

STABILIZATION OF GLAUBER'S SALT FOR LATENT HEAT STORAGE

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ABSTRACT

Thermal energy storage systems (TES) have attracted increasing interest for thermal applications such as hot water, space heating and cooling. These systems are useful to correct the mismatch between the supply and demand of energy. There are mainly two types of thermal energy storage systems, sensible and latent heat storage. Latent heat storage is particularly attractive due to its ability to provide a high energy storage density and its characteristics to store heat at a constant temperature corresponding to the phase transition temperature of the heat storage substance. Inorganic salt hydrates as latent heat storage materials have certain advantages over organic materials. However, some problems occur when salt hydrates are used as phase change material (PCM) in the latent heat storage applications. These are supercooling of salt hydrates when they freeze because of their weak nucleation properties and phase separation occurring because of incongruent melting. In this study, Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is stabilized with different concentrations of polyacrylamide and gelatin gels to prevent incongruent melting. A nucleating agent, which resembles crystal structure of Glauber's salt, was used to prevent supercooling. Thermal storage capacities of PCM samples which are stabilized with different concentrations of polymeric gels were determined both by DSC and temperature-history methods.

Keywords: Stabilization, Salt Hydrate, Polymeric Gel, Latent Heat Storage, Incongruent Melting, Supercooling

1. INTRODUCTION

Currently, consumption of energy increases considerably due to developments in technological area and population increase all over the world. Because of this, production and prolongation of energy is the most important problem. Usually fossil fuels are used as energy source. However, the fossil fuels have some harmful environmental effects for our earth. Greenhouse effect which harmful emissions of CO_2 , and NO_x from fossil fuels combustion is the most important environmental effect.

All over the world, renewable energy sources are investigated to decrease this effect. Utilization of the renewable energy sources can be done with thermal energy storage systems (TES). These systems give alternative solutions for existing energy problem. The mismatch between the energy demand and supply can only be overcome by the use of thermal energy storage systems. High capacity storage applications can be done with Phase Change Material (PCM)/latent heat storage in thermal energy storage systems. The latent heat storage is particularly attractive due to its ability to provide a high energy storage density and its characteristics to store heat at a constant temperature corresponding to the phase transition temperature of the PCM (Abhat, 1983; Bo He, 2004; Cabeza and et al., 2003; Farid and et al., 2004; Hong and et al., 2000; Sarı, 2003; Xiao and et al., 2002; Zalba et al., 2003).

Phase Change Materials (PCMs) are divided into two groups; these are organic and inorganic compounds. Organic compounds are paraffins and non-paraffinic materials, such as fatty acids. Inorganic compounds are salt hydrates, salts, metals and alloys. (Abhat, 1983; Bo He, 2004; Hasnain, 1998; Py and et al., 2001; Sarı, 2003; Zalba et al., 2003). Salt hydrates are attractive materials to be used in thermal energy storage due to their high heat storage capacity and high thermal conductivity compared with organic compounds (Bo He, 2004; Farid and et al., 2004; Py and et al., 2001; Ryu et al., 1992).

However, some problems occur in using salt hydrates as PCM in latent heat storage. One of them is incongruent melting which causes phase separation and the other one is supercooling of salt hydrates because of their weak nucleation properties (Abhat, 1983; Bo He, 2004; Cabeza and et al., 2003; Farid and et al. 2004; Ryu and et al, 1992). Anhydrous salts and aqueous solution of salts are formed when the inorganic salt hydrates melt. Anhydrous salts are considerably denser than the solution and precipitate to the bottom of the container. On freezing, rehydration may start only at the solution-precipitate interface. Thus, rehydration cannot be further proceed because the salt hydrate forms a contact barrier between the liquid and the anhydrous salt solution. The consequence is a bad crystallization of compound and a change in the thermophysical properties of the PCM. Phase separation can be prevented by changing the properties of the salt hydrate with the addition of another material that can hinder the heavier phases to sink to the bottom of the container. This can be achieved either with gelling or with thickening. Gelling means adding a crosslinked material (e.g. polymer) to the salt to create a three dimensional network that holds the salt hydrate together. Thickening means the addition of a material to

the salt hydrate that increases the viscosity and hereby holds the salt hydrate together (Cabeza and et al., 2003; Lane, 1983; Ryu and et al, 1992).

