

REPORT ON
HEAT STORAGE IN A SOLAR HEATING SYSTEM
USING SALT HYDRATES

WRITTEN IN 4 INDIVIDUAL PARTS

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The calculations of the densities of the salt water mixtures are given on p. 6 and 11 in part 3 of the report.

These calculations must be corrected in the following way: Considering a weight unit of the salt water mixture the density of the salt water mixture is calculated as follows with the assumption that the volume of the anhydrous salt and the volume of the water are additive:

Volume of salt water mixture = volume of anhydrous salt + volume of water. With the symbols this is:

$$\frac{1}{D_m} = \frac{F_{am}}{D_{as}} + \frac{1-F_{am}}{D_{water}}$$

Rearranging this equation the density of the salt water mixture is found from:

$$D_m = 1 / \left(\frac{F_{am}}{D_{as}} + \frac{(1-F_{am})}{D_{water}} \right) \text{ kg/m}^3 \text{ salt water mixture}$$

Measurements however gives slightly different densities than found by means of this equation, see this table:

Salt water mixture anhydrous salt/ F_{am}	$\text{Na}_2\text{SO}_4/0.33$	$\text{Na}_2\text{CO}_3/0.33$	$\text{NaCH}_3\text{COO}/0.58$	$\text{Na}_2\text{HPO}_4/0.27$	$\text{Na}_2\text{HPO}_4/0.40$
Density calculated kg/m^3	1243	1234	1241	1175	1296
Density measured at 58°C kg/m^3	1281	1323	1301	1272	1453
$f = \frac{\text{density measured}}{\text{density calcul.}}$	1.03	1.07	1.05	1.08	1.12

Table: Calculated and measured densities of salt water mixtures.

The fraction $f = \frac{\text{Density measured}}{\text{Density calculated}}$ varies for different anhydrous salts and F_{am} -values. With the assumption that f varies linearly with F_{am} in the interval going from $F_{am} = 0$ (f being 1) to the measured F_{am} values, the densities of all salt water mixtures can be found. Using this assumption the storage capacities per m^3 given in the tables and figures in part 3 should be multiplied by a factor, which is greater than or equal to the values given in this table:

Na_2SO_4	water mixture	0.83
Na_2CO_3	water mixture	0.88
NaCH_3COO	water mixture	1.00
Na_2HPO_4	water mixture	0.92

The storage capacities given in the tables and figures are calculated with the assumption that the temperature is 55°C .

HEAT STORAGE IN A SOLAR HEATING SYSTEM USING SALT HYDRATES

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AS STORAGE MEDIUM

PREFACE

As a result of the energy crises and the general world energy situation many R and D activities have been initiated both nationally and within international organizations with the purpose to decrease the dependency of oil as an energy source.

The Commission of the European Communities has initiated a Solar Energy R and D Programme. Project A under this programme deals with solar heating and cooling of buildings.

As most EEC-countries have only a moderate number of sunshine hours during the heating season, a widespread use of solar heating of houses depends very much on the possibilities for economic long term storage of heat.

The present report describes a research project with the objective to investigate the possibilities to use salt hydrates as storage medium, and how the difficulties associated with some of these types of storage media can be overcome, in a way which can be used in practice.

The expenditure related to the performance of this project amounts to D.kr. 450,300, which is shared on a 50% basis between the Commission and the Danish Government.

October 1977
Thermal Insulation Laboratory
Technical University of Denmark
V. Korsgaard
professor

INTRODUCTION AND SUMMARY

PART 1 OF REPORT ON
HEAT STORAGE IN A SOLAR HEATING SYSTEM
USING SALT HYDRATES

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JULY 1977

Introduction and summary.

Part 1 of report on
Heat storage in a solar heating system using salt hydrates.

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Figure 2 Schematical illustration of a heat storage based on a salt water mixture.

1. INTRODUCTION.

This report is part 1 of the final report on the research project no. 140-76 ESDK, Heat storage in a solar heating system using salt hydrates. The research project is carried out with support from the European Community.

The final report is divided in 4 parts. The aim of this 1st part is to give an introduction to the research project and a detailed description of the method, which was investigated, is given. Also a summary of the work done and a conclusion is given.

Part 2 - 4 of the final report describes in detail the major parts of the project as follows:

Part 2: Selection of salt water mixtures for heat storage.

Part 3: Calculation of storage capacity of the selected salt water mixtures.

Part 4: Experiments with the selected salt water mixtures in the storage system.

2. DESCRIPTION OF THE EXTRA WATER PRINCIPLE.

One of the possibilities to get a greater storage density and a higher efficiency of the solar heating system is to use latent heat storage based on salt hydrates instead of sensible heat storage using the temperature increases of the storage medium. The technical problems concerning the use of storage systems using salt hydrates must be solved before such a system can be used.

It will therefore be of great importance to find and solve the problems concerned with the use of heat storage using salt hydrates. In the following the problems are described and a solution to overcome these problems is given.

Almost all salt hydrates, which are possible as heat storage materials, melt incongruently. Therefore it is important to solve the problems arising when such salt hydrates are used as heat storage materials. The greatest problem concerning the use of incongruently melting salt hydrates as a heat storage

material is that phase separation will occur when nothing is done to prevent it. In other words, problems with the stability will occur. The storage capacity after repeated cooling/heating-cycles will decrease.

This project has the aim to investigate a new method for preventing phase separation and obtaining stability. To describe the method the behaviour of the melting and crystallization proces for both congruently and incongruently melting salt hydrates will be explained.

In figure 1 the salt hydrate is situated in a container without stirring. For the congruently melting salt hydrate the solubility of the salt is so great that all the anhydrous salt is soluble in the corresponding crystal water. Here no problems with separation occur by the phase change, see figure 1a. For the incongruently melting salt hydrate the solubility is not great enough to dissolve all the anhydrous salt in the corresponding crystal water. The molten salt hydrate therefore consists of a saturated solution and some anhydrous salt undissolved in the water. This settles down as sediment due to its higher density. By cooling salt hydrate crystals are formed in the dividing line between sediment and solution, by which a solid crust is formed. This solid crust prevents the anhydrous salt at the bottom and the upper layer of saturated solution in getting in contact with each other, and therefore no salt hydrate will be formed of these anhydrous salts, see figure 1b. It is only the salt in the solution that is active. At the same time the solidification will take place at decreasing temperature, since solidification only occurs from a saturated solution, and since the solubility decreases at decreasing temperature.

The content will be divided in 3 parts, at the bottom the anhydrous salt, then a layer of solid salt hydrate crystals and at the top of the container a layer of saturated solution. By heating the mixture the salt hydrate crystals will melt and form a saturated solution with a part of undissolved anhydrous

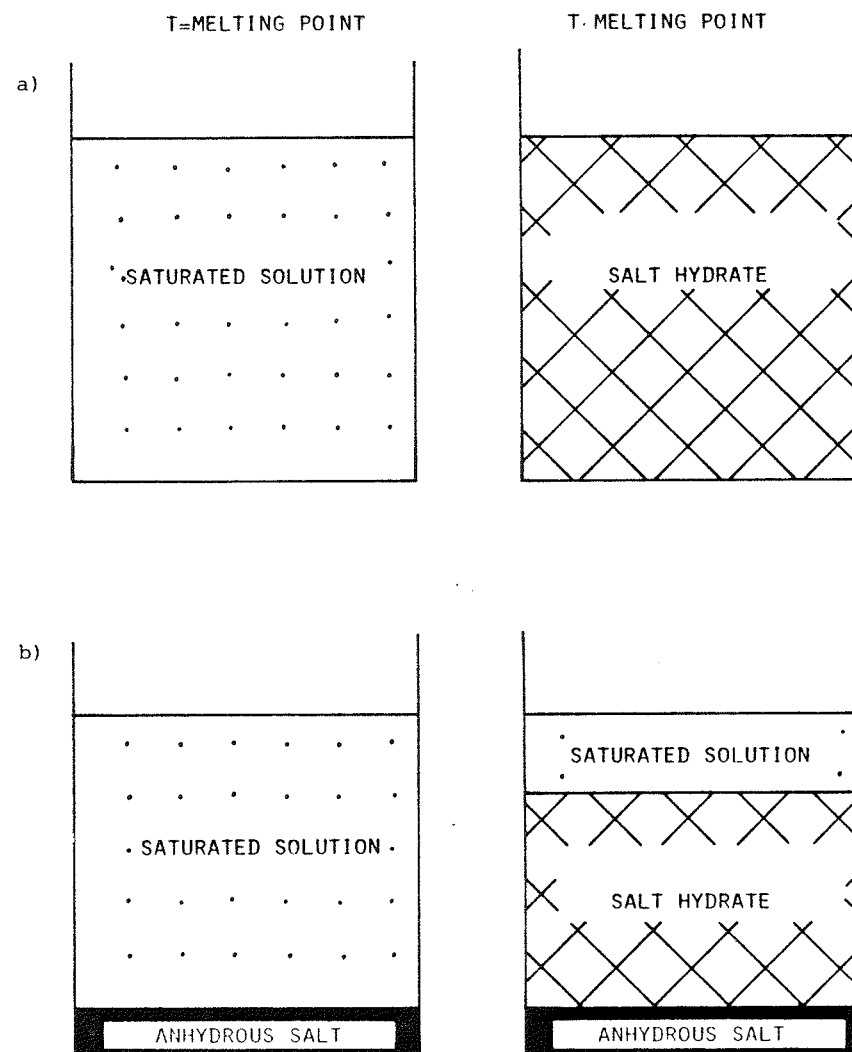


Figure 1. Schematic illustration of the melting/crystallization-proces for a) congruently melting salt hydrate, b) incongruently melting salt hydrate.

salt, which settles down as sediment. The amount of sediment increases in this way by each melting/crystallization cycle, and the heat storage capacity will decrease.

It is necessary to prevent this phase separation before it is possible to use incongruently melting salt hydrates. Several attempts have been made to solve this problem, for instance by adding different stiffening agents, but without good results. A possible solution is encapsulation of the salt hydrate, but layer thickness less than 1 cm is necessary to prevent phase separation and therefore the heat storage will be very expensive if normal container material is used.

This project deals with a new method which will have an effect on the incongruently melting salt hydrates in such a way that they will work stably.

The method consists in adding extra water to the salt hydrate so that all the salt can be dissolved in the water at the melting point. The salt dissolves completely in the water when the salt hydrate melts, if there is taken care of just a soft stirring at the same time. This stirring is necessary due to the very slow rate of natural mixing of the salt solution and the melted salt hydrate. If the mixture had time enough to reach equilibrium the stirring would not be necessary.

Since the salt solubility decreases at decreasing temperature for temperatures lower than the melting point and since crystallization only can take place from a saturated solution the solidification will take place by decreasing temperature. Melting will take place at increasing temperature.

By heating a salt water mixture consisting of solid and liquid phase the temperature increases and a part of the solid phase salt hydrate melts. Due to the temperature increase the solubility is increased too, and therefore the mixture also at the higher temperature will consist of a saturated solution and a solid phase salt hydrate. The mixture will for temperatures lower than the start solidification temperature consist of a salt hydrate solid phase and a saturated solution, and both melting

and solidification will take place in a temperature interval. With this method no phase separation or decrease in storage capacity will occur during repeated heating/cooling cycles and the heat storage will work stably.

For all incongruently melting salt hydrates this method can be used, and the greatest problem - to obtain stability, is solved. The other important problems are heat transfer and supercooling. These problems can also be solved by the new method.

A heat storage system where the extra water principle is used could be formed like the one shown schematically in figure 2. Oil is the heat transfer fluid, which is conducted in a pipe to the bottom of the container and through a nozzle system to the salt water mixture. The oil is immiscible with the salt water mixture, and due to density differences the oil will form a layer at the top of the heat storage container. Using such a heat storage system the heat transfer problems are solved due to the good contact between transfer- and storage-media. The oil drops take care of the soft stirring and this stirring prevents strong supercooling. Since there will always be a liquid phase in the salt water mixture, the oil will always be able to find its way to the top of the container. With such a heat storage system experiments were carried out in this project.

3. SUMMARY OF THE WORK DONE.

The work done is in detail described in part 2, 3 and 4 of the report, and a summary is given here.

A literature study concerning the selection of salt hydrates was carried out, and as a result of this 4 different salt hydrates were found as the best qualified components in the salt water mixture. Also a search for organic compounds suitable as heat storage materials was carried out by means of literature search and small scale experiments. Here a few organic compounds

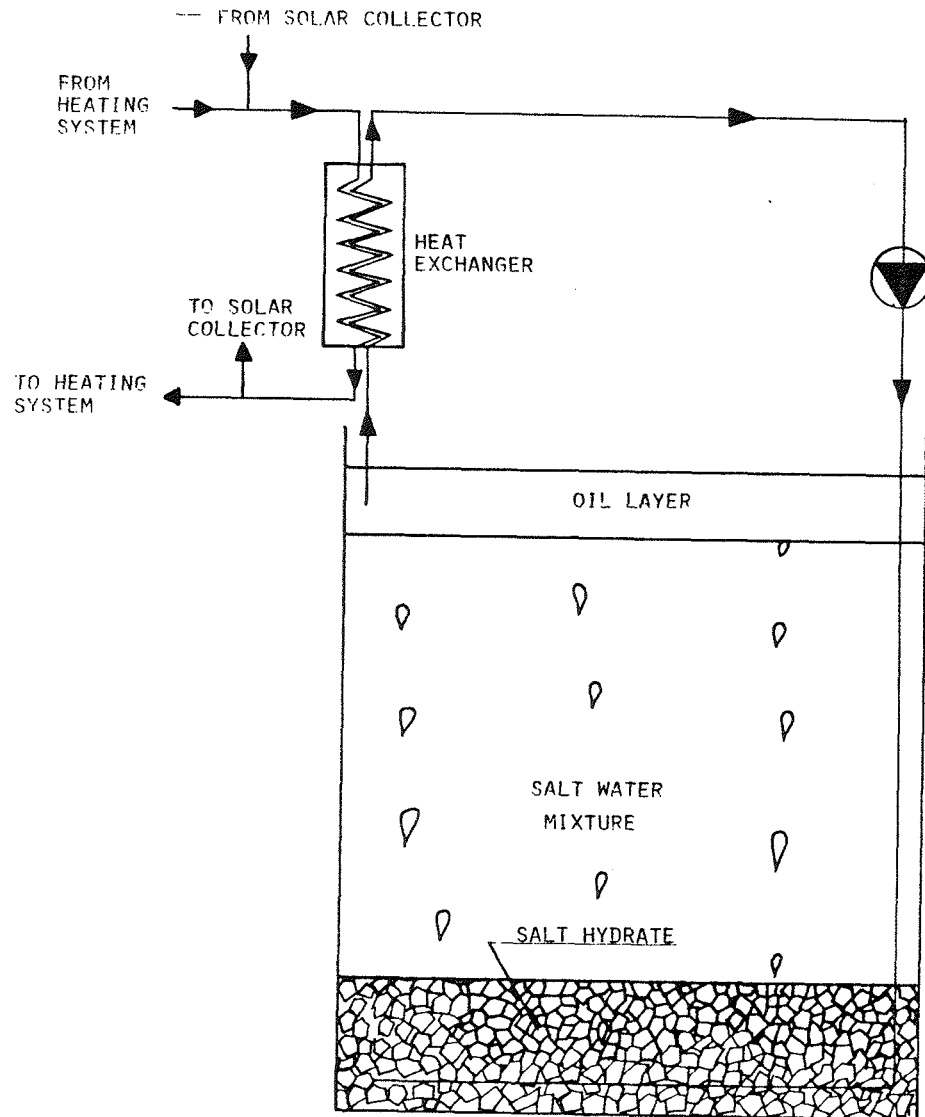


Figure 2. Schematic illustration of a heat storage based on a salt water mixture.

were found as promising possibilities.

Calculation of the storage capacity of the selected salt water mixtures was carried out. A general method for this calculation was set up, so that the storage capacity of any salt water mixture can be calculated when the data of the salt hydrates are known.

Small scale experiments with the selected salt water mixtures as heat storage material in a heat storage with oil as the heat transfer fluid in direct contact with the salt water mixture were carried out. A few heating/cooling cycles for each salt water mixture and measurements of the storage capacity during this time were carried out. The amount of the heat storage in these experiments was 0.2 m^3 . The results of the above mentioned measurements were compared with the calculated storage capacity. Important knowledge of the different salt water mixtures was obtained by these experiments.

4. CONCLUSION.

A new method, by means of which a salt water mixture consisting of an incongruently melting salt hydrate with additional water works stably as heat storage material, has been developed. The storage capacity of different promising salt water mixtures has been calculated and measured in a heat storage system using the method where oil was used as the heat transfer fluid. The storage system, which was of the amount of 0.2 m^3 seemed in all ways to work as planned during a few cycles.

In order to show that the heat storage system using a salt water mixture as heat storage material will work as planned in a solar heating system during a long period of time different improvements concerning the performance of the storage system must be carried out. Also a full scale heat storage must be built and tested under realistic conditions during a long period of time.

SELECTION OF SALT WATER MIXTURES
FOR HEAT STORAGE.

PART 2 OF REPORT ON
HEAT STORAGE IN A SOLAR HEATING SYSTEM
USING SALT HYDRATES

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Selection of salt water mixtures for heat storage.

Part 2 of report on

Heat storage in a solar heating system using salt hydrates.

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1. INTRODUCTION

This report is part 2 of the final report on the research project no. 140 - 76 ESDK, Heat storage in a solar heating system using salt hydrates, which financially is supported by the European Community.

The aim of the project to investigate a new method by which a heat storage based on an incongruently melting salt hydrate will work stably. Before describing this method some of the used expressions shall be explained.

Salt hydrate is the anhydrous salt with its corresponding crystal water. The expression is used for both the solid and the liquid phase.

Incongruently melting salt hydrate is a salt hydrate with an anhydrous salt which can not be dissolved completely in its corresponding crystal water at the melting point.

Salt water mixture is the salt hydrate with at least so much water added, that the anhydrous salt is completely dissolved at the melting point.

When an incongruently melting salt hydrate is melted the undissolved fraction of the anhydrous salt will form a layer at the bottom of the container. In the solidification part of a cycle this layer will not for normal container dimensions come in contact with the water, and it will therefore not work actively. This phase separation will in a few cycles diminish the performance of the heat storage.

The investigated method is mainly used to avoid the phase separation. It consists of adding so much extra water to the salt hydrate that all the anhydrous salt dissolves in the water. In order to secure that phase separation is avoided a soft stirring of the mixture is necessary.

The solidification will take place by decreasing temperature since crystallization only can take place from a saturated solution, and the solubility of the anhydrous salt decreases at decreasing temperature.

The aim of this part of the report is to investigate different inorganic salt hydrates, which are possible as heat storage materials in order to find the best qualified salt hydrates. Also organic compounds, which are possible as heat storage materials will be investigated. Also different storage systems based on a salt water mixture will be taken into consideration, and the most promising will be selected for the experiments.

2. METHOD OF SELECTION OF INORGANIC SALT HYDRATES

2.1. Criteria

In order to select the best qualified salt hydrates as storage medium a number of criterias were established. The criterias are mentioned in the following.

Toxic, flammable, dangerous, oxidizing and chemical unstable salt hydrates obviously must be left out as possible heat storage materials.

The melting point of the salt hydrate must be suitable, that is it must be situated in a temperature interval, so that the stored energy is of good use. This temperature interval goes from temperatures a little higher than room temperature to temperatures a little higher than the temperature of the hot water supply. This temperature interval was selected to the interval going from 25° C to 70° C.

The heat of fusion must be of a reasonable amount, that is salt hydrates having a heat of fusion much below the heat of fusion for normal salt hydrates must be left out. The storage capacity of such salt hydrates will not be much greater than the storage capacity of water. Only salt hydrates having a heat of fusion higher than 130 kJ/kg were therefore accepted.

Supercooling must be prevented. For many salt hydrates supercooling is prevented by stirring. Some salt hydrates have a tendency to strong supercooling, and for these salt hydrates the stirring does not prevent supercooling. Supercooling can for such salt hydrates be prevented by adding salt hydrate

crystals to the salt water mixture at the melting point or by keeping a part of the storage cold, so that solid salt hydrates always exist in this part of the container. A potential advantage of supercooling is that the supercooled mixture can be stored at low temperatures without thermal loss for a long period of time. The stored energy can be given out when salt hydrate crystals are added to the mixture resulting in solidification at a higher temperature level.

The salt hydrate must either be easily available in nature, produced in large quantities or produced of such materials that the price of the salt delivered in large quantities will not be much higher than the cost of the transport of the material. The cost limit, which was selected as criteria here, was 500 u.a./t salt hydrate.

Both congruently and incongruently melting salt hydrates will be taken into consideration since the extra water principle makes it possible to use incongruently as well as congruently melting salt hydrates.

2.2. Availability of data for inorganic salt hydrates.

Salt hydrates and their melting points are found from chemical handbooks. Characteristics of the salt hydrates, such as if supercooling occurs, if it is chemical unstable, toxic, dangerous or flammable is found from the chemical literature. The availability and price of the salt is found by information from chemical industries. The heat of fusion, which is of great importance, is only measured and reported for relatively few salt hydrates in the literature. Therefore an analysis of the heat of fusion of salt hydrates in order to find a crude estimate of the heat of fusion of an arbitrary salt hydrate was carried out. The analysis, which follows in the next section, was carried out and reported by the chemical consultant of the project, Erik Pedersen.

2.3. Regularities in enthalpies and entropies of fusion of salt hydrates.

It is well known that the entropies of vapourization are approximately the same (ca. 22 cal deg⁻¹ mole⁻¹) for a large number of nonpolar liquids. This is known as Troutons's Rule (1884). Polar solvents have a more complicated behaviour.

No similar simple rules of fusion have been established although it has been noted that there is a coarse correlation between the entropy of fusion and the number of atoms involved in the process of fusion (S. Procopiu: Compt. Rend. 224 (1947) 264). Such a correlation would imply that the entropies of fusion of salt hydrates should be simply related to the number of water molecules. Complications can, however, be expected in cases of incongruently melting hydrates where the change in number of water molecules in the solid and the solubility of the lower hydrate in the liquid must be considered.

From a heat storage point of view the enthalpies of fusion are more interesting than the entropies. The process of fusion is determined by the free energy difference

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium $\Delta G = 0$ and

$$\Delta H = T\Delta S$$

Since the melting points appear highly unpredictable no simple relation between the enthalpies of fusion and the number of molecules involved can be expected. For some classes of substances, however, notably the close-packed metal, regularities exist.

