

## Preparation and characterization of PCM from Glauber salt recoverable from the disposal of lead batteries

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**Abstract:** Glauber salt (sodium sulfate decahydrate) is a promising phase change material (PCM) to use in the building sector, thanks to the high enthalpy of fusion associated with a proper phase transition temperature. Also it offers economic and environmental advantages because it can be obtained as by product from the disposal process of lead batteries. However the Glauber salt, due to phenomena of phase segregation and subcooling, cannot be used in the pure state but requires the addition of rheological modifiers and nucleating agents. In this work the thermal performances of mixtures based on Glauber salt with different compositions are compared by using T-history method, by adopting sonication for mixing, and following the same preparation procedure for all the samples. Fixed the composition, also the effects of the sequence of addition of the reagents is examined. The analysis carried out by Turbiscan allowed to identify the kinetic of destabilization of each sample and revealed the need to specify in detail the preparation stages of PCM in order to make the composition reproducible in laboratory and on a wider scale.

**Keywords:** Glauber salt; PCM; T-history; Turbiscan.

## 1. Introduction

Generally PCM are enclosed in boards for the thermoregulation of internal environments. Panels can cover walls, floors or ceilings, therefore large quantities of such materials are required.

This need imposes limits in the choice of materials with regards to the economic aspects, making useful to address recycling or waste materials, for example the Glauber salt obtained as byproduct from the disposal process of lead batteries.

The recovery is carried out by crystallization of sulphate, which also allows the elimination of traces of heavy metals, toxic to the environment and damaging to health.

In particular in the phase of the pastel desulfurization in which the lead sulfate is treated by using carbonate or hydroxide of sodium, the following reactions take place [1, 2]:



Due to its thermal properties, the Glauber salt has been one of the first salts hydrates to be considered suitable for applications in the building sector for the thermoregulation [3].

In [4] data for the pure Glauber salt are available: the enthalpy of fusion equal to 251.2 kJ/kg, the phase transition temperature of 32.4°C, and the specific heat of the solid and liquid phase equal to 2.09 kJ/kgK e 3.35 kJ/kgK, respectively.

However, during the first investigations, problems of stability have been highlighted and, for consequence, difficulties in the long term performances.

These problems were mainly due to two phenomena common to many other hydrated salts: subcooling and phase segregation. The first prevents the release of heat at a defined temperature, while the second, due to the incongruent melting, limits the stability of the structure which is manifested by a progressive reduction of the enthalpy of fusion. The remedies proposed in the literature involve adding a nucleating substance [5] and a rheological modifier [6], in addition to an excess of water whose function is to counter the low solubility of the salt [7].

The study presented in this paper is based on the characterization and the thermal analysis of two compositions with different percentage of Glauber salt, obtained by using bentonite as a thickener and borax as a nucleating agent. The objective is to analyze their effect on the enlargement of solidification interval, on the lowering of solidification temperature, and on the fusion enthalpy and stability in comparison to the pure salt. Since the samples are dispersions, it was necessary to identify the most appropriate type of mixing, opting for the sonication considered more effective in respect

to the magnetic agitation technique in reducing the size of aggregates [8]. Two samples were prepared for each composition by varying the sequence of addition of the reagents. Each sample was analyzed successively by means of the t-history method for the determination of the thermal properties and by using the Turbiscan to get information on its stability.

## 2. Materials and methods

### 2.1 Reagents and preparation method of the samples

For the preparation of the sample the following reagents were utilized: distilled water, sodium sulfate 99.5%, borax 99.5%, potassium chloride 99%, purchased from Carlo Erba, and bentonite, provided by Sigma-Aldrich. Table 1 shows the two analyzed percentages of composition (by weight).

