SALT-WATER SOLUTIONS AS PCM FOR COOLING APPLICATIONS

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Abstract

The objective of the paper is for experimentally studying and analysing aqueous salt solutions of sodium chloride (NaCl) and potassium chloride (KCl) that could be candidates of phase change materials (PCM) for the cooling applications and cold storage systems. These salts were selected because of their easy availability at low cost. Total 16 aqueous salt solutions of 8 different concentrations each of the NaCl and KCl were prepared and analysed by cyclation and corrosion tests. Cyclation tests were performed in temperature range of -24 ºC to -10 ºC to check feasibility of their use for cooling applications. KCl-H_2O mixtures were analysed with 1% glycerine to avoid volume expansion. Results showed that KCl-H_2O has more phase segregation than NaCl-H_2O. Overall, melting-freezing temperature ranges of these mixtures are from -20 ºC to -3 ºC, which is feasible for the cold storage. However, all the 16 solutions showed subcooling. Corrosion tests were performed during 1 week and 1 month using 5 different common metals (Aluminium, Stainless steel, Laminated black steel, Copper and Galvanized steel) immersed in these 16 aqueous salt solutions to check their long term compatibility and corrosion rate of the metal-PCM pairs. 1 week results showed that 5% KCl with copper and galvanized steel and 21% NaCl with galvanized steel have highest corrosivity, while during 1 month, galvanized steel gave high corrosivity with 15% KCl and 21% NaCl.

1. Introduction

The energy demand has been increased during the last few years. Due to the limited sources of non-renewable energy, it is in great demand to find out other sources of energy using renewable energy sources. Energy storage using thermal energy storage (TES) technique could be proven as an efficient technique by which energy could be stored and that can be extracted later [1]. TES using latent heat of the phase change material utilizes renewable energy source. This technique is more efficient because phase change materials (PCM) have potential efficiency for heat and cold storage due to their high energy storage density per unit volume; phase change materials also allow isothermal operation at constant temperature [1]. Use of PCM for cooling applications provide many diverse applications such as protection of temperature sensitive products like food, beverages, pharmaceutical products, blood derivatives, electronic devices, bio medical products, air-conditioning, and many more [2]. Water, ice, eutectic mixtures, aqueous solutions of organic salts, and mixtures of salts are suggested as PCM for cold storage [3] [4]; but salt-water eutectic mixtures are convenient and cheap compared to alkane mixtures [5]. Eutectic salt-water solutions are PCM which generally melt below 0 ºC, usually have good storage density, and are available at low cost. All these factors attract the interest of their use for the cooling applications and for cold storage systems. On the other hand, this PCM could produce phase separation and subcooling, problems that should be addressed.

The main objective of this paper is to analyse salt-water solutions of sodium chloride (NaCl) and potassium chloride (KCl) salts as potential candidates as PCM. Their thermophysical properties, characteristics and behaviour during cyclation (heating-cooling), and corrosion tests will be analized. Cyclation tests were performed to study their behaviour during heating-cooling cycles. Moreover, 1% glycerine was added to KCl solutions in order to reduce the volume expansion [6]. Corrosion tests to check the compatibility of the metal-PCM pairs were performed.

2. Materials and methodology

2.1. Material selection

For cooling applications, especially for subzero applications, PCM should have a phase change temperature range from -24 ºC to -10 ºC. Gawron and Schöder [7] reported that the eutectic mixture of 22.4% NaCl-H_2O showed a melting point at -21.2 ºC. Based on that, eight different concentrations of NaCl and KCl salt-water solutions (5%, 10%, 15%, 20%, 21%, 22%, 23%, and 24%) were selected both for cyclation and corrosion tests. For the corrosion experiments, five different common, cheap, and widely used metals such as, aluminium (Al), stainless steel (SS), laminated black steel (LBS), copper (Cu), and galvanized steel (GS) were selected (Fig. 1). Their chemical composition can be found in Table 1.