During our literature work in connection with the present project we found a large number of melting data for salt hydrates. Some of these are shown in table 1 for hydrates ranging from monohydrates to dodecahydrates. Graphs showing ΔS_f and ΔH_f vs. the number of water molecules in the hydrates are given in figs. 1 and 2, respectively. It was tempting to perform

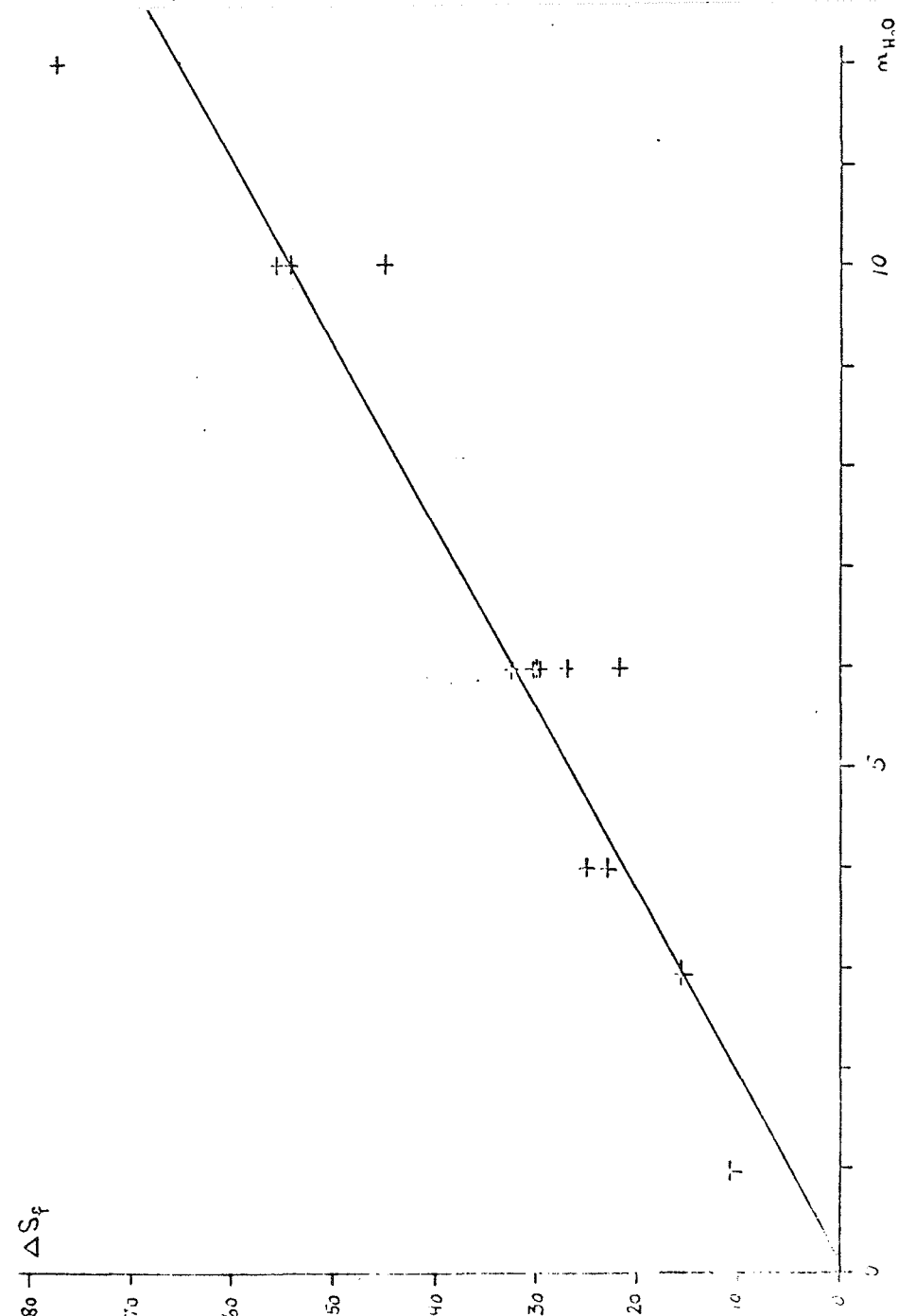


Figure 1. Entropies of fusion. Least squares best fit to straight line.

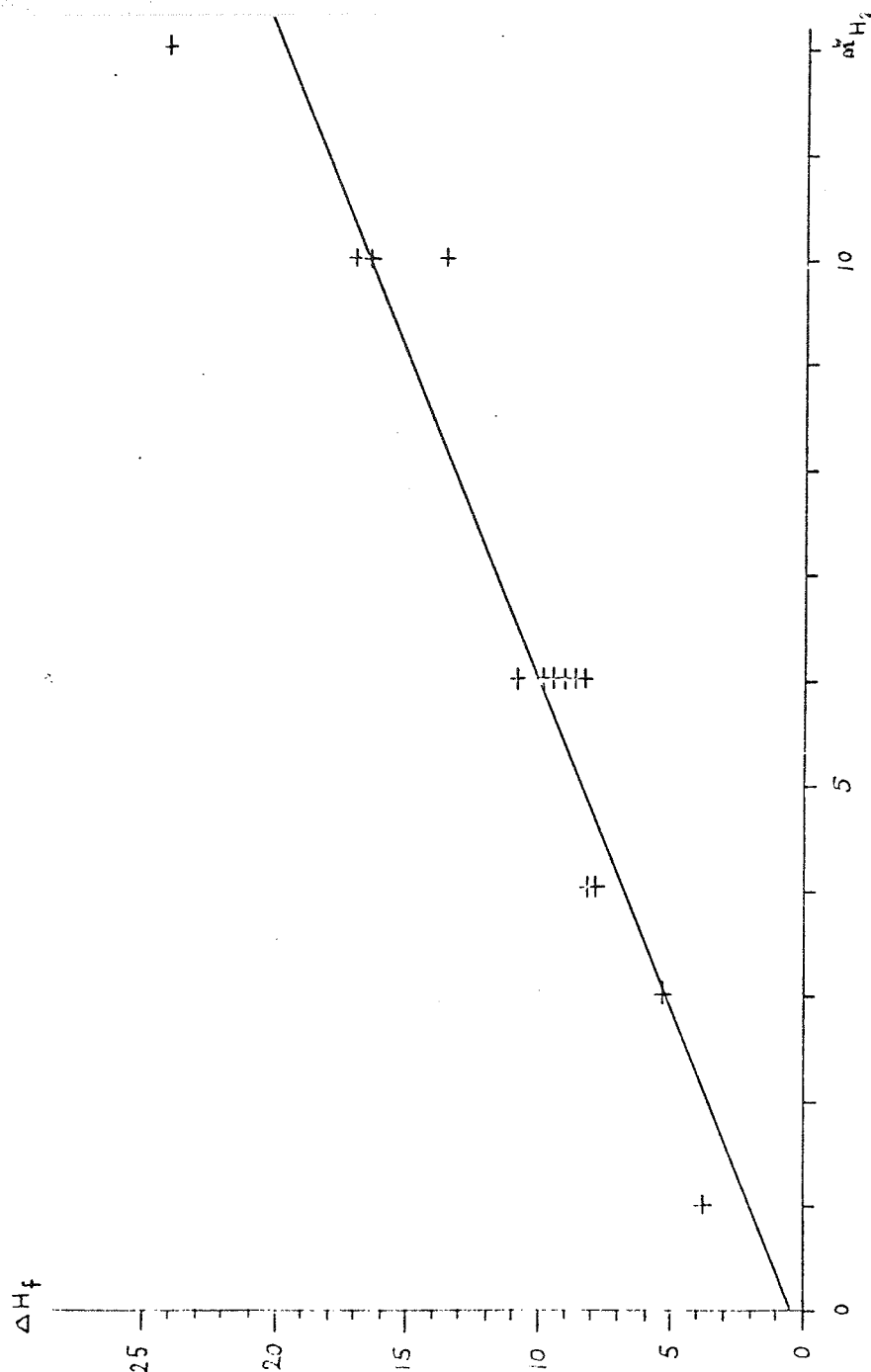


Figure 2. Enthalpies of fusion. Least squares best fit to straight line.

least squares best fits to straight lines. The results are shown in the figs. For the entropies were found a slope of $5.48 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1} \cdot (\text{moles of water})^{-1}$ an ΔS_f -axis intercept of -1.16 , and a correlation coefficient of 0.944 . For the enthalpies were found a slope of $1.62 \text{ kcal} \cdot \text{mole}^{-1} \cdot (\text{moles of water})^{-1}$ an ΔH_f -axis intercept of 0.41 , and a correlation coefficient of 0.944 . The linear relationships appear statistically significant.

Salt hydrate	t_f	ΔH_f	ΔS_f
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	59.5	7.79	23.4
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	29	8.91	29.5
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	42.1	7.89	25.4
$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	24.4	8.70	29.2
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	116.7	8.36	21.5
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	90	9.78	26.9
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	36.4	10.60	32.1
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	33	16.9	55.1
$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$	23	13.4	45.3
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	36.1	23.9	77.3
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	31	16.5	54.3
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	36.4	9.24	29.8
$\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$	58	5.29	16.0
$\text{NaOH} \cdot \text{H}_2\text{O}$	64.3	3.78	11.2

Table 1. Melting data of salt hydrates. Melting points in $^{\circ}\text{C}$, enthalpies of fusion in kcal per mole, and entropies of fusion in cal per deg per mole.

The linear relationship between ΔH_f and the number of water molecules is unexpected and is probably caused by the rather narrow interval of melting points selected. Incongruent melting appears to play a minor role. The slope is close to $\Delta H_f = 1.44 \text{ kcal mole}^{-1}$ for water.

A guide in finding the most efficient salt hydrate for heat storage in terms of heat content per unit of mass would thus be to look for high density hydrates with the highest percentage of water. Capacities slightly above the expected values are found for $\text{NaOH} \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

3. SEARCH FOR INORGANIC SALT HYDRATES

Salt hydrates having the melting point in the selected temperature interval $25^\circ \text{C} - 70^\circ \text{C}$ were found from literature, mainly from Glew and Lane; Thermal Energy Storage [1], M. Telkes; Solar energy storage [2], M. Telkes; Solar heat storage [3], Wettermark and Kowalewska; Storage of low temperature heat, solar energy thermal storage [4] and H. G. Lorsch; Latent heat and sensible heat storage for solar heating systems [5].

A list of the salt hydrates is given in table 2. If the salt is available in large quantities, the price is given. The heat of fusion is given. If the heat of fusion was not found from literature search it was calculated by means of the method found in section 2.3. Relevant remarks for some of the salt hydrates are given as well as it is pointed out, if the salt hydrate melts congruently or incongruently.

4. RESULT

For selection of salt hydrates as heat storage materials the criterias mentioned in section 2.1 were used for the salt hydrates listed in table 2.

Most of the salt hydrates were not commercially available in large quantities. Many of the salt hydrates are chemically

formula	melting point $^\circ \text{C}$	heat of fusion kJ/kg salt hydrate	price u.a./t salt hydrate 20 t delivery 1 u.a. = 7.5 D kr	congruent melting	remarks
$\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$	70	150*		no	
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	65	168		no	
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	64	200	82	no	unstable
$\text{NaOH} \cdot \text{H}_2\text{O}$	64	272	130	yes	dangerous, corrosive unstable
$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	61	181*			
$\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	60	125			unstable oxidizing toxic
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	59	98		no	
$\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$	58	160	234	no	
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	58	151			
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	57	168		yes	oxidizing
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	57	115		yes	oxidizing
$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	56	90*		no	unstable
$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	55	68*			oxidizing
$\text{Na}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	53	158			oxidizing
$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	51	104*		yes	strong supercooling
$\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$	48	99*	680	no	
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	48	135		no	
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	48	209	146	no	unstable
$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	48	168*	180		unstable, strong superc.
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	47	155*		yes	corrosive, oxidizing
$\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$	47	289*		no	

(cont.)

(cont.)

formula	melting point °C	heat of fusion kJ/kg salt hydrates	price u.a./t salt hydrate 20 t delivery 1 u.a. = 7.5 D kr	congruent melting	remarks
$K_3PO_4 \cdot 7H_2O$	45	145*			
$Zn(NO_3)_2 \cdot 4H_2O$	45	110*			oxidizing
$Ca(NO_3)_2 \cdot 4H_2O$	43	163		no	strong supercooling
$CaI_2 \cdot 6H_2O$	42	106*			
$KF \cdot 2H_2O$	42	162*		no	toxic
$MgI_2 \cdot 8H_2O$	42	133*		no	
$CaCl_2 \cdot 4H_2O$	39	158*		no	
$FeCl_3 \cdot 6H_2O$	37	223	360	no	unstable
$Mn(NO_3)_2 \cdot 4H_2O$	37	115*			oxidizing
$Zn(NO_3)_2 \cdot 6H_2O$	36	134			unstable, oxidizing
$Na_2HPO_4 \cdot 12H_2O$	35	266	417	no	
$LiBr \cdot 2H_2O$	34	124*			
$CaBr_2 \cdot 6H_2O$	34	138*		yes	
$KFe(SO_4)_2 \cdot 12H_2O$	33	173*			unstable
$Na_2CO_3 \cdot 10H_2O$	33	247	69	no	
$Na_2SO_4 \cdot 10H_2O$	32	251	88	no	
$LiNO_3 \cdot 3H_2O$	30	189*		no	oxidizing
$CaCl_2 \cdot 6H_2O$	29	174	106	no	
$FeBr_3 \cdot 6H_2O$	27	105*			unstable
$Mn(NO_3)_2 \cdot 6H_2O$	25	148*			oxidizing

Table 2. Data for inorganic salt hydrates melting in the temperature interval 25° C - 70° C.

* Heat of fusion calculated by means of the method found in section 2.3.

unstable, dangerous, toxic or too expensive.

The salt hydrates, which were selected as suitable storage materials from table 2 were:

$Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $NaCH_3COO \cdot 3H_2O$. For Na_2HPO_4 salt water mixtures $Na_2HPO_4 \cdot 7H_2O$ is the stable salt hydrate in the temperature interval 35.4° C - 48° C.

According to the literature study all the selected salt hydrates melt incongruently, and the extra water principle can be used. That is: the salt water mixtures consisting of the salt hydrate with additional water are candidates as heat storage materials, and they must be investigated in detail.

5. DATA FOR THE SELECTED SALT HYDRATES

The selected salt hydrates were examined and the result of the examination is given in table 3.

Sodium sulfate, $Na_2SO_4 \cdot 10H_2O$

All data for this salt were found in K. Kauffman and Y.C. Pan; Thermal energy storage in sodium sulfate decahydrate mixtures [6]. Furthermore the influence of temperature on the density and specific heats was investigated by means of a literature study. The result was, that it is a reasonable assumption, that both density and specific heats are independent of the temperature. The salt solubility is given as an approximated function of the temperature t found by a regression analysis. A small amount of borax added to the salt water mixture prevents supercooling.

Sodium carbonate, $Na_2CO_3 \cdot 10H_2O$

The heat of fusion was found from M. Telkes; Solar heat storage [3]. The solubility was found from W. F. Linke and A. Seidell; Solubilities of inorganic and metal organic compounds [7] and an approximated function of the temperature t was found by a regression analysis. The specific heat of both the anhydrous salt and the solid phase salt hydrate was found

p. 1461 in Zh.Fiz.Khim [8]. The density of the anhydrous salt was found from Handbook of Chemistry and Physics [9]. As result of a literature study it was found, that density and specific heats are independent of the temperature.

Sodium acetate, $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$.

The heat of fusion was found from Kolloid Z [10]. Specific heats and density of the anhydrous salt were found from Handbook of Chemistry and Physics [11] and [9]. The solubility was found from W.F. Linke and A. Seidell; Solubilities of inorganic and metal organic compounds [7] and the approximated curves were found by regression analysis.

Disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Salt water mixtures with Na_2HPO_4 as anhydrous salt can form two different salt hydrates, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ called 7-hydrate and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ called 12-hydrate, during cooling. 7-hydrate is stable for temperatures between 48°C and 35.4°C , and 12-hydrate is stable for temperatures lower than 35.4°C . With the extra water principle salt water mixtures with anhydrous salt weight % of the mixture lower than 27.5% only forms 12-hydrate during operation, and such salt water mixtures can be classified in the general case.

For salt water mixtures with anhydrous salt weight% in the interval going from 27.5% to 44.4% the 7-hydrate is formed during cooling until 35.4°C is reached. Until this temperature the salt water mixture acts like a general salt water mixture. When cooling is continued for temperatures lower than 35.4°C the stable 12-hydrate might be formed of the solution, which not already has solidified to 7-hydrate. On the other hand 12-hydrate might not be formed at all, since 7-hydrate, which is the basis for crystal growth might dominate the progress of the solidification in such a way, that 7-hydrate is formed also for temperatures lower than 35.4°C . These 2 possibilities will be investigated by means of experiments.

The salt solubilities were found from W. F. Linke and A. Seidell; Solubilities of inorganic and metal organic compounds [7] and approximated to functions of the temperature by regression analysis. Melting points and heat of fusion were found from T. L. Etherington; A dynamic heat storage system [12]. The specific heat of the solid phase 7- og 12-hydrate was found from National Bureau of Standards [13]. The specific heat and the density of the anhydrous salt were not found by literature search, and therefore measurements of these values were carried out. The results are given in table 3.

6. SEARCH FOR ORGANIC COMPOUNDS

Organic compounds, which commercially are available in large quantities, were investigated by means of literature studies and small scale experiments in order to give a crude estimate of the suitability of the different compounds as heat storage materials. This investigation was carried out by the chemical consultant Erik Pedersen, and his report covering this subject is given in the following.

Organic compounds as heat storage materials.

Earlier surveys on compounds suitable as isothermal solar heat storage materials (D.N. Glew and G.A. Lane: Internal working paper presented at the Nato Conference on Thermal Energy Storage, Turnberry, Scotland 1976) are based on the secondary chemical literature (R.C. Weast: Handbook of Chemistry and Physics, 53 Ed., The Chemical Rubber Co. Ohio, 1972, Landolt-Börnstein, 6 Ed. II, Springer-Verlag, Heidelberg 1962, and E.W. Washburn: International Critical Tables, McGraw-Hill, N.Y., 1926, etc.).

It was the purpose of our work to supplement the list of potentially suitable compounds by a search in the primary literature. This task is insuperable, however, unless narrow limitations are made. We chose the following conditions to be fulfilled:

salt hydrate	melting point °C	maximum fraction of an- hydrous salt in the salt water mixt. based on weight	fraction of anhydrous salt in the salt hydrate based on weight	approximated salt solubility in water at temperature t. (kg anhydrous salt/kg mix- ture) • t	Heat of fusion kJ/kg salt hydrate	specific heat of salt hydrate J/kg °C	density of anhydrous salt kg/m ³	specific heat of anhydrous salt J/kg °C
Na ₂ SO ₄ •10H ₂ O	32	0.33	0.44	0.0404•e ^{0.0652•t}	251	1930	2660	880
Na ₂ CO ₃ •10H ₂ O	33	0.33	0.37	0.0701•e ^{0.0469•t}	247	1990	2530	1040
NaCH ₃ COO•3H ₂ O	58	0.58	0.60	0° C - 40° C: 0.2646•e ^{0.00983•t} 40° C - 60° C: 0.2313•e ^{0.01345•t} 50° C - 58° C: 0.09667•e ^{0.03089•t}	160	2540	1530	1465
Na ₂ HPO ₄ •7H ₂ O	48	0.444	0.53	0.0812•e ^{0.0354•t}	135	1350	2460	1300
Na ₂ HPO ₄ •12H ₂ O	35	0.275	0.40	0.0130•e ^{0.0865•t}	266	1560	2460	1300

Table 3. Data for the selected salt hydrates.

1. The compounds themselves should be commercially available in large quantities.

or

2. The compounds should be accessible via simple chemical reactions between compounds in 1.

and

3. We further restricted ourselves to simple salts, carboxylic acids, amides, and esters. Alcohols were left out because of the unsuitable melting points expected, and hydrocarbons because of unsuitable heats of fusion expected. Other compounds were considered likely to be unstable.

Left were carboxylic acids and their salts, amides, and esters derived from acids with less 19 carbon atoms and furthermore salts and amides derived from ammonia, urea, ethylenediamine, triethylenediamine, hexamethylenediamine, triethylenetetramine, tetraethylenepentamine, alkylamines, ethanolamine, and triethanolamine. The compounds were rejected as candidates if their melting points were outside the interval 25 - 80° C and if difficulties of crystallization were reported.

The primary literature was found via Chemical Abstracts covering the literature till 1976.

We found the following addenda to the lists of Glew and Lane (see reference above):

Esters of stearic acid:

	m.p. °C
Benzyl stearate	45
Cyclohexyl stearate	44
Ethyl stearate	33.9
Cetyl stearate	56
Glycerol monostearate	58 and 81
Methyl stearate	39
Phenyl stearate	52

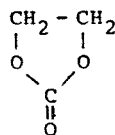
Esters of palmitic acid:

	m.p. °C
Benzyl palmitate	36
Cetyl palmitate	55
Ethyleneglycol dipalmitate	69
Glycerol tripalmitate	65
Methyl palmitate	29.5

Esters of ethyleneglycol and glycerol:

There is an extremely large selection of other esters of these alcohols, having suitable melting points. We feel, however, that their thermal properties are well represented in the present aspect by the members mentioned above. A special structure is found in

Ethyleneglycol carbonate 35



Amides:

2-hydroxyethylacetamide 40

Carbolic acids:

Pivalic acid 35.5

Salts:

Ethanolamine hydrochloride 80

Tetraethylammonium chloride
tetrahydrate 31

Free amines:

Hexamethylenediamine 42

(This compound can be excluded because of its corrosive character).

All the compounds mentioned above are reported to crystallize well or no comments are given.

The literature on salts of the polyamines is remarkably scarce. It was therefore decided to prepare acetates, propionates, palmitates, stearates, oxalates, and tartrates of the di- and polyamines mentioned above. Some of these could be expected to show strong hydrogen bonding effects which might be in favour of large heats of fusion.

The compounds were prepared by reacting stoichiometric amounts of pure grade amines and acids at 90° C. Most salts had melting points above 80° C. A few refused to crystallize. Triethylenetetramine tetrapalmitate and tetrastearate crystallized around 70° C, and they were the only candidates which deserved further study.

Cooling curves.

Semiquantitative estimates of the suitability of the compounds were further studied by recording cooling curves. 100 g samples of the melted compounds were placed in a double thin-walled calorimeter immersed in an ice/water bath. The temperature was measured with a Ni-Cr/Ni thermoelement and a Varian G 2000 recorder. Magnetic stirring in the calorimeter ensured good temperature equilibrium in the molten or partly molten states but introduced a large ac component in the thermocouple voltage, approx. 41 $\mu\text{V}\cdot\text{deg}^{-1}$. The system was therefore equipped with a RC-filter with a time constant of 2 sec. The thermocouple was calibrated against boiling and freezing water.

Assuming that the heat transport in the calorimeter is determined by conduction and not by radiation then the heat transport in the calorimeter is proportional to the temperature difference. Relative values of the heats of fusion can therefore be estimated from the cooling curves integrated over the ranges with constant or nearly constant temperatures.

To evaluate the qualifications of the compounds mentioned in this chapter their cooling curves were compared with those of

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$, and stearic acid, crf. Figs. 3-6, 10, respectively. It was noted that $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ had a very pronounced tendency to supercool. Crystallization could not be obtained without seeding. This behaviour has been investigated by W.T. Richards: JACS 54 (1932) 479, W.W. Conner: JACS 53 (1931) 2806, W. Quist, A. Salo, and G. Foessell: Acta Acad. Aboensis Math. Phys. 9 No. 2 (1936) 3, and A. Tschermak-Seysenegg: Microchemie 27 (1939) 96.