When the suitable thickener is added in PCMs, anhydrous salts are suspended homogeneously in the melt which may have greater chance contacting water so that the rehydration of salts can be improved. Many different thickening agents have been tested, including organics such as starch and various types of cellulose derivatives, as well as inorganics such as silica gel (Ryu and et al, 1992; Telkes, 1974). Cabeza and et al. (2003) studied thickening of sodium acetate trihydrate ($\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$) used as PCM with four different materials starch, methyl-cellulose, methylhydroxyethyl-cellulose and bentonite.

The use of cross-linked polymeric hydrogels which impart greatly improved stability to PCMs are presented in the literature. In 1992 Ryu H.W. et al. studied the gelling of the some salt hydrates as PCM with two different polymeric hydrogels, such as a super absorbent polymer (SAP) made from acrylic acid copolymer and carboxymethyl cellulose (CMC).

The aim of this study is to find effective gelling agent for Glauber's salt ($\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$) to prevent incongruent melting and phase separation for latent heat storage. Polyacrylamide and gelatin gels are used as gelling agent in this study.

2. MATERIALS AND METHOD

2.1. Materials

2.1.1 Phase Change Material

Glauber's salt (sodiumsulphate decahydrate- $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$, Merck-Germany) was stabilized as PCM with different concentrations of polyacrylamide and gelatin gels. Glauber's salt melting point is 32°C and heat of fusion is 251 kJ/kg (www.fskab.com/annex17).

A nucleating agent which resembles crystal structure of Glauber's salt, which is borax ($\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$, Merck-Germany) was used. The percentage of the Borax used was 1-2% by weight.

2.1.2. Gelling Agent

For the preparation of polyacrylamide gel the following materials were used:

- Acrylamide ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$, Fluka Chemie-Switzerland)
- N, N-Methylene-bis-acrylamide ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$, Fluka Chemie-Switzerland)
- TEMED (N,N,N,N-Tetrametyletilendiamin- $\text{C}_6\text{H}_{16}\text{N}_2$, Serva-Germany)
- Amoniumpersulfate ($\text{H}_8\text{N}_2\text{O}_8\text{S}_2$, Fluka Chemie-Switzerland)
- Buffer Solution of Tris-HCl (0,1M ; pH=7): Trizma Base ($\text{C}_4\text{H}_{11}\text{NO}_3$, Sigma-Aldrich Chemie-Germany, Trizma Hydrochloride ($\text{C}_4\text{H}_{11}\text{NO}_3\cdot \text{HCl}$, Sigma-Aldrich Chemie-Germany)

Glauber's salt was stabilized with different percentages (40, 30, 20, and 10 %) of the polyacrylamide gel.

For preparation of gelatin gel, gelatin powder (Merck-Germany) and hot water were used. Glauber's salt was supported with different percentages (30, 20, and 10 %) of the gelatin gel.

Polyacrylamide gel is a porous material. The total solids content (%T) of the polyacrylamide gel is a parameter that is used to determine the size of its pores. The %T is the ratio of the sum of the weights of the acrylamide monomer and cross-linker to the volume of solution, expressed as % w/v (Maurer, 1971). %T value for the polyacrylamide gel prepared in this study was 10.

