



Research Article

Hand warmer types, silica and zeolite 4A as potential hand warmers

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ABSTRACT

Hand warmers are used in cold environmental conditions to warm hands. Disposable air activated hand warmers and reusable hand warmers which generate heat by crystallization are present in the market. In the present study utilizing heat of wetting of silica gel and zeolites in warming hands was tested in a system simulated to warm hands by inserting warmer packages in knitted wool gloves. Sodium acetate solution was also tested as a reusable hand warmer by melting and recrystallization. While the commercial warmers released heat slowly for long period, dry silica gel and dry zeolite 4A released heat fast. Around 25% water and inert dilution materials should be used to limit the temperature rise in silica gel and zeolite 4A within reasonable limits.

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INTRODUCTION

Hand warmers are small packets, creating heat when needed, to warm the cold hands. They are activated by opening to air or triggering crystallization or dissolution depending on their type. They are placed in hands under a glow after heat activation. Exothermic reactions take place in hand warmers. There are various exothermic reaction such as air oxidation of charcoal [1], iron [2], gasoline [3,4], redox reactions of ingredients [5], salt dissolution [6] or crystallization in water [7]. Preventing heat transfer from hands by a heat insulator is another method of keeping hands warm in cold [8].

Air Activated Hand Warmers

Charcoal hand warmer

First hand warmers provide heat up to 6 h by slow combustion of charcoal. A charcoal stick was used for this purpose. The stick was lit from one or two ends and then extinguished for slow combustion. The slow burning stick was placed inside metal case coated with felt. The combustion was continued to create heat for long periods [1].

Iron powder hand warmer

Disposable hand warmers in the market such as Grabber Mycoal™ or heat factory™ gives the heat by the reaction of iron and oxygen. Iron powder, salt, water, an

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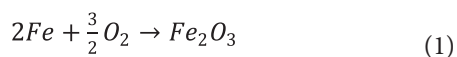
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absorbent material, and activated carbon were present in small packages with semipermeable containers in impermeable packages. When the impermeable package is open oxygen diffuses through permeable layer into powder part. Nylon or viscose nonwoven membranes are used to allow oxygen pass through into powder phase [9].

Oxygen reacts with the iron powder by an exothermic reaction with salt catalyst to form iron oxide (Fe_2O_3) as shown by Equation 1. The heat produced is dispersed in the powder with carbon. Adsorbent material which could be vermiculite slows down the heat dissipation [9-11]. Pulverized wood, polyacrylate or vermiculite are present in the mixture to control moisture [2]. Weiland et al. [2] and Tam et al. [11] reported an example for the composition of hand warmers with 50% iron powder, 25% distilled water, 20% activated carbon, 3% vermiculite and 2% sodium chloride.

The iron oxidation reaction shown in Equation 1 has enthalpy change of $-798.0 \pm 6.6 \text{ kJ mol}^{-1}$ [12].



The reaction rate depends on the surface area of metallic iron and oxygen pressure. While at atmospheric pressure the maximum temperature attained was around 48°C , for pure oxygen at 3 bar pressure it was above 110°C [13]. The effects of temperature and the humidity of the air medium were investigated by Klarzak et al. [14]. It was found that temperature rather than the humidity significantly affected the heat effect of the air activated hand warmers. The shape of the hand warmer rather than its presence in a protective glove impaired the skill of using hands [15].

Gasoline hand warmers

The PEACOCK™ and Zippo™ pocket warmers make use of the flameless combustion of gasoline vapor to carbon dioxide and water with the catalytic effect of platinum. The activation of the catalyst is done by heating gasoline with a match, cigarette lighter or an electric cell. The PEACOCK™ pocket warmer utilizes oxidation heat generated during the catalytic process. This is an advanced pocket warmer, safe, clean, and environmentally friendly [3,4].

Redox reaction hand warmers

Hypochlorite salts such as sodium hypochlorite or calcium hypochlorite in water and lignocellulosic material mixture is a source of exothermic reaction. The alcohol groups of cellulose are oxidized to ketones first than carboxylic acids with hypochlorite by an exothermic reaction. It was possible to obtain different temperatures for different periods by regulating the proportions of the reactants [5].

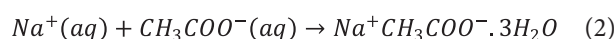
Heat of solution of crystals hand warmers

Vannatta et al. [6] designed a hand warmer by using the exothermic heat of solution of anhydrous calcium chloride in water. Dynarax(TM) heat pack in the market uses heat of solution of magnesium sulphate in water. Water present in a rupturable container is mixed with salt by squeezing the package.

Heat of Crystallization Hand Warmers

Sodium acetate trihydrate hand warmers

Sodium acetate trihydrate is also used in making hand warmers. When it is heated above 58°C it starts to lose its water of hydration and dissolves in that water up to 79°C . When the solution temperature is lowered to 20°C , it is unsaturated with respect to anhydrous sodium acetate, but it is supersaturated with respect to sodium acetate trihydrate. When a seed crystal of sodium acetate trihydrate is added, sodium acetate trihydrate crystallizes out with an exothermic reaction releasing $19.7 \text{ kJ mole}^{-1}$ energy [16]. If a flexible metal disc is placed in supersaturated solution and it is bended, the crystallization of sodium acetate trihydrate is triggered as indicated by Equation 2.



The latent heat of phase change for sodium acetate trihydrate for 25% and 33% aqueous solutions was reported as 243 kJ kg^{-1} and 264 kJ kg^{-1} respectively [7] or $237\text{-}243 \text{ kJ kg}^{-1}$ [17]. The seed crystals trapped in metal disc act as nucleation centers. Various metal appliances such as screws, paper clips etc. also triggered the crystallization of sodium acetate trihydrate [18].

