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Calculation of the volume ratio of salt filling the pores of a porous material for latent Heat storage application.

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Abstract
The performance of the PCM composite depends on the amount of PCM absorbed into the metal foam [1]. The preparation procedure of the PCM composite includes three important steps: the preparation of water-PCM solution, the addition of the metal foam, the impregnation of the water-PCM solution into the metal foam and finally the drying of the sample in order to evaporate the remained water inside the pores which will lead to the creation of void inside it. In order to overcome this problem, In this study, equations were developed to estimate the volume ratio of salt that could fills the pores as a function of treating cycle (adding the PCM + penetration of PCM into the pores + drying), solubility of the PCM in water and temperature of use. The results of the calculations shows that the number of cycles needed for each type of PCM is different depending on the solubility of the PCM in water and temperature of use.

Keywords: *PCM, metal foam, solubility.*

1. Introduction

The use of phase change materials (PCMs) in latent heat storage attracts more and more attention in recent years [2-3]. However, their low thermal conductivity presents one of the issues that should be resolved [4]. In order to overcome this issue, the impregnation of PCM into porous body has been investigated in many studies [5-6].

Recently, some studies were done about preparing the PCM composite using the impregnation method. Zhong et al [7] used this method to prepare three kinds of porous heterogeneous composite PCMs where the Expanded graphite was chosen as the porous matrix and binary salts ($LiNO_3$-KCl, $LiNO_3$-$NaNO_3$, $LiNO_3$-NaCl) s the PCMs. They conclude that the advantages of this method is that the water was used as a medium which is suitable for the

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dispersion of the PCM in the expanded graphite, comparatively to the melting method which lead to less uniform adsorption in the porous body. Adopting the expanded graphite as a supporting material and hydrated salts as the PCM; Wu and Wang [8] used also the impregnation method to prepare a new shape-stabilized PCM, and they found out that there was a good combination between the expanded graphite and the hydrated salts.

Hawes and Feldman [1] investigated in their paper the effect of some parameters, such as temperature, on the amount of PCM penetrated into a porous concrete. For that, one equation was developed in order to estimate the mass of absorbed PCM into the porous concrete and they found out that the temperature should not be as high as possible after removing the porous concrete from the bath because rising the temperature will decrease both the surface tension and the density of the liquid which will lead to a reduction in the amount of liquid retained in the capillaries.

The impregnation method could be a promising method for preparing PCM composite based on the fact that it is suitable method for dispersion of the PCM inside the porous body. It was demonstrated that many parameters affect the amount of PCM penetrated into the porous matrix.

One of the important steps during the impregnation method is drying the PCM composite in the aim of evaporating the water remained inside the pores. We believe that, after this step, voids are created inside the pores. In literature; there was not enough data on investigating how this issue could be resolved or on how to increase the amount of PCM penetrated into the porous body as function of treating cycle and temperature. The main goal of this study is to resolve this issue by developing equations in order to estimate the volume ratio of salt that could fills the pores as a function of treating cycle (adding the PCM + penetration of PCM into the pores + drying), solubility of the PCM in water and temperature of use.

2. The calculation of the volume ratio salt filling the metal foam pores $\phi_{s(i)}$

First, the metal foam is prepared, containing metal and some pores. Then, a water solution is prepared by saturating water by a salt at given temperature. After that, the metal foam MF with a porous structure is added to this solution and the pores of MF are filled with the solution. Then, the MF with water solution in its pores is heated and dried. Finally water is removed by drying and a composite is obtained containing metal with pores, the latter partly filled by the salt, crystallized from water solution upon the evaporation of water.

MF initially (before being treated by the solution) contains two phases: metal (m) and pores (p). The sum of the two volume ratios of these two phases equal 1:

$$\phi_m + \phi_p = 1 \quad (1)$$

After the treatment of the MF by the solution and after filtering and drying, the pores contain two phases: salt (s) and air (a), so the following equation is valid:

$$\phi_p = \phi_s + \phi_a \quad (2)$$

Suppose a saturated solution fills the pores during the process. After drying the solution the volume ratio of the salt at room temperature can be expressed from the initial volume ratio of the pores as:

$$\phi_s = \frac{C_{max}}{100} \cdot \frac{\rho_{ss}}{\rho_s} \cdot \phi_p \quad (3)$$

Where C_{max} (w%) is the solubility of salt in water, ρ_{ss} (g/cm^3) is the density of the saturated water solution at its temperature, ρ_s (g/cm^3) is the density of the dry salt at room temperature. The last expression relates to the result obtained after the 1st cycle. In the aim of filling the pores with higher amount of salt, treatment (adding the MF to water solution + drying) is repeated several times. Then, the volume ratio of the salt filling the pores will be:

$$\phi_{s(i)} = \phi_{s(i-1)} + \frac{C_{max}}{100} \cdot \frac{\rho_{ss}}{\rho_s} \cdot \left(\phi_p - \phi_{s(i-1)}\right) \quad (4)$$

Where i is the number of cycle. One can see that at i = 1 Eq.(4) reduces to Eq.(3), as $\phi_{s(0)}$ = 0.

