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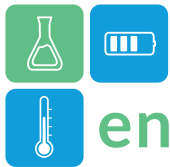
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Thermocline thermal storage material based on reclaimed and low-cost materials.

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Abstract

In response to the challenge raised by climate change, industries, and various sectors must transform to decarbonize their activities and facilitate the energy transition. To this end, thermal energy storage systems offer promising solutions. This study aims to explore the feasibility and performance of utilizing second-life materials as sensible thermal storage components integrated into high-temperature thermocline technologies, crucial for some industries facing this transition. The investigation ensures these materials possess the requisite energy density, operational stability, and cost-effectiveness. The materials were formulated by shaping reclaimed refractory fillers with low-cost clay-based binding matrices.

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Keywords: Sensible thermal energy storage, Formulation, Waste refractory ceramic, Thermocline, Design of experiments

Introduction

In 2021, France's industrial sector consumed 311.7 TWh (Sédillot, 2022), ranking third in energy usage, just behind transport and residential sectors. According to the ADEME (French Environment and Energy Management Agency), a third of this energy is lost through heat that could be used for other applications (La chaleur fatale, n.d.). However, this energy could be valorised if it were collected and stored (Récupération de chaleur fatale Etats des réalisations et évolution du gisement à fin 2020, 2022), reducing by the way raw energy consumption and greenhouse gas emissions.

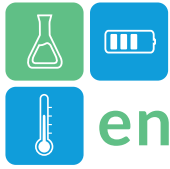
Such valorisation exists and the company Eco-Tech Ceram provides such a system with their Eco-Stock®, a sensible thermal energy storage system (STESS) (Lalau et al., 2022). Previous work showed that this system environmental performances could be improved by using Sensible Thermal Energy Storage Material (STESM) made from wastes or secondary raw materials (Jacob et al., 2022). Furthermore, a local and abundant supply is a strategic asset.

Our work focuses on the development of a new STESM composed of local, abundant, low-impact and low-cost materials. The STESM formulation is based on a clay matrix including second-life refractory ceramics. Their elaboration is optimized by a design of experiments (DOE) planning to meet the IEA recommendation on energetic density that should be above $2.6 \text{ MJ.m}^{-3}.\text{K}^{-1}$ (Meffre, 2013).

Methodology

Upon reception, the different clays and minerals fillers were prepared by passing through a jaw crusher (except the SD clay which was already fine) and reduced to centimetric dimensions.

The prepared materials were then dried at 105°C for a minimum of 24 hours before batch crushing in a mill grinder at a constant filling ratio. Post grind milling, the products passed through sieves; mineral fillers with a sieve diameter above $800 \mu\text{m}$ and clay above $200 \mu\text{m}$ remained in the mill, while the complementary fraction was added to maintain a constant grinding rate. Refractory fillers were



categorized as fine (passing through a 200 μm sieve), intermediate (passing through a 500 μm sieve), and coarse (below 800 μm).

Following material preparation, powder mixtures were prepared according our L₉ DOE, (detailed in Table 1). These mixtures, composed of fine clay and fillers of varying size distribution, were shaped using a uniaxial press at 48.8 MPa.

The resulting samples were fired in an electric kiln, with a temperature increase rate of 5°C/min and a step stage of 1 hour.

Table 1: Design of experiment

Sample	Clay	Particle size fraction of fillers	Mass ratio of filler / clay	Sintering temperature
T01	A	Fine	30/70	1050 °C
T02	B	Fine	70/30	1125 °C
T03	C	Fine	50/50	1200 °C
T04	A	Intermediate	50/50	1125 °C
T05	B	Intermediate	30/70	1200 °C
T06	C	Intermediate	70/30	1050 °C
T07	A	Coarse	70/30	1200 °C
T08	B	Coarse	50/50	1050 °C
T09	C	Coarse	30/70	1125 °C

Finally, the fired samples and powders underwent analysis. Powders were subjected to granulometry using laser diffraction analysis, X-ray Fluorescence (XRF) employing an Epsilon3-XL from Malvern Panalytical, and pycnometer, while sample density was measured following ISO 5017 standards.