The compounds studied, their melting points, densities, and their heat storage capacity under isothermal or nearly isothermal conditions are tabulated in Table 4, crf. Figs. 7-9, 11-13.

Although the present method of investigating cooling curves gives only a very crude estimate of the suitability of compounds as heat storage materials it does, however, indicate that ethylene carbonate, benzyl stearate and related compounds have volume capacities comparable with those of inorganic salt hydrates. Disadvantages will be their somewhat higher prices and perhaps their higher solubilities in heat exchange oils.

The storage capacity relative to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ given in table 4 is the heat of fusion per weight unit found by reading of the cooling curves. The used method gives only a crude estimate of the heat of fusion of the materials. For the salt hydrates no extra water was added and changes in enthalpies caused by incongruent melting will lead to results differing from those of part 3 and 4 of the report.

Compound	m.p. °C	Density	Storage capacity rel. to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	32.3	1.46	1.0
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	32.5	1.44	1.6
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	40-32	1.52	2.3
$\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$	58	1.53	2.9
Pivalic acid	31	0.91	0.2
Ethylenecarbonate	32	1.32	1.9
Benzylstearate	40	0.91	1.6
Stearic acid	67	0.85	1.1
Ethanolamine hydrochloride	78	?	0.6
Triethylenetetramine tetrastearate	ca. 70	?	0.5
$(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 4\text{H}_2\text{O}$	30	ca. 1	1.1

Table 4. Thermal data for compounds studied by recording of cooling curves.

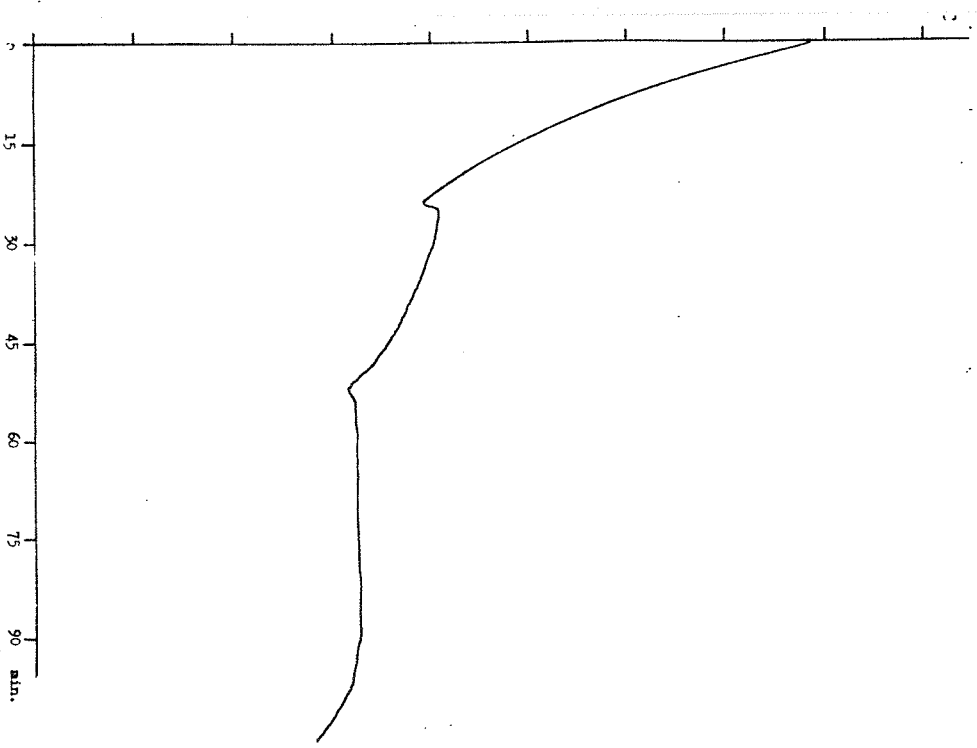


Figure 5. Cooling curve for $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

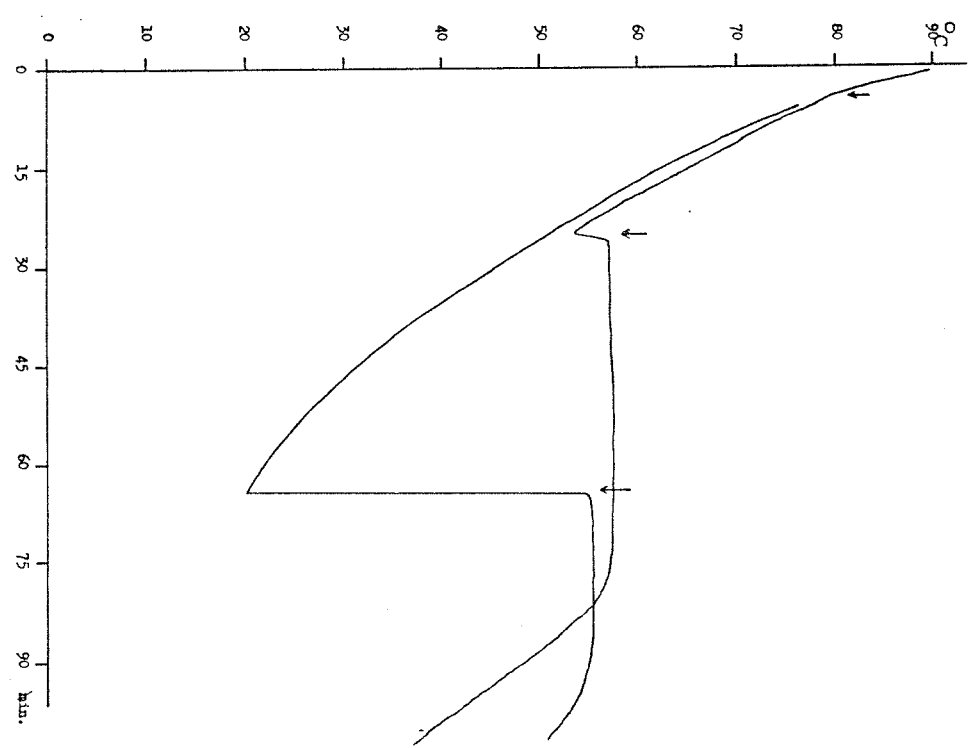


Figure 6. Cooling curves for $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$. Arrows indicate seeding with the trihydrate.

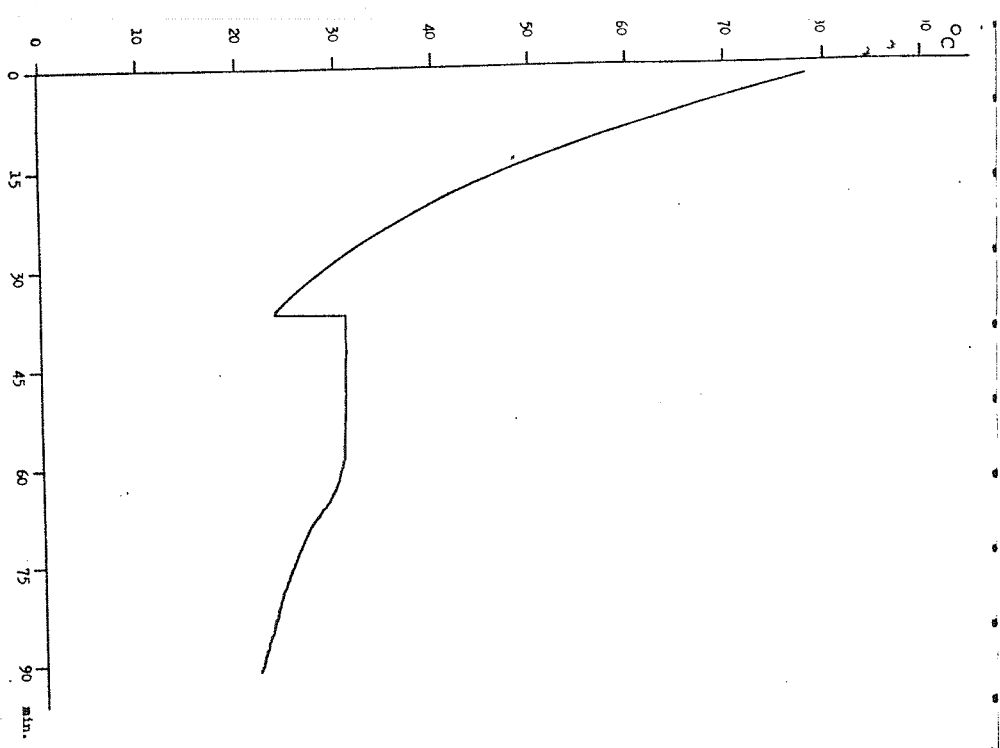


Figure 3. Cooling curve for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

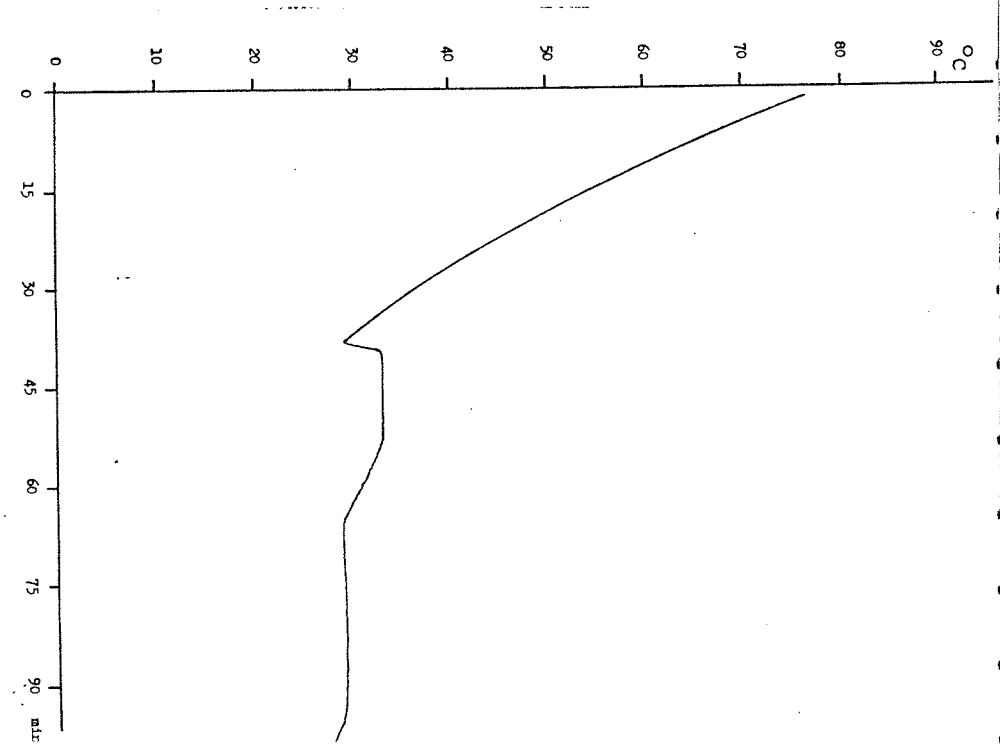


Figure 4. Cooling curve for $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

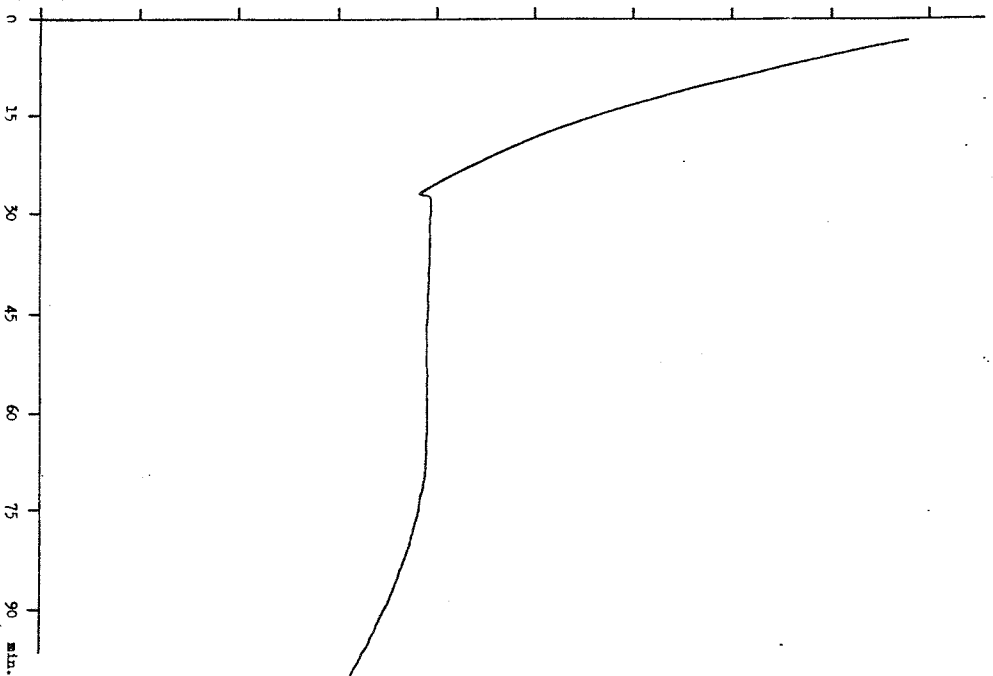


Figure 9. Cooling curve for benzylstearate
 $C_{17}H_{35}COOCH_2C_6H_5$.

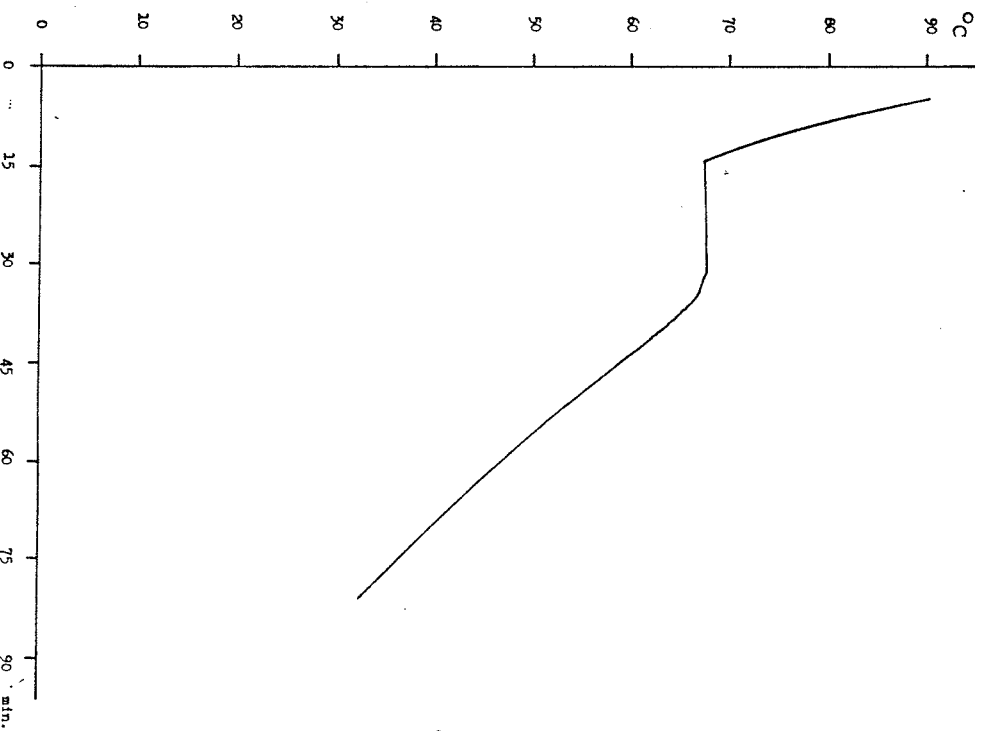


Figure 10. Cooling curve for stearic acid,
 $C_{17}H_{35}COOH$.

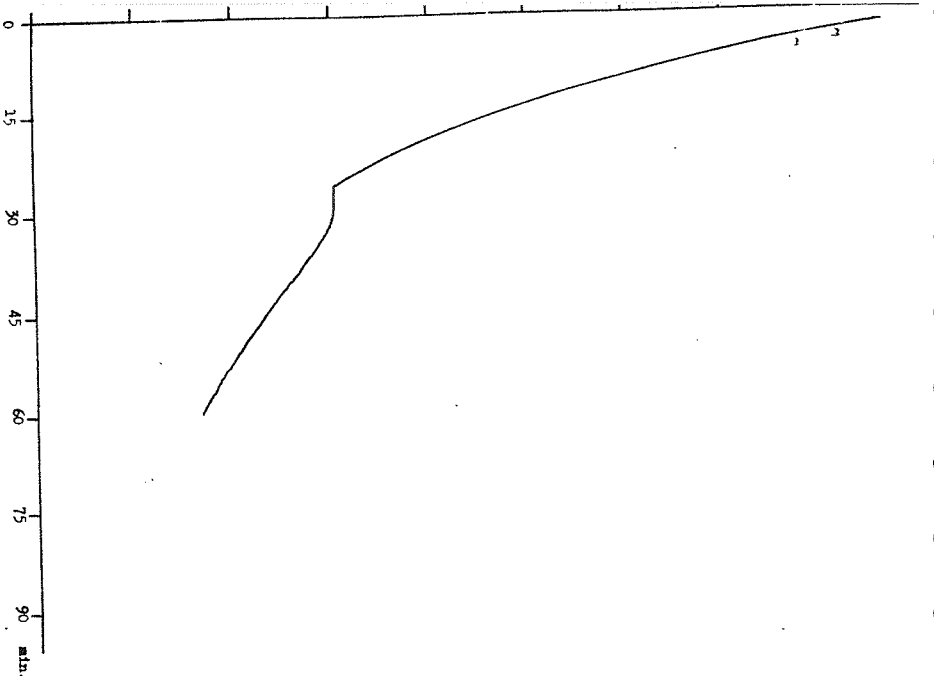


Figure 7. Cooling curve for pivalic acid,
 $(CH_3)_3CCOOH$.

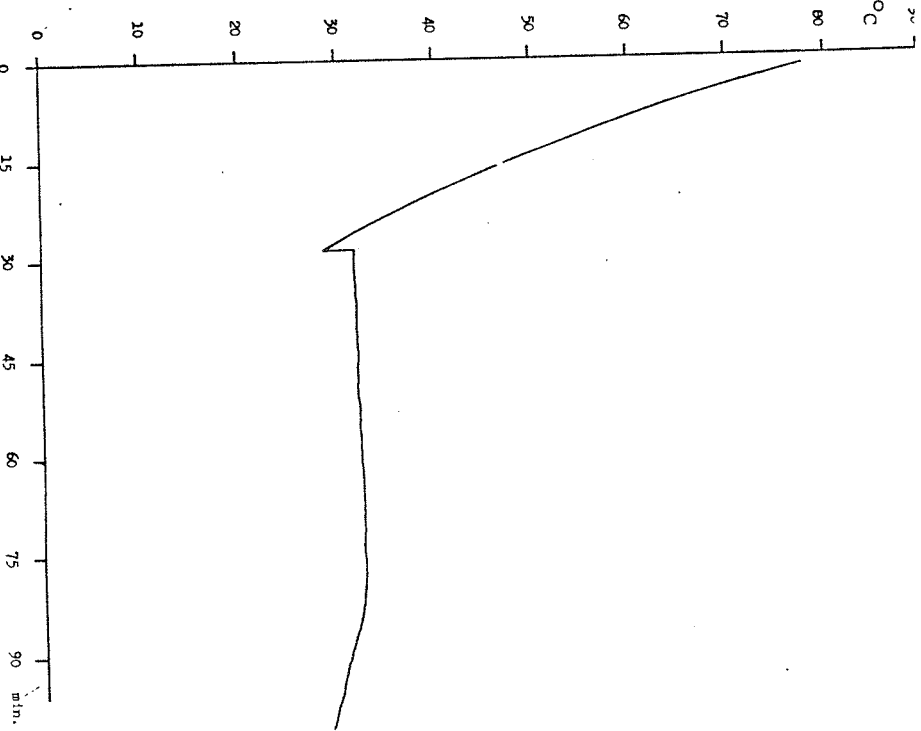
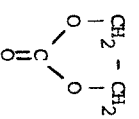


Figure 8. Cooling curve for $CH_2=CH_2$ -
ethylenecarbonate



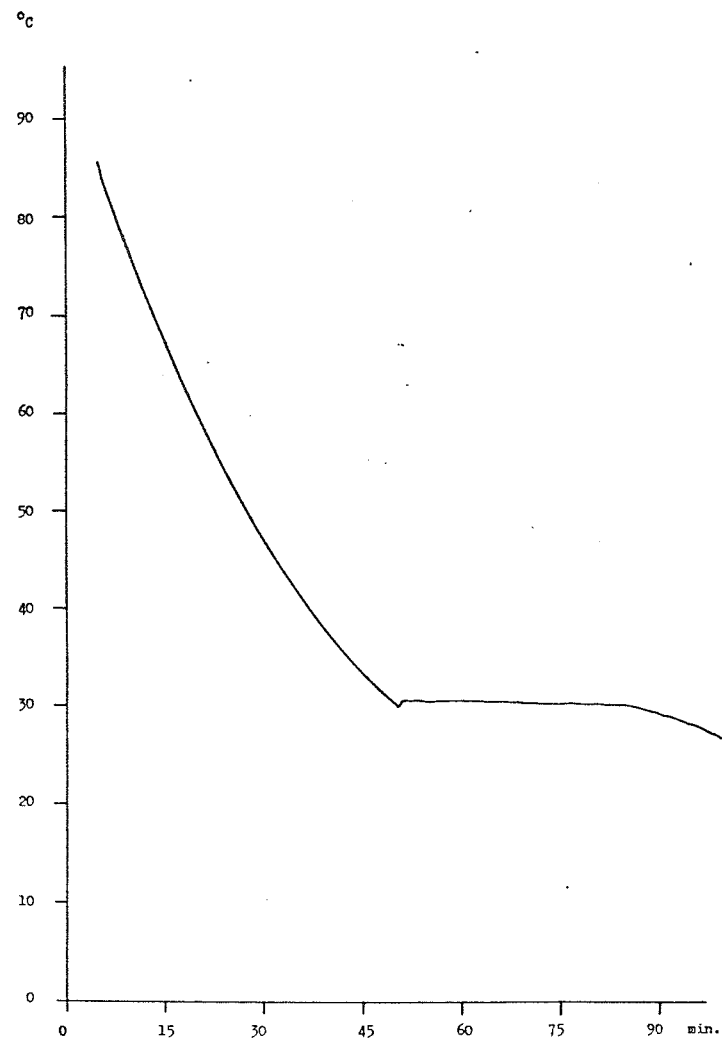


Figure 13. Cooling curve for $(C_2H_5)_4NCl \cdot 4H_2O$.