Fig. 1. Metal pieces used in the corrosion experiments. From left to right: stainless steel, laminated black steel, copper, aluminium, and galvanized steel

2.2. Methodology for cyclation test

5 ml of each solution were poured in a plastic test tube. These tubes were immersed in a thermostatic water bath (Huber CC1) filled with 60% of water-glycol solution to reach the desired low temperature of -27 ºC [8]. One PT100 temperature sensor was immersed in each test tube and the tubes were sealed with paraffin films. The sensors were connected to a data logger (DL-01 Register from step). The sensors were calibrated by comparing with a reference temperature probe before the experiments. Temperature response of PT100 sensors and reference temperature probe was measured by thermostat (TM6612-AOIP) in a thermostatic furnace (Eurotron) at -20 ºC, 0 ºC and 10 ºC temperatures. During the freezing cycle, the temperature of the thermostatic bath was set at -27 ºC to observe the freezing behaviour and melting cycle was performed in ambient temperature for the melting behaviour. Temperature gradient used was 0.2 ºC/min and the temperature response during freezing and melting was recorded at the time interval of 20 seconds by data logger. Three parallel cyclation tests of KCl solutions were performed to check reproducibility of the solutions.

2.3. Methodology for corrosion test

At first metal pieces were cleaned with acetone. Then only the metal pieces were directly immersed in glass test tubes in such a way that they were in direct contact with PCM solution and the tubes were sealed with paraffin films. Later on these test tubes were placed in a thermostatic water bath (P Selecta) at 25 ºC. The metal pieces were removed from the test tubes after 1 week and 1 month and were evaluated with the following procedure:

Table 1. Chemical composition of the metals used in the experiments

Element/Metal (identification)	Aluminium (1050-H14)	Stainless steel (SAE 304)	Laminated black steel	Copper	Galvanized steel
%Al	≥99.5	---	<0.005	---	---
%Cu	≤0.050	---	0.21	99.9	---
%Fe	≤0.40	66.34-74		---	---
%Mg	≤0.050	---		---	---
%Pb	---	---		---	---
%Zn	≤0.050	---		---	---
%C	---	Max 0.08	0.26	---	≤0.120
%Si	≤0.25	Max 1	0.27	---	≤0.500
%Mn	≤0.050	Max 2	1.10	---	≤0.600
%P	---	Max 0.045	0.01	---	≤0.100
%Ti	≤0.030	---	<0.005	---	≤0.300
%V	≤0.050	---	<0.005	---	---
%S	---	Max 0.03	0.03	---	≤0.045
%Cr	---	18-20	0.05	---	---
%Ni	---	8-10.5	0.07	---	---
%N	---	---		---	---
%Mo	---	---	<0.01	---	---
%Nb	---	---	<0.01	---	---
%B	---	---	<0.0005	---	---
%W	---	---	<0.01	---	---
%Sn	---	---	0.02	---	---
%Co	---	---	0.01	---	---
%Zr	---	---	<0.01	---	---
Other,each	≤0.030	---		---	---

- Change in the appearance of the solution and metal and their characteristics were evaluated to identify qualitatively the precipitate formed.
- The metal pieces were cleaned thoroughly with tap water and their change in appearance was evaluated visually.
- Later on, metal pieces were polished with abrasive paper.
- Gravimetric analysis prior to and following the corrosion tests provided mass loss, Δm (g), with respect to the initial mass [$m(t_0)$]:

$$\Delta m = m(t_0) - m(t) \quad (1)$$

- Measurements prior to and following the tests provided reduction in sample thickness, and length (mm).
- Corrosion rate was defined as mass loss per square meter of surface and day (g/m^2d).

$$CR = \Delta m / (t_0 - t) \cdot A \quad (2)$$

Although the samples were measured before and after the treatment, the differences in the thickness were not significant enough to be taken into consideration. This is why comparison between samples was made with the mass loss and the qualitative evaluation of the solutions after treatment [9].

3. Results and discussion

3.1. Cyclation test

Results obtained in the heating-cooling test of NaCl-H_2O and KCl-H_2O solutions are shown in Fig. 2 and Fig. 3, respectively. Clearly, the subcooling effect can be detected in both figures. It can be seen that subcooling and melting temperature range remains similar for every cycle of all solutions. This is a good indication that these solutions could be used for cooling applications. Table 2 shows the freezing-melting temperature range, their associated degree of subcooling, and the freezing point depression for the NaCl and KCl solutions; values obtained from the heating-cooling curves. Freezing point depression is the phenomena in which the freezing point of a liquid (a solvent) is depressed when another compound is added, meaning that a solution has a lower freezing point than a pure solvent; this happens whenever a solute is added to a pure solvent, such as water [10].