Thermal energy can be stored in supercooled liquids where the material is in thermal equilibrium with its surroundings [7]. The stored latent heat of fusion is released by triggering the crystallization of the supercooled substance. Enthalpy-temperature curves including the effect of supercooling are measured for some well-known supercooling salt hydrates (disodium hydrogen phosphate dodecahydrate, sodium acetate trihydrate and STL-47) by Sandnes and Rekstad [7]. It was found that the maximum temperature reached during crystallization generally decreases with increased degree of supercooling. The supercooling and nucleation of sodium acetate can be controlled by nucleating agents such as disodium hydrogen phosphate (DSP), tetrasodium pyrophosphate decahydrate (TPD), anhydrous sodium acetate (SAA), sodium tetraborate decahydrate (STD), sodium metasilicate nonahydrate (SMN) and the viscosity can be controlled by carboxymethyl cellulose sodium (CMC), polyacrylic acid sodium salt (PASS), xanthan gum (XG) and palygorskite (PAS) thickeners [19]. Bentonite and starch were successfully used as thickener with a loss of 20-35% loss in enthalpy [17].

Nano-copper (Nano-Cu), which possesses high thermal and electrical conductivity, as an additive, can improve the supercooling properties of sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$), SAT and enhance its thermal conductivity. Nano-Cu can be used for enhancing thermal conductivity of SAT [20]. To investigate the effect of Nano-Cu content on the degree of supercooling of SAT, composite phase change materials containing SAT, Nano-Cu (0.4%, 0.5%, 0.6%, 0.7% and 0.8%), carboxymethyl cellulose (CMC) (thickening agent) and sodium dodecyl sulfonate ($C_{12}H_{25}NaO_3S$, dispersant)

were prepared by Cui et al. [20]. Carboxymethyl cellulose, extra water, liquid polymer HD 310, metal-based graphite flakes, and silicone oil were applied as additives to form the different sodium acetate trihydrate compositions [21]. The volume change of sodium acetate trihydrate on crystallization can be controlled by using additives. While the volume reduction was 16.2% for pure sodium acetate trihydrate, it is reduced to 11.6% for the mixture of sodium acetate trihydrate, xanthan gum and disodium hydrogen phosphate [19]. The densities of solid and liquid sodium acetate trihydrate are 1.636 and 1.406 g cm⁻³ respectively. On the other hand the mixture had solid and liquid densities of 1.406 and 1.268 g cm⁻³ respectively [19].

Disodium hydrogen phosphate hand warmers

Disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O) is an attractive candidate for phase change materials [22]. Additives such as sodium polyacrylate, sodium alginate and water are used as additives to keep heat storage capacities constant [22].

Heat Insulating Hand Warmers

Hand warmers made out of beavers fur could be used for long periods when they were placed in gloves with the fiber side contacting with the palm [8]. The warming is the result of very high insulating ability of heat by the fibers and the skin of the beaver's fur.

Heat of Wetting Hand Warmers

Heat of wetting of adsorbents such as zeolites and silica gel can also be used as heat source for warming hands. The dried adsorbents can be wetted by rupturing the microcapsules with water and the released heat of wetting could be used for warming hands. For example zeolite 4A and natural clinoptilolite could be used for this purpose [23]. The energy storage intensity was measured by flow micro calorimetry in the range 464-201 J g⁻¹ and 48-97 J g⁻¹ for zeolite 4A and the tuff respectively. Specific heats of zeolite 4A and the zeolitic tuff were measured as 1.42 and 1.01 J g⁻¹ K⁻¹, respectively [23]. Silica gel had 94.3 ± 15 J g⁻¹ heat of wetting of water [27].

Table 1. Hand warmers present in the market

Reactants	Additives	Reaction	Heat released	Ref
Cellulose, calcium hypochloride		Oxidation	n.a.	[5]
Calcium chloride and water		Dissolution of crystals in water	81.8 kJ mol ⁻¹	[6]
Magnesium sulfate and water		Dissolution of crystals in water	85 kJ mol ⁻¹	
Gasoline and air		Oxidation with platinum catalyst	5460 kJ mol ⁻¹ For octane	[3,4]
Iron and air	Graphite Vermiculate cellulose	Oxidation with sodium chloride catalyst	798 kJ mol ⁻¹	[10], [11], [2]
Sodium acetate trihydrate	Nucleating agents Viscosity regulators dispersants	Crystallization of supercooled liquid	19.7 kJ mol ⁻¹ 264-269 kJ kg ⁻¹	[7], [16], [24]
Sodium acetate trihydrate 25% aqueous solution		Supercooled liquid	243 kJ kg ⁻¹	[7]
Sodium acetate trihydrate 33% aqueous solution		Crystallization of supercooled liquid	264 kJ kg ⁻¹	[7]
Sodium acetate trihydrate 60% in urea		Crystallization of supercooled material	226 J g ⁻¹	[25]
Sodium acetate trihydrate 50% in urea		Crystallization of supercooled material	255 kJ kg ⁻¹	[25]
Sodium acetate trihydrate	Bentonite starch	Crystallization of supercooled liquid	153-237 kJ kg ⁻¹	[17]
Sodium acetate trihydrate	Water CMC Xantan gum Tartaric acid EDTA Polymers with different chain lengths	Crystallization of supercooled liquid	161-216 J g ⁻¹	[26]
Disodium hydrogen phosphate dodecahydrate	Sodium polyacrylate	Crystallization of supercooled liquid	200 J g ⁻¹	[22], [7]
Silica gel		Heat of wetting	94.43±15 J g ⁻¹	[27]

In Table 1 hand warmer types, the reaction occurring, additives used and the amount of heat released per unit mass are summarized.