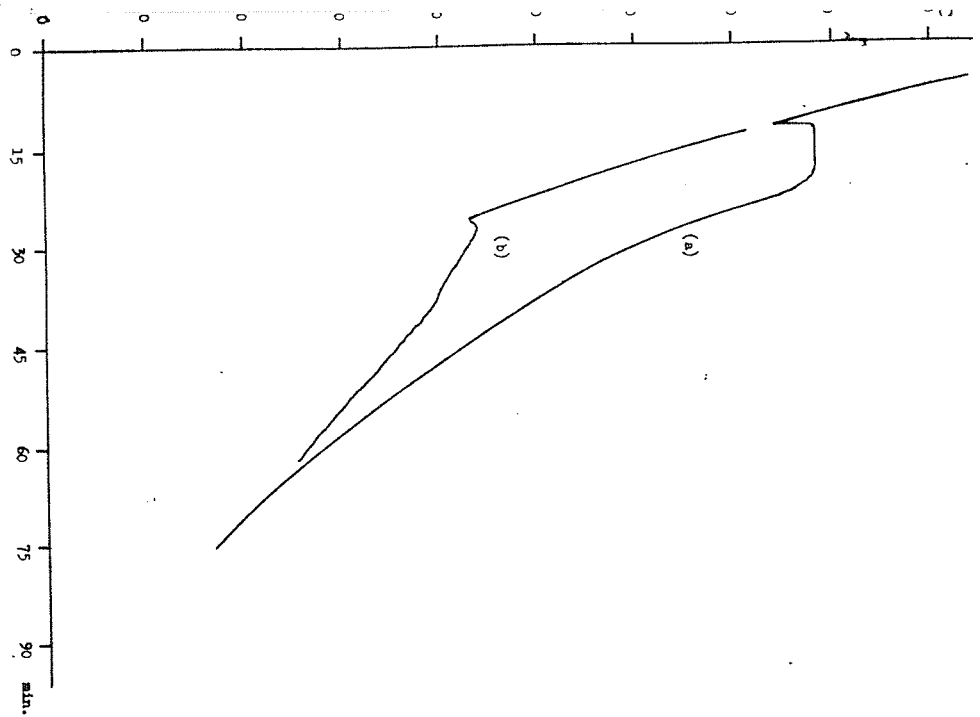


Figure 11. Cooling curve for (a) 2-ethanolamine hydrochloride, (b) 2-ethanolamine hydrochloride with addition of one molecule of water.

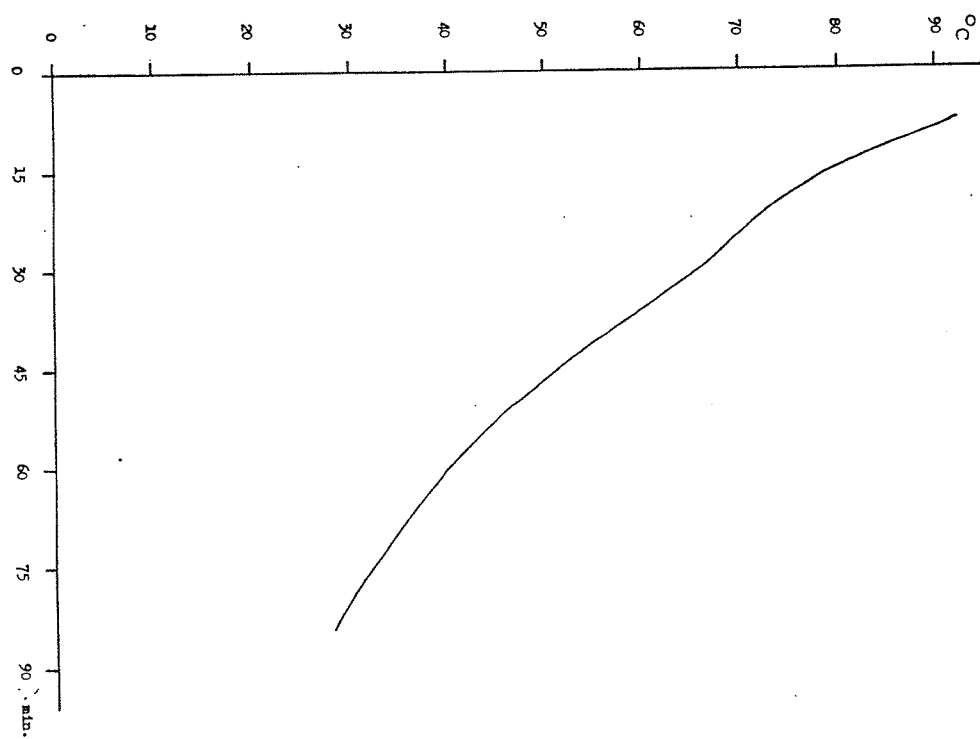


Figure 12. Cooling curve for 1,4,7,10-tetraazadodecane tetrasulfate, $H_2N-C_2H_4-NH-C_2H_4-NH-C_2H_4-NH_2 \cdot 4Cl^{17}H_{35}COOH$.

7. STORAGE SYSTEM SELECTION

Storage systems using the extra water principle can be constructed in different ways.

A possible construction is the one described in part 1 of the report, where heat transfer oil is the heat transfer fluid in direct contact with the salt water mixture. This storage system was selected for the experiments.

Another construction could be formed as schematically shown in figure 14. There will always be a liquid phase in which the stirrer can be situated. The stirrer was supposed to improve the heat transfer due to a flow in the liquid phase. However, this construction was not selected due to expected problems concerning salt hydrate growth on the heat exchanger and the stirrer resulting in a poor heat transfer from the heat storage.

Furthermore the system, where the salt water mixture itself is pumped in the pipes to the solar collector from a storage container, should be mentioned. This system was not selected due to expected problems concerning solidification in the pipes.

8. CONCLUSION

Four salt hydrates, which are suitable as heat storage materials using the extra water principle have been selected. The data for calculating the storage capacity of the salt water mixture have been found by literature studies or measurements. Also a search for organic compounds as heat storage materials have been made, and a few promising candidates have been found. These compounds must, like the selected salt hydrates, be investigated in detail in order to evaluate the problems occurring when such materials are used as heat storage materials.

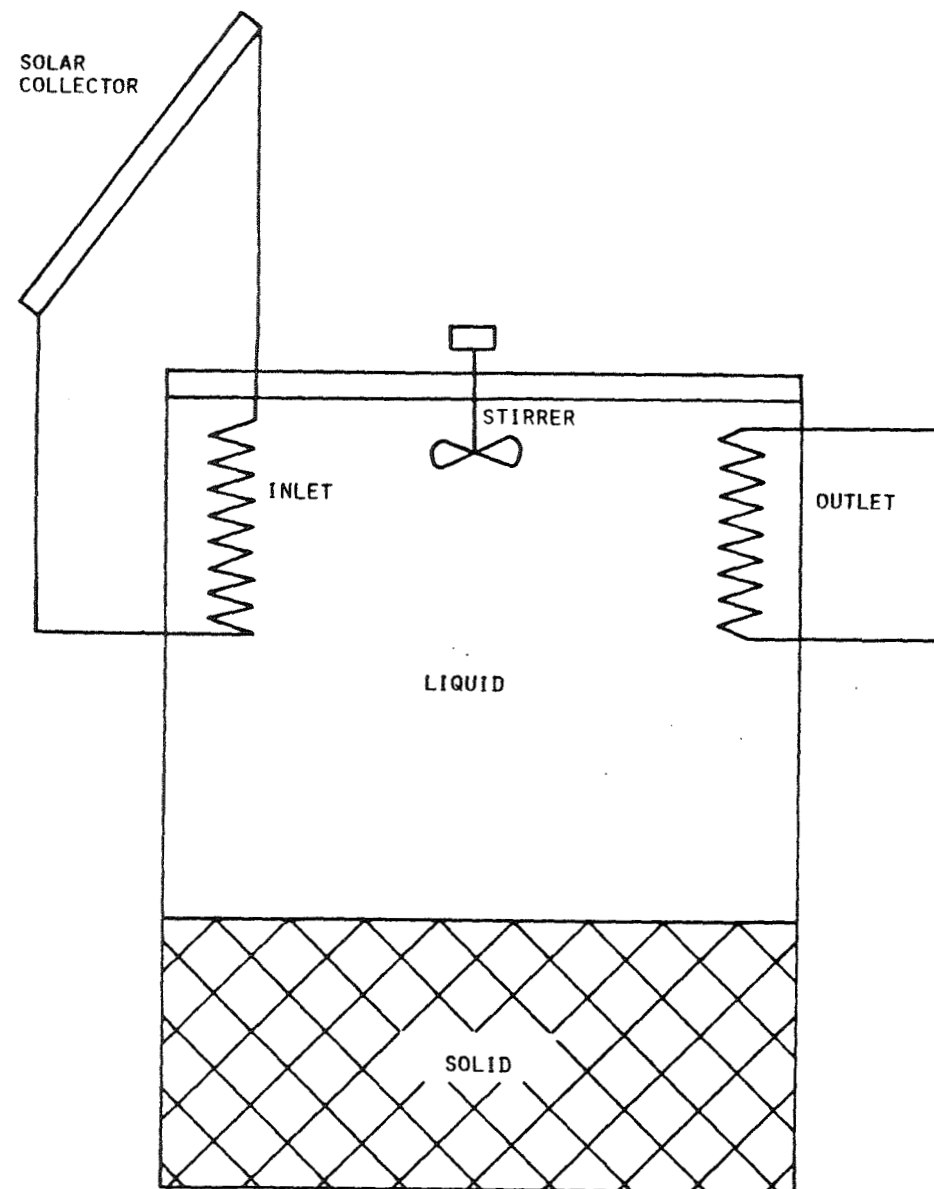


Figure 14. Schematic illustration of a heat storage based on a salt water mixture.

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CALCULATION OF THE STORAGE CAPACITY
OF SELECTED SALT WATER MIXTURES

PART 3 OF REPORT ON
HEAT STORAGE IN A SOLAR HEATING SYSTEM
USING SALT HYDRATES

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JULY 1977

Calculation of the storage capacity of selected salt water mixtures.

Part 3 of report on
Heat storage in a solar heating system using salt hydrates.

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1. INTRODUCTION

This report is part 3 of the final report on the research project no. 140 - 76 ESDK, Heat storage in a solar heating system using salt hydrates, which financially is supported by the European Community.

The aim of the project is to investigate a new method by which a heat storage based on an incongruently melting salt hydrate will work stably. Before describing this method some of the used expressions shall be explained.

Salt hydrate is the anhydrous salt with its corresponding crystal water. The expression is used for both the solid and the liquid phase.

Incongruently melting salt hydrate is a salt hydrate with an anhydrous salt which can not be dissolved completely in its corresponding crystal water at the melting point.

Salt water mixture is the salt hydrate with at least so much water added that the anhydrous salt is completely dissolved at the melting point.

When an incongruently melting salt hydrate is melted the undissolved fraction of the anhydrous salt will form a layer at the bottom of the container. In the solidification part of a cycle this layer will not for normal container dimensions come in contact with the water and it will therefore not work actively. This phase separation will in a few cycles diminish the performance of the heat storage.

The investigated method is mainly used to avoid the phase separation. It consists of adding so much extra water to the salt hydrate that all the anhydrous salt dissolves in the water. In order to secure that phase separation is avoided a soft stirring of the mixture is necessary.

The solidification will take place by decreasing temperature since crystallization only can take place from a saturated solution and the solubility of the anhydrous salt decreases at decreasing temperature.

The aim of this part of the report is to set up a general method for calculation of the storage capacity of a salt water mixture consisting of an incongruently melting salt hydrate with additional water. The storage capacity of the salt water mixtures selected in part 2 of the final report is calculated by means of this method and given in tables and figures. The storage capacity of the Na_2HPO_4 -salt water mixture, where both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ are assumed to be formed during cooling, is also calculated.

2. ASSUMPTIONS FOR THE CALCULATION

Specific heats and densities for the water, anhydrous salt and solid phase salt hydrate are assumed to be independent of the temperature. This assumption is reasonable in the temperature interval going from 0°C to 100°C , see part 2 of the final report. The amount of heat is assumed additive and the heat of dilution is ignored. This have been confirmed as reasonable assumptions by small scale experiments. Also all phase changes in the solid phase are ignored.

3. GENERAL METHOD FOR CALCULATION OF THE STORAGE CAPACITY OF A SALT WATER MIXTURE

3.1. Definition of used symbols.

- F_{am} : Fraction of anhydrous salt in the salt water mixture based on weight.
- F_{as} : Fraction of anhydrous salt in the salt hydrate based on weight.
- $S_a(t)$: Solubility of anhydrous salt in water, that is the fraction of anhydrous salt in a saturated salt solution based on weight at the temperature t .
- $F_{\text{sol}}(t)$: Fraction of the solid phase salt hydrate in the salt water mixture based on weight at the temperature t .

- L : Heat of fusion of the salt hydrate. The unit is kJ/kg salt hydrate.
- C_{sh} : Specific heat of the solid salt hydrate with the unit $\text{J}/^\circ\text{C kg}$.
- D_{as} : Density of the anhydrous salt with the unit kg/m^3 .
- C_{as} : Specific heat of the anhydrous salt with the unit $\text{J}/\text{kg}^\circ\text{C}$.
- T_s : Start solidification temperature.
- $C_{\text{ml}}(t)$: Specific heat of the salt water mixture at the temperature t , where t is lower than T_s . The unit is $\text{J}/^\circ\text{C kg}$ salt water mixture.
- C_{mh} : Specific heat of the salt water mixture for temperatures higher than T_s . The unit is $\text{J}/^\circ\text{C kg}$ salt water mixture.
- C_{ls} : Specific heat of the liquid phase of saturated solution for temperatures lower than T_s with the unit $\text{J}/^\circ\text{C kg}$.
- C_{water} : Specific heat of water with the unit $\text{J}/^\circ\text{C kg}$.
- D_{water} : Density of water with the unit kg/m^3 .
- D_m : Density of the salt water mixture with the unit kg/m^3 salt water mixture.
- T_o : Temperature point of origin, where the heat content is 0.
- Q_s : Storage capacity of the salt water mixture.

3.2. Calculation of storage capacity.

Since the fraction of the solid phase salt hydrate in the salt water mixture for temperatures lower than T_s is changing with temperature, it is necessary to find both the amount of liquid phase and solid phase as a function of the temperature. Figure 1 shows schematically the composition of the salt water mixture for temperatures lower than T_s . Start solidification temperature T_s is found from $S_a(T_s) = F_{\text{am}}$.

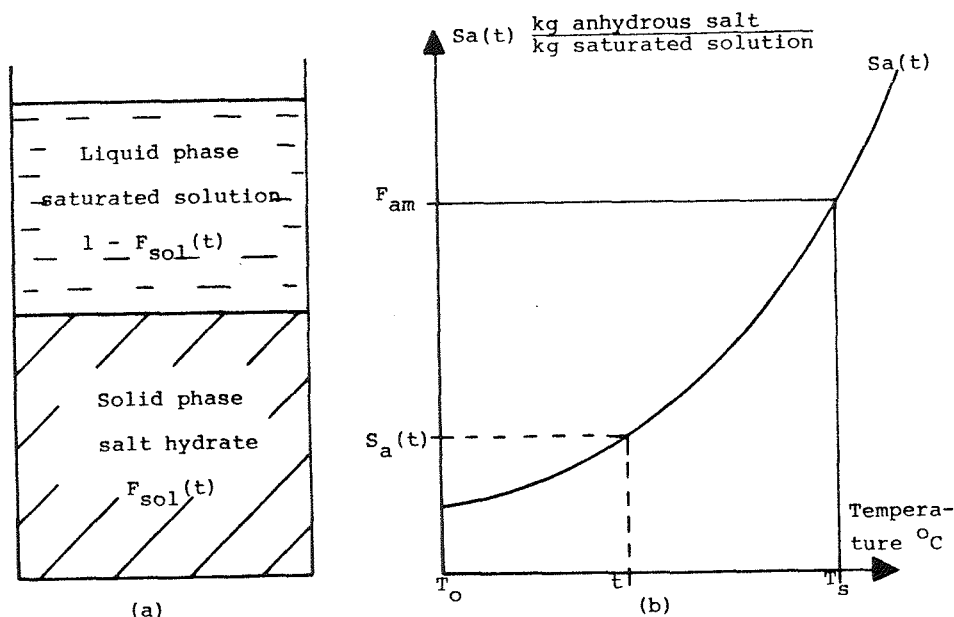


Figure 1. Schematic illustration of the composition of the salt water mixture at temperatures lower than T_s . (a) Weight fractions of the salt water mixture at temperature t . (b) Solubility of the anhydrous salt in water.

3.2.1. Latent heat.

As the solidification/melting-process takes place in a temperature interval from T_s and down the latent heat is released or absorbed in the same temperature interval.

For temperatures lower than T_s the salt water mixture consists of a liquid phase of saturated salt solution and a solid phase of salt hydrate, see figure 1.

Considering a weight unit of the salt water mixture, the weight fraction of the salt water mixture, which is solid phase salt hydrate at the temperature t , $F_{sol}(t)$ is calculated as follows:

Weight of anhydrous salt in the mixture = weight of anhydrous salt in solid phase salt hydrate + weight of anhydrous salt in the saturated solution. With the symbols this is:

$$1 \cdot F_{am} = 1 \cdot F_{sol}(t) \cdot F_{as} + 1 \cdot (1 - F_{sol}(t)) \cdot S_a(t)$$

Rearranging this equation we get:

$$F_{sol}(t) = \frac{F_{am} - S_a(t)}{F_{as} - S_a(t)}$$

The weight fraction of the salt water mixture, which undergoes phase change in the temperature interval going from T_0 to t is: $F_{sol}(T_0) - F_{sol}(t)$. The amount of latent heat situated in the same temperature interval then is $L \cdot (F_{sol}(T_0) - F_{sol}(t))$ kJ/kg salt water mixture.

3.2.2. Sensible heat.

Calculation of the specific heat of the salt water mixture must be divided into the 2 temperature intervals: $t > T_s$ and

$$t < T_s.$$

$$t > T_s$$

The salt water mixture consists of a mixture of anhydrous salt and water, and the specific heat of the salt water mixture is found from the following balance:

Specific heat of the salt water mixture = (fraction of anhydrous salt in the salt water mixture based on weight) \times (specific heat of anhydrous salt) + (fraction of water in the salt water mixture based on weight) \times (specific heat of water).

With the symbols this is:

$$C_{mh} = F_{am} \cdot C_{as} + (1 - F_{am}) \cdot C_{water} \text{ J/}^\circ\text{C kg salt water mixture.}$$

$$t < T_s$$

The salt water mixture consists of solid phase salt hydrate and liquid phase saturated salt solution, see figure 1, and the specific heat of the salt water mixture at the temperature t is found from the following balance:

Specific heat of salt water mixture at the temperature t = (fraction of solid phase salt hydrate in the salt water mixture based on weight) \times (specific heat of solid phase salt hydrate)

+ (fraction of liquid phase in the salt water mixture based on weight) x (specific heat of liquid phase). With the symbols this is:

$$C_{ml}(t) = F_{sol}(t) \cdot C_{sh} + (1 - F_{sol}(t)) \cdot C_{lss} =$$

$$F_{sol}(t) \cdot C_{sh} + (1 - F_{sol}(t)) \cdot [S_a(t) \cdot C_{as} + (1 - S_a(t)) \cdot C_{water}]$$

J/°C kg salt water mixture.

3.2.3. Total storage capacity.

The density of the salt water mixture is calculated as follows:

Density of salt water mixture = (fraction of anhydrous salt in the salt water mixture based on weight) x (density of anhydrous salt) + (fraction of water in the salt water mixture based on weight) x (density of water). With the symbols this is:

$$D_m = F_{am} \cdot D_{as} + (1 - F_{am}) \cdot D_{water} \text{ kg/m}^3 \text{ salt water mixture}$$

The storage capacity of the salt water mixture at the temperature $T_O < T_s$ is fixed to 0. At a higher temperature t the storage capacity per m^3 salt water mixture is calculated as follows:

Storage capacity = Latent heat + sensible heat. With the symbols this is:

$$\text{For } t < T_s:$$

$$Q_s = L \cdot (F_{sol}(T_O) - F_{sol}(t)) \cdot \frac{D_m}{10^3} + \int_{T_O}^t C_{ml}(t) \cdot \frac{D_m}{10^6} dt \text{ MJ/m}^3$$

$$\text{For } t > T_s:$$

$$Q_s = L \cdot F_{sol}(T_O) \cdot \frac{D_m}{10^3} + \int_{T_O}^{T_s} C_{ml}(t) \cdot \frac{D_m}{10^6} dt + \int_{T_s}^t C_{mh} \cdot \frac{D_m}{10^6} dt \text{ MJ/m}^3$$

Using the above formula it is possible to calculate the storage capacity of any salt water mixture if only the following data are known for the salt water mixture: F_{am} , F_{as} , $S_a(t)$, L , C_{sh} , D_{as} and C_{as} . For the selected salt hydrates, mentioned in part 2 of the final report, the data are given in table 1.

3.3. Results.

With the data given in table 1 and the values $C_{water} = 4180 \text{ J/kg}^\circ \text{C}$ and $D_{water} = 985 \text{ kg/m}^3$ the storage capacity of the salt water mixtures was calculated using a computer program with temperature steps of 0.5°C for the integral calculation. T_O was fixed to 0°C in these calculations.

The results are shown in figure 2 - 5 and table 2 - 5 for Na_2SO_4 -, Na_2CO_3 -, NaCH_3COO - and Na_2HPO_4 -salt water mixtures.

Figure 2 - 5 show the storage capacity for different salt water mixtures. Each figure shows the storage capacity of 3 different salt water mixtures with more or less water added to the salt hydrate. In the temperature interval $0^\circ \text{C} - 100^\circ \text{C}$ mixtures with increasing fraction of water have decreasing storage capacity. It is clearly seen that the heat of fusion is situated at still lower temperatures for salt water mixtures with increasing action of water. The storage capacity of a salt water mixture in an arbitrary temperature interval can be found from the curve as the difference of the reading of the storage capacity at the temperature limits.

For each 2°C the storage capacity of the salt water mixtures with the smallest fraction of water, which is the most relevant case, is also given in table 2 - 5.

salt hydrate	melting point °C	F _{am} max	F _{as}	approximated solubility S _a (t)	L kJ/kg	C _{sh} J/kg °C	D _{as} kg/m ³	C _{as} J/kg °C
Na ₂ SO ₄ ·10H ₂ O	32	0.33	0.44	0.0404·e ^{0.0652·t}	251	1930	2660	880
Na ₂ CO ₃ ·10H ₂ O	33	0.33	0.37	0.0701·e ^{0.0469·t}	247	1990	2530	1040
NaCH ₃ COO·3H ₂ O	58	0.58	0.60	0° C - 40° C: 0.2646·e ^{0.00983·t}	160	2540	1530	1465
				40° C - 60° C: 0.2313·e ^{0.01345·t}				
				50° C - 58° C: 0.09667·e ^{0.03089·t}				
Na ₂ HPO ₄ ·7H ₂ O	48	0.444	0.53	0.0812·e ^{0.0354·t}	135	1350	2460	1300
Na ₂ HPO ₄ ·12H ₂ O	35	0.275	0.40	0.0130·e ^{0.0865·t}	266	1560	2460	1300

Table 1. Data for 5 different salt hydrates.