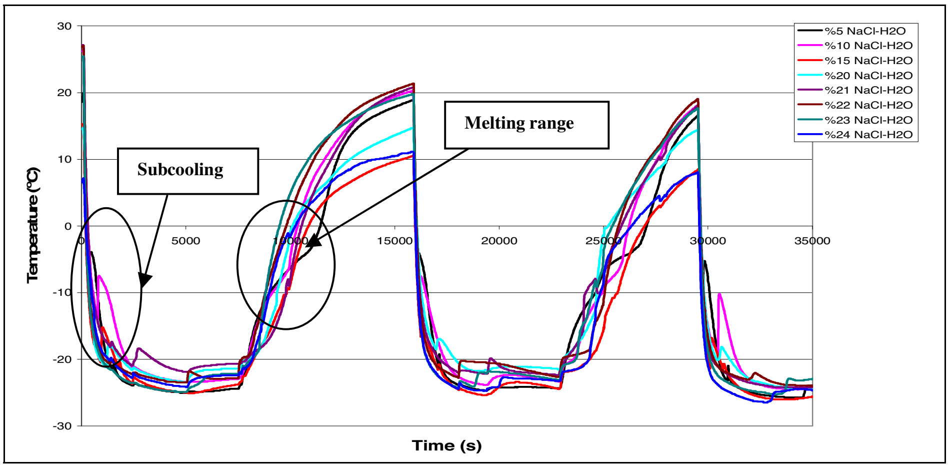

Fig. 2. Temperature vs. time curves obtained in cyclation test of NaCl-H_2O solutions

Subcooling is a common problem for eutectic salt-water solutions because the thermal conductivity of these solutions is similar to water and they can subcool like water by several Kelvin or more. Subcooling is the effect in which many PCM do not solidify immediately upon cooling below the melting temperature, but start crystallization only after a temperature well below the melting temperature is reached. During the heat storage there is no effect of subcooling, but during the heat extraction the latent heat is not released when the melting temperature is reached due to subcooling. To avoid the subcooling it is necessary to reduce the temperature well below the phase change temperature. To initiate solidification, nucleation should occur. Nevertheless, if nucleation does not happen at all, the latent heat is not released at all and the material only stores sensible heat. Therefore subcooling can be a serious problem for the technical applications. Subcooling can be considered as a drawback of these solutions; however it has advantage of melting-freezing point below 0 ºC.

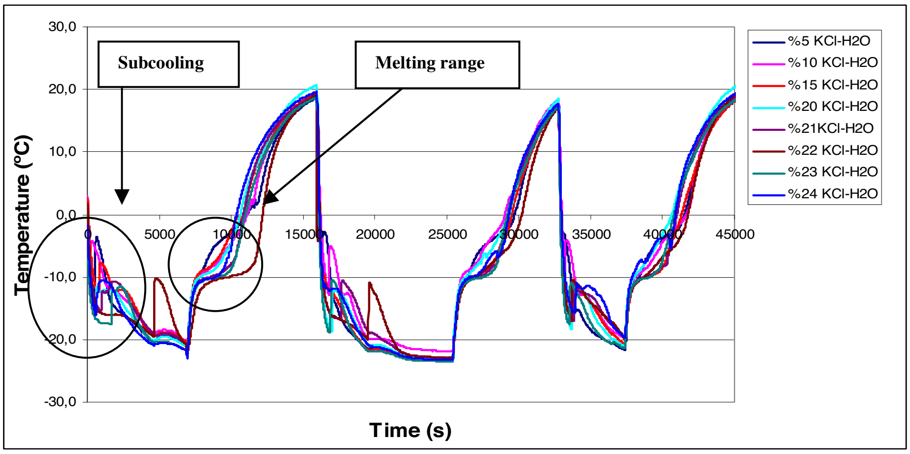

Fig. 3. Temperature vs. time curves obtained in cyclation test of KCl-H_2O solutions

In addition, these solutions showed phase separation. Phase separation occurs due to the two different components, water and salt. The density of water and salt is different and thus high density component sinks earlier compared to the lower density component; then phase separation tkes place.

