13 that exhibits a higher value, with the composite 15 that has even less than 1% discrepancy. In light of this, we can affirm that this calorimetric analysis is a suitable method for conducting preliminary energy density screening on novel composite materials, saving time and enabling the selection of the most promising ones for indepth analysis and further development.

4. Preliminary cost analysis

The preliminary cost analysis is an important instrument to assess the potential economic feasibility in terms of costs of the installed storage capacity of the novel developed materials. The ratio between the price of the raw materials, C (\notin /ton), and the cycled heat, Q_u (kWh/ton), is the *key performance indicator* (KPI) used in this work as a figure of merit to evaluate the economic appeal of the synthesized materials[7].

To calculate the KPI for the novel composite materials, we used the Q_u values obtained by Salustro et al.[7] through the cycle illustrated in figure 3 for each of these materials. To evaluate *C*, neglecting all other costs except for raw materials, we assumed: 100 \notin /ton for PC[8], 400 \notin /ton for CAC[9], 300 \notin /ton for CSA cement[10], 100 \notin /ton for sepiolite[11], 160 \notin /ton for anhydrous magnesium sulfate[12], and the results are shown in table 5.

As can be observed, composite 8 has the higher KPI among the novel synthesized composite, and so it should be discarded. Composite 14 is not provided in table 5 because it has a similar composition to composite 15 but worst KPI, so the latter has been taken as representative. It is important to notice that composite 8 has a Q_u value better than others, but the higher cost of CAC makes its KPI not competitive. Composite 15, thanks to the presence of a small percentage of PC cement, balance the higher cost of CAC in relation to CSA, and so the composite 15 results the best among the tested ones in terms of KPI and economical appealing.

Material	Salt (%)	<i>T_c</i> (°C)	Q_u (kWh/ton)	E_d (GJ/ton)	C (€/ton)	KPI (€/kWh)	Ref.
CAC; 70% sep.; w/c=1.5	21.4	150	23.37	0.095	233.3	10	Composite 8 and Salustro [7]
CSA; 70% sep.; w/c=1.5	21.5	150	22.61	0.084	212.4	9.4	Composite 13 and Salustro [7]
CAC(77.5%)-PC(22.5%); 70% sep.; w/c=1.5	21.5	150	22.83	0.085	212.4	9.3	Composite 15 and Salustro [7]
PC/MgSO ₄	21	140	-	0.18	132.6	1.7 - 2.7	[5]
Vermiculite/CaCl ₂	57.3	85	-	1	329	1.18	[13]
Zeolite 13X	-	160	-	0.12	84.3	2.7 - 4.2	[14]
Zeolite 13X/MgSO ₄	10 - 25	150	-	0.65	1805	10.03	[14]
Silica Gel/CaCl ₂	33.7	90	-	0.58	3483.5	26.39	[14]

Table 4. Comparison of the best composites developed with other materials in literature. The KPI column shows the values in terms of raw materials costs variations.

Finally, it is important to compare the performances of these composites to that of other materials already characterized in literature and reported in table 5. The novel synthesized composites perform better than Zeolite $13X/MgSO_4$ and silica gel/CaCl₂ in terms of cost and KPI, but are far from the performances of the other materials in terms of energy density and KPI, while the cost remains competitive.

5. Conclusion

The goal of this study was to synthesize and thermally characterize cement-based CSPM materials for thermochemical energy storage. Three cement types were explored: PC cement, CAC and CSA cement, with sepiolite investigated as an additive to reduce costs and enhance porosity. An "*in situ*" technique facilitated the synthesis, offering advantages in speed, thermal performances and reproducibility. A preliminary calorimetric analysis was conducted to obtain energy density values, and this data have been confirmed to be reliable and helpful to perform affordable and time-saving screening analysis. Despite not being fully optimized, the cost-effective CSPM materials show promise, and further optimization could enhance KPI. CAC and CSA, while costlier, may benefit from cost reductions through scale economies. The mixture of CAC with PC cement proves interesting, providing stability against liquid water and sulfate resistance at lower costs. Clearly, this is a preliminary work that is focused only on material aspects and characterization and not on the entire

thermochemical storage system. So, we are aware that in the future a more complete characterization of the material, e.g. thermal conductivity, heat and mass transfer models and kinetics should be investigated in order to pave the way for a real plant application of the novel materials synthesized in this work.

Acknowledgement

We acknowledge financial support from: PNRR - M4C2 - AVVISO 341/2022 - NEST - PE00000021 CUP - E13C22001890001 SPOKE 6 - Energy Storage.

References

- McBain J W 1909 XCIX. The mechanism of the adsorption ("sorption") of hydrogen by carbon The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 18 916–935.
- [2] Zhang Y and Wang R 2020 Sorption thermal energy storage: Concept, process, applications and perspectives *Energy Storage Mater.* **27** 352–369.
- [3] Aristov Y I 2007 Novel Materials for Adsorptive Heat Pumping and Storage: Screening and Nanotailoring of Sorption Properties *Journal of Chemical Engineering of Japan* **40** 1242–1251.
- [4] Brancato V, Gordeeva L G, Sapienza A, Palomba V, Vasta S, Grekova A, Frazzica A and Aristov Y 2019 Experimental characterization of the LiCl/vermiculite composite for sorption heat storage applications *International Journal of Refrigeration* **105** 92–100.
- [5] Lavagna L, Burlon D, Nisticò R, Brancato V, Frazzica A, Pavese M and Chiavazzo E 2020 Cementitious composite materials for thermal energy storage applications: a preliminary characterization and theoretical analysis *Sci. Rep.* **10** 12833.
- [6] Cangelmi L 2021 Development of Cementitious Composite Materials for Sorption Thermal Energy Storage *Msc Thesis* Politecnico di Torino.
- [7] Salustro S, Lavagna L, Fernicola V, Smorgon D, Mondello A, Chiavazzo E and Pavese M 2024 Thermal characterization and cost analysis of cement-based composite materials for thermochemical energy storage J. Energy Storage submitted.
- [8] European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs 2018 Competitiveness of the European cement and lime sectors: final report *Publications Office*.
- [9] Lea F M and Hewlett P C 1998 Lea's Chemistry of Cement and Concrete (London: Arnold)
- [10] Aranda M A G, De la Torre A G 2013 Sulfoaluminate cement *Eco-Efficient Concrete* (Cambridge: Woodhead Publishing) p 488–522.
- [11] Song N, Hursthouse A, McLellan I and Wang Z 2021 Treatment of environmental contamination using sepiolite: current approaches and future potential *Environ. Geochem. Health* **43** 2679–2697.
- [12] Trausel F, de Jong A-J and Cuypers R 2014 A Review on the Properties of Salt Hydrates for Thermochemical Storage *Energy Procedia* **48** 447–452.
- [13] Aristov Y I, Tokarev M M, Cacciola G, and Restuccia G 1996 Selective water sorbents for multiple applications, 1. CaCl2 confined in mesopores of silica gel: Sorption properties *Reaction Kinetics & Catalysis Letters* 59 325–333.
- [14] Yu N, Wang R Z and Wang L W 2013 Sorption thermal storage for solar energy Prog. Energy Combust. Sci. 39 489–514.