Other Applications of Hand Warmers

There are cases for the use of hand warmers for cancer treatment [28]. Phase change material hand warmers were used for external heating of blood without any side effects [29]. Hand warmers could be used as heat patches to treat headaches. Phase change material mixed mortar had better insulating ability from hot and cold of the walls of the buildings [30].

Developing disposable and reusable hand warmers is aimed in the present study. Since the composition of commercial hand warmers are not publicly known, practical hand warmers from powder form and granular silica gel and zeolite A were aimed to be developed by utilizing their heat of wetting with water. A simple test system was used to show the heating effect obtained by wetting silica gel and zeolite 4A with water for disposable hand warmer. Also heat release by sodium acetate trihydrate supersaturated solution crystallization is shown to be used as reusable hand warmer.

MATERIALS AND METHODS

Materials

Silica gel powder (Sigma aldrich), Silicagel granules (Sigma aldrich), zeolite 4A powder (Sigma Aldrich), zeolite 4A granules (Sigma Aldrich) were tested as potential hand warmers. Sodium acetate trihydrate (Merck) was tested as a reusable hand warmer. Commercial air activated hand warmer (Grabber) having 33 g mass with 14 cmx11 cm dimensions with ingredients of iron powder, water, salt, activated charcoal and vermiculite and commercial sodium acetate hand warmer (Touchpack) with 330 g mass were used as reference materials.

Methods

Potential powder hand warmers

5 g material that was dried at 200°C and cooled in a desiccator was placed in plastic bags and mixed with 100 mg drop of water. The bags were placed in a wool knitted cloth instantly after mixing with water. The temperature at the surface of the bags was monitored with a Testo 945 K-type thermocouple with one minute intervals up to 60 minutes. The set up for measurement is shown in Figure 1.

Sodium acetate hand warmer

1.06 grams of sodium acetate trihydrate and 1.8 cm³ water were placed in a bottle. Bottle contents was mixed and heated in a temperature controlled water bath till a clear solution of sodium acetate was obtained. A supersaturated solution was obtained by cooling the sodium acetate solution to room temperature. Bottle was taken from water bath and the lid was opened. The crystallization was triggered as soon as the Testo 945 K-type thermocouple was immersed in solution. The temperature change with time was recorded.

Test for commercial air activated hand warmer

First of all, plastic packaging is opened in the air at 21.2 °C. By this way, it was activated by exposing the contents to air. Next, Testo 945 K-type thermocouple was fixed to the chemical warmer via a small square piece of duct tape. The thermocouple and warmer were then placed inside the knitted wool as seen in Figure 2. Temperature was measured at 5 minute intervals via the thermocouple.

Test for commercial sodium acetate bag

The metal disc inside the plastic packet containing sodium acetate solution was snapped to trigger crystallization. By doing this, the crystallization of sodium acetate was activated. Then, the thermocouple was fixed to the surface of the chemical warmer via a small square piece of duct tape. The thermocouple and warmer were then placed

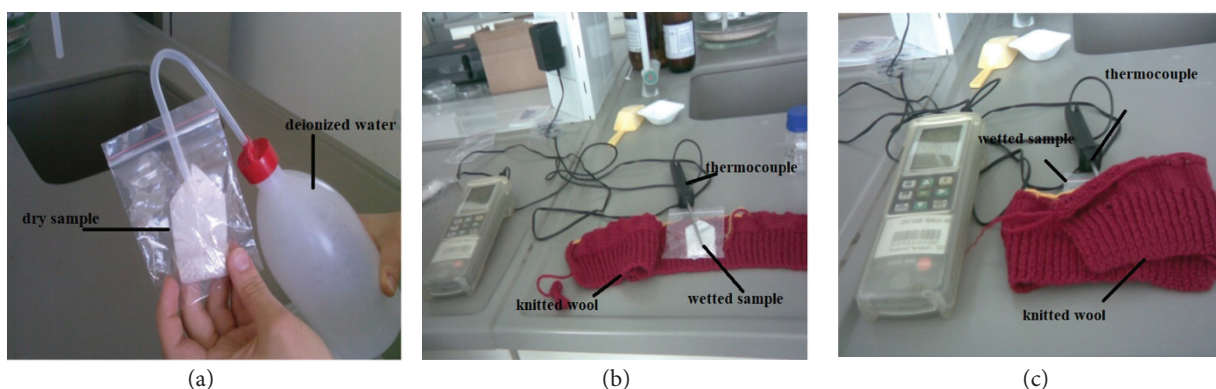


Figure 1. a. Wetting of dry sample by a droplet of water, b. placing thermocouple on wetted sample on knitted wool, c. Covering the sample and thermocouple with knitted wool and recording temperature.

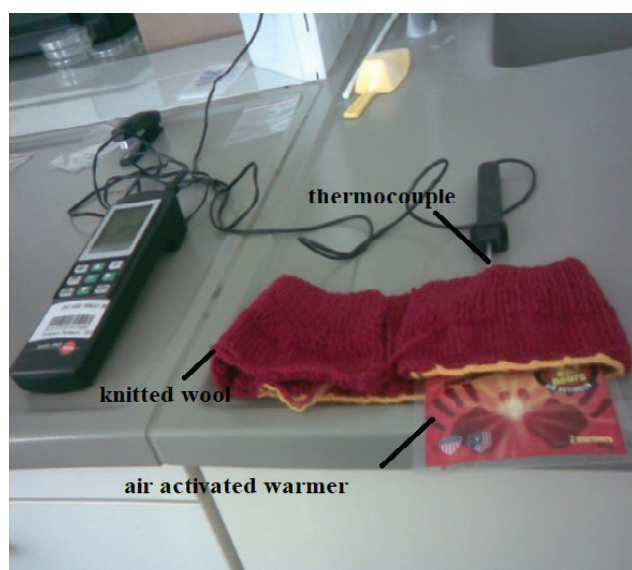


Figure 2. Air activated warmer opened to air and placed in knitted wool for measurement of temperature.

inside the knitted wool. Temperature was monitored at 1 minute intervals by the thermocouple.

