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INVESTIGATION OF HEAT STORAGES
WITH SALT HYDRATE
AS STORAGE MEDIUM BASED ON
THE EXTRA WATER PRINCIPLE

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PREFACE

As a result of the 1973 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 project which is described in the present report is a continuation of 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 first phase of the project is described in report no. 70 of July 1977.

The expenditure related to the performance of the second phase of this project amounts to D.kr. 485.000, which is shared on a 50% basis between the Commission and the Danish Government.

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ABSTRACT

This report describes the work of the research project nr. 275-77 ESDK, Experimental and computational investigation of a full scale heat storage with salt hydrate as storage medium and based on the extra water principle, which is carried out with support from the European Communities. The project is a prolongation of the research project no. 140-75 ESDK, which also is supported by the European Communities.

Two different types of full scale heat storage, both making use of an incongruently melting salt hydrate as storage medium and based on the extra water principle, are examined by means of long term experiments. In the first heat storage type oil as heat transfer fluid in direct contact with the storage medium is used. The second storage type is a mantle storage where water as heat transfer fluid is circulated in the mantle. No decrease in the performance of the storages during the long term experiments is observed, and experiences for both storage types are obtained.

By means of computer calculations heat of fusion storages with oil as the heat transfer fluid in direct contact with the storage medium are compared with hot water storages as part of solar heating systems with the Danish Reference Year as basis. With results of these calculations examples of economical comparisons between heat of fusion storages and hot water storages are carried out.

Considerations and experiments concerning storage material, stability of heat storage and heat transfer capacity are carried out.

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1 INTRODUCTION

This report is the final report on the research project nr. 275-77 ESDK, Experimental and computational investigation of a full scale heat storage with salt hydrate as storage medium and based on the extra water principle. The research project was carried out with support from the European Communities.

The report is divided into a number of main sections, dealing with an introduction to the project, the experiments which were carried out, the analysis concerning the influence of the heat storage on the thermal performance of a solar heating system on yearly basis, and considerations concerning construction of a heat storage making use of a phase change material. At last a conclusion is given.

The aim of the project is partly to find the stability of a full scale salt hydrate storage making use of the extra water principle by means of repeated heating/cooling cycles, partly to compare such a phase change storage with a traditional hot water storage as part of a solar heating system by means of computer calculations. The project deals with more advanced studies of the investigations made in the research project nr. 140-76 ESDK, Heat Storage in a solar heating system using salt hydrates, which was also financially supported by the European Communities. In the latter project short term experiments with small scale storages making use of the extra water principle were carried out, and the work is described in Report on Heat Storage in a Solar Heating System Using Salt Hydrate [1].

Both in the previous and in this project the extra water principle was investigated. Therefore a short description of this method, by which a heat storage based on an incongruently melting salt hydrate will work stably, will be given here.

Description of the extra water principle

The behaviour of the melting and crystallization process for the incongruently melting salt hydrate is of great importance for the understanding of the extra water principle.

An incongruently melting salt hydrate is a salt hydrate with an anhydrous salt which cannot be dissolved completely in its corresponding crystal water at the melting point. The molten salt hydrate therefore consists of a saturated solution and some anhydrous salt undissolved in the water. This will settle down as sediment due to its higher density, when the salt hydrate is situated in a container without stirring. 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. The content of the container is divided into three 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. When heated, a part of the layer of solid salt hydrate crystals will melt and form a saturated solution with a part of undissolved anhydrous salt, which will settle down as sediment. The amount of sediment increases in this way by each melting/crystallization cycle, and the storage capacity decreases rapidly. Therefore this phase separation must be prevented if a heat storage should make use of an incongruently melting salt hydrate.

The extra water principle investigated in our projects is a method which has the effect of avoiding phase separation on the incongruently melting salt hydrates, and making the storage 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. When the salt hydrate melts the salt dissolves completely in the water, merely by 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 can only take place from a saturated solution, the solidification will take place by decreasing temperature. Melting will take place by 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, which still is lower than the melting point, 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.