3. The calculation of the target value ϕ_s

The target value of $\phi_{s,max}$ is the maximum value, that allows melting the salt in the pores without extending the volume of the pore. So, if the density of the salt is known as function of Temperature (T), then the maximum target value is calculated as:

$$\phi_{s,max} = \phi_p \cdot \frac{\rho_{s,maxT}}{\rho_s} \quad (5)$$

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Where $\rho_{s,maxT}$ (g/cm^3) is the density of the molten salt at the maximum temperature in the heat storage cycle.

4. Results and discussion

Using Eq.(3) and Eq.(4), the volume ratio of some inorganic salts filling the pores of metal foam will be calculated at different temperatures : 25°C, 50°C and at high temperature (70°C and 80°C).The results are presented in the figures 1-3.

The density of molten salt, density of pure salts at room temperature and the target value of ϕ_s are given in Table 1. The data about different densities and solubility are taken from the 'International Critical Tables of Numerical Data' [9] and Molten Salts Handbook [10].

Table 1: *Densities and the maximum target value of ϕ_s of different salts*

	ρ_s(g/cm^3)	$\rho_{s,maxT}$(g/cm^3)	$\phi_{s,max}$
$NaNO_3$	2.26	1.88	0.83
KNO_3	2.10	2.02	0.96
$RbNO_3$	3.09	2.42	0.78
$CsNO_3$	3.63	2.75	0.76
KCl	1.99	1.48	0.75
NaCl	2.16	1.53	0.71
CsCl	3.97	2.70	0.68
RbCl	2.80	2.19	0.78

The obtained results at room temperature (25°C) are shown in Fig. 1. As we can see from this figure, the higher temperature of the solution, the more salts fill the pores; because of the salts solubility that increase with the temperature (see also Eq-s 3-4). For some kind of salts, the temperature dependence was not taken into consideration because of the missing data. However, for all salts, the volume ratio of the salt was studied for different cycles and the number of cycles are found which is sufficient for the given salt to reach the maximum target value, calculated by Eq.(5).

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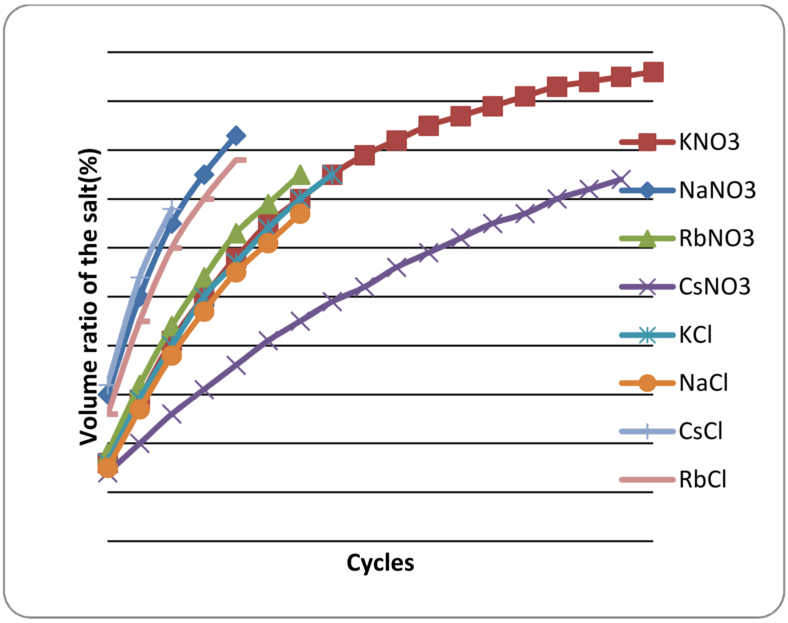

***Fig. 1**: Volume ratio of salt filling the pores of the MF as a function of treating cycle at room temperature (25°C)*

The volume ratio of salt filling the pores of MF at 50°C is given in figure 2. Comparatively to the results obtained at room temperature (Fig. 1), we can observe that the number of treating cycles is reduced when the temperature is increased from room temperature to 50°C.