2.2. Method

2.2.1. Thermal Analysis of Stabilized Glauber's Salt Samples

Stabilized Glauber's salt samples at various percent ratio of gel to salt hydrate, were melted and frozen with water bath and air bath to investigate their thermal properties. Figure 1 shows the experimental setup. Samples of stabilized salt hydrate, pure salt hydrate and pure polymer gel were placed into the water bath (Technique TU-16A). Three identical glass tubes are used as containers for all the samples in the water bath. Then, water bath was heated until $40 - 50^\circ\text{C}$. At the same time, the temperature of the samples was measured and recorded by a data-logger (Campbell CR10X) to obtain heating curves of the samples. Three temperature sensors (Campbell T107) were used to measure the temperatures of all the samples in the water bath. Then the heater was

switched off and the temperature of the water bath was decreased suddenly by removing part of the water from the surrounding water bath and adding ice and cold water. The temperature was decreased to 15 – 20°C with this method. The cooling curves of samples were obtained with temperature measurements made during this cool down experiment. In the second method a cooling air-bath (a styrofoam container) was used. The air-bath method was used to obtain a slower temperature change that would allow better observation of the phase change process.

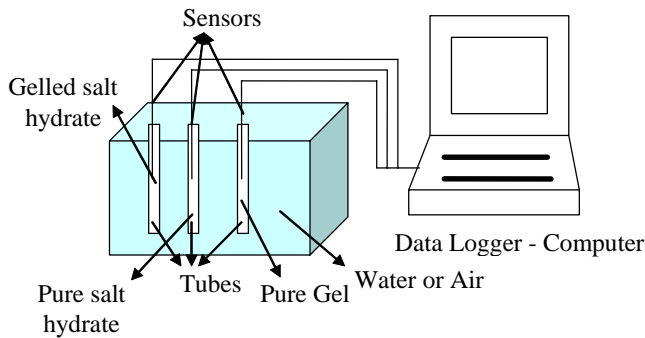


Figure 1. Water/Air bath

2.2.2. Latent Heat Storage Capacity of the PCMs

2.2.2.1. Temperature-History (T-History) Method

The Temperature-History Method, proposed by Yinping et al. (1999), is a simple and economic way to determine the main thermophysical properties of materials used in thermal energy storage based on solid-liquid phase change. It is based on comparing the temperature history of a PCM sample and a reference material upon cooling down. A comparison of curves, using a mathematical description of the heat transfer, allows the determination of the heat capacity, C_p , and the enthalpy, H , of the PCM from the known C_p of the reference material. A hot water bath, two identical tubes, insulated cool down chamber, three temperature sensors, a data-logger and computer are used in this method. The PCM to be tested is placed into one of two identical tubes and distilled water is placed into the other tube as reference material. Both of them are heated up in the water bath to 65 – 70°C. Then, the tubes are placed in the cool down chamber and the temperatures of the samples are recorded by the data-logger and the computer. In conclusion T_{PCM} , T_{water} , T_{air} and two temperature curves of the samples are obtained. The experimental set-up is shown in the Figure 2.

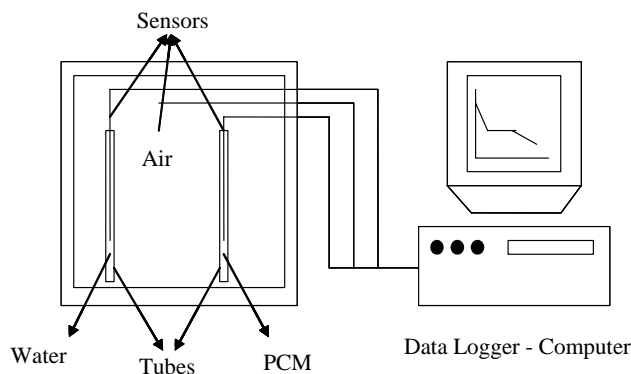


Figure 2. Experimental set-up of temperature - history (T-History) method (Marin et al., 2003; Yinping et al., 1999).