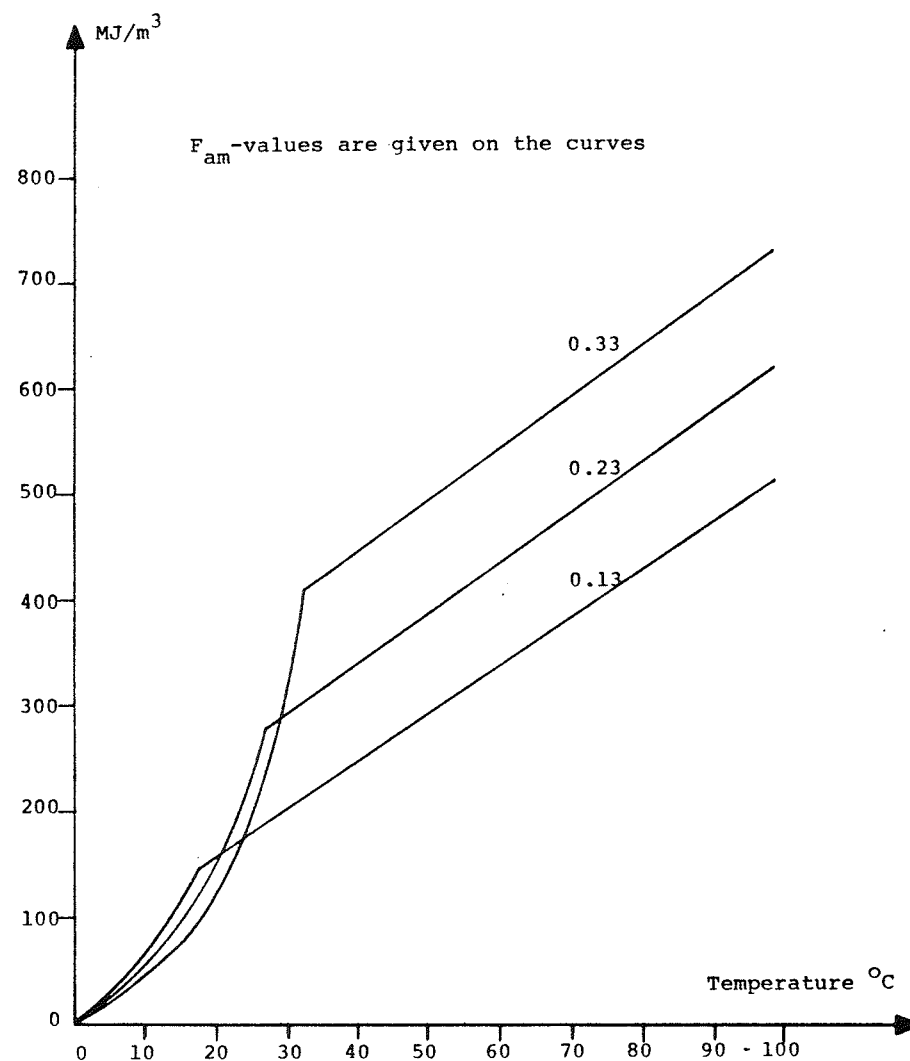


Figure 2. Storage capacity of Na₂SO₄-salt water mixtures.

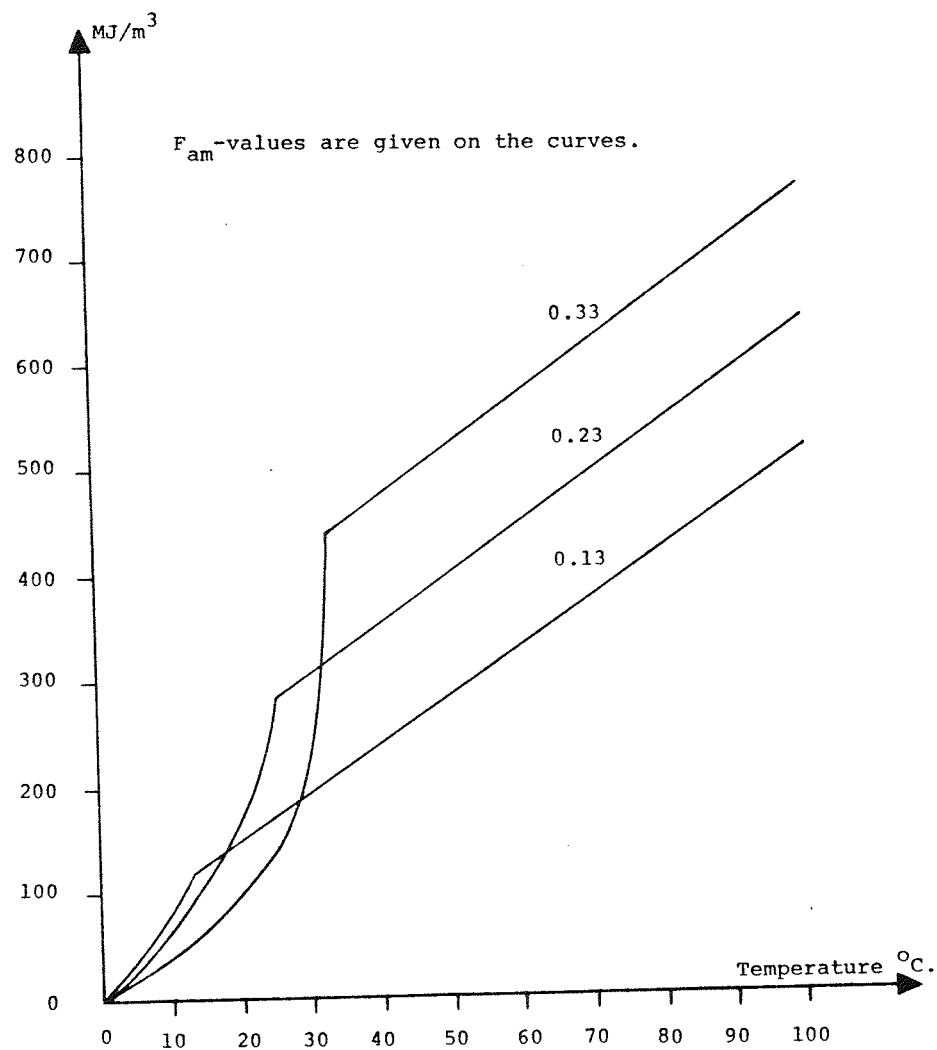


Figure 3. Storage capacity of Na₂CO₃-salt water mixtures.

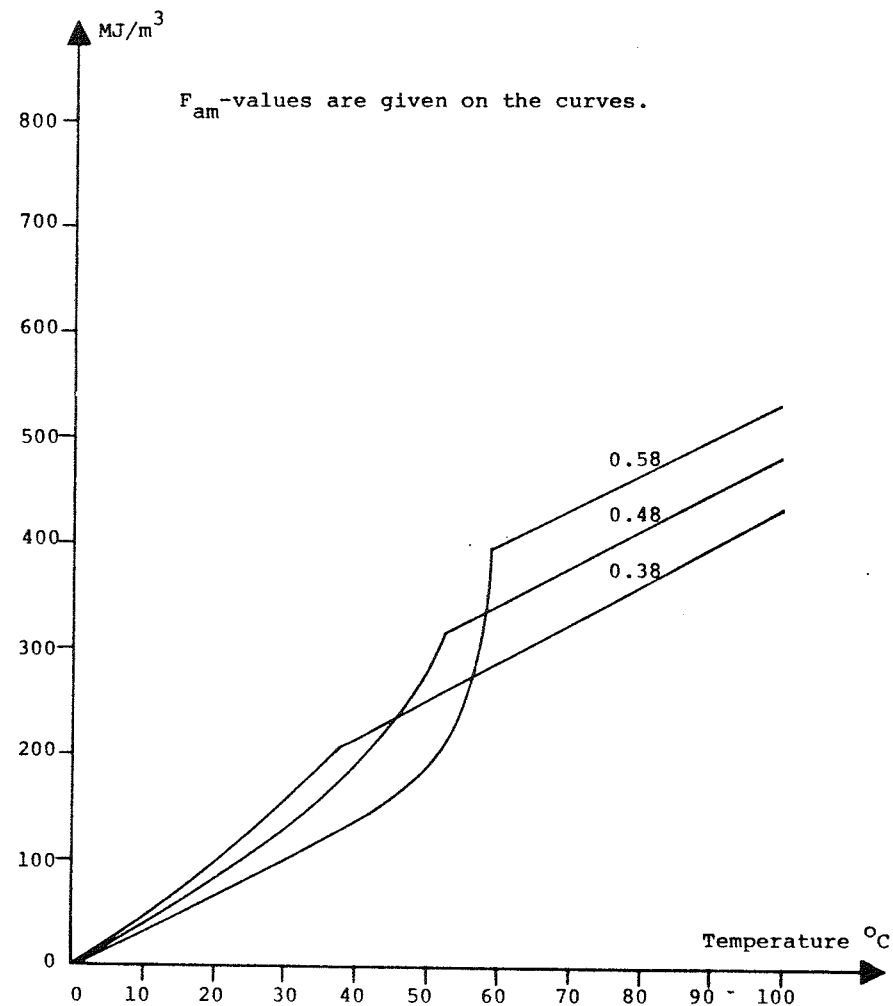


Figure 4. Storage capacity of NaCH₃COO-salt water mixtures.

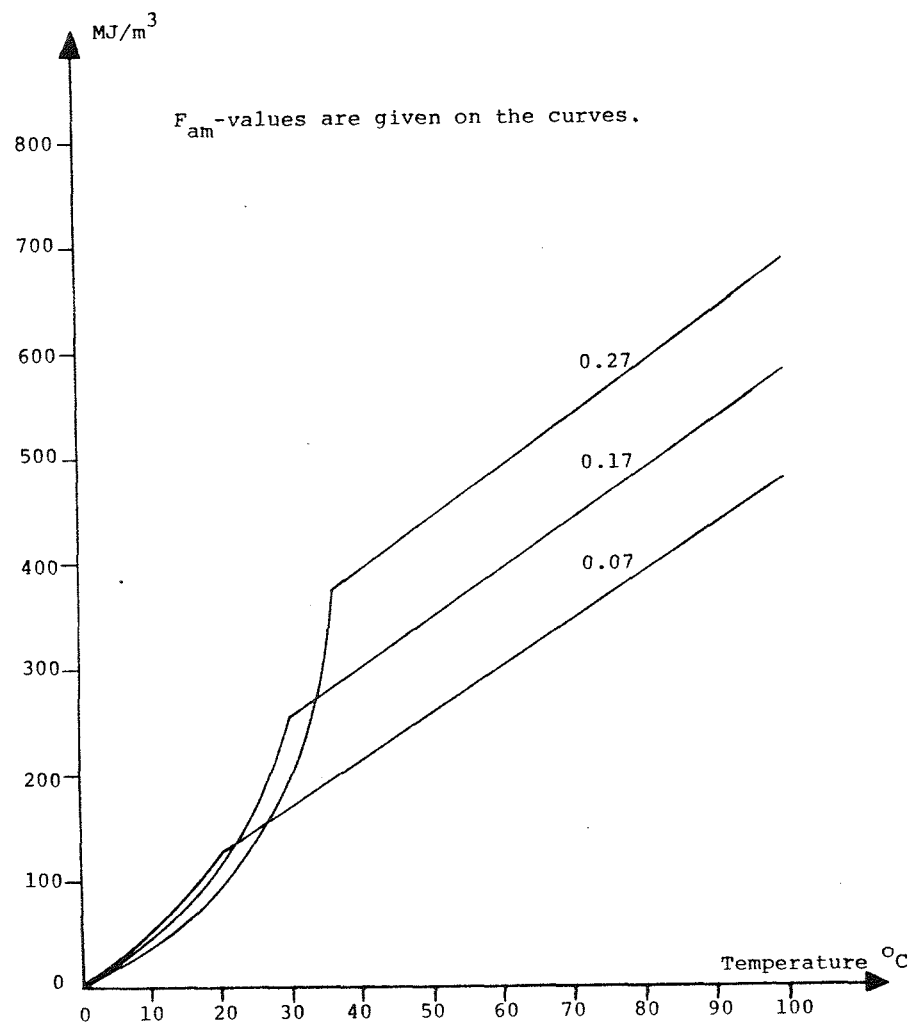


Figure 5. Storage capacity of Na_2HPO_4 -salt water mixtures.

Temperature $^{\circ}\text{C}$	Sensible heat MJ/m^3	Latent heat MJ/m^3	Total heat MJ/m^3
0	0	0	0
2.0	7.7	1.5	9.3
4.0	15.5	3.3	18.8
6.0	23.2	5.4	28.6
8.0	31.0	7.9	38.9
10.0	38.8	10.9	49.7
12.0	46.6	14.5	61.1
14.0	54.4	18.8	73.3
16.0	62.3	24.2	86.5
18.0	70.2	31.0	101.2
20.0	78.2	39.5	117.7
22.0	86.2	50.7	136.9
24.0	94.3	65.7	160.0
26.0	102.5	86.6	189.2
28.0	110.9	117.8	228.7
30.0	119.6	168.3	287.9
32.0	128.7	263.2	391.9
34.0	137.0	279.7	416.7
36.0	146.5	279.7	426.2
38.0	156.0	279.7	435.7
40.0	165.5	279.7	445.2
42.0	175.0	279.7	454.7
44.0	184.5	279.7	464.2
46.0	194.0	279.7	473.7
48.0	203.5	279.7	483.2
50.0	213.0	279.7	492.7
52.0	222.5	279.7	502.2
54.0	232.0	279.7	511.7
56.0	241.5	279.7	521.3
58.0	251.0	279.7	530.8
60.0	260.5	279.7	540.3
62.0	270.0	279.7	549.8
64.0	279.6	279.7	559.3
66.0	289.1	279.7	568.8
68.0	298.6	279.7	578.3
70.0	308.1	279.7	587.8
72.0	317.6	279.7	597.3
74.0	327.1	279.7	606.8
76.0	336.6	279.7	616.3
78.0	346.1	279.7	625.8
80.0	355.6	279.7	635.3
82.0	365.1	279.7	644.8
84.0	374.6	279.7	654.3
86.0	384.1	279.7	663.8
88.0	393.6	279.7	673.3
90.0	403.1	279.7	682.9
92.0	412.6	279.7	692.4
94.0	422.1	279.7	701.9
96.0	431.6	279.7	711.4
98.0	441.2	279.7	720.9
100.0	450.7	279.7	730.4

Table 2. Storage capacity of Na_2SO_4 - salt water mixture with $F_{am} = 0.33$.

Temperature °C	Sensible heat MJ/m ³	Latent heat MJ/m ³	Total heat MJ/m ³
0	0	0	0
2.0	6.7	1.2	7.9
4.0	13.5	2.5	16.0
6.0	20.3	4.0	24.3
8.0	27.0	5.9	32.9
10.0	33.8	8.0	41.8
12.0	40.6	10.6	51.2
14.0	47.5	13.6	61.1
16.0	54.3	17.4	71.8
18.0	61.3	22.1	83.4
20.0	68.2	28.1	96.3
22.0	75.2	35.9	111.2
24.0	82.3	46.6	128.9
26.0	89.5	61.9	151.4
28.0	96.9	85.6	182.5
30.0	104.5	126.7	231.2
32.0	112.7	215.3	328.0
34.0	119.8	320.0	439.8
36.0	129.2	320.0	449.2
38.0	138.6	320.0	458.6
40.0	148.0	320.0	468.0
42.0	157.4	320.0	477.4
44.0	166.8	320.0	486.8
46.0	176.2	320.0	496.2
48.0	185.6	320.0	505.6
50.0	195.0	320.0	515.0
52.0	204.4	320.0	524.4
54.0	213.8	320.0	533.8
56.0	223.2	320.0	543.2
58.0	232.6	320.0	552.6
60.0	242.0	320.0	562.0
62.0	251.4	320.0	571.4
64.0	260.8	320.0	580.8
66.0	270.2	320.0	590.2
68.0	279.6	320.0	599.6
70.0	289.0	320.0	609.0
72.0	298.4	320.0	618.4
74.0	307.8	320.0	627.8
76.0	317.2	320.0	637.2
78.0	326.6	320.0	646.6
80.0	336.0	320.0	656.0
82.0	345.4	320.0	665.4
84.0	354.8	320.0	674.8
86.0	364.2	320.0	684.2
88.0	373.6	320.0	693.6
90.0	383.0	320.0	703.0
92.0	392.4	320.0	712.4
94.0	401.8	320.0	721.8
96.0	411.2	320.0	731.2
98.0	420.6	320.0	740.6
100.0	430.0	320.0	750.0

Table 3. Storage capacity of Na₂CO₃-salt water mixture with F_{am} = 0.33.

Temperature °C	Sensible heat MJ/m ³	Latent heat MJ/m ³	Total heat MJ/m ³
0	0	0	0
2.0	6.8	0.2	7.0
4.0	13.5	0.4	13.9
6.0	20.3	0.6	20.9
8.0	27.0	0.9	27.9
10.0	33.8	1.1	34.9
12.0	40.5	1.4	41.9
14.0	47.3	1.6	48.9
16.0	54.0	1.9	55.9
18.0	60.8	2.2	63.0
20.0	67.5	2.6	70.1
22.0	74.3	2.9	77.2
24.0	81.0	3.3	84.3
26.0	87.8	3.7	91.5
28.0	94.5	4.1	98.7
30.0	101.3	4.6	105.9
32.0	108.0	5.1	113.2
34.0	114.8	5.7	120.5
36.0	121.6	6.2	127.8
38.0	128.3	6.9	135.2
40.0	135.1	8.0	143.1
42.0	141.8	9.1	151.0
44.0	148.6	10.4	159.0
46.0	155.3	12.0	167.3
48.0	162.1	13.8	175.8
50.0	168.8	15.9	184.7
52.0	175.6	22.8	198.4
54.0	182.3	35.2	217.6
56.0	189.1	63.6	252.7
58.0	195.9	195.8	391.6
60.0	202.7	195.8	398.4
62.0	209.4	195.8	405.2
64.0	216.2	195.8	412.0
66.0	223.0	195.8	418.7
68.0	229.8	195.8	425.5
70.0	236.5	195.8	432.3
72.0	243.3	195.8	439.1
74.0	250.1	195.8	445.9
76.0	256.9	195.8	452.6
78.0	263.7	195.8	459.4
80.0	270.4	195.8	466.2
82.0	277.2	195.8	473.0
84.0	284.0	195.8	479.8
86.0	290.8	195.8	486.5
88.0	297.6	195.8	493.3
90.0	304.3	195.8	500.1
92.0	311.1	195.8	506.9
94.0	317.9	195.8	513.7
96.0	324.7	195.8	520.4
98.0	331.5	195.8	527.2
100.0	338.2	195.8	534.0

Table 4. Storage capacity of NaH₃COO-salt water mixture with F_{am} = 0.58.

Temperature °C	Sensible heat MJ/m ³	Latent heat MJ/m ³	Total heat MJ/m ³
0	0	0	0
2.0	6.7	0.8	7.5
4.0	13.5	1.7	15.2
6.0	20.2	2.9	23.1
8.0	27.0	4.3	31.2
10.0	33.7	6.0	39.7
12.0	40.5	8.1	48.6
14.0	47.3	10.7	58.0
16.0	54.2	13.8	68.0
18.0	61.1	17.8	78.9
20.0	68.0	22.9	90.9
22.0	75.1	29.4	104.4
24.0	82.2	37.9	120.1
26.0	89.4	49.4	138.7
28.0	96.7	65.3	162.0
30.0	104.3	88.5	192.8
32.0	112.2	124.8	237.0
34.0	120.7	188.2	309.0
36.0	127.9	244.3	372.3
38.0	137.3	244.3	381.7
40.0	146.8	244.3	391.1
42.0	156.2	244.3	400.5
44.0	165.6	244.3	409.9
46.0	175.0	244.3	419.3
48.0	184.4	244.3	428.7
50.0	193.8	244.3	438.1
52.0	203.2	244.3	447.6
54.0	212.6	244.3	457.0
56.0	222.1	244.3	466.4
58.0	231.5	244.3	475.8
60.0	240.9	244.3	485.2
62.0	250.3	244.3	494.6
64.0	259.7	244.3	504.0
66.0	269.1	244.3	513.4
68.0	278.5	244.3	522.9
70.0	287.9	244.3	532.3
72.0	297.4	244.3	541.7
74.0	306.8	244.3	551.1
76.0	316.2	244.3	560.5
78.0	325.6	244.3	569.9
80.0	335.0	244.3	579.3
82.0	344.4	244.3	588.7
84.0	353.8	244.3	598.2
86.0	363.2	244.3	607.6
88.0	372.6	244.3	617.0
90.0	382.1	244.3	626.4
92.0	391.5	244.3	635.8
94.0	400.9	244.3	645.2
96.0	410.3	244.3	654.6
98.0	419.7	244.3	664.0
100.0	429.1	244.3	673.5

Table 5. Storage capacity of Na_2HPO_4 -salt water mixture with $F_{am} = 0.27$.

4. STORAGE CAPACITY OF SALT WATER MIXTURES WHERE $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ IS FORMED DURING SOLIDIFICATION.

4.1 Assumption for the calculation.

$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, from now on called 7-hydrate, is formed during solidification for salt water mixtures with Na_2HPO_4 as the anhydrous salt and the fraction of the anhydrous salt in the salt water mixture based on weight F_{am} situated in the interval $0.275 < F_{am} < 0.444$. The solubility versus the temperature is shown in figure 6, where also the stable salt hydrate is shown. The 7-hydrate is stable in the temperature interval $35.4^\circ\text{C} < t < 48.1^\circ\text{C}$ corresponding to the interval $0.275 < S_a(t) < 0.444$, and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, from now on called 12-hydrate is stable for temperatures lower than 35.4°C , corresponding to $S_a(t) < 0.275$.

By cooling a salt water mixture with $0.275 < F_{am} < 0.444$ 7-hydrate is formed in the temperature interval going from T_s down to 35.4°C . For temperatures lower than 35.4°C either the stable 12-hydrate with the great heat of fusion or the 7-hydrate which has already formed 7-hydrate as a basis for growth is formed. Due to insufficient knowledge of the behavior of this solidification the heat capacity will be calculated for both assumptions. Only experiments will show what is right.

With the assumption, that only 7-hydrate is formed during cooling, the heat capacity is calculated as described above, and the result is shown in table 6 for $F_{am} = 0.40$. $F_{am} = 0.40$ is used because the salt hydrate is bought in that form. In the following the heat capacity will be calculated with the assumption, that 12-hydrate is formed for temperatures lower than 35.4°C and that no crystal change between 7-hydrate and 12-hydrate takes place.