DSC analysis of sodium acetate trihydrate

2.5 mg sodium acetate trihydrate was heated from 25 °C up to 600 °C at 10 °C min⁻¹ rate up to 600 °C under 50 cm³ min⁻¹ N₂ flow using Shimadzu DSC 60 for DSC analysis.

RESULTS AND DISCUSSION

Results

Tests for silica gel and zeolite 4A

A schematic view of the system used in the present study is shown in Figure 3a. The thermocouple measures the temperature at one point close to the water droplet in the adsorbent layer as a function of time. The temperature increased in a short time due to heat of wetting of silica gel

or zeolite by a drop of water. Then it decreased slowly due to heat transfer to nonwetted silica gel or zeolite in hand warmer tests as seen in Figures 4 and 5. The heat transfer to surroundings could be neglected since silica gel or zeolite was covered with wool cloth acting as insulating layer. Higher (8.6 °C) temperature increase (ΔT_{\max}) was observed for silica gel in granular form than that of silica gel powder (5.7 °C). The temperature increase rate of the silica gel granules was also higher than the silica gel granules. The temperature rise for zeolite 4A was much higher than silica gel due to higher heat of wetting as reported in Table 1. The powder form had higher ΔT_{\max} (22.2 °C) than that (19.6 °C) of the granular form of zeolite 4A indicating different heat transfer behavior was present for silica gel and zeolite 4A.

The temperature increased in a short time due to heat of wetting of silica gel or zeolite by a drop of water. Then it decreased slowly due to heat transfer to nonwetted silica gel or zeolite in hand warmer tests as seen in Figures 4 and 5. The heat transfer to surroundings could be neglected since silica gel or zeolite was covered with wool cloth acting as insulating layer. A schematic view of the system used in the present study is shown in Figure 5. The thermocouple measures the temperature at one point close to the water droplet in the adsorbent layer as a function of time. Higher (8.6 °C) temperature increase (ΔT_{\max}) was observed for silica gel in granular form than that of silica gel powder (5.7 °C). The temperature increase rate of the silica gel granules was also higher than the silica gel granules. The temperature rise for zeolite 4A was much higher than silica gel due to higher heat of wetting as reported in Table 1. The powder form had higher ΔT_{\max} (22.2 °C) than that (19.6 °C) of the granular form of zeolite 4A indicating different heat transfer behavior was present for silica gel and zeolite 4A.

The information obtained in the present study is not sufficient in designing a hand warmer. However the heating effects of the two adsorbents even by a droplet of water are clearly observed. In a real hand warmer sufficient and evenly dispersed water will be added to completely wet the adsorbents to take the full advantage of heat of wetting. Silica gel adsorbed 24±1.5 mass% water at saturation [27]. Thus in order to obtain maximum heat of wetting the total

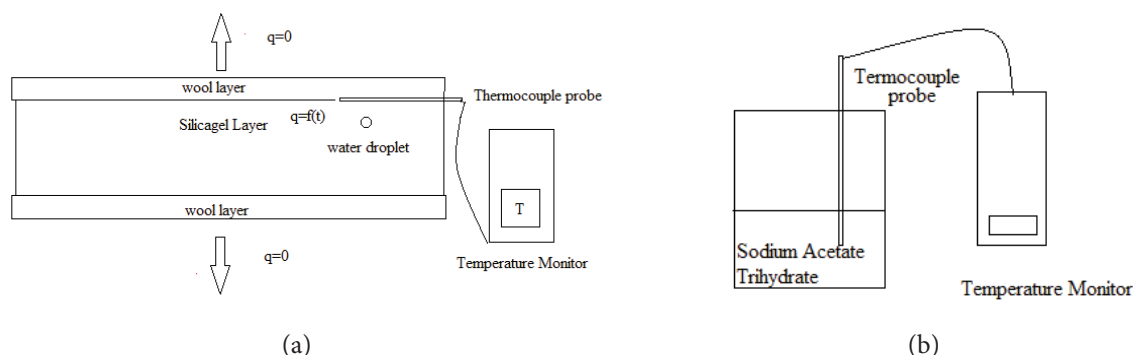


Figure 3. Schematic view of a. silica gel hand warmer test, b. reusable hand warmer test.

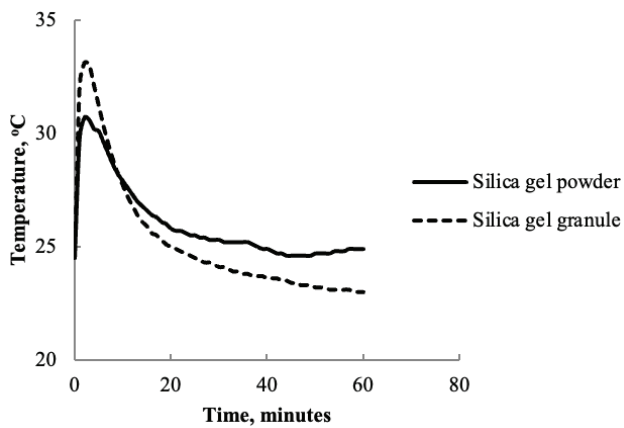


Figure 4. Temperature change with time for the wetted silica gels.

amount of water should be around 25% of dry mass of the silica gel. Using the heat of wetting values of 94.3 J g^{-1} [27] and 201 J g^{-1} [23] from Table 1 and specific heats of 0.68 and $1.4 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ [23] the temperature rise (ΔT) could be calculated using Equation 3.

$$q = (m_1 c_{p1} + m_2 c_{p2}) \Delta T \quad (3)$$

Where m_1 is the mass of dry silica gel or zeolite 4A, m_2 is mass of added water for saturation. Assuming 25% liquid water per dry mass is added and taking the specific heat of water as $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ 54.6 and $82.2 \text{ }^\circ\text{C}$ temperature rise was calculated for silica gel and zeolites respectively. Since the theoretical temperature rise is above the suitable temperatures for warming hands the silica gel or zeolites should be mixed with an inert material to lower the temperature rise to around body temperature.