The heat of fusion of the PCM is calculated using the following equation. In this equation, H_m is the heat of fusion of the PCM, $C_{p,w}$, $C_{p,t}$ are the mean specific heats of the water and of the material of the tube, respectively,

m_w , m_t , m_p are the masses of the water, of the tube and of the PCM, respectively, T_0 , T_s are the temperatures of the start of the experiment and the supercooling of the PCM, respectively. (Marin et al., 2003; Yinping et al., 1999).

$$H_m = \frac{m_w \cdot c_{p,w} + m_t \cdot c_{p,t}}{m_p} \cdot \frac{A_2}{A_1} \cdot (T_0 - T_s) \quad (1)$$

2.2.2.2. Differential Scanning Calorimeter (DSC) Method

Thermophysical properties of PCMs were also measured by differential scanning calorimetry (Perkin Elmer Diamond DSC) method. The heating rate was 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Thermal Analysis of Gelled Salt Hydrate Samples

Heating and cooling curves of Glauber's salt stabilized with 30 % and 20 % gelatin gel are shown in Figure 3 and Figure 4, respectively. 1 % Borax was used as nucleating agent. In the heating curves, Glauber's salt stabilized with both 20 % and 30 % gelatin gel samples melted around 32 – 34°C temperature interval. In the cooling curves this situation changed; the Glauber's salt stabilized with 30 % gelatin gel froze at 26–30°C, showing 4°C of supercooling. However, Glauber's salt stabilized with 20 % gelatin gel showed only 2°C of supercooling and froze at 28-30°C.

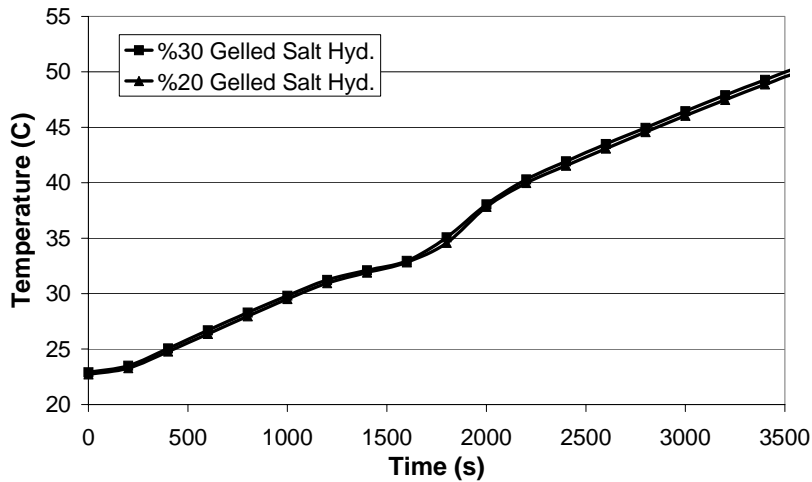


Figure 3. Heating curves of Glauber's salt stabilized with different percentages of gelatin gel

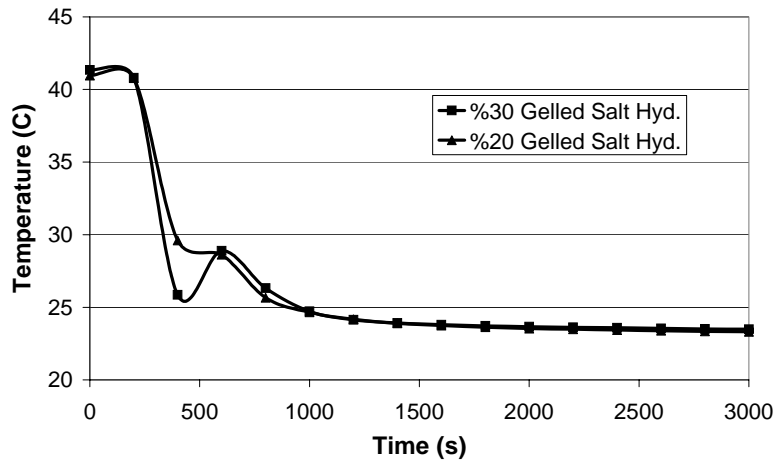


Figure 4. Cooling curves of Glauber's salt stabilized with different percentages of gelatin gel