Table 2. Freezing-melting temperature range and subcooling for aqueous NaCl and KCl solutions

Solutions	**Subcooling [ºC]**	**Freezing temperature [ºC]**	**Melting temperature [ºC]**	**Δ (Freezing point depression)** [11]
5% NaCl	3.87	-3.87/-4.27	-4.87/-3.18	3.04
10% NaCl	6.28	-7.60/-7.70	-7.80/-6.10	6.56
15% NaCl	5.30	-15.19/-15.29	-10.40/-9.20	10.88
20% NaCl	2.79	-18.22/-17.92	-18.92/-14.62	16.45
21% NaCl	2.20	-18.46/-18.36	-18.86/-18.26	17.77
22% NaCl	1.60	-21.95/-21.85	-20.15/-19.65	19.17
23% NaCl	0.20	-20.89/-21.39	-22.39/-20.89	20.66
24% NaCl	0.30	-20.19/-19.79	-22.08/-19.59	-
5% KCl	1.59	-3.38/-3.58	-3.28/-2.08	2.32
10% KCl	7.48	-6.60/-7.10	-11.79/-6.00	4.80
15% KCl	4.40	-12.80/-13.20	-11.40/-9.60	-
20% KCl	5.59	-12.93/-13.13	-10.23/-9.43	-
21% KCl	4.80	-10.35/-10.65	-10.15/-9.65	-
22% KCl	6.90	-1045/-11.25	-10.95/-9.15	-
23% KCl	7.48	-12.12/-12.82	-12.32/-9.83	-
24% KCl	5.10	-10.80/-11.10	-11.10/-9.10	-

3.2. Corrosion test

Results for NaCl and KCl solutions are presented in Fig. 4 and Fig. 5, respectively.For NaCl, after one week most solutions containing galvanized steel were blurry with white precipitates, there were few precipitates on the metal and these metals showed high corrosion rate (between 4.0 to 5.7 g/ m^2·d). After one month, there were white precipitates on the metal but the corrosion rate was decreased compared to 1 week. This metal-PCM pair is not recommended because of the high corrosion rate measured.

Samples with copper also showed high corrosion rate for 1 week (for 5% and 10% 3.2 and 3.3 g/ m^2·d, respectively). Corrosion rate decreased as the concentration increased. For 1 month, corrosion rate values decreased drastically probably due to the good passivation of the metal. This metal could be used with this PCM, nevertheless caution is recommended.

Laminated black steel gave few orange precipitates in the solutions and few precipitates were present on the metal in case of 1 week testing. In case of 1 month testing, in most cases there were lots of precipitates in the solution and also there were few precipitates on the metal but the corrosion rate decreased very much for 1 month testing compared to 1 week, that could be probably because of the passivating effect of the metal.

Aluminium and stainless steel showed no corrosion with all the eight solutions, but there was presence of air bubbles in the case of aluminium with 15%, 20%, 21%, 22%, and 24%. Caution is recommended for aluminium-PCM pairs.

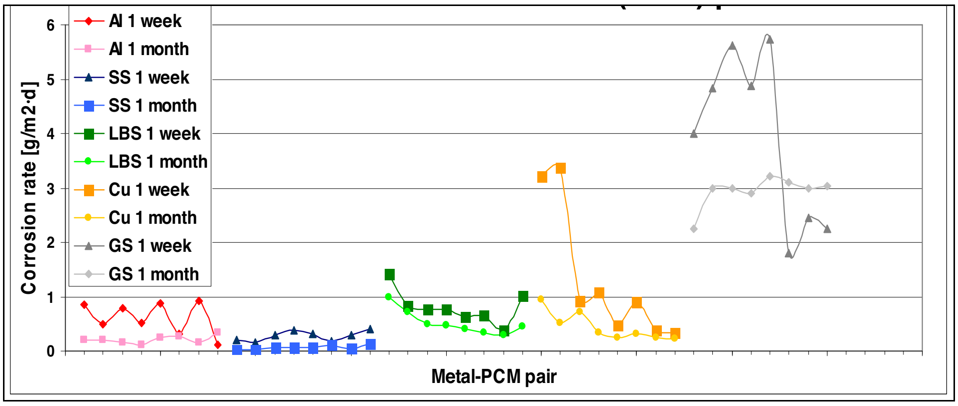

Fig. 4. Corrosion rate of experiments with different concentrations of NaCl. X-axe shows different metal-PCM concentration pairs: from left to right - (Al, SS, LBS, Cu and GS) + (5%, 10%, 15%, 20%, 21%, 22%, 23%, and 24% PCM).

