Crystallization in Phase Change Materials

Mohammed Jaafer Ali Alatabe

ORCID ID orcid.org/0000-0002-0919-3596

Environmental Engineering Department, Mustansiriyah University. Baghdad, Iraq

ABSTRACT

There are large numbers of phase change materials that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. Hydrated salts have larger energy storage density and higher thermal conductivity but experience super cooling and phase segregation, and hence, their application requires the use of some nucleating and thickening agents. Sodium carbonate, sodium phosphate and sodium sulfate tested as phase change material by crystallization in this work. Salt hydrate phase change materials used for thermal storage in space heating and cooling applications have low material costs, but high packaging costs. A more economic installed storage may be possible with medium priced, high latent heat. Latent heat storage is one of the most efficient ways of storing thermal energy. Unlike the sensible heat storage method, the latent heat storage method provides much higher storage density, with a smaller temperature difference between storing and releasing heat.

Keywords : Crystallization, Salt Hydrate , Phase Change Material.

I. INTRODUCTION

Today, classic cooling systems are used for room cooling, and these ensure that the rooms are cooled to a comfortable temperature in all environment climates. These systems are effective, however they would be a lot more energy-efficient if they used the natural temperature differences between day and night for cooling purposes. The use of the building mass as a storage medium is well known. This concept of night-time cooling has already been successfully implemented in many construction projects. The application of PCMs in buildings can have two different goals. First, the PCMs can be used to utilize natural heat and cold sources. For instance, solar energy for heating during the evening/night or the use of night cold for cooling during the day. Second, PCMs can use manmade heat or cold sources. In addition, different ways of using PCMs are available. In buildings, these again fall into two groups. PCMs can be located in building components such as walls or ceilings, or can be arranged in separate heat or cold stores. Using PCMs within buildings components are generally passive systems. The heat or cold is stored automatically and released when indoor or outdoor temperatures rise or fall beyond the phase change point of the material. Using PCMs in separate heat or cold stores are usually based on active systems. The stored heat or cold is in containment separated from the building itself and heat or cold transfer is not automatic, but used on demand(Abhat .A, *et al.* ,1983).

Crystallization is an important operation in the chemical industry , as a method of purification and a method of providing crystalline materials in the desired size range . In a crystal the constituent molecules , ion or atoms are arranged in a regular manner with the result that the crystal shape is independent of size ,and if a crystal grows, each of the faces develops in a regular manner . The presence of impurities will, however, usually result in the formation of an irregular crystal . Generally large regular crystals are a guarantee of the purity of the material .Though a number of pairs of materials from ''mixed crystal''. In recent years considerable development has taken place in techniques for growing perfect single crystals which are used in the production of semiconductor devices , laser beams , and artificial gems.

The crystallization process consists essentially of two stages which generally proceed simultaneously but which can to some extent be independently controlled.

The first stage is the formation of small particles or nuclei, and the second stage is the growth of the nuclei. If the number of nuclei can be controlled, the size of the crystals ultimately formed can be regulated(Ryu, H.W., *et al.,*1992).

II. Theoretical Aspects

Saturation:

If melt is slowly cooled, the temperature will gradually fall until the melting point is reached and further cooling will then produce, either super-cooling of the liquid, or solidification with the temperature remaining approximately constant. Generally a definite degree of super-cooling must be achieved before change of phase will occur, and a meta stable condition therefore exists at temperatures a little below the melting point because the rate of spontaneous nucleation is here negligible. On the other hand, if a small seed crystal or other nucleus is introduced, it will increase in size until the solution is no longer super cooled(Ryu, H.W., *et al.,*1992).

Nucleation:

Nuclei may form spontaneously if conditions are suitable, but in many cases small seed crystals may be added and small quantities of impurities may also act as nuclei. Spontaneous nucleation is a process which takes place with some reluctance and is thought to depend upon the existence of random variations in concentration or temperature on the molecular scale.