The heating and cooling curves of Glauber's salt stabilized with 10 % gelatin gel and pure Glauber's salt and pure gelatin gel are shown in Figure 5 and Figure 6, respectively. 2 % Borax was used as nucleating agent. In the heating curves, Glauber's salt stabilized with 10 % gel melted at 32 – 34°C and pure Glauber's salt melted at 33 – 34°C. In the cooling curves, Glauber's salt stabilized with 10 % gel froze at 28-30 °C without supercooling. In this experiment, no phase change was observed for pure Glauber's salt, and this was due to incongruent melting of the material. For pure gelatin gel, no phase change was observed during heating and cooling. The best result for preventing supercooling was obtained with 10% gel. It could be seen that at higher gel percentages supercooling effect tends to increase.

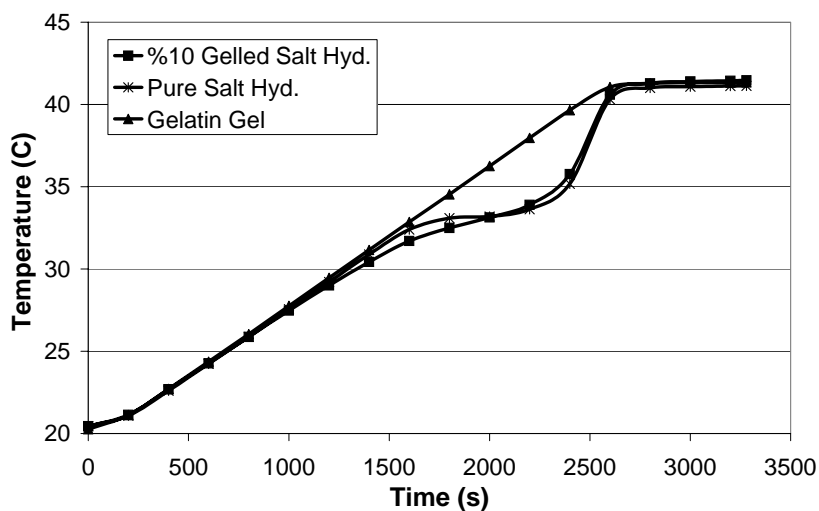


Figure 5. Heating curves of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) stabilized with 10 % gelatin gel and pure Glauber's salt and pure gelatin gel

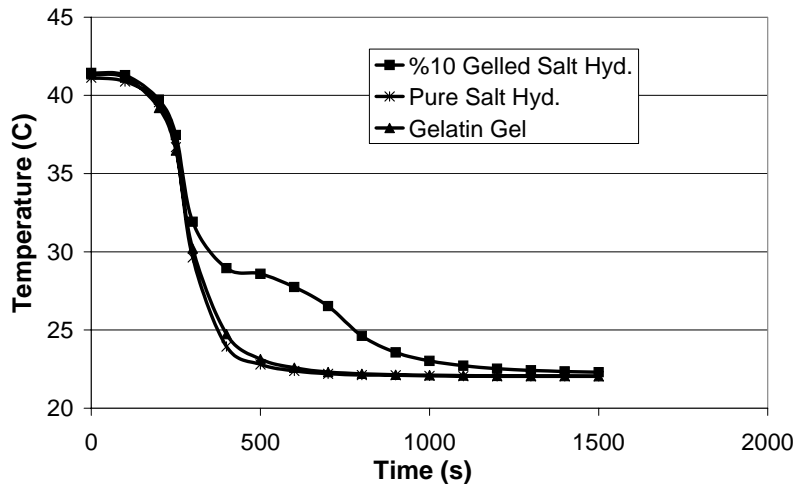


Figure 6. Cooling curves of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) stabilized with 10 % gelatin gel and pure Glauber's salt and pure gelatin gel

The heating and cooling curves of Glauber's salt stabilized with different percentages of polyacrylamide gel are shown in Figure 7 and Figure 8, respectively. 2 % Borax was used as nucleating agent. Air bath was used for cooling down in this measurement. In the heating curves, Glauber's salt stabilized with 10 % polyacrylamide gel sample melted at 33 – 35°C while phase change was not observed for the other samples of Glauber's salt stabilized with polyacrylamide gel. Rapid heating in the water bath may have prevented the detection of the phase change. In the cooling curves, Glauber's salt stabilized with 10 % polyacrylamide froze at 29 – 31°C. This sample had 4°C of supercooling.