Sodium acetate acetate trihydrate as a reusable hand warmer

The schematic view of the test made in a bottle for 37% sodium acetate trihydrate solution is shown in Figure 3b and the result of the test is shown in Figure 6. ΔT_{max} was observed at the 3rd minute as $9.3 \text{ }^\circ\text{C}$. The supercooled sodium acetate solution was crystallized as seen in Equation 2 giving heat to the surroundings. The crystallization occurred as soon as the thermocouple probe was inserted in super saturated solution. This showed that a clean surface without any sodium acetate trihydrate nuclei [18] can also induce crystallization by mechanical action. The theoretical temperature rise (ΔT) was calculated from Equation 4.

$$\Delta H_c m_1 = (m_1 c_{p1} + m_2 c_{p2} + m_3 c_{p3}) \Delta T \quad (4)$$

Where ΔH_c is enthalpy of crystallization in J g^{-1} of sodium acetate trihydrate, m_1 and m_2 are mass liquid and solid of sodium acetate trihydrate and m_3 is mass of water

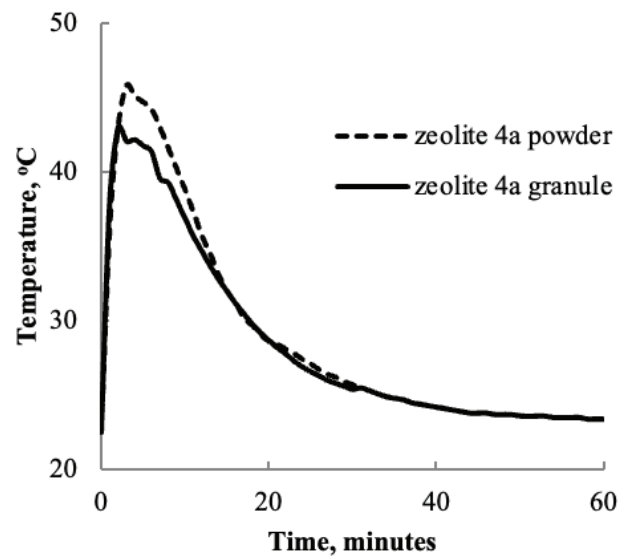


Figure 5. Temperature change with time for the wetted zeolite 4A.

in g, c_{p1} and c_{p2} are specific heats of solid and dissolved sodium acetate trihydrate in water and c_{p3} is the specific heat of water in $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$ in sodium acetate trihydrate solution having crystallized sodium triacetate hydrate. The theoretical temperature rise was found as $5 \text{ }^\circ\text{C}$ taking specific heat of solid and liquid sodium acetate trihydrate as $2.26 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ and $3.3 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ [31] and ΔH_c as 248 J g^{-1} as reported in Table 2. When supercooled sodium acetate trihydrate solution is stressed crystals of sodium acetate trihydrate in a saturated solution of sodium triacetate forms [31]. The solubility of sodium triacetate trihydrate in water at $20 \text{ }^\circ\text{C}$ is $46.5 \text{ g } 100 \text{ g}^{-1}$ water [31].

A higher temperature rise ($9.3 \text{ }^\circ\text{C}$) than expected ($5 \text{ }^\circ\text{C}$) was observed since the thermocouple probe immersed in solution measured the temperature at a single point. The system was not heat insulated and cooled with time by dissipating to the surrounding.

Placing and sealing of appropriate amount of sodium acetate trihydrate with few drops of water [31] together with a flexible metal disc into a heat resistant plastic bag in size appropriate to be placed in a wool glove would make it a reusable hand warmer. The crystals will be melted when immersed in hot water and super cooled solution will be obtained on cooling. When the metal disc moved exothermic crystallization will occur. The released heat will be used to warm hands.

Commercial air activated hand warmer, grabber

The temperature increased at a fast rate from $21.2 \text{ }^\circ\text{C}$ to $31.5 \text{ }^\circ\text{C}$ in 5 minutes and at a slow rate to maximum $37 \text{ }^\circ\text{C}$ in 25 minutes for air activated hand warmer as seen in Figure 7. ΔT_{max} was $15.8 \text{ }^\circ\text{C}$ for it. The temperature decreased towards ambient temperature at a very slow rate due to

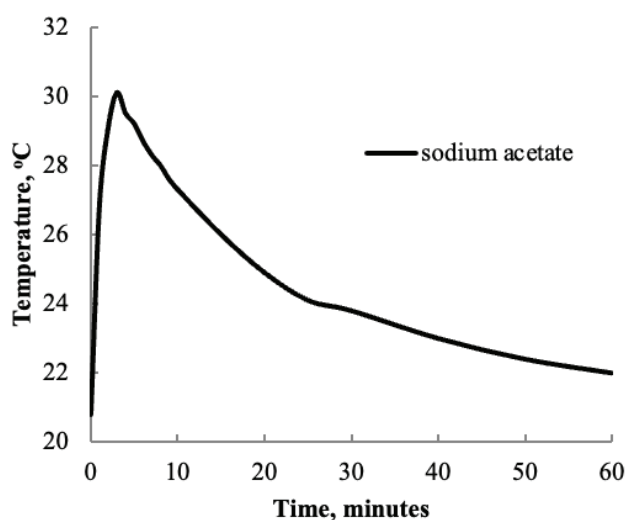


Figure 6. Temperature change with time after activation for super saturated sodium acetate Commercial air activated hand warmer, Grabber.

slow exothermic reaction of iron powder in its contents according to reaction 1. There are simultaneous heat and mass transfer reactions occurring in this hand warmer that contains iron powder, purified water, activated carbon, vermiculite and sodium chloride [2, 11]. Rather than explaining the reactions, the heat generation characteristics were determined to determine the limits for future design of the hand formers in the present study.