Crystallization Rate :-

The rate of growth of crystal in a solution is dependent on the temperature and concentration of the liquid at the crystal face. These condition are not generally the same as those in the bulk of the solution because a concentration gradient is necessary for the transfer of solute towards the face, and a temperature gradient for the dissipation of the heat of crystallization. The problem thus involves both heat transfer and mass transfer, though in most cases the heat transfer may be negligible. In the case of melts, the problem is one of heat transfer alone. Since the resistance to heat and mass transfer lies predominantly in the laminar sub–layer close to the surface of the crystal, the rate of growth of the crystal is improved by increasing the

relative velocity between the solid and the liquid(Mohammed, J. A., *et al.,*2012).

Nucleation and Growth :-

It is clear that no discussion of a crystallizing system can be meaningful until the combined effects of nucleation rate , growth rate , heat balance, and material balance can be combined into a single equation. Theoretical analysis of nucleation and crystal growth is the subject of a large amount of literature. Tammann (1925) discussed the theory of nucleation and crystal growth, and outlined the various parameters involved in terms of, a probabilistic model involving a functional relation to pressure, temperature, and time. Many later studies deal with the nucleation and growth of crystals on an atomistic level. Although such studies a revere significant data on nucleation and crystal-growth kinetics are required for the system under study prior to development of atomistic models. Quantitative data on nucleation and crystal growth are available for only a few systems of geological importance, and the purpose of this section is to present a brief introduction to theories of nucleation and crystal growth as a prelude to the results of crystal-growth experiments. Nucleation involves the addition of atoms or molecules to a nucleus having the structure of the solid. If the nucleus is larger than a certain critical size, it will grow spontaneously, but if it is smaller than the critical size, the nucleus will be unstable. Critical size is dependent upon the amount of under cooling [$\Delta T = T(liquidus)-T(growth)$] and varies from an infinite size at liquidus temperatures to smaller sizes at greater degrees of under cooling. Another factor in the nucleation of crystals from a melt is the mobility of atoms and molecules in the melt as measured by the diffusion coefficient. As the temperature drops below the liquidus, nucleation will increase from zero to a maximum at some under cooling. Diffusion rates are then very low and nucleation decreases with further decrease in temperature. This explains the pattern of nucleation in liquids where the liquid diffusivity decreases with temperature. Crystal growth from a melt proceeds by attachment of chemical species from the liquid to the crystal nuclei. Rate of growth is thus a function of mobility of crystal-forming species within the melt. Mobility, as measured by the diffusion coefficient, drops with decreasing temperature, and growth rate, like nucleation, is expected to rise from zero at the liquidus to a maximum at some under cooling and then

decrease. This is the expected pattern of growth rate of crystals from a viscous liquid(Zalba, B., *et al.,*2003)

Crystals :-

A crystal may be defined as a solid composed of atoms arranged in an orderly repetitive array . The inter atomic distances in a crystal of any definite material are constant and are characteristic of that material . Because the pattern or arrangement of the atoms is repeated in all directions ,there are definite restriction on the kinds of symmetry that crystals can possess (MOHAMMED, j. A., *et al.,*2012).

Heat Effects In a Crystallization Process:-

The heat effects in a crystallization process can be computed by two methods:-

1-A heat balance can be made where in the individual heat effects such as sensible heats, latent heats , and the heat of crystallization can be combined into an equation for the total heat effects: or,2-An enthalpy balance can be made in which the total enthalpy of all leaving streams minus the total enthalpy of all entering streams is equal to the heat absorbed from external sources by the process . In using the heat-balance method, it is necessary to make a corresponding mass balance , since the heat effects are related to the quantities of solids produced through the heat of crystallization .With compounds whose solubility increases with increasing temperature there is an absorption of heat when the compound dissolves which is called the heat of solution. In compounds with decreasing solubility, as the temperature increases there is an evolution of heat when solution occurs.