The heat capacity of the samples was assessed through a mixture law (1) based on elements analyzed with XRF and the Shomate equation (2) using the NIST dataset (Linstrom, 1997). Differential scanning calorimetry (DSC) was conducted to confirm the heat capacity evaluation using a Labsys Evo.

$$C_{p_{sample}} = \sum_i w_i * M_i * C_{p_i} \quad \#(1)$$

$$C_{p_i} = A + B * t + C * t^2 + D * t^3 + \frac{E}{t^2} \quad \#(2)$$

$C_{p_{sample}}$: heat capacity of the sample ($\text{J.g}^{-1}.\text{K}^{-1}$)

C_{p_i} : heat capacity of i-element ($\text{J.mol}^{-1}.\text{K}^{-1}$)

w_i : weight percent of i-element

t : temperature (K/1000)

The energetic density U were defined as the products of the bulk density with the heat capacity of the sample

$$U = \rho_{bulk} * C_{p_{sample}} \quad \#(3)$$

U : energetic density of the sample (J.cm^{-3}).

Results and Discussion

XRF (Table 2) reveal the elemental composition of the raw material after calcination. The heat capacity of the sample is calculated for each sample as function of the temperature with equations (1) and (2) and compared to DSC measures (Table 3). The indices "e" and "m" in the data series T01e to T09e and T01m to T09m signify estimated and measured values, respectively.

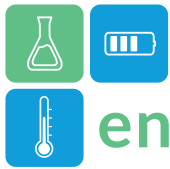
Table 2: XRF Element analysis of clay and filler

Element	Clay 1	Clay 2	Clay 3	Filler
Na ₂ O	0	0	0	2.9
MgO	0	0.1	0.7	0
Al ₂ O ₃	23.1	24.1	18.5	94.3
SiO ₂	64.3	63.5	66.6	1.7
K ₂ O	1.4	3.6	4.1	0.4
CaO	0	0.3	0.3	0.2
TiO ₂	0.9	0.7	1.3	0
MnO ₂	0	0.1	0	0
Fe ₂ O ₃	9.8	7.2	8.1	0.9
I	0.5	0.4	0.4	0.3
ZrO ₂	0	0	0	0.2

The Table 3 illustrates the C_p increase with the temperature and shows a slightly superior value for the DSC measures (11 to 16% at high temperature). A slight drop is observed on estimated data near 600°C at 573°C due to the polymorphic transformation of α -quartz to β -quartz. This transformation does not appear on our measures but the heat capacity in this range of temperature varies little.

Table 3: Heat capacity of samples estimated and measured

Sample	C_p ($\text{J.g}^{-1}.\text{K}^{-1}$)		
	100 °C	400 °C	600 °C
T01e	0.87	1.11	1.15
T01m	1.06	1.30	1.36
T02e	0.90	1.13	1.18
T02m	1.17	1.32	1.34
T03e	0.89	1.12	1.17
T03m	1.12	1.30	1.34
T04e	0.89	1.12	1.17
T04m	1.08	1.30	1.35
T05e	0.88	1.11	1.15
T05m	1.20	1.35	1.36
T06e	0.90	1.13	1.18
T06m	1.13	1.30	1.34
T07e	0.90	1.13	1.18
T07m	1.11	1.29	1.34
T08e	0.89	1.12	1.17
T08m	1.18	1.33	1.35
T09e	0.88	1.12	1.15
T09m	1.10	1.31	1.35



Bulk and absolute densities of our samples were measured. Values varying from 2.10 ± 0.09 to $2.56 \pm 0.09 \text{ g.cm}^{-3}$ for the bulk density and from 2.85 to 3.27 g.cm^{-3} for the absolute density.

Further analysis, employing our L_9 design structure, reveals the average effects attributable to the different parameters studied (Figure 1). Clay type plays a crucial role, with the second and third clays demonstrating superior properties compared to the first. An X-ray Diffraction (XRD) analysis on the clays indicates higher content in illite and halloysite in clay 1 and 2. Additionally, unlike clay 2 and 3, clay 1 lacks a muscovite phase. These elements are believed to facilitate the densification of samples during sintering. Samples using an intermediate size fraction of mineral fillers and a higher proportion of filler exhibit increased density, facilitating shaping and densification. However, excessive filler amounts negatively impact shaping quality, hindering clay's binding role and resulting in reduced density and mechanical strength. The sintering temperature emerges as a critical parameter impacting density, revealing that a temperature of at least 1200°C is optimal for firing. Investigations into higher sintering temperatures demonstrated a decrease in bulk density after 1225°C due to increased closed porosity.