2. EXPERIMENTS

2.1 Aim

The aim of the experiments is to built and during repeated heating/cooling cycles examine the stability of two full scale storage units.

2.2 Arrangement for testing the heat storage

An arrangement for testing the heat storages was built. The arrangement is schematically illustrated in figure 1. With this arrangement it is possible to examine a heat storage under realistic conditions, that is the amount of heat power which is possible to remove from or transfer to the storage by means of a heat transfer fluid is to some extent adjustable in a large interval going from about 8000 W of heat power removal from the storage to about 20000 W of heat power transfer to the storage. The flow velocity of the fluid is adjustable too.

The arrangement is divided in 3 different pipe systems: a heating system with water as the heat transfer fluid, a cooling system with a glycol/water mixture as the cooling medium and a system for the heat transfer fluid for the storage. Each system will be described in the following.

The heating system consists of a hot water tank in which 3 6kW heating elements are placed, resulting in a heating power of 0, 6, 12 or 18 kW. A circulation pump circulates the water in the system from the hot water tank to a heat exchanger where the water is cooled and back to the hot water tank.

The heat exchanger is a common heat exchanger which usually is used in connection with district heating.

The cooling medium from the refrigerating plant in the cooling system is a glycol/water mixture. When cooling is wanted, a magnet valve opens and the mixture streams through a heat exchanger. The flow velocity of the cooling

medium in the heat exchanger is adjustable by means of two valves: an automatically controlled valve and a valve mechanically controlled by the temperature difference in the heat transfer fluid to the storage across the heat exchanger. The latter valve works in such a way that the mentioned temperature difference, and with that the heat power removed from the storage, is constant for each adjustment of the automatically controlled valve. With this system it is possible to remove a constant amount of heat power up to about 8000 W.

A centrifugal pump takes care of the circulation of the heat transfer fluid for the storage in the arrangement. The fluid is conducted through both the above mentioned heat exchangers where the fluid either is heated or cooled. The fluid is heated as it streams along a 2700 W heating element situated inside the pipe. Further an instrument, where the flow velocity is read, is placed in the pipe system.

The pipe systems consist mostly of stainless steel of different dimensions. The pipes are insulated in order to minimize thermal losses. The pumps, heating elements and valves and with that the experiments are controlled from a control panel.

Temperature measurements are made by use of copper/constantan thermocouples and a recorder. The temperature is measured in the fluid entering and leaving the 2700 W heating element, in the fluid entering and leaving the heat storage, that is leaving and entering the arrangement. The temperature of the ambient air is measured too in order to calculate the thermal loss from the heat storage. Two temperature differences are measured with copper/constantan thermopiles and a 2-channel recorder. The temperature difference across the 2700 W heating element is measured in order to calculate the flow velocity of the fluid. The temperature difference between the fluid entering and leaving the arrangement is measured in order to calculate the heat transferred to or from the heat storage. Figures 2 - 7 show photos of the arrangement.

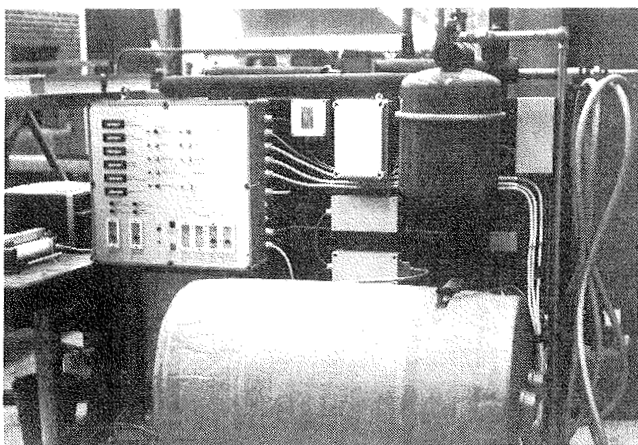


Figure 2 . Control panel from which the experiments are controlled. The hot water tank in the heating system is shown in the front of the photo.