When there is no change in solubility with temperature there is no heat effect. The solubility curve will be continuous as long as the solid substance of a given phase is in contact with the solution , and any sudden change in the slope of the curve will be accompanied by a change in the heat of solution and a change in the solid phase(Xiao, M., *et al.,*2002).

Heats of solution are generally reported as the change in enthalpy associated with the dissolution of large quantity of solute in an excess of pure solvent . At equilibrium the heat of crystallization is equal and opposite in sign to the heat of solution using the heat of

solution at infinity dilution as equal, but opposite in sign to the heat of crystallization is equivalent to neglecting the heat of dilution . With many materials the heat of dilution is small in comparison with the heat of solution and the approximation is justified ,however , there are some exception . Relatively large heat effects are usually found in the crystallization of hydrated salts . In such cases the total heat released by this effect may be a substantial portion of the total heat effects in a cooling-type crystallizer . In evaporation –type crystallizers the heat of crystallization is usually negligible when compared with the heat of vaporizing the solvent (I. Dincer ,*et al.,*2002).

Thermo chemical heat storage

An important contribution to sustainable energy is an efficient use of solar heat and industrial waste heat. Storage of energy is an important issue in this context. Traditional sensible heat storage techniques offer a number of disadvantages. Substantial heat loss and relatively low energy density are the most serious drawbacks. An alternative to heat storage in water tanks is the thermo chemical heat storage utilizing reversible physical chemical processes offering the advantage of high energy density and very low energy losses. The sorption-desorption equilibrium of water vapor in micro porous materials such as zeolithes is one such example. More recently, research has been conducted in the use of chemical reactions such as hydration-dehydration reactions of metal salts for the thermo chemical storage of energy(Belenzalba , *et al.,* 2003).

The use of salt hydrates in a thermo chemical system is based on the release of the heat of hydration. Hence, a salt hydrate storage system is charged by the endothermic thermal dehydration of the respective higher hydrated salt. Many salts can be dehydrated at temperatures that can well be achieved using solar thermal collectors. In this state, the energy can be stored over long periods of time implying its application for seasonal storage. The exothermic back reaction may be initiated by simply increasing the water vapor partial pressure. The performance of a salt hydrate storage system largely depends on the kinetics of the hydration and dehydration reactions. The objectives of our research are as follows: (1) Selection of appropriate metal salts based on their thermodynamic properties and the kinetics of the respective hydration and dehydration reactions. (2)

Testing of different porous substrates including meso-porous materials for the salt hydrate(Mohammed J. A., Ahmed A., et al., 2017).

III. Experimental work

The experimental work complete in the chemical engineer department laboratory by using hydrated salts as phase change material like , sodium carbonate decahydrate (Na2CO3.10H2O) , a pure and analytical material was used in this work (Merck –Germany) . The procedure for these experiments by pass cooling air through hydrated salt solution putted in the(2L) glass container , on this container fixed thermometer to measuring the temperature .The cooling air agitated the solution by bubbling in constant velocity and temperature ,every (5 minutes) record the thermometer temperature (temperature of the system) .Fig(1) refer to the experimental rig which this research tests done by it, it consists the parts coded from one (1) to fourteen (14) as shown in figure.
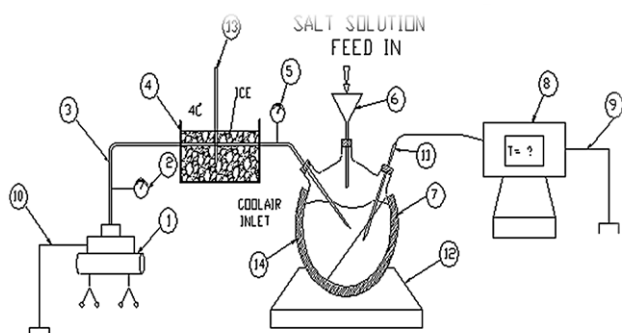

Figure 1. Experimental rig for the experimental work (1(- Air-Compressor)2(- Air-flow indicator ,)3(- Copper pipe ,)4(- Ice container ,)5(- Temperature indicator ,)6(- Funnel , (7(- Conical flax (2L) , (8)- Temperature indicator,(9&10)- Electrical connection , (11)- Thermocouple , (12)-Bench , (13)- Thermometer , (14)-Insulators.