Commercial sodium acetate trihydrate hand warmer

A commercial reusable warmer with 330 g mass was tested for comparison. Its size was bigger than a hand warmer but it showed as how a commercial reusable warmer acted. It was activated by flexing the metal disc inside the clear solution. As seen in Figure 6 temperature was increased to 51.8 °C in 1 minute and it reached to

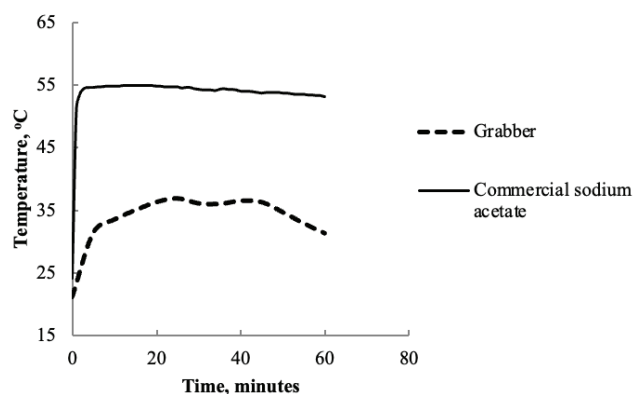


Figure 7. Temperature versus time after air activation of grabber hand warmer and mechanical activation of commercial sodium acetate.

maximum 54.8 °C in 8 minutes. ΔT_{\max} was 30.7 °C for commercial reusable hand warmer. The warmer kept its high temperature till the end of the test period due to its low heat transfer area per unit mass. The temperature was 53.3 °C at the 60th minutes. Also there could be transparent additives to control viscosity, density and heat capacity of sodium acetate trihydrate solution.

In Table 2 the experimental results obtained from potential hand warmers silica gel and zeolite 4A, sodium acetate trihydrate and commercial hand warmers are reported.

DSC analysis of sodium acetate trihydrate

DSC analysis curve of sodium acetate trihydrate used in the present study is shown in Figure 8.

The onset, peak and end set temperatures for the first peak which is the fusion endotherm of sodium acetate trihydrate are 58.55, 63.59 and 100.36 °C respectively in Figure 8. The enthalpy change of the melting of sodium acetate trihydrate was calculated as 227 J g⁻¹ considering the area of the first peak in the range of 53 to 70 °C since evaporation

Table 2. The maximum temperature attained and time to attain T_{\max} , ΔT_{\max} specific heat, sample mass, adiabatic temperature rise, rate

Reactants	Time, min	T_{\max} , °C	ΔT_{\max} , °C	Specific heat, Jg ⁻¹ °C ⁻¹	Sample mass, g	Adiabatic temperature rise	Rate
Silica gel granules	2	33.1	8.6	0.68	5	54.6	fast
Silica gel powder	4	30.2	5.7	0.68	5	54.6	fast
Zeolite 4A powder	4	44.7	22.2	1.4 [23]	5	82.2	fast
Zeolite 4 A granules	4	42.2	19.6	1.4 [23]	5	82.2	fast
Sodium acetate trihydrate	3	30.1	9.3	3.33 (l) 2.26 (s) [32]	2.86	5	fast
Grabber	25	37.0	15.8	0.5	30	--	slow

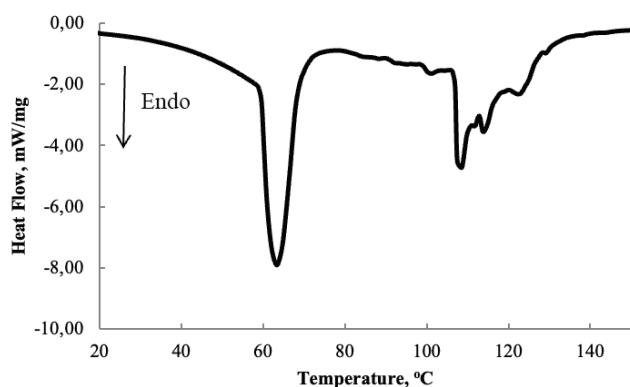


Figure 8. DSC analysis curve of sodium acetate trihydrate.

of water was considerable at higher temperatures. During melting of sodium acetate three mols of water is separated and sodium acetate was dissolved by ionizing in this water. In cooling this solution without making any disturbance the supersaturated solution is obtained.

Hua et al. [19] also measured heat of fusion of sodium acetate trihydrate and reported the heat of fusion as 268.8 J g^{-1} . They found the starting and termination temperature of fusion of sodium acetate trihydrate as $58.8 \text{ }^\circ\text{C}$ and $68.2 \text{ }^\circ\text{C}$ respectively. Jin et al. [33] reported that SAT started to melt at about $59.0 \text{ }^\circ\text{C}$. The maximum heat-flow point occurred at a temperature of about $63.0 \text{ }^\circ\text{C}$. The calculated heat of fusion was 257.2 kJ kg^{-1} with a melting temperature range of $58.9 \text{ }^\circ\text{C}$ to $67.3 \text{ }^\circ\text{C}$. During the cooling process, the results showed that SAT did not release the latent heat even when it was cooled to $-40 \text{ }^\circ\text{C}$. However, if it is partially molten it releases heat on cooling due to nucleating effect of remaining SAT crystals. The additives to avoid precipitation of sodium acetate trihydrate also changed its enthalpy of fusion. Kong et al. [26] reported the heat of crystallization of sodium acetate trihydrate with different additives as $161\text{--}216 \text{ J g}^{-1}$.

