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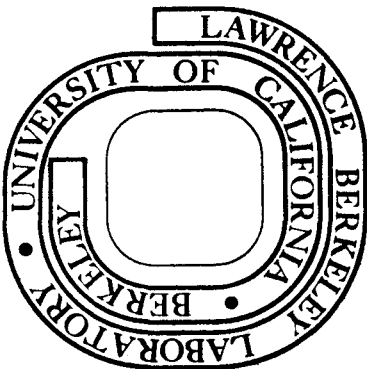
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THERMAL ENERGY STORAGE USING SODIUM SULFATE DECAHYDRATE
AND WATER*

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Water is commonly considered to be the most suitable material for thermal energy storage (TES) primarily because it is cheap and has a reasonably high heat capacity. An alternate means for TES is to use the latent heat of a reaction. If the latent heat of reaction is large, this method has the advantage of making possible smaller systems (as illustrated in Table I).

As a practical matter, two criteria limit reactions that can be considered for such systems:

- (1) The reaction must occur in the temperature range of interest (normally for solar heating 30°C to 50°C) and
- (2) The reacting materials must be as inexpensive as possible.

On the basis of these considerations, the dehydration reaction of sodium sulfate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ looked promising, and considerable work has been done [1,2] using decahydrate as a TES material. But it has been found [2] that the effective heat storage of the system degrades and is not reproducible after 5 or 10 cycles.

Sodium sulfate decahydrate decomposes peritectically on heating to 32.4°C to yield anhydrous sodium sulfate and a saturated solution of Na_2SO_4 in water. This mixture when cooled below 32.4°C can undergo the reverse reaction of water with anhydrous sodium sulfate only as rapidly as water can diffuse through solid sodium sulfate decahydrate to the

anhydrous sodium sulfate particles on which the decahydrate particles form. Peritectic solidification reactions [3] are characteristically much slower than congruent solidification or eutectic solidification, and because the rate limiting process is solid state diffusion, stirring has no significant effect on the rate.

The purpose of this note is to describe a means for obtaining many of the advantages of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ reaction while eliminating the solid state diffusion problem.

The partial equilibrium phase diagram [2] is shown in Fig. 1. All the previous TES work [1,2] reported used stoichiometric $\text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O}$, (44% Na_2SO_4 and 56% H_2O by weight, point 3 in Table II), at 20°C. When this salt decomposes above 32.4°C, the composition changes to 16.4 w/o anhydrous rhombic Na_2SO_4 and 83.6 w/o solution of composition 33 w/o Na_2SO_4 and 67 w/o H_2O (point 4, at 36°C). This reaction can reverse on cooling only as rapidly as solid state diffusion permits the peritectic reaction to proceed.

Solid state diffusion can be eliminated as a reaction step by using a mixture of decahydrate and water as the starting material (68.2 w/o $\text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O}$ and 31.8 w/o H_2O). At 15°C (point 2), the mixture consists of 58.1 w/o $\text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O}$ and 41.9 w/o solution of composition 10.6 w/o Na_2SO_4 and 89.4 w/o H_2O . When the temperature of the mixture is raised, the solubility of decahydrate increases with the increase in temperature.

With the composition chosen, all the decahydrate dissolves when the system is heated above 32°C. The overall composition of the solution then is 30 w/o Na_2SO_4 and 70 w/o H_2O . Now if the solution is cooled from 36°C (point 5 in Fig. 1), as it reaches the liquidus line (at 30°C),

decahydrate crystals should begin to separate.* As the temperature is further decreased, the system enters into a two-phase region, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and liquid. The amount of each constituent can be easily calculated at any temperature by using the Lever rule. The stored thermal energy in the system is released when the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals separate from the solution.

The heat that can be stored in a cycle such as just described can be calculated [4] from the heats of formation and heat capacities of Na_2SO_4 in H_2O . The heat of solution of Na_2SO_4 in water is only -0.5 ± 0.2 kcal/mole, essentially independent of concentration between infinite dilution and 100 moles. The heat of solution of the hydrate per unit weight, therefore, is almost identical to the heat of decomposition per unit weight of the hydrate to water and anhydrous Na_2SO_4 . From Table I it is found that a mass 50% larger and a volume 71% larger than for an ideally-efficient system based on pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ would be required for a million BTU heat storage. But the mass and volume are much smaller than for a system using water alone.

In summary, it appears that the major problem preventing use of sodium sulfate decahydrate for thermal/^{energy} storage can be avoided by using a different composition. The appropriate composition is at or slightly to the water rich side of the invariant point C in the phase diagram. A mixture of 68.2 w/o $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and 31.8 w/o H_2O is suggested for a TES material.

*Supercooling can be prevented by adding 3 to 4% borax as reported by Telkes [1].