**Table 1.** Percentages of composition of the tested mixtures.

Composition	Water (%)	Bentonite (%)	Sodium sulfate (%)	Borax (%)
1	67	4	25	4
2	60	5	31	4

The samples have been made by the sonicator UP200S provided by Hielscher (sonotrode S14 with diameter of 14 mm), proceeding with 0.8 cycles of impulse followed by 0.2 s of pause at 100% of the length amplitude. Each composition (in total 100 g) has been obtained by application of two different modalities:

Modality (1): water and bentonite were sonicated for 10 minutes. After the addition of salts the dispersion is submitted for sonication for further 30 minutes.

Modality (2): water and salts are submitted for sonication for an interval of 30 minutes, in a second step the bentonite was added and the sonication was applied for 10 minutes.

The samples will be identified in the paper following the nomenclature showed in table 2.

**Table 2.** Identification of the four samples in relation to the modality of preparation.

Sample	Composition	Modality of preparation
C1(1)	1	1
C1(2)	1	2
C2(1)	2	1
C2(2)	2	2

### 2.2 Thermal analysis: T-history method

The thermal analysis was carried out by using the t-history method [9] in the range of temperature from 10°C to 40°C. A refrigerated thermostat was utilized in order to obtain an adequate control of the environmental conditions, as suggested by Stankovic et al [10].

The results are presented with reference to the method of Marin et al [11] in which, in addition to the enthalpy of fusion, the representation of the trend enthalpy-temperature is showed in the examined range. Such representation takes into account that PCMs do not have homogeneous composition and, therefore, they have rather a wide solidification range. The curve has been obtained by considering the changes in enthalpy on small temperature ranges according to eq. (3):

$$\Delta h_p(T_i) = \left( \frac{m_w \cdot c_{pw}(T_i) + m_t \cdot c_{pt}(T_i)}{m_p} \right) \cdot \frac{I_i}{I_i'} \cdot \Delta T_i - \frac{m_t}{m_p} \cdot c_{pt}(T_i) \cdot \Delta T_i \quad (3)$$

where  $m_w$ ,  $m_t$  and  $m_p$  is the mass of water, test and PCM, respectively [kg];  $c_{pw}$ ,  $c_{pt}$  is the specific heat of water and test material [kJ/kg K];  $\Delta T_i$  is the temperature range [°C] with medium value  $T_i$ , to whom corresponds the enthalpy variation  $\Delta h_p(T_i)$  [kJ/kg];  $I_i$  is the integral with respect to time of the difference in temperature between PCM and environment;  $I_i'$  is the integral with respect to time of the difference in temperature between water and environment.

The latent heat of solidification was obtained as  $[\Delta h_p(T_i) - \Delta h_p(T_f)]$  where  $T_i$  is the initial temperature of solidification calculated as the maximum value reached after sub-cooling and  $T_f$  is the final temperature, calculated according to as a point of inflection on the cooling curve of PCM [12].

The specific heat of fluid state ( $C_{pl}$ ) and solid state ( $C_{ps}$ ) were calculated in reference to the article of Marin as the gradients of the two straight lines observable in the enthalpy vs temperature trend [5].

### 2.3 Kinetic of destabilization: Turbiscan

The turbiscan technique was utilized for the characterization of the dispersions [13-15]. The principle of operating is based on the multiple light scattering. The instrument scans samples with a volume of about 25 ml and draws transmission and backscattering profiles along all the height of the test cell. The scan can be repeated for long times, and at fixed intervals of time. The more the profiles are distinguished from the initial one the more the dispersion is unstable.

By means this comparison the instrument elaborates the destabilization kinetics based on the computation of the TSI (Turbiscan Stability Index) in different time step  $i$  [16]:

1) by comparing every  $scan_i(h)$  of a measurement to the previous one  $scan_{i-1}(h)$ , on the selected height  $h$ ;

2) by dividing the result by the total selected height (H) in order to obtain a result which does not depend on the quantity of product in the measuring cell.

$$TSI = \sum_i \frac{\sum_h |scan_i(h) - scan_{i-1}(h)|}{H} \quad (4)$$

The analysis was conducted considering a period of 24 hours and the temperature was fixed at the maximum value in the observation range (40°C) in which the sample remains in the liquid phase.