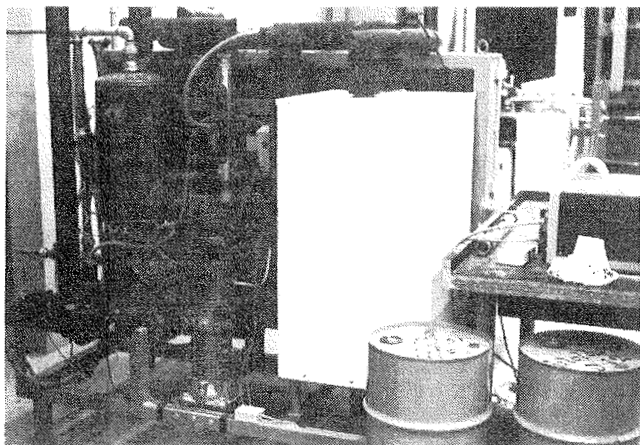


Figure 3 . The pipe system through which the heat transfer fluid to the storage is conducted with the centrifugal pump. The heat exchanger where the fluid is heated to the right and the heat exchanger where the fluid is cooled to the left.

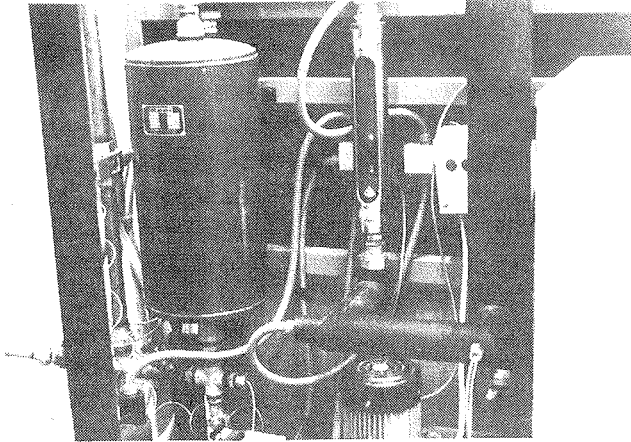


Figure 4 . A part of the pipe system for the heat transfer fluid with the heating element, the flow velocity measurement and the heat exchanger for cooling.

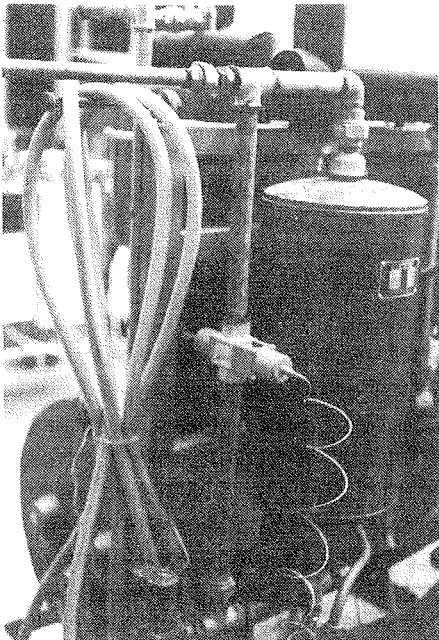


Figure 5 . The cooling system with the heat exchanger for cooling and the 3 different valves which control the cooling fluid flow velocity.

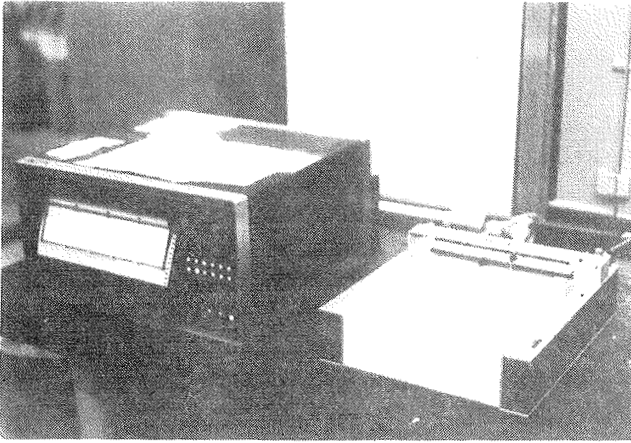


Figure 6 . The recorders which registrate the measured temperatures and temperature differences.