Results for KCl-PCM pairs are shown in Fig. 5. Solutions with galvanized steel and copper gave blurry solutions, white precipitates (GS) and blue precipitates (Cu) both in the solutions and on the metal pieces, and the highest corrosion rate with these salt solutions for 1 week testing. For 1 month the corrosion rate decreased, especially for copper.

Laminated black steel gave blurry solutions and few precipitate in the solution and on the metal for 1 week and for 1 month. For 1 week this metal gave moderate corrosion rate but the corrosion rate for the 1 month decreased very much and probably that could be because of the formation of the passivating layer on the metal. This metal could be used in contact with these PCM but caution is recommended.

Most solutions with aluminium showed presence of bubbles for 1 week and 1 month. For 1 week, experiments showed corrosion at low rate but for the 1 month, corrosion rate almost decreased except for the 20% solution (1.512 g/m^2·d). And finally, stainless steel showed no corrosion at all with any of the concentration. In case of the formation of a passivating layer, the passivating layer effect on the heat conductivity of the metals and its resistance to temperature cycling should be evaluated [10].

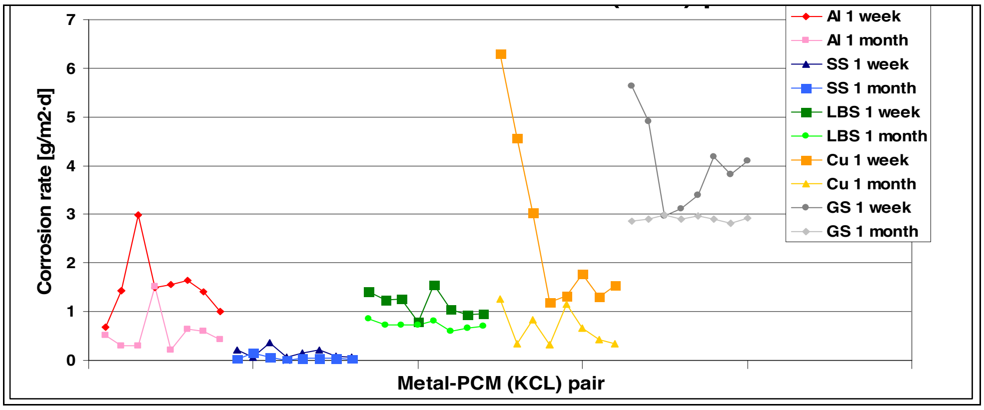

Fig. 5. Corrosion rate of experiments with different concentrations of KCl. . X-axe shows different metal-PCM concentration pairs: from left to right - (Al, SS, LBS, Cu and GS) + (5%, 10%, 15%, 20%, 21%, 22%, 23%, and 24% PCM).

4. Conclusions

- Aqueous salt-water solutions of NaCl and KCl are good PCM candidates because of their low cost and melting-freezing point below 0 ºC. Melting-freezing temperatures are in the range of -20 ºC to -3 ºC.
- However, all the 16 salt-water solutions tested showed subcooling. The degree of subcooling for NaCl solutions is less compared to KCl. Thus, NaCl solutions are more efficient PCM than KCl solutions for cooling applications.
- The density of NaCl, KCl, and water is different, so during the freezing cycle phase, separation occurs. Gelling and thickening of the PCM could be applied to minimize this effect.
- Five different common, cheap, and widely used metals with these PCM were studied in present work for the cooling applications that could be used for the short term (7 days) and long term (30 days) but some cautions are recommended as follows:
    - Aluminium: It could be used for short and long term applications with NaCl solutions, but caution is recommended because some combinations tested produced bubbles. With KCl solutions, it could be used without problems with the exception of 20% KCl solution.
    - Stainless steel: For the short term applications, this metal could be used without any problem with both NaCl and KCl solutions. For long term applications, the metal with high concentrations of NaCl (21%, 22%, 23%, and 24%) presented a little bit of precipitate, and with KCl solutions it could be used without problems for all the concentrations except 5% KCl solution because it gave some oxidation.

- Laminated black steel: Caution is recommended with both solutions for short and long term experiments because of precipitate.
- Copper: Avoid it with NaCl for short term applications. It could be used for long term (except 5% and 21%) however caution is recommended because of precipitate on the metal.
- Galvanized black steel: Should never be used because of the high corrosivity.

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