### 3. Experimental results

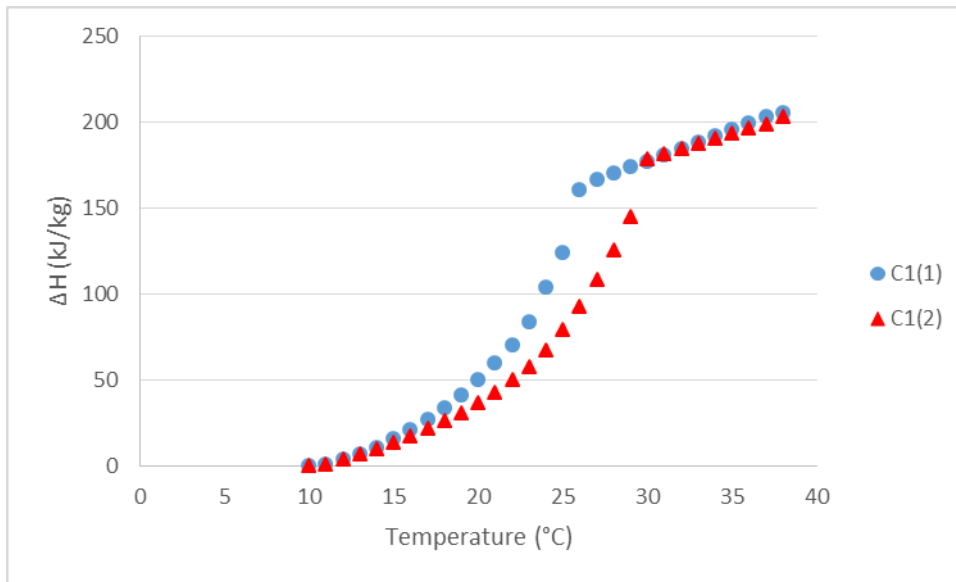
#### 3.1 Thermal analysis of the samples

By preparing the sample following the modality 1 or 2 it is possible to observe significant and visible differences in the structure. In particular the first sample has an appearance more viscous than the second. Figure 1 shows the comparison between the composition C1(1) and C1(2).

**Figure 1.** Sample with composition C1(1) on the right in comparison to the sample with composition C1(2) on the left.



By considering the cooling curves and the equation (3), the enthalpy vs temperature curves were determined for all the samples. In figure 2 are represented the results obtained for the sample C1.

**Figure 2.** Sample C1. Enthalpy vs temperature curves at variation of the modality of preparation.

The thermal properties of the first sample, estimated considering the method described in the section 2.1 are summarized in table 3.

**Table 3.** Thermal properties of the first sample C1 prepared by means the modality (1) and (2).

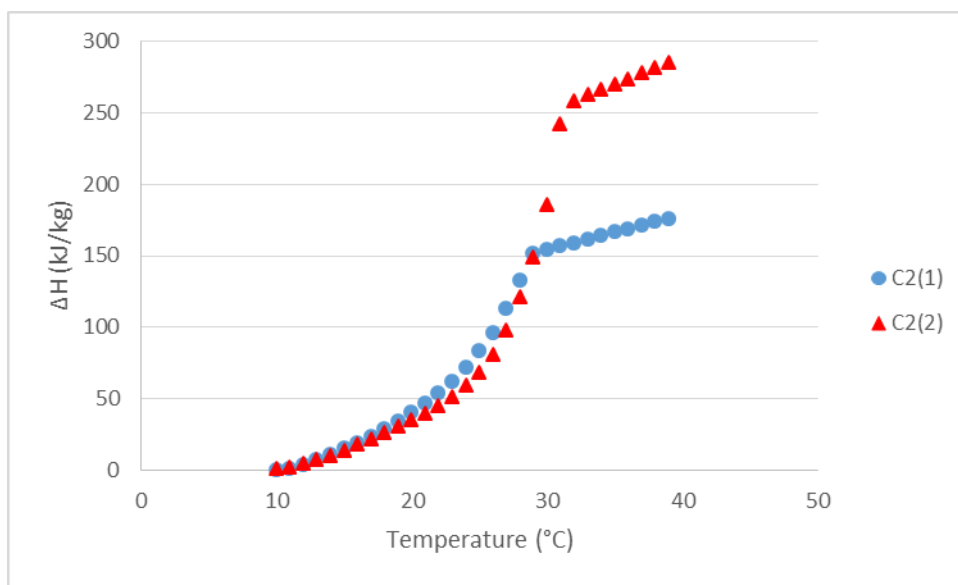
Sample	$T_{in}$ (°C)	$T_{fin}$ (°C)	$\Delta H$ (kJ/kg)	$C_{ps}$ (kJ/kgK)	$C_{pl}$ (kJ/kgK)
C1(1)	29.75	19.26	122.28	4.10	2.70
C1(2)	25.63	21.07	87.99	3.24	3.63