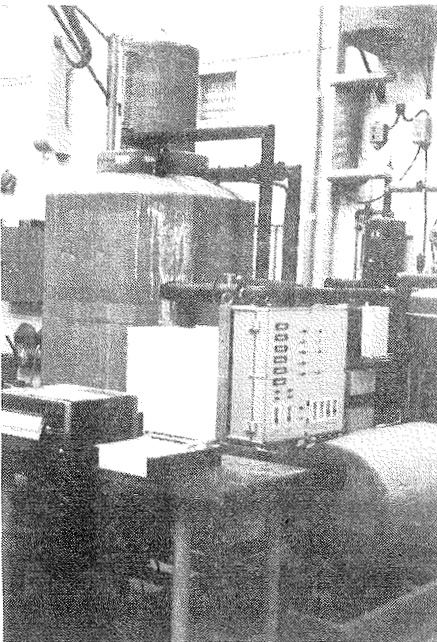


Figure 7 . The arrangement with the heat storage making use of mineral oil as the heat transfer fluid.

Besides the mentioned temperatures and temperature differences only the temperature inside the examined heat storage is measured, so that the heat capacity of the storage can be found.

2.3 Heat storages

Two different storage units both making use of the extra water principle were built and examined.

2.3.1 Storage with oil as the heat transfer fluid

In the first storage system which in detail is described in [1], a mineral oil, Gilotherm D12 is the heat transfer fluid, which in a pipe system is conducted to the bottom of the storage tank and through a nozzle system to the salt water mixture.

The storage is a 1500 l cylindrical steel tank with a gauge of metal of 4 mm, a diameter of 1.15 m and a height of approximately 1.60 m. The tank is supplied with an inside surface treatment of polyester materials. The storage medium is a sodium sulfate water mixture with a fraction of anhydrous salt in the salt water mixture equal to 0.33. A 60 l expansion tank is connected with the storage through a pipe branche at the top of the storage and placed above the storage. Both tank and expansion tank are insulated with 10 cm of mineral wool. The amount of salt water mixture is 1800 kg, that is 594 kg of Na_2SO_4 and 1206 kg of water. In order to diminish supercooling 1°/oo borax, that is 1.8 kg borax, was added to the mixture. The amount of Gilotherm D12 oil is 150 l.

The pipe system, through which the oil is conducted to the storage, is led through a pipe branche into the container. The pipe system consists of two copper pipes with diameters of 22 and 12 mm. In the pipe with the large diameter 16 holes, each with a diameter of 3 mm, are placed. This pipe is conducted to the bottom of the container and here formed in such a way that the jets of

oil from the 16 holes produce an effective stirring all over the container. The pipe with the smaller diameter is conducted along the other pipe and back to the top of the container and through a safety valve into the pipe, in which the oil is conducted away from the storage. This valve is open if all the nozzles are blocked with solid salt hydrate crystals and closed when the crystals are melted and the oil allowed to enter the salt water mixture again. The pipes are in close connection with each other, and if any crystals are situated in the nozzles only a few minutes circulation of warm oil in the pipe with the small diameter is necessary to melt these crystals. Normally the oil will only be conducted through the nozzles, and the small diameter pipe is only used if the normal circulation is stopped.

The outlet system is placed at the top of the container and formed in such a way that there will only be pumped oil from the stationary upper part of the oil layer at the top of the container. This is done to diminish the salt content in the circulated oil.

Figure 8 shows a photo of the storage.