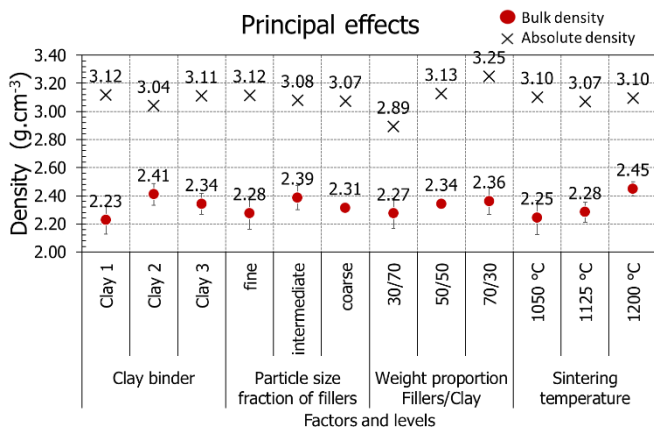


Figure 1 : Principal effect of the DOE parameters on density

Given the proximity of the sample's heat capacity, principal effects behave in the same way for the energetic density (3) (Figure 2) than for the bulk density. (Figure 1). The energetic density of all our samples (Table 4), with the exception of T01, surpasses the IEA recommendation of $2.6 \text{ J.cm}^{-3}.\text{K}^{-1}$ for temperatures above 200°C , corresponding to the operating zone of STESS.

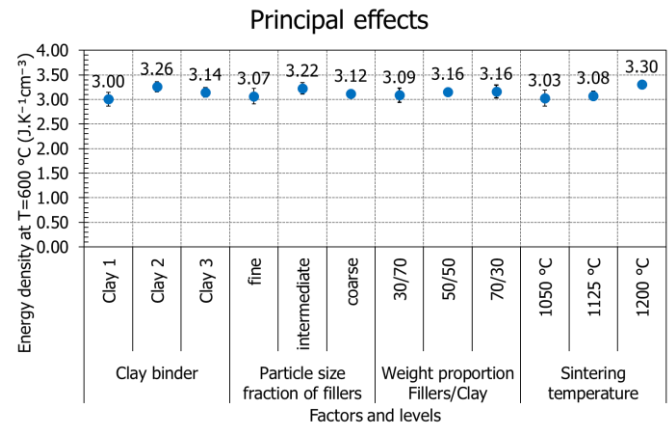


Figure 2: Principal effect of DOE parameters on energetic density

Table 4: Samples energetic density ($\pm 0.12 \text{ J.cm}^{-3}.\text{K}^{-1}$)

Sample	U (J.cm ⁻³ .K ⁻¹)		
	100 °C	400 °C	600 °C
T01m	2.16	2.66	2.78
T02m	2.75	3.10	3.15
T03m	2.71	3.17	3.26
T04m	2.45	2.94	3.05
T05m	3.05	3.44	3.47
T06m	2.66	3.06	3.15
T07m	2.63	3.07	3.18
T08m	2.76	3.11	3.15
T09m	2.47	2.92	3.02

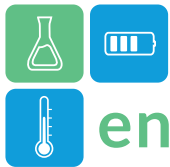
Conclusions

Our initial observations of clay and reclaimed refractory fillers reveal promising outcomes, indicating their suitability for integration into thermocline systems like the Eco-Stock®. The energy density exhibited by these materials aligns with the recommendations set forth by the IEA, positioning them as strong candidates for such applications while offering a way of recovering mineral waste.

Ongoing investigations using mixtures of clay and reclaimed refractory minerals are underway to identify an optimal composition that not only maintains a high energy density but also ensures a prolonged lifespan. This avenue of research seeks to enhance the performance and longevity of these materials, contributing to their efficacy in sustainable and efficient energy storage solutions.

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