Engmair et al. [21] determined maximum water content as 40.8% of the commercial sodium acetate trihydrate stored in laboratory for different periods up to 26 months after drying at $120 \text{ }^\circ\text{C}$.

The DSC curve of sodium acetate trihydrate in Figure 8 has a second endothermic peak with $95.21 \text{ }^\circ\text{C}$ onset, $108.65 \text{ }^\circ\text{C}$ peak and $110 \text{ }^\circ\text{C}$ endset temperature belonging to evaporation of released crystal water. The enthalpy change for this second peak is -366 J g^{-1} .

DISCUSSION

In the present study a water droplet was added to the dried silica gel and zeolite 4A to test the temperature rise effect for warming hands. However both silica gel and zeolite 4A had much higher capacity of water for complete wetting. Thus when a real hand warmer is produced this

effect should be taken in consideration. Water encapsulated in microcapsules could be placed together with silica gel or zeolite 4A in a water impermeable package. Also an inert material should be present in the mixture to limit the temperature rise to plausible limits. The warming effect could be obtained releasing water by crushing the microcapsules by squeezing the package between fingers.

Sodium acetate trihydrate hand warmer could be produced and tested for different solution concentrations by placing in packages in suitable size to be placed between the glove and the hand.

For air activated hand warmers iron powder and other additives are placed in an air permeable bag and placed in a second package impermeable to air. When the impermeable bag is opened air enters through the permeable bag to react with iron powder to create heat. The heat effects produced could be measured and predicted using temperature-time data, specific heats reported in Table 2 and reaction heats.

There are previous studies testing commercial air activated hand and foot warmers present in the market [10] or use of different semipermeable covering [9] or their effect in human comfort [15]. However in the present study new materials silica gel, zeolite 4A are tested for their potential use in hand warmers. Future experimental and model work about hand warmers should be planned and done by considering the previous studies [34] and the results of the present study.

CONCLUSION

The commercial hand warmers and potential hand warmers were tested for heat release, maximum temperature attained and the amount of heat released in one hour. Supersaturated sodium acetate hand warmer gives more heat than the air-activated one. Since the sodium acetate trihydrate hand warmer can be used repeatedly, and air activated hand warmer can be used once, it should be preferred when there are means for melting by heating. Air activated ones are efficient in circumstances when reheating is not possible, such as on top of a mountain. Silica gel and zeolite 4A in their powder and granule form could be one use hand warmers releasing sufficient heat to warm hands in cold weather. While the commercial warmers released heat slowly for long term and dry silica gel and dry zeolite 4A could be used for short term heating of hands by placing them in gloves.

NOMENCLATURE

- cp_1 Specific heat of silica gel or zeolite 4A, or solid sodium acetate trihydrate in of solid in $\text{J g}^{-1}\text{ }^\circ\text{C}^{-1}$
- cp_2 Specific heat of water or dissolved sodium acetate trihydrate, $\text{J g}^{-1}\text{ }^\circ\text{C}^{-1}$
- cp_3 Specific heat of water in mixture of solid, liquid and water mixture, $\text{J g}^{-1}\text{ }^\circ\text{C}^{-1}$

m_1	Mass of dry silica gel or zeolite 4A or mass of liquid sodium acetate trihydrate, g
m_2	Mass of added water for saturation of silica gel or zeolite 4A or the mass of crystalline sodium acetate trihydrate, g
m_3	Mass of water in the mixture of partially crystallized sodium acetate trihydrate and water, g
ΔH_c	Enthalpy of crystallization in J g^{-1} of sodium acetate
q	Heat, J
T	Temperature, $^{\circ}\text{C}$
t	Time, sec