By considering purely the stoichiometric point of view and neglecting the interactions and solubility problems, the first composition should have a percentage of Glauber salt equal to 56.8%. In both cases a decrement of the solidification point in respect to the value of the pure salt is observed. The phenomenon is correlated to the presence of additives that determine also an extension of the solidification interval that results grater for the first composition remarking a major degree of inhomogeneity.

The specific heats, for the solid and liquid phase, are bigger than the values of the pure Glauber salt because it is worked in excess of water known for the elevate specific heat.

In figure 3 the enthalpies of fusion of the two samples with composition 2 are compared and a significant difference in the values is noticed.

**Figure 3.** Sample C2. Enthalpy vs temperature curves at variation of the modality of preparation.



The thermal properties of the second sample are presented in table 4.

**Table 4.** Thermal properties of the first sample C2 prepared by means the modality (1) and (2).

Sample	$T_{in}$ (°C)	$T_{fin}$ (°C)	$\Delta H$ (kJ/kg)	$C_{ps}$ (kJ/kgK)	$C_{pl}$ (kJ/kgK)
C2(1)	28.06	21.15	72.65	4.64	2.43
C2(2)	30.97	24.45	171.9	3.62	3.80

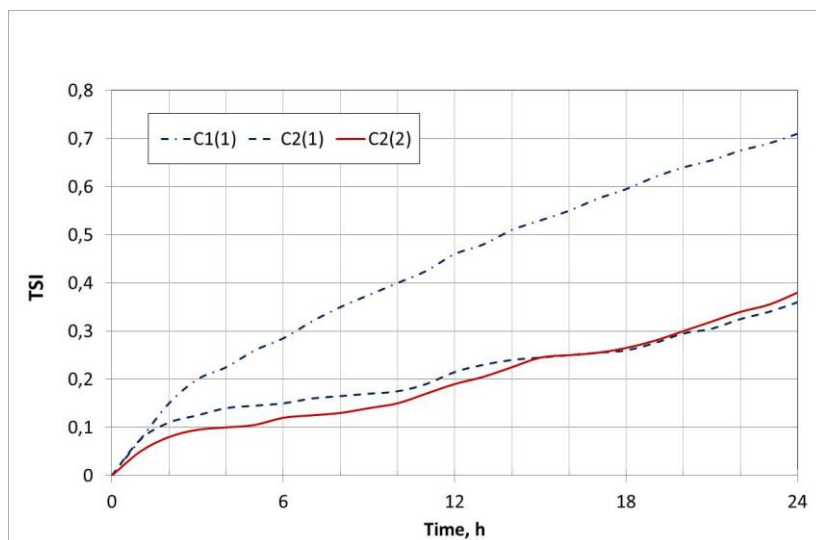
The composition C2 contains a theoretical percentage by weight of Glauber salt equal to 70.5%, therefore it results little effective on the point of view of the thermal performances if the sample is obtained by means the modality (1). In respect to the composition C1(1) it is possible to evidence some differences in the preparation: salts are added to a dispersion characterized by a ratio bentonite/water higher and thus more viscose.