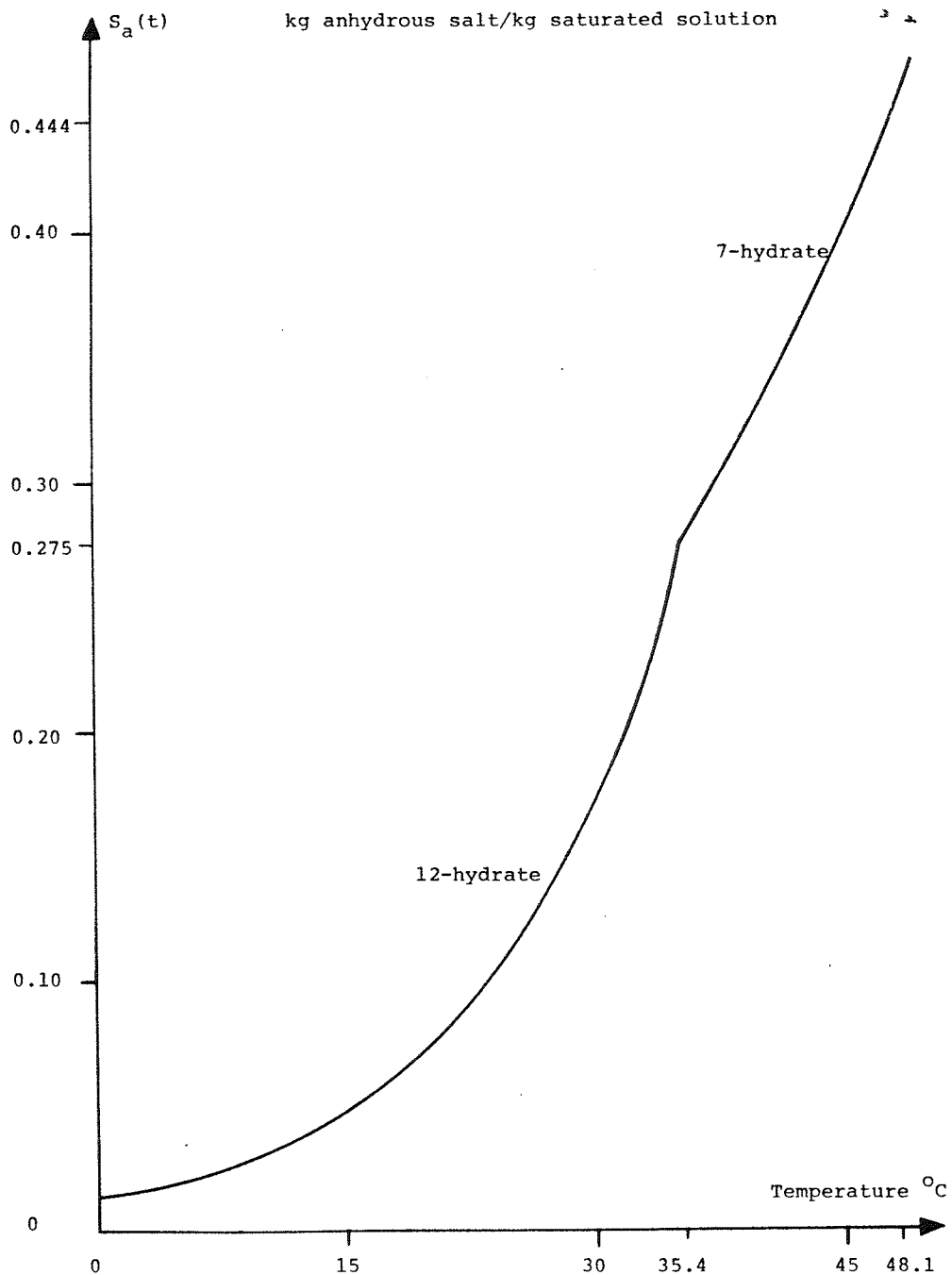


Figure 6. Solubility of Na_2HPO_4 in water.

Temperature $^{\circ}\text{C}$	Sensible heat MJ/m^3	Latent heat MJ/m^3	Total heat MJ/m^3
0	0	0	0
2.0	6.6	0.8	7.5
4.0	13.3	1.7	15.0
6.0	19.9	2.8	22.7
8.0	26.6	3.9	30.5
10.0	33.2	5.1	38.5
12.0	40.1	6.5	46.6
14.0	46.8	8.1	54.9
16.0	53.6	9.8	63.5
18.0	60.5	11.8	72.3
20.0	67.4	14.1	81.5
22.0	74.3	16.7	91.0
24.0	81.3	19.7	100.9
26.0	88.3	23.1	111.4
28.0	95.4	27.2	122.6
30.0	102.6	32.0	134.7
32.0	109.0	37.8	147.8
34.0	117.4	44.9	162.3
36.0	125.0	53.7	178.7
38.0	132.7	65.0	197.7
40.0	140.8	79.7	220.5
42.0	149.2	100.0	249.2
44.0	158.1	129.4	287.5
46.0	165.5	151.0	316.5
48.0	175.0	151.0	326.0
50.0	184.5	151.0	335.6
52.0	194.1	151.0	345.1
54.0	203.6	151.0	354.6
56.0	213.1	151.0	364.2
58.0	222.7	151.0	373.7
60.0	232.2	151.0	383.3
62.0	241.8	151.0	392.8
64.0	251.3	151.0	402.3
66.0	260.8	151.0	411.9
68.0	270.4	151.0	421.4
70.0	279.9	151.0	430.9
72.0	289.5	151.0	440.5
74.0	299.0	151.0	450.0
76.0	308.5	151.0	459.6
78.0	318.1	151.0	469.1
80.0	327.6	151.0	478.6
82.0	337.1	151.0	488.2
84.0	346.7	151.0	497.7
86.0	356.2	151.0	507.3
88.0	365.8	151.0	516.8
90.0	375.3	151.0	526.3
92.0	384.8	151.0	535.9
94.0	394.4	151.0	545.4
96.0	403.9	151.0	554.9
98.0	413.4	151.0	564.5
100.0	423.0	151.0	574.0

Table 6. Storage capacity of Na_2HPO_4 -salt water mixture with $F_{am} = 0.40$ and the assumption, that only $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ is formed during cooling.

4.2. Calculation of storage capacity of salt water mixtures, where both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ are formed.

4.2.1. Definition of symbols used.

Besides the symbols used in the general case the following symbols will be used:

- L_{7h} : Heat of fusion of the 7-hydrate with the unit kJ/kg salt hydrate.
- L_{12h} : Heat of fusion of the 12-hydrate with the unit kJ/kg salt hydrate.
- $F_{7h}(t)$: Fraction of solid phase 7-hydrate in the salt water mixture based on weight at the temperature t , where t is situated in the temperature interval $35.4^\circ\text{C} < t < T_s$.
- $F_{12h}(t)$: Fraction based on weight of solid phase 12-hydrate at the temperature $t < 35.4^\circ\text{C}$ in the liquid phase part, that existed at 35.4°C .
- C_{7h} : Specific heat of the 7-hydrate solid phase with the unit $\text{J}/^\circ\text{C kg}$.
- C_{12h} : Specific heat of the 12-hydrate solid phase with the unit $\text{J}/^\circ\text{C kg}$.
- C_{ss} : Specific heat of a saturated salt solution with the unit $\text{J}/^\circ\text{C kg}$.
- $C_{mi}(t)$: Specific heat of the salt water mixture at the temperature t in the temperature interval $35.4^\circ\text{C} < t < T_s$ with the unit $\text{J}/^\circ\text{C kg}$ salt water mixture.
- $C_{ml}(t)$: Specific heat of the salt water mixture for temperatures lower than 35.4°C with the unit $\text{J}/^\circ\text{C kg}$ water mixture.

4.2.2 Calculation of storage capacity.

Calculation of the storage capacity must be divided into 3 temperature intervals. The temperature intervals are:

$$t > T_s, \quad 35.4^\circ\text{C} < t < T_s \quad \text{and} \quad t < 35.4^\circ\text{C}.$$

$$t > T_s$$

The salt water mixture is completely melted and consists of anhydrous salt and water. The specific heat of the salt water mixture is found in the following way:

Specific heat of the salt water mixture = (fraction of anhydrous salt in the salt water mixture based on weight) \times (specific heat of anhydrous salt) + (fraction of water in the salt water mixture based on weight) \times (specific heat of water).

With the symbols this is:

$$C_{mh} = F_{am} C_{as} + (1 - F_{am}) C_{water} \quad \text{J}/^\circ\text{C kg salt water mixture.}$$

$$35.4^\circ\text{C} < t < T_s$$

The salt water mixture consists of a saturated solution and solid crystals of 7-hydrate. Figure 7 shows a schematical illustration of the composition of the salt water mixture.

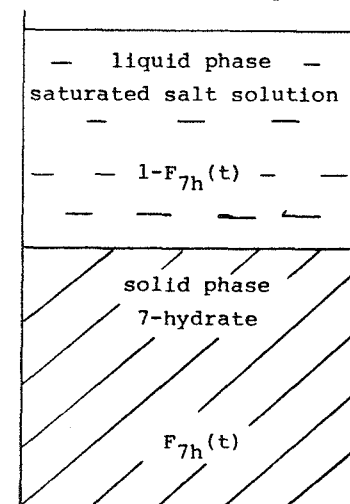


Figure 7. Schematical illustration of the composition of the Na_2HPO_4 -salt water mixture in the temperature interval $35.4^\circ\text{C} < t < T_s$.

As described in the previous, in section 3.2.1., $F_{7h}(t)$ can be found from:

$$F_{7h}(t) = \frac{F_{am} - S_a(t)}{0.53 - S_a(t)}$$

since the fraction of anhydrous salt in the 7-hydrate based on weight is 0.53, see table 1.

The fraction based on weight of the salt water mixture, which change phase between 35.4°C and t is: $F_{7h}(35.4^\circ\text{C}) - F_{7h}(t)$. The heat of fusion situated in the same temperature interval then is:

$$L_{7h} \cdot (F_{7h}(35.4^\circ\text{C}) - F_{7h}(t)) \cdot \frac{D_m}{10^3} \text{ MJ/m}^3.$$

D_m is above the density of the salt water mixture, which is found from:

Density of salt water mixture = (fraction of anhydrous salt in the salt sater mixture based on weight) x (density of anhydrous salt) + (fraction of water in the salt water mixture based on weight) x (density of water).

With the symbols this is:

$$D_m = F_{am} \cdot D_{as} + (1 - F_{am}) \cdot D_{\text{water}} \text{ kg/m}^3 \text{ salt water mixture.}$$

The specific heat of the salt water mixture is found in the following way:

Specific heat of salt water mixture = (fraction of solid phase 7-hydrate in the salt water mixture based on weight) x (specific heat of solid phase 7-hydrate) + (fraction of liquid phase saturated solution based on weight) x (specific heat of saturated solution).

With the symbols this is:

$$C_{mi}(t) = F_{7h}(t) \cdot C_{7h} + (1 - F_{7h}(t)) \cdot C_{ss}.$$

With the salt hydrate data this is:

$$C_{mi}(t) = F_{7h}(t) \cdot C_{7h} + (1 - F_{7h}(t)) \cdot [S_a(t) \cdot C_{as} + (1 - S_a(t)) \cdot C_{\text{water}}]$$

J/ $^\circ\text{C}$ kg salt water mixture.

$t < 35.4^\circ\text{C}$.

The salt water mixture consists of a saturated salt solution, solid phase 12-hydrate crystals formed of the saturated solution and solid phase 7-hydrate crystals, which was already formed at 35.4°C , see figure 8.

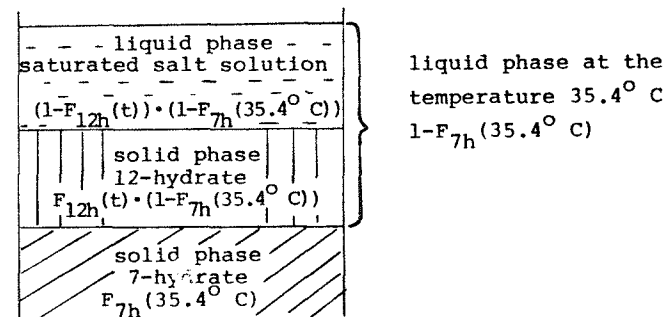


Figure 8. Schematic illustration of the composition of the Na_2HPO_4 -salt water mixture for temperatures t lower than 35.4°C .

As described in section 3.2.1. the fraction based on weight of the 35.4°C -salt solution, which at the temperature t has solidified to 12-hydrate, is found from the following formula:

$$F_{12h}(t) = \frac{0.275 - S_a(t)}{0.40 - S_a(t)}$$

since the fraction based on weight of the anhydrous salt in the 35.4°C -salt solution is 0.275 and in the salt hydrate is 0.40.

The fraction based on weight of the salt water mixture, which changes phase between T_o and t is $(F_{12h}(T_o) - F_{12h}(t)) \cdot (1 - F_{7h}(35.4^\circ\text{C}))$. The heat of fusion situated in the same temperature interval then is $L_{12h} \cdot (F_{12h}(T_o) - F_{12h}(t)) \cdot (1 - F_{7h}(35.4^\circ\text{C})) \cdot \frac{D_m}{10^3} \text{ MJ/m}^3 \text{ salt water mixture.}$

The specific heat of the salt water mixture is found from:
 specific heat of the salt water mixture = (fraction of solid phase 7-hydrate in the salt water mixture based on weight) x (specific heat of solid phase 7-hydrate) + (fraction of solid phase 12-hydrate in the salt water mixture based on weight) x (specific heat of solid phase 12-hydrate) + (fraction of saturated solution in the salt water mixture based on weight) x (specific heat of saturated solution).

With the symbols this is:

$$C_{ml}(t) = F_{7h}(35.4^\circ \text{C}) \cdot C_{7h} + F_{12h}(t) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot C_{12h} + (1 - F_{12h}(t)) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot C_{ss} = F_{7h}(35.4^\circ \text{C}) \cdot C_{7h} + F_{12h}(t) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot C_{12h} + (1 - F_{12h}(t)) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot [S_a(t) \cdot C_{as} + (1 - S_a(t)) \cdot C_{water}] \text{ J/}^\circ \text{C kg salt water mixture.}$$

4.2.3. Total storage capacity.

The storage capacity of the salt water mixture at the temperature $T_o < 35.4^\circ \text{C}$ is fixed to 0. At a higher temperature t the storage capacity per m^3 salt water mixture is calculated as follows:

Storage capacity = latent heat + sensible heat.

With the symbols this is:

For $t < 35.4^\circ \text{C}$:

$$Q_s = L_{12h} \cdot (F_{12h}(T_o) - F_{12h}(t)) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot \frac{D_m}{10^3} + \int_{T_o}^t C_{ml}(t) \cdot \frac{D_m}{10^6} dt \text{ MJ/m}^3$$

For $35.4^\circ \text{C} < t < T_s$:

$$Q_s = L_{12h} \cdot F_{12h}(T_o) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot \frac{D_m}{10^3} + L_{7h} \cdot (F_{7h}(35.4^\circ \text{C}) - F_{7h}(t)) \cdot \frac{D_m}{10^3} + \int_{T_o}^{35.4^\circ \text{C}} C_{ml}(t) \cdot \frac{D_m}{10^6} dt + \int_{35.4^\circ \text{C}}^t C_{ml}(t) \cdot \frac{D_m}{10^6} dt \text{ MJ/m}^3$$

For $t > T_s$:

$$Q_s = L_{12h} \cdot F_{12h}(T_o) \cdot (1 - F_{7h}(35.4^\circ \text{C})) \cdot \frac{D_m}{10^3} + L_{7h} \cdot F_{7h}(35.4^\circ \text{C}) \cdot \frac{D_m}{10^3} + \int_{T_o}^{35.4^\circ \text{C}} C_{ml}(t) \cdot \frac{D_m}{10^6} dt + \int_{35.4^\circ \text{C}}^{T_s} C_{ml}(t) \cdot \frac{D_m}{10^6} dt + \int_{T_s}^t C_{mh} \cdot \frac{D_m}{10^6} dt \text{ MJ/m}^3$$

Using the above formula it is possible to calculate the storage capacity of the salt water mixture at any temperature t .

4.3. Results

With the data given in table 1 and the values $C_{water} = 4180 \text{ J/}^\circ \text{C kg}$ and $D_{water} = 985 \text{ kg/m}^3$ the storage capacity was calculated with the computer program using $T_o = 0^\circ \text{C}$ and $F_{am} = 0.40$, since the salt hydrate, which is commodity has $F_{am} = 0.40$. The result is shown in table 7 and in figure 9, where the heat capacity is shown for both the mentioned assumptions. For temperatures higher than 35.4°C the heat capacity is the same for both assumptions, and the difference of the curves is obtained for temperatures lower than 35.4°C .

Temperature °C	Sensible heat MJ/m ³	Latent heat MJ/m ³	Total heat MJ/m ³
0	0	0	0
2.0	5.9	0.4	6.4
4.0	11.9	1.0	12.8
6.0	17.8	1.6	19.4
8.0	23.8	2.4	26.2
10.0	29.7	3.3	33.1
12.0	35.7	4.5	40.2
14.0	41.7	5.9	47.6
16.0	47.7	7.7	55.4
18.0	53.7	10.0	63.7
20.0	59.8	12.8	72.6
22.0	65.9	16.4	82.3
24.0	72.0	21.2	93.2
26.0	78.2	27.6	105.8
28.0	84.5	36.4	121.0
30.0	90.9	49.4	140.3
32.0	97.5	69.7	167.2
34.0	104.5	105.1	209.5
36.0	111.9	151.5	263.5
38.0	119.7	162.7	282.5
40.0	127.8	177.5	305.3
42.0	136.2	197.8	334.0
44.0	145.1	227.2	372.3
46.0	152.4	248.8	401.3
48.0	162.0	248.8	410.8
50.0	171.5	248.8	420.3
52.0	181.1	248.8	429.9
54.0	190.6	248.8	439.4
56.0	200.1	248.8	449.0
58.0	209.7	248.8	458.5
60.0	219.2	248.8	468.0
62.0	228.8	248.8	477.6
64.0	238.3	248.8	487.1
66.0	247.8	248.8	496.6
68.0	257.4	248.8	506.2
70.0	266.9	248.8	515.7
72.0	276.4	248.8	525.3
74.0	286.0	248.8	534.8
76.0	295.5	248.8	544.3
78.0	305.1	248.8	553.9
80.0	314.6	248.8	563.4
82.0	324.1	248.8	572.9
84.0	333.7	248.8	582.5
86.0	343.2	248.8	592.0
88.0	352.7	248.8	601.6
90.0	362.3	248.8	611.1
92.0	371.8	248.8	620.6
94.0	381.4	248.8	630.2
96.0	390.9	248.8	639.7
98.0	400.4	248.8	649.3
100.0	410.0	248.8	658.8

Table 7. Storage capacity of Na_2HPO_4 -salt water mixture with $F_{\text{am}} = 0.40$ and the assumption, that both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ are formed during cooling.

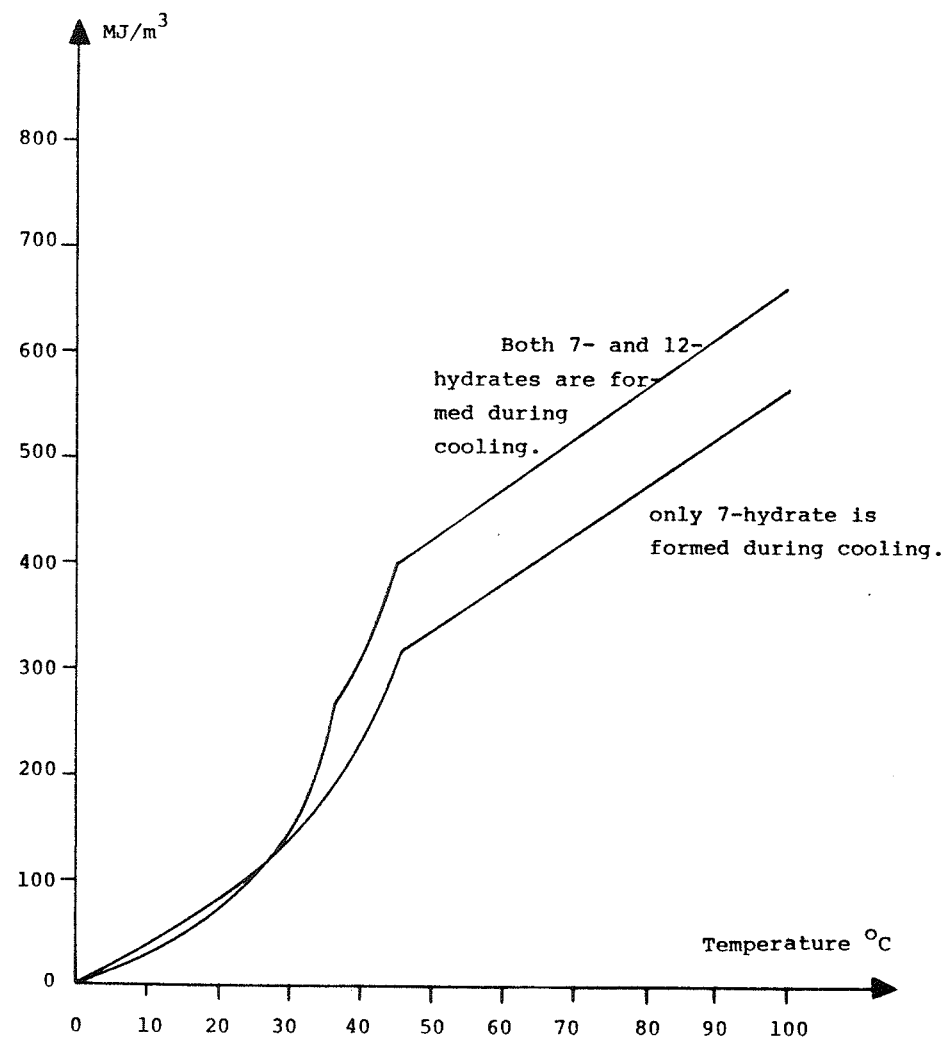


Figure 9. Heat capacity of Na_2HPO_4 -salt water mixtures with $F_{\text{am}} = 0.40$ for two different assumptions concerning the solidification.

EXPERIMENTS WITH THE SELECTED SALT
WATER MIXTURES AS STORAGE MEDIUM

PART 4 OF REPORT ON
HEAT STORAGE IN A SOLAR HEATING SYSTEM
USING SALT HYDRATES

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Heat storage in a solar heating system using salt hydrates.

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1. INTRODUCTION

This report is part 4 of the final report on the research project no. 140 - 76 ESDK, Heat storage in a solar heating system using salt hydrates, which financially is supported by the European Community.

The aim of the project is to investigate a new method by which a heat storage based on an incongruently melting salt hydrate will work stably. Before describing this method some of the used expressions shall be explained.

Salt hydrate is the anhydrous salt with its corresponding crystal water. The expression is used for both the solid and the liquid phase.

Incongruently melting salt hydrate is a salt hydrate with an anhydrous salt which can not be dissolved completely in its corresponding crystal water at the melting point.

Salt water mixture is the salt hydrate with at least so much water added, that the anhydrous salt is completely dissolved at the melting point.

When an incongruently melting salt hydrate is melted the undissolved fraction of the anhydrous salt will form a layer at the bottom of the container. In the solidification part of a cycle this layer will not for normal container dimensions come in contact with the water, and it will therefore not work actively. This phase separation will in a few cycles diminish the performance of the heat storage.