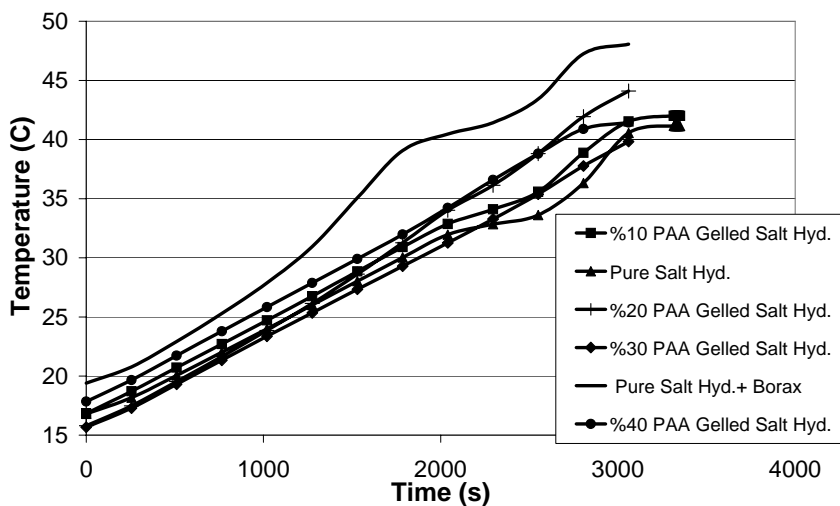


Figure 7. Heating curves of Glauber's salt stabilized with different per cent % polyacrylamide gel

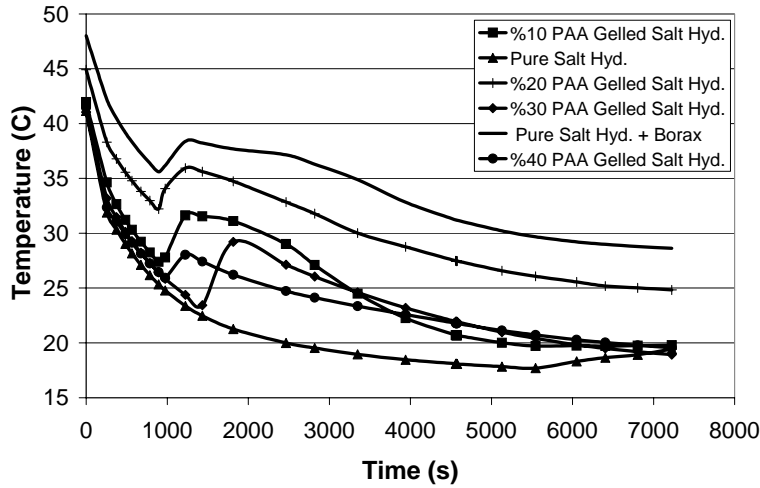


Figure 8. Cooling curves of Glauber's salt stabilized with different per cent % polyacrylamide gel

3.2. Thermophysical Properties

The T-History Method, proposed by Yinping et al in 1999, is used to determine the thermophysical properties of the Glauber's salt stabilized with gelatin gel and polyacrylamide gel samples. Moreover, the thermophysical properties of the samples were also measured by differential scanning calorimeter (DSC). The thermophysical properties obtained are compared in Table 1.