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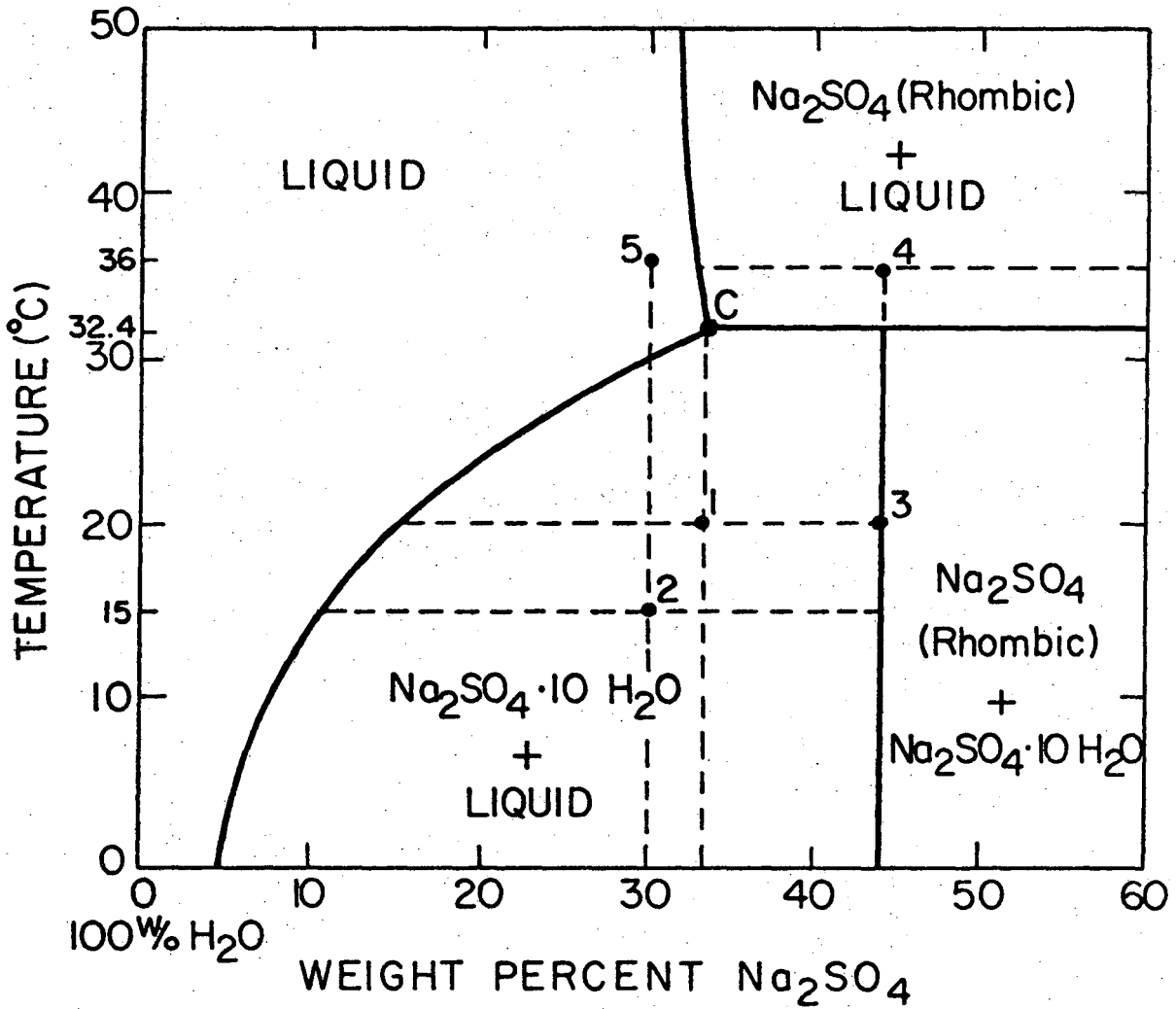
Table I. Properties for storage of one million BTU heat using water or sodium sulfate decahydrate

Materials	Density lb/ft ³	Sp. ht $\frac{\text{BTU}}{\text{lb } ^\circ\text{F}}$	Heat of reaction BTU/lb of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Heat storage of 10^6 BTU with 20°F temperature limit	
				Mass lbs	Volume ft ³
Water	62.5	1.0	-	50,000	800
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	91.0	0.46	108	8,530	94
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and water	79.5	-	105	12,800*	161*

*Does not include the contribution from Sp. ht.

Table II. Compositions at difference temperatures

Point (see Fig. 1)	Temperature °C	Compositions, % by weight		
		Na_2SO_4	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Liquid (solution)
1	20	-	62.6	37.4
2	15	-	58.1	41.9
3	20	-	100.0	-
4	36	16.4	-	83.6
5	36	-	-	100.0



PARTIAL PHASE DIAGRAM OF THE SODIUM SULFATE - WATER SYSTEM

XBL758-6939

Fig. 1

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