The investigated method is mainly used to avoid the phase separation. It consists of adding so much extra water to the salt hydrate that all the anhydrous salt dissolves in the water. In order to secure that phase separation is avoided a soft stirring of the mixture is necessary.

The solidification will take place by decreasing temperature since crystallization only can take place from a saturated solution and the solubility of the anhydrous salt decreases at decreasing temperature.

The aim of this part of the report is to describe the experiments, which were carried out with the selected salt water mixtures in a heat storage system with oil as the heat transfer fluid in direct contact with the salt water mixture.

2. PERFORMANCE OF THE STORAGE SYSTEM.

The storage system, which was selected for the experiments was the system with heat exchange oil as the heat transfer fluid in direct contact with the salt water mixture. The oil is conducted in a pipe to the bottom of the container and through a nozzle system to the salt water mixture. Since there will always be a liquid phase in the mixture the oil will always be able to find its way to the top of the container, where the immiscible oil will form a layer. The oil drops take care of the stirring, and the stirring prevents strong supercooling.

3. PRELIMINARY EXPERIMENTS WITH THE STORAGE SYSTEM AND THE SELECTED SALT HYDRATES.

3.1. Experiments with the storage system.

Experiments with the storage system described above were carried out with a container in the size 14 l. In order to find a heat exchange oil, which was suitable for the experiments, different mineral heat exchange oils with low viscosity were examined in the arrangement with water instead of a salt water mixture as the heat storage medium. The different oils had different tendency to form a layer of emulsion with the water. This emulsion must be avoided, and the heat exchange oil: Gilotherm D12 from the Rhone-Poulenc Industries with excellent specific heat and viscosity properties had no tendency to emulsion at all, so this oil was selected for the experiments.

With this oil the storage system was examined in the arrangement mentioned above. When the oil continuously is circulated no blocking of the nozzles will occur for normal salt water mixtures, not even by strong cooling to low temperatures.

If the circulation of the oil is stopped at a low temperature for a long period of time the salt water mixture will have time to form a block of solid salt hydrate, so that the nozzles will be blocked. The oil is not able to enter the storage by an attempt to start the circulation of the oil if there have been no circulation in a long period of time due to this solid block in the nozzles.

The above mentioned experiences concerning the nozzle system resulted in a new improvement of the inlet system. In figure 1 the system is schematically shown. Using this system no blocking problems will occur, not even after a long period of time without circulation of oil. If any salt hydrate crystals are blocking the nozzles circulation of warm oil in the inside pipe melts these crystals so that circulation through the salt water mixture again will be possible. During the time of melting these crystals the oil is conducted to the salt water mixture from the top of the container as shown in figure 1 resulting in a poorer heat transfer from the oil to the storage. On the other hand the system will work stably and safely.

In order to diminish the salt content in the circulated oil the outlet system, that is the system, where the oil is conducted from the top layer of the container to the pipe system, is formed in such a way, that there only will be pumped from the stationary upper part of the oil layer.

3.2. Solubilities of salt hydrates in Gilotherm D12 heat exchange oil.

The solubility of the salt on the heat exchange oil should be as little as possible in order to avoid salt in the pipe system. In order to obtain an estimate of the solubilities of the salt hydrates in the heat exchange oil, experiments were carried out by the chemical consultant Erik Pedersen. These experiments are described by Erik Pedersen in this section.

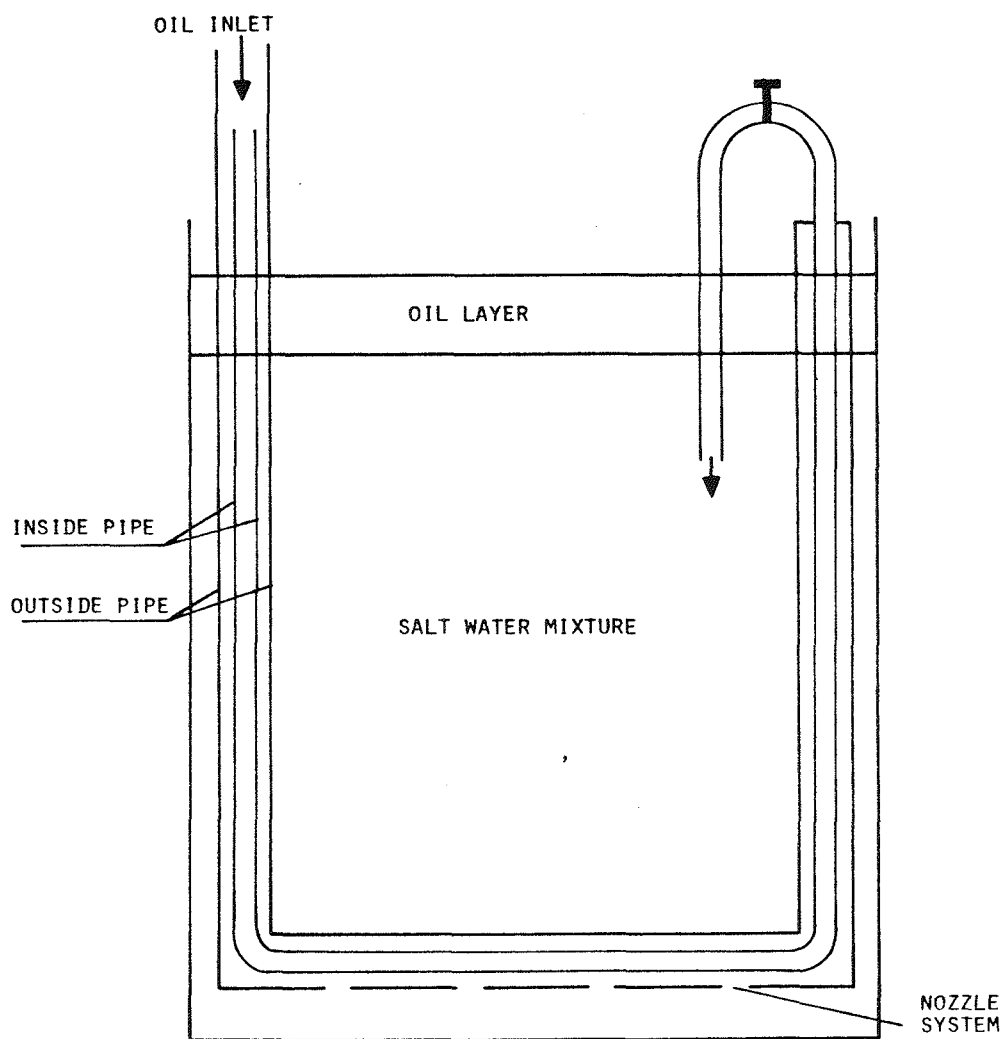


Figure 1. Schematic illustration of the inlet system.

The following four mixtures of salts and water have been used as heat storage materials in direct contact with the heat exchange oil "Gilotherm D 12".

Salt/water mixture	Weight-% anhydrous salt
$\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$	0.33
$\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$	0.33
$\text{Na}_2\text{HPO}_4/\text{H}_2\text{O}$	0.40
$\text{NaCH}_3\text{COO}/\text{H}_2\text{O}$	0.58

A combination of high solubilities and large solubility vs. temperature coefficients will result in rapid crystallization of salt in the heat exchanger.

"Gilotherm D12" (Rhone-Poulenc Industries) is a mixture of aliphatic hydrocarbons with an average molecular weight of 170. The solubilities of the salts mentioned above were therefore expected to be very small. Trace analyses were therefore first performed.

The salt/water mixtures were vigorously stirred with the oil for 8 hours at 25° C and 70° C (corresponding to partly solid and melted salt/water mixtures, respectively). The following phase separation occurred rapidly. There was no evidence of formation of suspensions or emulsions. 10 ml samples of the oil were evaporated to dryness and tested in the following ways:

Test for sulfate: Precipitation of BaSO_4 in the presence of MnO^- .

Test for carbonate: Conversion to CO_2 and decolorization of carbonate solution containing phenolphthalein.

Test for phosphate: Oxidation of benzidine by phosphomolybdate.

Test for acetate: Conversion to hydroxamic acid and colour reaction with Fe^{3+} .

All tests were negative. The identification limits of the reactions were determined with standard solutions. The results were: Sulfate 10^{-8} mol, carbonate 10^{-7} mol, phosphate $5 \cdot 10^{-10}$ mol, and acetate $2 \cdot 10^{-7}$ mol. These results agree well with

F. Feigl: Spot Tests in Inorganic Analysis, Elsevier 1958,
and F. Feigl: Manual of Spot Tests, A.p. 1943.

On this basis we reached the following conclusions about
upper limits of solubilities:

Salt	Solubilities at 25° C and 70° C			
$\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$	less than 140 μg Na_2SO_4 per liter			
$\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$	-	-	1 mg Na_2CO_3	-
$\text{Na}_2\text{HPO}_4/\text{H}_2\text{O}$	-	-	7 μg Na_2HPO_4	-
$\text{NaCH}_3\text{COO}/\text{H}_2\text{O}$	-	-	2 mg NaCH_3COO	-

3.3. Experiences with the salt water mixtures.

Experiments with salt water mixtures consisting of the selected salt hydrates, see part 2 of the report, with additional water were carried out. The container was in the size 14 l, and the aim of these experiments was to examine the problems occurring by the use of the different salt water mixtures in the heat storage.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ water mixture.

The fraction based on weight of the anhydrous salt in the salt water mixture, which was examined, was 0.33. As the solidification takes place crystal particles of loose consistency are formed. The crystal don't grow as one big block but settles as crystal particles of very small size. This is very favourable since the jet of oil, which is conducted through the nozzles to the salt water mixture easily is able to sweep away the salt hydrate crystal particles, so that the salt water mixture consists of a lot of small crystal particles drifting in the water. With such a progress of the solidification no heat transfer problems occur.

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ water mixture.

The fraction of the anhydrous salt in the salt water mixture based on weight was 0.33. During solidification the crystals have a tendency to form large solid blocks at calm places in the storage container. The oil makes at low temperatures its way to the top of the container through channels in these solid blocks. Since the solid phase salt hydrates have poor thermal conductivity, the heat transfer to and from the storage therefore will be poor.

Na_2HPO_4 water mixtures.

2 different salt water mixtures were examined. The fraction of anhydrous salt in the salt water mixture based on weight was 0.40 respectively 0.27. The salt water mixture with the great amount of anhydrous salt forms in the start of the solidification $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ crystals while the other salt water mixture only forms $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystals.

Unfortunately the $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ crystals have a strong tendency to block the nozzles even when oil is circulated in the pipes. The salt hydrate is first formed at the coldest places around the inlet system and in the nozzles. The heat transfer for storage temperatures lower than the start solidification temperature is poor since the oil only is circulated in the inside pipe with no direct contact between oil drops and salt water mixture. Salt water mixtures, where $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ is formed during cooling therefore will not be suitable in connection with the selected storage system.

For salt water mixtures where only $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ is formed during cooling the solidification behaves in the same manner as the solidification for sodium sulfate mixtures, which is favourable.

$\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ water mixture.

The fraction of the anhydrous salt in the salt water mixture based on weight was supposed to be 0.58. Unfortunately the bought salt hydrate was not crystalline, and the fraction of water in the salt hydrate had neither the supposed value nor a constant value for all deliveries. Therefore the right fraction of anhydrous salt in the salt water mixture was not obtained, anhydrous salt floated up in the oil layer and formed in connection with the oil a layer of mush which made the oil circulation in the pipes impossible. For this reason no measurements of the storage capacity were carried out in the small scale experiments described in section 4.

4. SMALL SCALE EXPERIMENTS

4.1. Aim of the experiments.

The aim of these experiments is to test the storage system using a salt water mixture as storage medium and a heat exchange oil as transfer fluid in a realistic small scale heat storage. The storage capacities of the selected salt water mixtures will be found in short term experiments by means of measurements, and they will be compared with the theoretically calculated storage capacities. Experiences concerning the construction of a full scale heat storage will be obtained.

4.2. Arrangement

The arrangement is shown schematically in figure 2. Each part of the arrangement will be described in the following.

The container consists of an inside polyethylen container and an outside steel container. The container is cylindrical, and the amount of the container is approximately 0.2 m^3 . The container is insulated with 5 cm of mineral wool all over the surface of the container.

The pump, which circulates the oil is a motor pump unit with nitrile impellers, which by rotation carries the liquid through the pump. The pump can be used for many different liquids.

The heating element is placed inside the pipe. The power of the heating element is of the amount of 1600 W. The temperature of the oil increases as it streams along the heating element. The power of the heating element is measured with a kWh-recorder and a stop-watch for each cooling or heating part of a cycle.

The heat exchanger is a common heat exchanger, which usually is used in connection with district heating. Flowing through this the oil can both be warmed up or cooled as hot or cold water is led to the heat exchanger.

The pipe system consists mostly of stainless steel of different dimensions. The system of pipes is insulated in order to

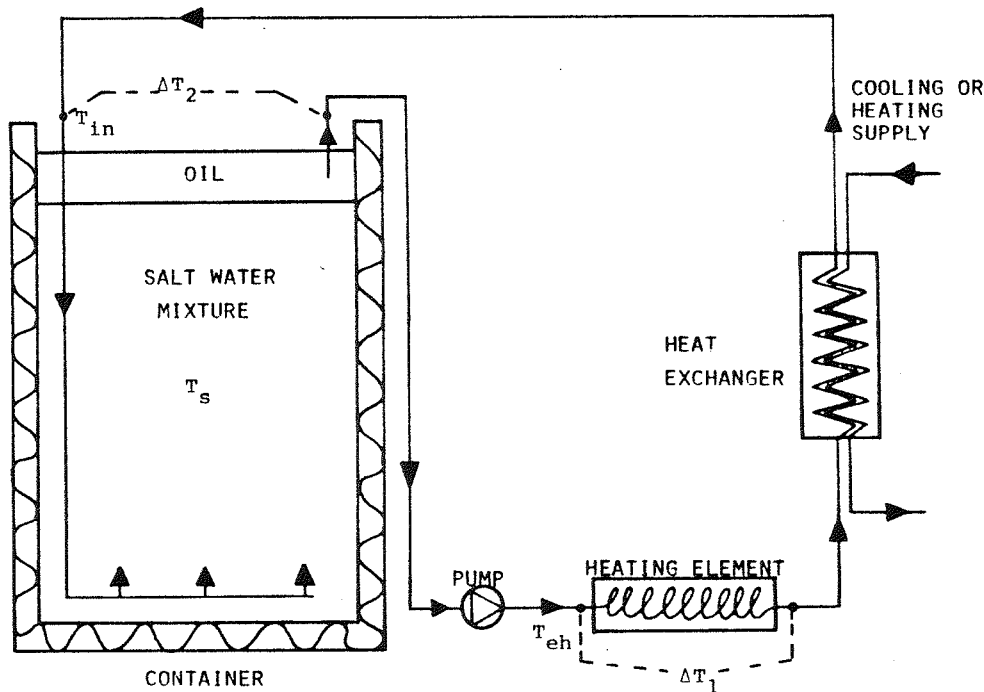


Figure 2. Schematic illustration of the arrangement with the pipe system. The measured temperatures and differences in temperatures are given.

minimize thermal losses.

The fundamental performance of the inlet system is described in section 3.1. Both the inside and the outside pipes are made of copper. Through 6 holes in the outside pipe the oil is conducted to the container. Each hole has the diameter size 2 mm. The holes are placed in such a way, that the jet of oil is pointing obliquely downwards in such a way, that the stirring is as effective as possible. The inside pipe is kept away from the holes with small screws.

Temperature measurements are made by use of Cu/Ko-thermoelements, and a 6-channel recorder. The temperature is measured in 3 levels of the salt water mixture, in the oil entering the heating element and in the oil entering the storage. Furthermore the temperature on the outside of the insulation of the container is measured. 2 temperature differences are measured with Cu/Ko-thermopiles and a 2-channel recorder. The temperature difference across the heating element is measured in order to calculate the flow of the oil. Also the temperature difference between oil entering and leaving the heat storage is measured in order to calculate the heat transferred to or from the heat storage. Figures 3-11 show photoes of the arrangement.

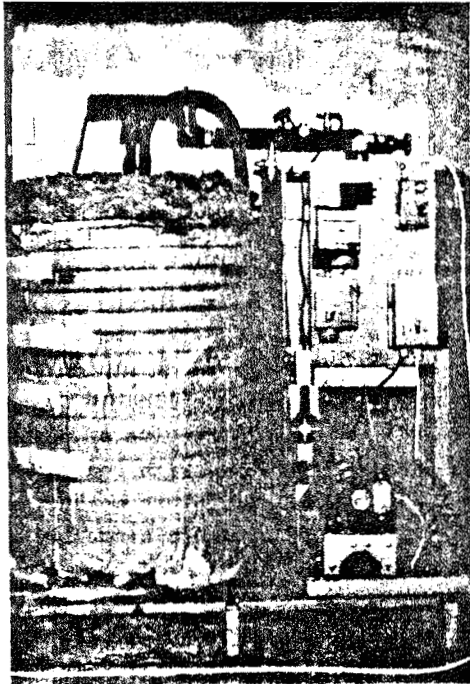
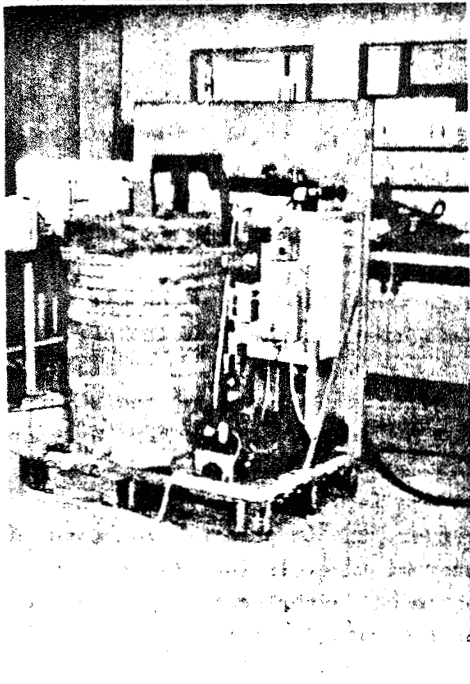


Figure 3 and 4. The arrangement of the experiments. The heat storage container and the pipe system from long and short distance.

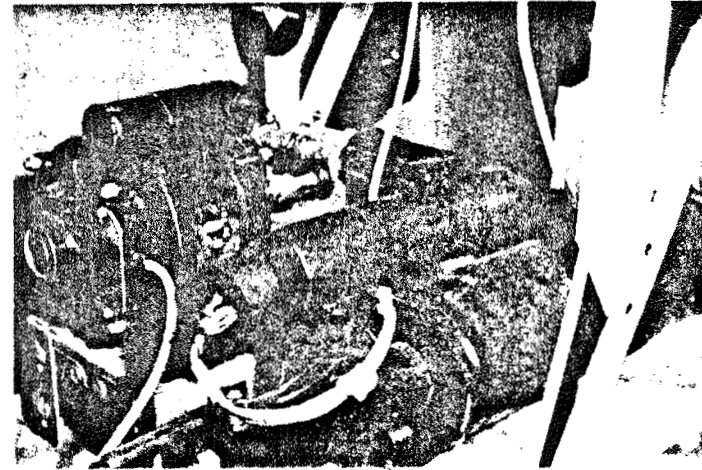


Figure 6. Pump and heating element. In the front also a part of the arrangement used for measuring the temperature of the oil entering the pipe, in which the heating element is situated, is shown.

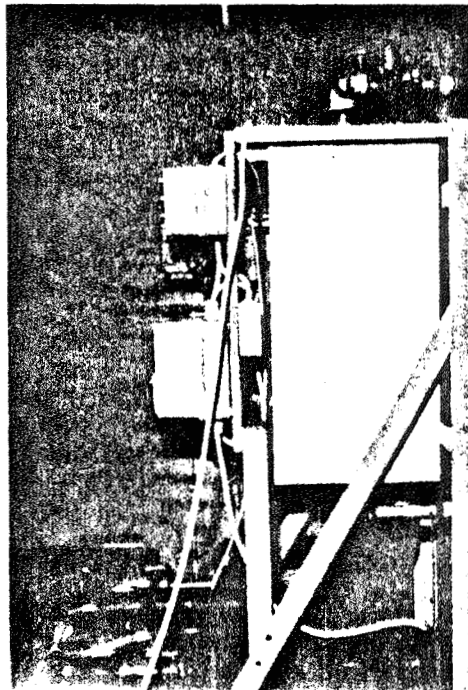


Figure 5. Arrangement seen from the side. The heat exchanger is seen in the front.



Figure 7. Pump and heating element. The heating element is placed in the front.



Figure 8. The inlet system. The oil can be conducted to the top of the container through the inside pipe.

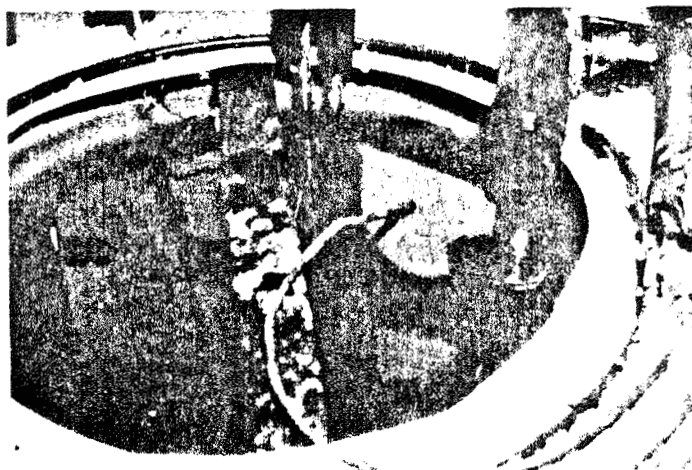


Figure 9. Top of the container. View in the top of the container with the insulation removed with the oil layer. The inside pipe, through which the oil is conducted to the top of the container, is seen. Also the outlet system is seen to the right.



Figure 10. Inside of the container. View from the top inside the container. In the bottom of the container the inlet system is seen. The thermoelements are situated in the container at a bar of wood.

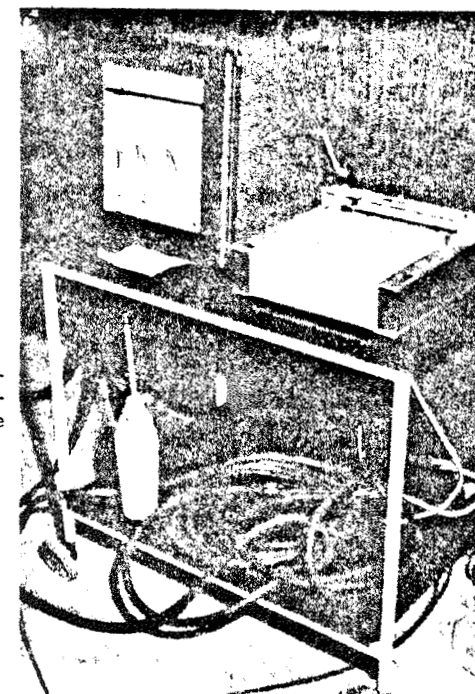


Figure 11. Recorders. The temperatures and temperature differences are measured with the recorders.