IV. The Result

There are   many experiments done to study the crystallization rate of this hydrated salt ,but selected the best tow results of the experiments for each state of the following salt and plot it as in Fig.(3):

1-Sodium Carbonate Decahydrate (Na2CO3.10H2O) Commonly known as washing soda. The decahydrate contains 37% sodium carbonate and 63% water . It

forms several salt hydrates with different crystal habits . The decahydrate changes to heptahydrateat(32oC) and to monohydrate at (36oC) ,this dissolves almost completely. The material must be nucleation to form decahydrate crystals and formation of the heptahydrate must be avoided. Sodium carbonate is one of the least expensive and most available chemical. It is produced in large quantities from such natural sources as salt lakes and dry deposits . Sodium carbonate decahydrate melts at(32 oC), Sodium carbonate decahydrate is a good candidate for the storage of solar energy. Although its melting point, at (32oC), is somewhat on the low side, its relatively high heat of fusion of (247kj\kg) is definite advantage (Hawes DW, et al., 1992).

For this material at transition temperature 500gm of sodium carbonate dissolved in (1L) of water , fixed the temperature of cooling air for bubbling at 15oC. This solution being saturated with sodium carbonate at the transition temperature and nucleation from glass container can observe, no problem in nuclei contained. Crystallization started invariably when the bubbling cooling air maintained the temperature inside the glass container (29-30)oC. The cooling cycles could be carried out with such sealed container without any appreciable under cooling .Fig.(2) represented the diagram of 37% sodium carbonate solubility in water vs the temperature , Fig.(3) show the (time-temperature) curve of experiment which represented the crystallization process of this state.
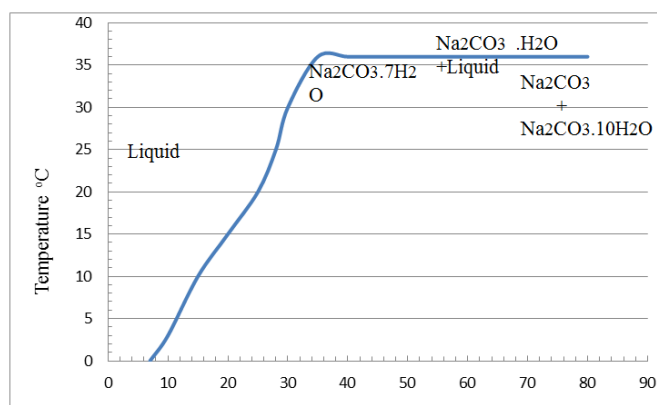

Figure 2. Phase Diagram Of Sodium Carbonate-Water System (Solubillity Diagram(Peippo K,et al., 1991).
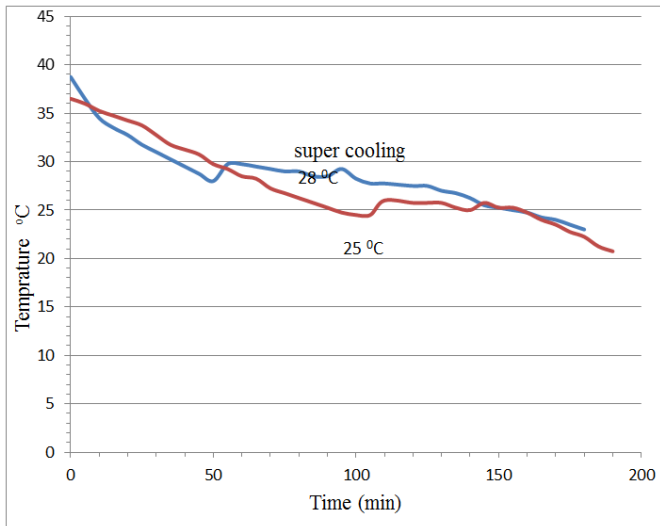
Figure 3. Cooling curves of Sodium Carbonate Deca-hydrate.