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

REFERENCES

- [1] Patel AN, Wernham AGH, Varma S. Charcoal pocket hand warmers - a rare cause of BCC carcinogenesis? *Australas J Dermatol* 2019;60:156–157. [CrossRef]
- [2] Weiland JL, Sherrow LK, Jayant DA, Katz KD. Chemical Hand Warmer Packet Ingestion: A Case of Elemental Iron Exposure. *Wild Environ Med* 2017;28:246–248. [CrossRef]
- [3] Hakkin..Available at: <http://hakkin.co.jp/index.html> Last Accessed Date: 12.03.2024
- [4] Zippo Hand Warmers. Available at: <https://www.zippo.com/pages/hand-warmers> Last Accessed Date: 12.03.2024
- [5] Littlefield TKT, Tock RW, Cox LV. Chemical Heater. US patent 4573447. 1986.
- [6] Vannatta MW, Richards-Babb M, Sweeney RJ. Thermochemistry to the rescue: A novel calorimetry experiment for general chemistry. *J Chem Educ* 2010;87:1222–1224. [CrossRef]
- [7] Sadnes B, Rekstad J. Supercooling salt hydrates: Stored enthalpy as a function of temperature. *Sol Energy* 2006;80:616–625. [CrossRef]
- [8] Aurora Heat Natural Reusable Hand Warmers Available at: <https://auroraheat.ca/products/natural-reusable-hand-warmers> Last Accessed Date: 12.03.2024
- [9] Irzmańska E, Jurczyk-Kowalska M, Bil M, Płocińska M. Experimental investigation of the properties of laminated nonwovens used for packaging of powders in mineral warmers. *Autex Res J* 2019;21:163–171. [CrossRef]
- [10] Sands WA, Kimmel WL, Wurtz BR, Stone MH, Jeni R, McNeal JR. Comparison of commercially available disposable chemical hand and foot warmers. *Wild Environ Med* 2009;20:33–38. [CrossRef]
- [11] Tam AYB, Chan C, Lau FL. A case series of accidental ingestion of hand warmer. *Clin Toxicol* 2008;46:900–904. [CrossRef]
- [12] Majzlan J, Navrotsky A, Schwermann U. Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite (similar to $\text{Fe}(\text{OH})_3$), schwertmannite (similar to $\text{FeO}(\text{OH})_{3/4}(\text{SO}_4)_{1/8}$), and epsilon- Fe_2O_3 . *Geochim Cosmochim Acta* 2004;68:1049–1059. [CrossRef]
- [13] Raleigh G, Rivard R, Fabus S. Air-activated chemical warming devices: Effects of oxygen and pressure. *J Geophys Res* 2005;32:445–449.
- [14] Klarzak I, Ura-Bińczyk E, Płocińska M, Jurczyk-Kowalska M. Effect of temperature and humidity on heat effect of commercial chemical warmers based on iron powder. *Thermal Sci Eng Prog* 2018;6:87–94. [CrossRef]
- [15] Irzmańska E, Kropidłowska P, Adamus-Włodarczyk A. Chemical hand warmers in protective gloves: Design and usage. *Autex Res J* 2021;21:13–19. [CrossRef]
- [16] Supersaturation of Sodium Acetate Available at: <https://chem.washington.edu/lecture-demos/supersaturation-sodium-acetate> Last Accessed Date: 12.03.2024
- [17] Cabeza LF, Svensson G, Hiebler S, Mehling H. Thermal performance of sodium acetate trihydrate thickened with different materials as phase change energy storage material. *Appl Therm Eng* 2003;23:1697–1704. [CrossRef]
- [18] Sandnes B. The physics and the chemistry of the heat pad. *Am J Phys* 2008;76:546–550. [CrossRef]
- [19] Hua WS, Zhang XL, Muthoka MJ, Han X. Preparation and performance analysis of modified sodium acetate trihydrate. *Materials* 2018;11:1016. [CrossRef]

- [20] Cui WL, Yuan YP, Sun L, Cao X, Yang X. Experimental studies on the supercooling and melting/freezing characteristics of nano-copper/sodium acetate trihydrate composite phase change materials. *Renew Energ* 2016;99:1029–1037. [CrossRef]
- [21] Englmaier G, Jiang YL, Dannemand M, Moser C, Schranzhofer H, Furbo S, Fan J. Crystallization by local cooling of supercooled sodium acetate trihydrate composites for long-term heat storage. *Energy Build* 2018;180:159–171. [CrossRef]
- [22] Lan X, Tan ZC, Yue DT, Shi Q, Yang CG. Heat storage performance of disodium hydrogen phosphate dodecahydrate: Prevention of phase separation by thickening and gelling methods. *Chinese J Chem* 2007;25:921–925. [CrossRef]
- [23] Ulku S, Balkose D, Alp B. Dynamic heat of adsorption of water vapour on zeolitic tuff and zeolite 4A by flow microcalorimetry. *Oxid Commun* 2006;29:204–215.
- [24] Chemistry Matters: Warmer Available at: https://www.ncpedia.org/sites/default/files/documents/chemistry-matters_warmer.pdf Last Accessed Date: 12.03.2024
- [25] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Therm Eng* 2003;23:251–283. [CrossRef]
- [26] Kong W, Dannemand M, Johansen JB, Fan J, Dragsted J, Englmaier G, Furbo S. Experimental investigations on heat content of supercooled sodium acetate trihydrate by a simple heat loss method. *Sol Energy* 2016;139:249–257. [CrossRef]
- [27] Tahat MA. Heat-pump/energy-store using silica gel and water as a working pair. *Appl Energy* 2001;69:19–27. [CrossRef]
- [28] Honma M, Hashimoto M, Iwasaki T, Iinuma S, Takahashi H, Ishida-Yamamoto A, et al. Primary cutaneous anaplastic large cell lymphoma successfully treated with local thermotherapy using pocket hand warmers. *J Dermatology* 2008;35:748–750. [CrossRef]
- [29] McEwen MP, Roxby D. Can latent heat safely warm blood? - in vitro testing of a portable prototype blood warmer. *BMC Emerg Med* 2007;7:8. [CrossRef]
- [30] Kabay N, Kizilkanat AB. A comparative study on the thermal performance of mortars with different formulations. *Sigma J Eng Nat Sci* 2023;8:183–189.
- [31] Oliver DE, Bissell AJ, Liu X, Tang CC, Pulham RC. Crystallisation studies of sodium acetate trihydrate - suppression of incongruent melting and sub-cooling to produce a reliable, high performance phase-change material. *CrystEngComm* 2021;23:700–706. [CrossRef]
- [32] Yinping Z, Yi J, Yi J. A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measurement Sci Technol* 1999;10:201–205. [CrossRef]
- [33] Jin X, Medina MA, Zhang X, Zhang S. Phase-change characteristic analysis of partially melted sodium acetate trihydrate using DSC. *Int J Thermophys* 2014;35:45–52. [CrossRef]
- [34] Javidana M, Asgari M, Gholinia M, Nozari M, Asgari A, Gani DD. Thermal energy storage inside the chamber with a brick wall using the phase change process of paraffinic materials: A numerical simulation. *Theor Appl Mech Lett* 2022;12:100329. [CrossRef]