BIM-GIS Modelling for Sustainable Urban Development

Original
BIM-GIS Modelling for Sustainable Urban Development / TORABI MOGHADAM, Sara; Lombardi, Patrizia; Ugliotti, FRANCESCA MARIA; Osello, Anna; Mutani, Guglielmina. - In: NEWDIST. - ISSN 2283-8791. - ELETTRONICO. - SPECIAL ISSUE:(2016), pp. 339-350.

Publisher:
DIST, Politecnico e Università di Torino

Published
DOI:

Journal of Physics: Conference
Series

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

9th European Thermal Sciences Conference (Eurotherm 2024) IOP Publishing
Journal of Physics: Conference Series **2766** (2024) 012218 doi:10.1088/1742-6596/2766/1/012218

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

A Mondello[1], M Morciano[1], L Lavagna[2], M Pavese[2] 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 *in-situ* 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 low-temperature 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 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 low-temperature 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-sulfo-aluminate (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 $MgSO_4$ (in the form of the eptahydrate $MgSO_4{\cdot}7H_2O$) 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 x 20 x 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 $MgSO_4$ 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 $MgSO_4{\cdot}7H_2O$. 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	✗	7	-	1.5	✗	11	-	1.0	✗	14	70	1.5	✓
2	-	1.5	✗	8	70	1.5	✓	12	70	1.5	✗				
3	30	1.0	✗	9*	70 (H_2O)	2.2	✓	13	70	1.5	✓				
4	30	1.5	✗	10*	70 ($MgSO_4$)	2.2	✓					**CAC 77.5% - PC 22.5%**			
5	70	1.0	✗									Label	Sep (%)	*w/c*	*In Situ*
6	70	1.5	✗									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)	ρ_s (g/cm^3)	T_i (°C)	T_f (°C)	E_d (MJ/m^3)	$\bar{E}_d$ (MJ/m^3)
4	3.74	1.07	21.90	26.60	65.01	69.77
	3.04	1.07	20.50	25.00	74.53	
5	4.23	1.15	22.00	27.50	71.73	70.96
	4.47	1.15	21.90	27.50	70.19	
6	3.56	1.06	21.60	27.70	85.92	85.92
8	2.68	1.12	20.40	25.20	92.58	102.04
	2.58	1.12	16.90	22.20	116.75	
	2.02	1.12	21.60	25.30	92.98	
	2.90	1.12	19.40	25.30	105.85	
12	3.12	1.01	20.00	23.80	57.34	66.42
	2.98	1.01	20.50	24.90	69.13	
	2.07	1.01	21.10	24.40	72.79	
13	2.70	1.04	16.20	21.10	85.37	110.33
	2.74	1.04	21.00	26.80	99.31	
	2.67	1.04	21.60	28.80	127.22	
	2.47	1.04	18.30	24.30	113.16	
	2.51	1.04	19.60	26.30	125.10	
	2.24	1.04	20.30	25.70	111.82	
14	1.41	1.06	22.20	24.90	89.72	94.25
	2.62	1.06	22.70	28.00	98.78	
15	1.61	1.04	22.50	25.40	84.47	84.52
	2.64	1.04	23.50	28.00	84.56	

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 ($\bar{E}_d$) of 22 samples from 8 different composite materials.

According to the data in Table 2, considering 80 MJ/m^3 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.

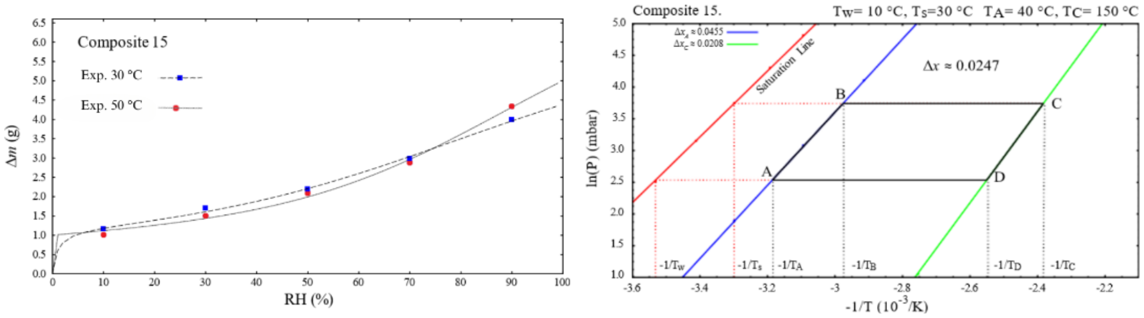

Figure 2. On the left, experimental adsorption isotherms at 30 °C and 50 °C for composite 15, with the related fitting curve. On the right, charging/discharging thermodynamic cycle for the same composite with the operational boundaries that are average winter temperature (T_W), average summer hot temperature (T_S), user operating temperature (T_A) and heat source temperature (T_C).

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
$E_{d\,(\text{Salustro et al.}[7])}$	(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 ($\bar{E}_d$) 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 in-depth 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 (€/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 €/ton for PC[8], 400 €/ton for CAC[9], 300 €/ton for CSA cement[10], 100 €/ton for sepiolite[11], 160 €/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 (%)	T_c (°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/$CaCl_2$ 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.

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