4.3. Measurements.

4.3.1. Definition of used symbols.

- T_s : Temperature of the salt water mixture with the unit $^{\circ}\text{C}$.
- T_a : Temperature on the outside surface of the insulation of the container with the unit $^{\circ}\text{C}$.
- T_{in} : Temperature of the oil entering the heat storage with the unit $^{\circ}\text{C}$.
- T_{eh} : Temperature of the oil entering the heating element with the unit $^{\circ}\text{C}$.
- ΔT_1 : Temperature difference of the oil across the heating element with the unit $^{\circ}\text{C}$.
- ΔT_2 : Temperature difference of the oil entering and leaving the heat storage with the unit $^{\circ}\text{C}$.
- Q_p : The power of the heating element with the unit W.
- ρ_{oil} : Density of the heat exchange oil, Gilotherm D 12, with the unit kg/m^3 .
- C_{oil} : Specific heat of the heat exchange oil, Gilotherm D 12, with the unit $\text{J}/\text{kg } ^{\circ}\text{C}$.
- \dot{m} : The oil flow in the pipes with the unit m^3/s .
- Q_{loss} : Thermal loss from storage container with the unit W.
- Q_t : The power, which is transferred to or from the storage with the unit W.
- Q_s : Storage capacity of the storage material with the unit Wh.
- τ : Time with the unit h.
- ΔQ_s : Increase in storage capacity with the unit Wh.
- $\Delta \tau$: Increase in time with the unit h.

4.3.2. Thermal loss from container.

The container is cylindrical with the diameter 58 cm and the height 87 cm. 5 cm mineral wool insulation is situated around the container. The thermal loss from the container is calculated as:

$$Q_{loss} = 1.9 \cdot (T_s - T_a) \text{ W.}$$

In order to measure the thermal loss an experiment with 190 kg water in the container was carried out. The content was warmed up to 45°C , and the temperatures were measured during 15 hours without circulation of oil. During this time the average temperature difference $T_s - T_a$ was 19.7°C , and the decrease in the temperature of the water was 2.7°C . With $4180 \text{ J}/\text{kg } ^{\circ}\text{C}$ as the specific heat for water the thermal loss is found from:

$$Q_{loss} = 2.7^{\circ}\text{C} \cdot 190 \text{ kg} \cdot 4180 \text{ J}/\text{kg } ^{\circ}\text{C} \cdot \frac{1}{15 \cdot 3600 \text{ s}} = 39.7 \text{ W.}$$

Since the average temperature difference $T_s - T_a$ is equal 19.7°C , the thermal loss is measured as:

$$Q_{loss} = \frac{39.7}{19.7} (T_s - T_a) = 2.0 (T_s - T_a) \text{ W.}$$

This is in good agreement with the theoretically calculated thermal loss, and therefore the above formula is used in the following.

4.3.3. Method for calculation of the storage capacity of the storage medium.

The oil flow in the pipe system is found in the following way. All the power Q_p , which is given off from the heating element, is assumed to be absorbed of the oil resulting in the increase ΔT_1 in the oil temperature across the heating element. This gives with the symbols:

$$Q_p = \dot{m} \cdot C_{oil} \cdot \rho_{oil} \cdot \Delta T_1$$

Rearranging this equation the oil flow is found from:

$$\dot{m} = \frac{Q_p}{C_{oil} \cdot \rho_{oil} \cdot \Delta T_1} \text{ m}^3/\text{s}.$$

The power, which either is removed from or added to the heat storage, Q_t is found from

$$Q_t = \dot{m} \cdot C_{oil} \cdot \rho_{oil} \cdot \Delta T_2 \text{ W}.$$

The density ρ_{oil} and the specific heat C_{oil} of Gilotherm D12 are changing with the temperature, see figure 12 and 13. Since the temperature of the oil in the heating element not is equal the temperature in the storage ρ_{oil} and C_{oil} therefore have not the same values in the 2 formulas above.

Both ΔT_2 and Q_t can both be positive and negative as both warming and cooling of the heat storage can take place.

The energy balance for the heat storage is, using the storage capacity of the storage Q_s :

$$\frac{dQ_s}{d\tau} = Q_t - 2.0 \cdot (T_s - T_a)$$

For a finite increment in time the equation can be rewritten as:

$$\Delta Q_s = Q_t \cdot \Delta \tau - 2 \cdot (T_s - T_a) \cdot \Delta \tau$$

Using the above formula the storage capacity at different storage temperatures can be found when the temperature in the storage medium is measured at the same time. The storage capacity of the storage is with a reasonable assumption equal the storage capacity of the heat storage material.

In order to obtain correct measurements of the temperature in the salt water mixture 3 thermoelements as mentioned were placed in 3 different levels in the storage container. During the cooling period the temperature will not be the same in all the levels due to differences in the progress of the solidi-

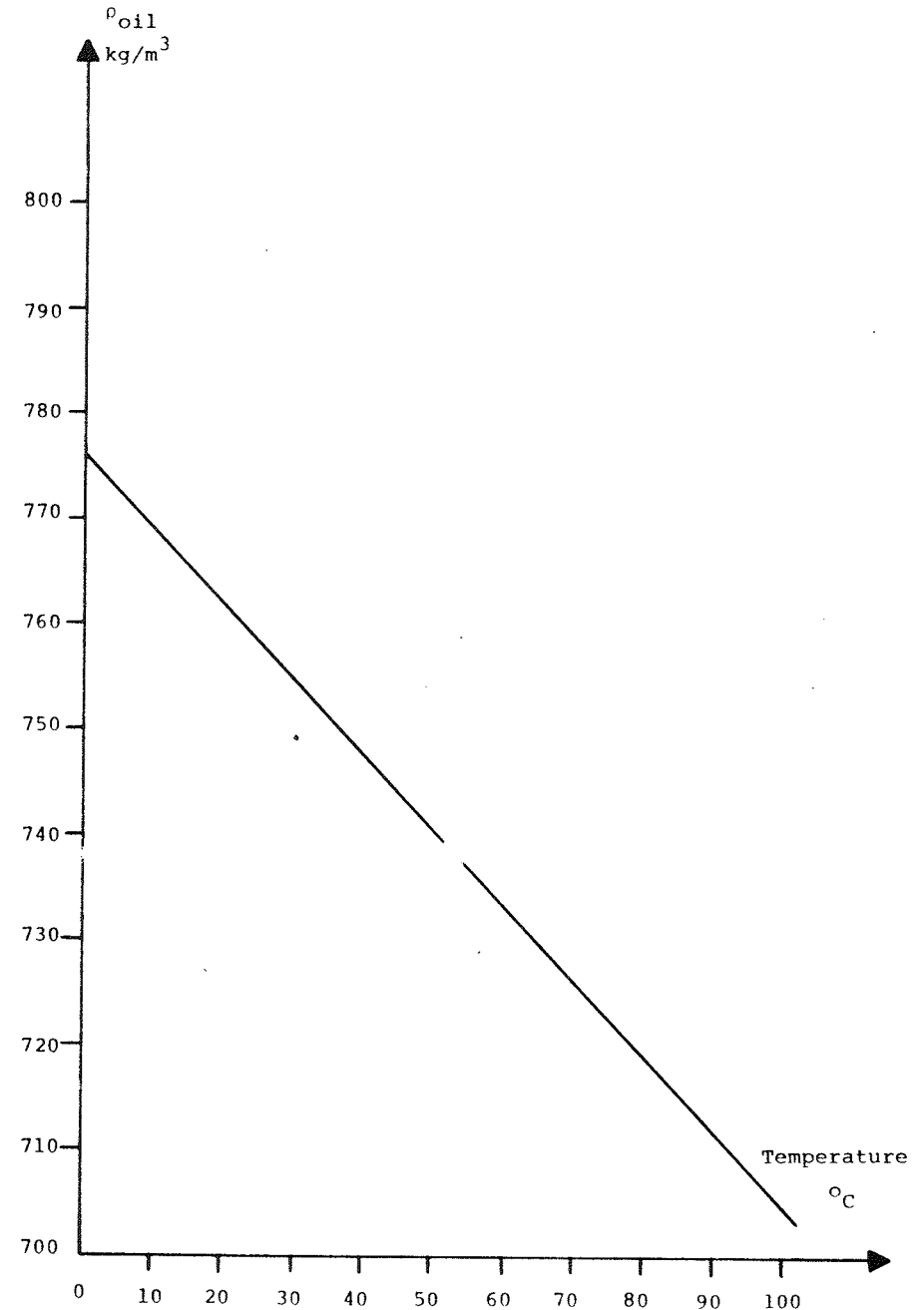


Figure 12. Density of Gilotherm D12 versus temperature.

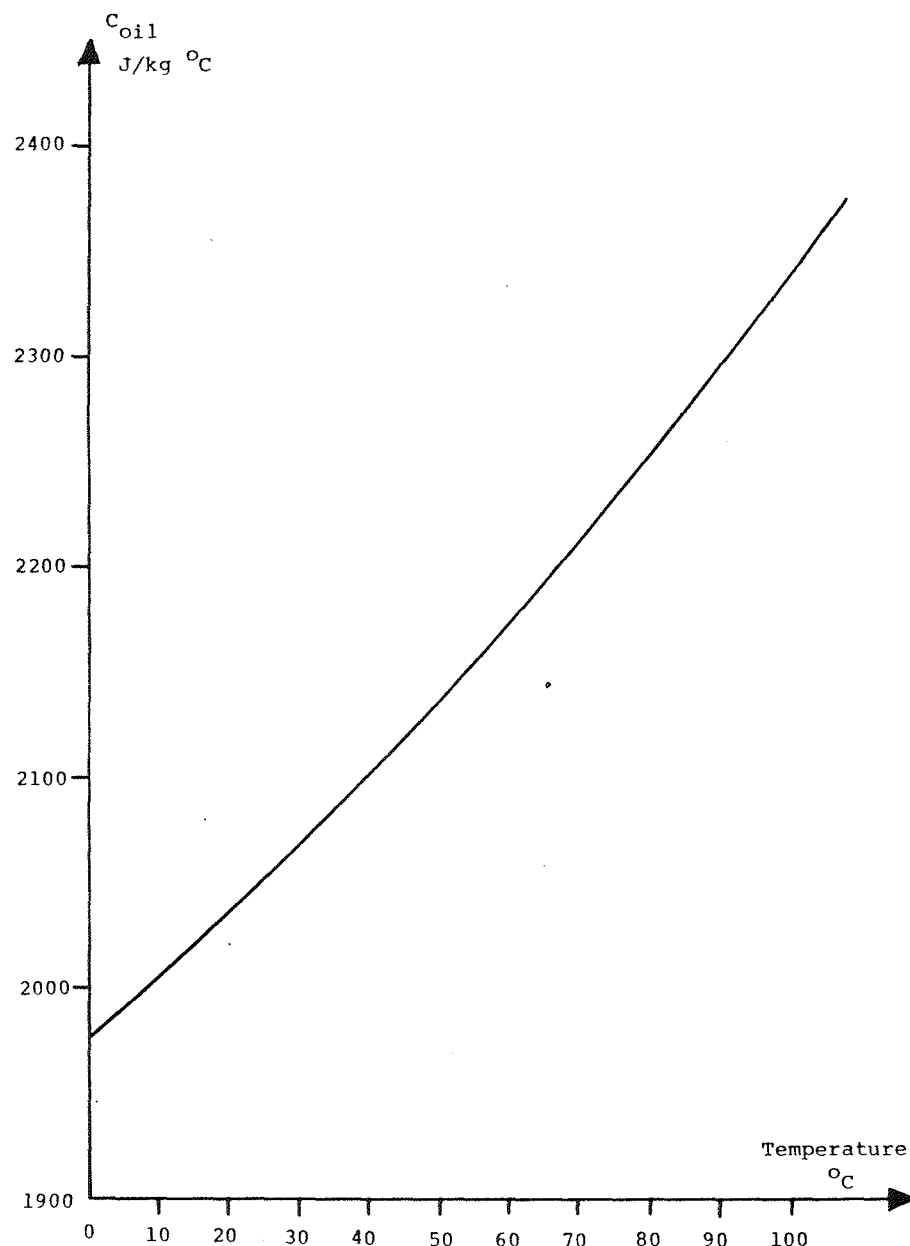


Figure 13. Specific heat of Gilotherm D12 versus temperature.

fication, local formation of salt hydrate crystals with a small thermal conductivity and so on. These differences in temperature must be equalized in order to obtain correct measurements of the temperature. Therefore the oil after a period of cooling or heating is circulated in the pipe system without heating or cooling until all temperature measurements show the same result. First then the temperature measurement of the salt water mixture is reliable.

Using the formulas described in this section the storage capacities of the salt water mixtures in different temperature intervals were measured.

4.4. Results.

4.4.1. Experiences with the storage system.

The extra water principle worked in such a way, that no decrease in the storage capacity of the salt water mixture after a few heating/cooling-cycles for all the examined salt hydrates was observed.

The nozzle system with an inside and an outside pipe worked as planned, that is the oil could always be circulated, also after a long period of time without circulation at a low temperature. In other words the oil could be circulated through the inside pipe and only a short period of time was necessary before the nozzles would work again.

The supercooling was planned to be prevented by means of the stirring, which was produced by the oil drops penetrating through the salt water mixture. The supercooling for some of the salt hydrates seems, however, to be so strong, that this stirring is not enough to eliminate supercooling totally.

The heat transfer was excellent as long as no solid blocks of salt hydrate were formed. This can in an actual heat storage be prevented by making the nozzle system more branching in such a way, that it will cover all the ground area of the heat storage container.

Another problem which must be solved is to avoid salt in the

pipe system. At low temperatures without circulation the salt in the pipes will solidify and form blocks. The solubility of the salt in the oil is small, see section 3.2. Therefore it is possible to avoid great amounts of salt in the pipes if the outlet system is formed in such a way, that only stationary oil without salt in excess is taken in the pipe system. This can be done by placing the outlet system in the top of a high layer of oil. This high layer of oil does not necessarily mean that the amount of oil is increased. For instance the container can grow narrow in the top. Another possibility is in the outlet system to put a filter, which prevents salt in entering the pipe system, but using this method cleaning of the filter is necessary from time to time.

4.4.2. Measured storage capacities of the salt water mixtures.

The experiments were carried out with the 4 salt water mixtures, which are given in table 1.

anhydrous salt	fraction of anhydrous salt in the salt water mixture based on weight	amount of salt water mixture kg
Na_2SO_4	0.33	240
Na_2CO_3	0.33	250
Na_2HPO_4	0.40	170
Na_2HPO_4	0.27	220

Table 1. Salt water mixtures examined by experiments.

A number of heating/cooling cycles was carried out for each salt water mixture, and the storage capacity in different tem-

perature intervals was measured and calculated as described in section 4.3.3. The behaviour of the solidification was as described in section 3.3. The results of the measurements are mentioned in the following for each salt water mixture.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ water mixture.

4 heating/cooling cycles without additional borax were carried out. The supercooling in the cooling part of these cycles varied from 1.0°C to 8.8°C . The highest temperature, where the solidification took place varied from 31.6°C to 31.9°C .

With the same mixture and 240 g borax, that is 1 o/oo added to the salt water mixture, a cycle was carried out. For this cycle no supercooling occurred, and the start solidification temperature was 32.0°C .

The results of the measurements are given in table 2.

cooling/ heating	temperature interval $^\circ\text{C}$	storage capacity		
		measured Wh	calculated Wh	$\frac{\text{measured}}{\text{calculated}}$
cooling	40.5 - 25.1	10800	11800	0.92
heating	24.3 - 46.8	12890	13440	0.96
cooling	36.6 - 22.0	11900	12640	0.94
heating	22.0 - 41.0	12890	13540	0.95
cooling	41.0 - 28.8	8020	8440	0.95
heating	28.4 - 44.3	9670	9580	1.01
cooling	42.0 - 27.4	9810	9820	1.00
heating	26.2 - 43.6	11370	11390	1.00
cooling*	43.6 - 27.7	9960	10070	0.99
heating	28.1 - 43.8	9750	9700	1.00

Table 2. Storage capacity of the 240 kg Na_2SO_4 salt water mixture.

*1 o/oo borax added to the salt water mixture.

The measured storage capacities are in good agreement with the in part 3 of the report calculated storage capacities. The solidification progress is favourable, see section 3.3, and the salt water mixture and the storage system seem in all ways to act as planned.

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ water mixture.

For this salt water mixture supercooling was not prevented by means of the stirring produced by the oil drops. A number of heating/cooling cycles was carried out, and the supercooling varied from 0.5°C to 2.8°C . Unfortunately supercooling seemed to have the influence on the salt water mixture, that the temperature of the mixture varied in steps during the cooling progress. The temperature increased suddenly after a period of cooling with a uniform decrease in temperature. This process was during the cooling progress repeated several times, and therefore the result of the measurements of the temperature and with that the measurements of the storage capacity were very doubtful. In these cycles the highest temperature, where solidification took place, varied from 30.4°C to 32.1°C .

In order to obtain reliable measurements 3 heating/cooling cycles, where a few salt hydrate crystals were added to the mixture at the melting point during the cooling parts of the cycles, were carried out. This prevented supercooling effectively, and a uniform and calm progress of the decrease in temperature resulted, so that correct measurements were obtained. In these cycles the start solidification temperature varied from 32.6°C to 33.1°C . The result of these measurements are shown in table 3.

cooling/ heating	temperature interval $^\circ\text{C}$	storage capacity		
		measured Wh	calculated Wh	measured calculated
cooling	37.1 - 27.9	11710	12150	0.96
heating	27.8 - 38.8	12370	12610	0.98
cooling	36.0 - 27.2	12790	12550	1.02
heating	27.2 - 36.4	11080	12640	0.88
cooling	36.4 - 29.4	10350	10750	0.96
heating	29.4 - 42.2	10650	12020	0.89

Table 3. Storage capacity of the 250 kg Na_2CO_3 salt water mixture.

The measured storage capacities are a little lower than the storage capacities calculated in part 3 of this report. The solidification progress is not as favourable as for the sodium sulfate mixture, see section 3.3.

Na_2HPO_4 water mixtures.

Salt water mixtures with 0.40 and 0.27 as the fraction of anhydrous salt in the salt water mixture based on weight were examined in the storage.

As mentioned in section 3.3 the salt water mixture with 0.40 as the fraction of anhydrous salt in the salt water mixture based on weight would form $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ crystals in the nozzles during cooling resulting in a poor heat transfer. Nevertheless a heating/cooling cycle was carried out in order to examine the behaviour of the solidification, that is if only $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ crystals or both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystals are formed during cooling. No supercooling occurred, and the results are given in table 4, where also the storage capacities calculated in part 3 of this report for the two different assumptions are given.

cooling/ heating	temperature interval °C	storage capacity		
		measured Wh	calculated Wh *	calculated Wh **
cooling	50.0 - 32.1	9080	7600	5630
heating	32.1 - 48.1	8550	7310	5350

Table 4. Storage capacity of 170 kg Na_2HPO_4 salt water mixture with 0.40 as the fraction of anhydrous salt in the salt water mixture based on weight.

* Both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystals are formed during cooling

** Only $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ crystals are formed during cooling.

The results show, that both $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystals are formed during cooling.

The measured storage capacities are a little greater than the calculated storage capacities, that is the heats of fusion could be a little greater than the values, which were used for the calculation. Due to the poor heat transfer the salt water mixture must be left out in connection with the selected storage system.

The salt water mixture with 0.27 as the fraction of anhydrous salt in the salt water mixture based on weight was examined too. Only $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystals are formed during solidification. No supercooling occurred, and the start solidification temperature varied from 34.9°C to 35.1°C . The measured storage capacities are given in table 5.

cooling/ heating	temperature interval °C	storage capacity		
		measured Wh	calculated Wh	measured calculated
cooling	51.3 - 30.0	13070	11110	1.18
heating	30.0 - 38.2	9560	8390	1.14
cooling	36.3 - 30.8	8900	7210	1.23
heating	30.8 - 42.5	10110	8500	1.19
cooling	42.0 - 34.5	3410	3340	1.02
heating	34.5 - 51.0	5740	5400	1.06

Table 5. Storage capacity of the 220 kg Na_2HPO_4 salt water mixture with 0.27 as the fraction of anhydrous salt in the salt water mixture based on weight.

The solidification progress was as mentioned in section 3.3 favourable, and the heat of fusion seems also here to be greater than the value, which was used for the calculations.

5. AN EXAMPLE OF COSTS OF INVESTMENT OF STORAGES BASED ON A SALT WATER MIXTURE AND WATER.

Comparing different storages the influence of the storage on the other parts of the solar heating system must be taken into consideration. Comparisons must therefore be carried out with the use of computer programs using data for weather, solar collector, heating system, heat demands and so on.

The suitability of different storages can also be found without computer programs. Then parameters such as storage temperature level, heat transfer to and from the storage, safety, required house volume for the storage, costs of investment, working expenses and costs of maintenance must be taken into consideration.

A crude comparison of the suitability of a storage based on a salt water mixture with oil as heat transfer fluid in direct contact with the storage material and a traditional hot water storage can be found by tabulating the costs of investment and costs of required house volumes for the storage systems with the same amount of heat content in a temperature interval going from 25° C to 80° C. In this temperature interval the heat capacity for water and the examined Na₂SO₄ water mixture is 227 MJ/m³ respectively 462 MJ/m³.

With 10³ MJ as the heat content in the selected temperature interval the water and the Na₂SO₄ water mixture has the amount 4.4 m³ respectively 2.2 m³. With these values a cost estimate is given in table 6.

	costs for 2.2 m ³ Na ₂ SO ₄ water storage u.a.	costs for 4.4 m ³ hot water storage u.a.
cost of heat storage material (97% salt water mixture, 1.083t anhydrous salt) 90 u.a./t anhydrous salt	97	0
cost of heat transfer fluid (3% heat exchange oil, 66 l oil) 1.3 u.a./l oil	86	0
cost of insulated steel tank with corrosion resistant lining 150 u.a./m ³	330	660
cost of heat exchanger, circulation pump, connecting pipes and pipe fittings	450	250
cost of required house volume 250 u.a./m ² basement storage	375	750
Total	1338	1660

Table 6. Cost estimate of heat storages with storage capacity 10³ MJ in the temperature interval 25° C - 80° C.
1 u.a. = 7.5 D kr.

These cost estimates give only a crude estimate of the suitability of the storage system. With other temperature intervals and storage dimensions the results would be otherwise. However, costs of the salt water mixture storage seem to be somewhat lower than the costs of the traditional hot water storage.

As mentioned above a better comparison would be to compare the storage systems as part of a solar heating system by means of computer calculations.

6. CONCLUSION.

Experiments with the selected salt water mixtures in connection with the storage system, where oil is the heat transfer fluid in direct contact with the salt water mixture, were carried out. The nozzle system was formed in such a way, that the storage system worked stably and safely under alle conditions. Experiences with the salt water mixtures in connection with the storage system were obtained. Short term experiments of the amount 0.2 m^3 gave as result, that the measured storage capacities of the salt water mixtures were close to the theoretically calculated storage capacities. The storage system seems very promising for a few of the salt water mixtures.