DSC measurement equipments are complicated and expensive, and the samples tested by it are very small. Therefore the thermophysical properties of the samples can be different from the bulk phase change materials and phase change processes of the samples cannot be observed clearly. However, T-history method is very useful to determine the thermophysical properties of the phase change materials because the melting point, heat of fusion and specific heat can be determined, while the phase change process of the samples can be observed visually.

While the heat of fusion of the salt hydrate stabilized with 10% polyacrylamide gel was determined as 180,01 (J/g) and the heat of fusion of the salt hydrate stabilized with 10 % gelatin gel was determined as 113,00 (J/g), the heat of fusion of the pure salt hydrate was determined as 234,58 (J/g). As the result of the measurements that the heat of fusion of the samples decrease when they are mixed with polymeric gels.

Figures 9-10 show measured T-history curves of the Glauber's salt stabilized with 10% polyacrylamide gel as PCM and distilled water was used as reference material. The enthalpy of the PCM was calculated as 274,49 J/g by using equation 3 mentioned above.

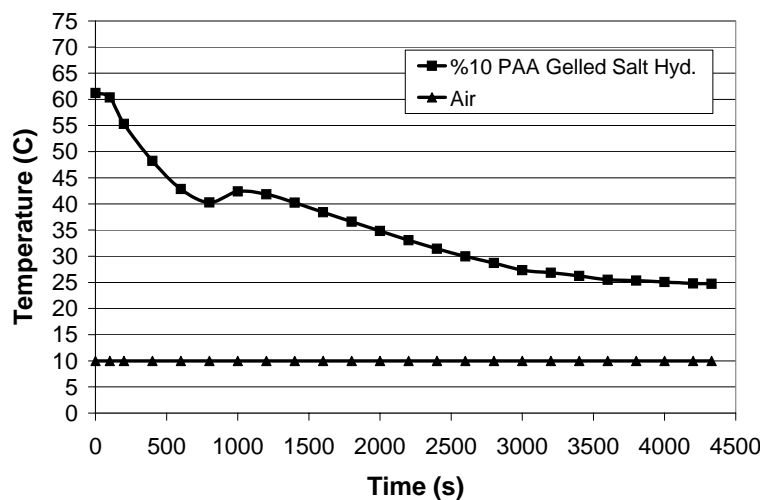


Figure 9. The t-history curve of the Glauber's salt stabilized with 10 % polyacrylamide gel

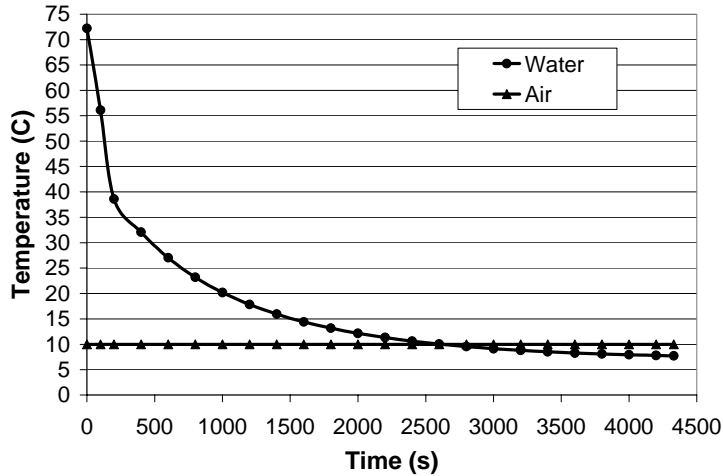


Figure 10. The t-history curve of the distilled water

Figures 11-12 show measured T-history curves of the Glauber's salt stabilized with 10% gelatin gel as PCM and distilled water as reference material. The enthalpy of the PCM was calculated as 253,53 J/g by using equation 3 mentioned above.