Discusson :-

The hydrates show a strong tendency to super cooling. This implies that in the phase of discharging the heat of fusion cannot be extracted at the melting point but only at temperature several degrees lower at which spontaneous crystallization occurs .The degree of super cooling is more or less random and influenced by effects such as impurities ,it may be reduced or even decreased to zero by adding solid material which initiates the crystallization .Such nucleation may be caused , for example , by crystals of a material which resembles the storage medium in structure and lattice parameters but which does not dissolve at operational temperatures   (NeeperD,et al.,2000).

Table 1. show the properties and cost of the hydrate salts [13]

hydrate Salt	Water Mols	Melting Point (^{o}C)	Heat of Fusion kj\kg	Density kg\m^3	$\100 kg	kj\$	Cost of storage kj.$
Sodium Carbonate	10	32-36	247	1361	4.41	559 1.5	200.5

From the Figs.(1and 2) respectively can noticed that the hydrated salts which used in these experiments was a good material in nucleation and growth of crystal when the temperature decreases ,but, in decahydrate sodium sulfate state the salt solution needed to catalyst for enhanced the formation of nuclei. The problem of super cooling can observe in Fig.(1) between (25-28)^{o}C, from fig.(2) super cooling between (23-32)^{o}C . That mean the melting state returned to liquid phase and needed more time to back the system to the melting state, the reason of all these in the above experiments come from the velocity and temperature of air that used in bubbling the system not fixed ,and the container effected by the ambient temperature ,thus must isolated it to get best resulted .Super cooling affect on the energy storage in the crystals, because its draw out some of the energy at form of heat and decreases the amount of energy storage. From Fig. (2), the solubility diagram of 37% sodium carbonate, that show the saturated state of these salt and can detected the weight percent of the salt solution converted to solid phase at any temperature of the system multiplied this value by percent of molecular weight of (Na_2CO_3) to the molecular weight of ($Na_2CO_3.10H_2O$) (Hadjieva M, *et al.,* 2000)

Hydrated salts are attractive materials for use in thermal energy storage due to high volumetric storage density, relatively high thermal conductivity and moderate costs compared to organic material like paraffin waxes (Mehling R, *et al.,* 2003) . The selection of such material as PCM for a specific application should be based on thermodynamic properties, kinetic properties and chemical properties(Feldman, D., *et al.,* 1986). For low temperature applications ranging from 0°C to 99°C, Salt Hydrates would be the best option owing to their availability in a less temperature range with a reasonable specific heat capacity of 0.56(kj/deg.mol), thermal conductivity of 0.987 W/m-K, density of 1552 kg/m3 in the solid phases respectively and phase transfer temperature ranging from 35°C - 39°C (Khudhair, A. M., et al., 2004)

V. CONCLUSIONS

The applications of inorganic PCMs require the use of nucleating and thickening agents to minimize sub cooling and phase segregation. Significant efforts are continuing to discover those agents by commercial companies. The applications in which PCMs can be applied are vast, ranging from heat and coolness storage in buildings to thermal storage in satellites and protective clothing. A PCM with an easily adjustable melting point would be a necessity as the melting point

is the most important criterion for selecting a PCM for passive solar applications. Many more applications are yet to be discovered.

VI. ACKNOWLEDGMENT

VII.   CONFLICT OF INTERESTS

The author declare that there is no conflict of interests regarding the publication of this manuscript.

Abbreviations

^{0}C	degree centigrade
deca	ten (10)
dedo	twelve (12)
kg	kilograms
$\Delta H°$	Standard enthalpy change
$\Delta G°$	Free energy change
$\Delta S°$	Entropy change
m^3	cubic meter
Min	minutes
kj	kilojoules
PCMs	phase change materials
W	watt
$	dollar

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