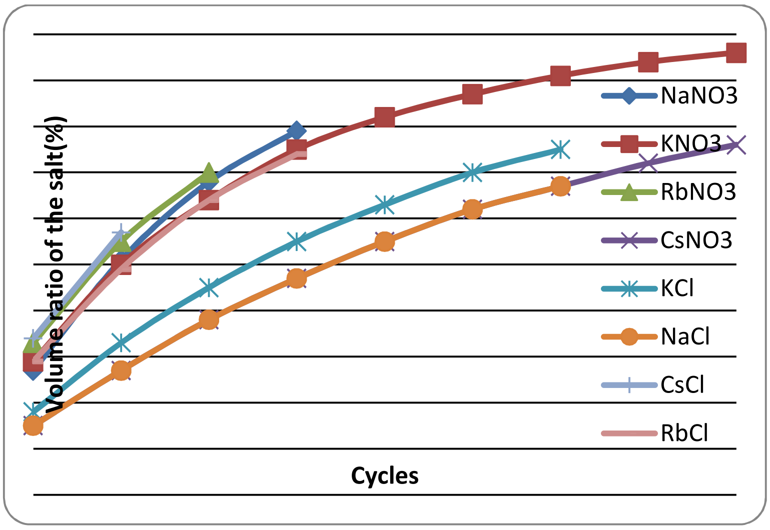

***Fig. 2**: Volume ratio of salt filling the pores of the MF as a function of treating cycle at 50°C*

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The same results are obtained when the temperature is increased from 50°C to 70 and 80°C (Fig. 3).The number of cycles needed to fill the pores before reaching the target value $\phi_{s.max}$ is different from salt to another because of the solubility term that appears in the previous equations (see also Eq-s 3-4).At room temperature, we can see that the number of cycles in case of nitrate is much higher than that of chloride salts.

The calculated target value $\Phi_{s.max}$ in case of nitrate was found higher, so more cycles are needed in case of nitrate than chloride salts. The solubility of nitrate salts, as a function of temperature is higher than that of chloride salts; that's why, when the temperature is increased, we can observe that in case of nitrate salts; the number of cycles is significantly influenced by the temperature, while in the case of chlorides it was minimal. The solubility of NaCl, RbCl and KCl doesn't vary significantly as a function of temperature; that's why; the number of cycles in their cases has not been decreased too much when the temperature is increased.

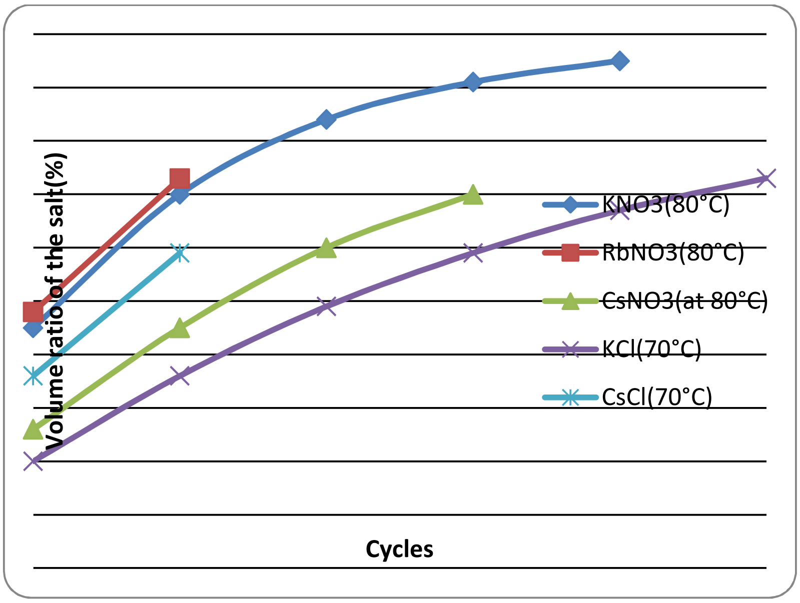

Fig. 3: *Volume ratio of salt filling the pores of the MF as a function of of treating cycle at 70 and 80°C*

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5. Conclusion

The impregnation method has became one of promising method of preparing the PCM composite that could be used in latent heat storage application. It is based on the penetration of a saturated salt solution into a porous matrix. One of issue that should be taken by consideration, before obtaining the final PCM composite, is how to control the amount of PCM inside the porous matrix; cause after drying the PCM composite samples, water will be evaporated from the pores and voids will be created inside it. Our idea is to repeat the treating cycles (adding the MF+ penetration of salt into the pores + drying) several times. In order to estimate the volume ratio of salt that could fill the pores, some equations are developed, and we found the followings:

- The solubility of salt in water is one of the main parameters that affect the volume ratio of salt filling the pores of the MF.
- The numbers of treating cycles and the volume ratio and of salt filling the pores are different for the studied salts due to the term of solubility in the equations.
- The number of cycles needed to fill the pores is reduced when the temperature is increased and it was significantly influenced by temperature in case of nitrate salts more than the other salts.
- Salts with high number of treating cycles are not worth using.

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