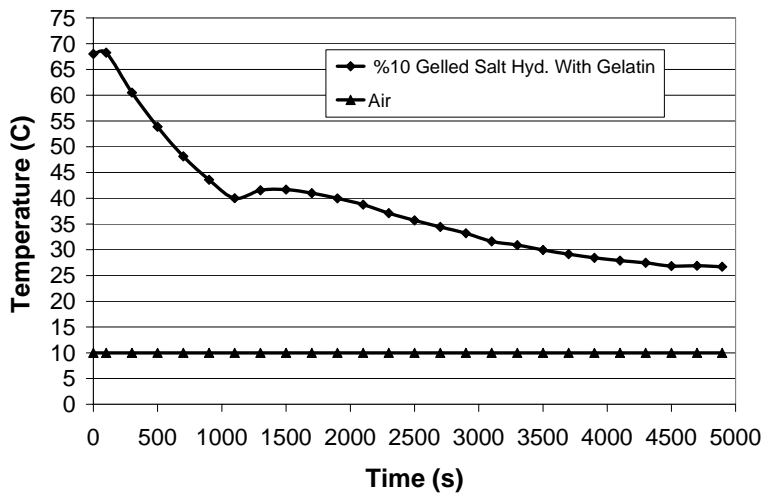


Figure 11. The t-history curve of the Glauber's salt stabilized with 10 % gelatin gel

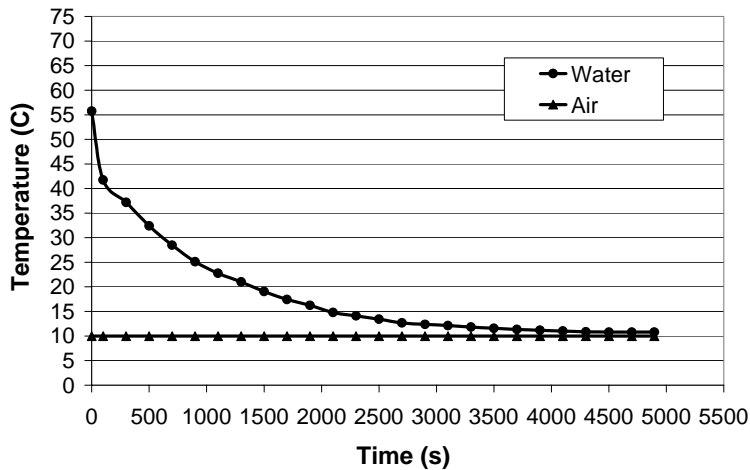


Figure 12. The t-history curve of the distilled water

Table 1. Latent Heat Values which are determined by both T-History Method and DSC Method of the PCM

PCM	DSC Method	T-History Method
Salt hydrate stabilized with 10% polyacrylamide gel	180,01 (J/g)	274,49 (J/g)
Salt hydrate stabilized with 10 % gelatin gel	113,00 (J/g)	253,53 (J/g)
Pure (Na ₂ SO ₄ .10H ₂ O) Glauber's salt	234,58 (J/g)	-

4. CONCLUSIONS

In the latent heat storage systems, salt hydrates exhibit some problems when they are used as PCM. One of the problems is (incongruent melting) phase segregation and the other problem is supercooling. In this paper, supercooling is solved by adding a nucleating agent.

Incongruent melting which occurs in the salt hydrate is prevented through stabilization with a polymer gel. In this study, the use of polyacrylamide gel and gelatin gel is proposed to prevent phase segregation (incongruent melting). Glauber's salt is stabilized with different gel percentages; 40, 30, 20, 10%. Among these, 10% gelled sample gives significantly better results than the other compositions.

As a result of the measurements, for Glauber's salt stabilized with 10 % gelatin gel, incongruent melting and supercooling are prevented completely. However, supercooling of Glauber's salt stabilized with 10 % polyacrylamide gel is about 4°C, although a nucleating agent was used.

Polyacrylamide gel and the gelatin gel can both be used to stabilize Glauber's salt to prevent phase separation. The stabilized Glauber's salt can be used as PCM at 28-32°C temperature interval applications. The thermal stability of the samples should be determined in the repetitive thermal cycles of heating and cooling.

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