It is deduced the same sonication power is not able to break up effectively the anhydrous sodium sulphate promoting the formation of the decahydrate form (Galuber salt). In all the analyzed compositions the size of subcooling is 2-3 °C and it can be considered very reduced in comparison to the values superior than 15°C indicated in literature for the pure salt [17], revealing the efficacy of the adopted nucleant.

### 3.2 Stability analysis of the samples

Stability analysis has been carried out by considering the Turbiscan Stability Index (TSI) behavior and comparing the trends obtained in 24 hours. As already said, such index could be used as a measure of the progressive destabilization of the system. In Figure 4 TSI values are reported with reference to the sample C1 with the two different preparation modalities. It appears evident that the modality 2 is not adequate for the preparation of the Glauber salt, as discussed observing the feature of samples in Figure 1. Values of TSI that increase progressively until 15, for the sample C1(2), permit to confirm that sonication of water and bentonite has to be carried out preliminarily with respect to sonication of water and salt. That allows to achieve samples more homogeneous.

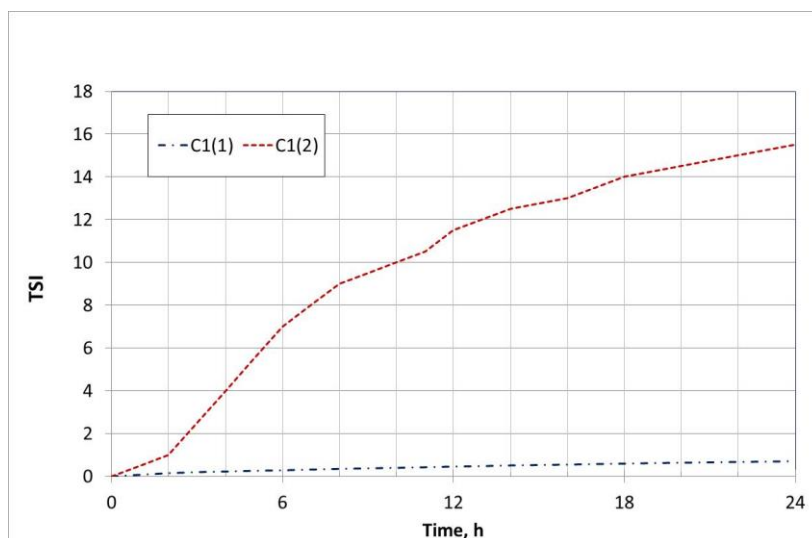
**Figure 4.** Sample C1. Comparison of time evolution of TSI as function of modality of preparation.



In order to evaluate the influence of composition, in Figure 5 TSI behavior has been reported, for the sample C1(1), C2(1) and C2(2). That permit to compare the influence of composition on stability (sample C1(1) and C2(1)) and the influence of modality in the case where more concentrated solution were used, (sample C2(1) and C2(2)). It is interesting to underline that TSI for C1(1) is almost double than TSI of C2(1). No significant difference can be observed for C2(1) and C2(2). That could be due to the fact that the sample C2 is characterized by higher thickener (as bentonite)/water ratio, able to guarantee greater stability to the solution.



**Figure 5.** Comparison of time evolution of TSI as function of composition and modality of preparation.



In any case the compositions C2(1) and C2(2) are more stables than C1(1).

However the sample C2(2) offers better thermal performances in comparison to C2(1), consequently it could be preferred for further studies.

#### 4. Conclusions

The nucleant selected in order to limit the subcooling has produced in all the analyzed cases satisfactory results as it is able to reduce this phenomenon at few celsius degree. With reference to the thickener, it was observed that the stability of the dispersion improves for the samples that present a greater rate bentonite/water thanks to the higher viscosity.

In defining the optimal composition of Glauber salt and additives, the results underlined that the thermal performances and the stability of a dispersion cannot be defined by considering only the percentage of composition. The final properties depend on the preparation method and in particular on the sequence used for adding the reagents and on the viscosity of the mixture.

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