2.3.2 Storage with air circulation as the stirring

In the second storage system the heat transfer fluid which is water is circulated in a mantle around the surface of the storage tank. The tank is cylindrical and has an amount of approximately 500 l. The height is approximately 1.70 m and the diameter is 70 respectively 65 cm with and without the mantle. The container is insulated with 10 cm of mineral wool. The heat transfer fluid is conducted to and from the mantle through pipe branches situated in the mantle. The heat is conducted through the container wall to and from the storage medium.

The storage medium is 520 kg of a Na_2SO_4 salt water mixture with a fraction of anhydrous salt in the mixture of 0.33 based on weight. In order to diminish super cooling 1% borax, that is 0.5 kg borax, was added to the mixture.

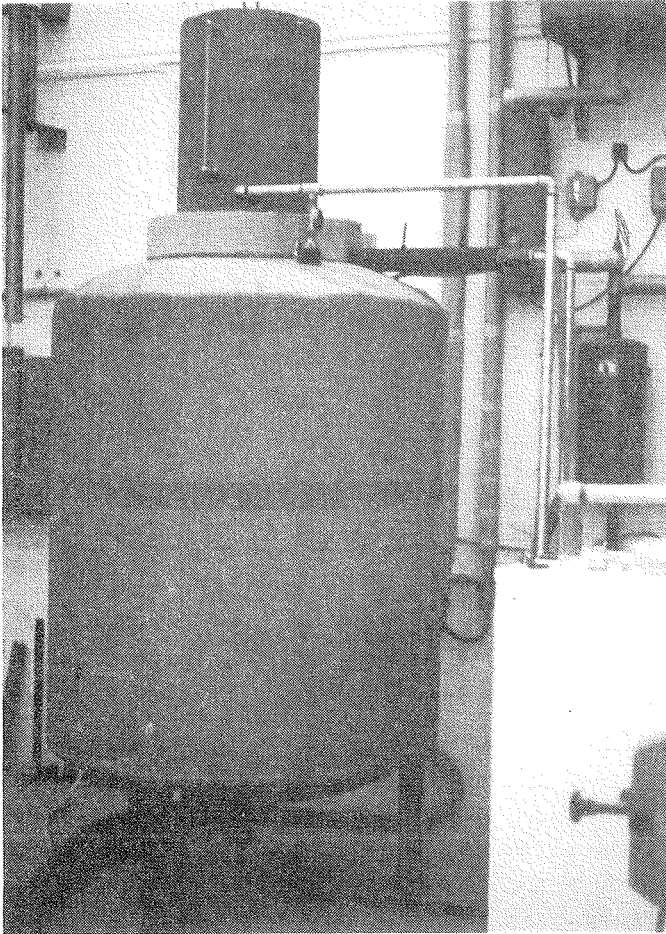


Figure 8 . 1500 l heat storage with the expansion tank in the top of the storage container.

The top of the tank serves as expansion possibility, and the tank is closed. The air situated at the top of the container is conducted through a pipe to the bottom of the container by means of an air pump, and the air bubbling through the salt water mixture produces a soft stirring so that phase separation is avoided. A heating element situated in the pipe takes care of any salt hydrate crystals which prevent the circulation of the air. A safety valve situated at the top of the container opens if the pressure of the air at the top of the container exceeds a critical amount.

Figures 9 and 10 show a schematical illustration and a photo of the storage.

2.4. Measurements

Repeated heating/cooling cycles were carried out with both storages in order to find the stability and the heat transfer capacity for the storages.

2.4.1 Measurements with the storage using oil as the heat transfer fluid

For the first storage unit the measurements were carried out as described in [1] in order to measure the storage capacity of the salt water mixture in different temperature intervals. The only difference from the calculations, described in [1], is the thermal loss from the container. This thermal loss was calculated, and by means of measurements with water as storage medium during 48 hours without circulation of oil confirmed to be:

$$Q_{\text{loss}} = 5.4 \cdot (T_s - T_a) W$$

T_s and T_a are the temperatures of the storage medium respectively the ambient air.

In order to elucidate the heat transfer capacity the effectiveness of the heat exchanger inside the storage from the oil to the salt water mixture and reversely was measured. This effectiveness ϵ is found from:

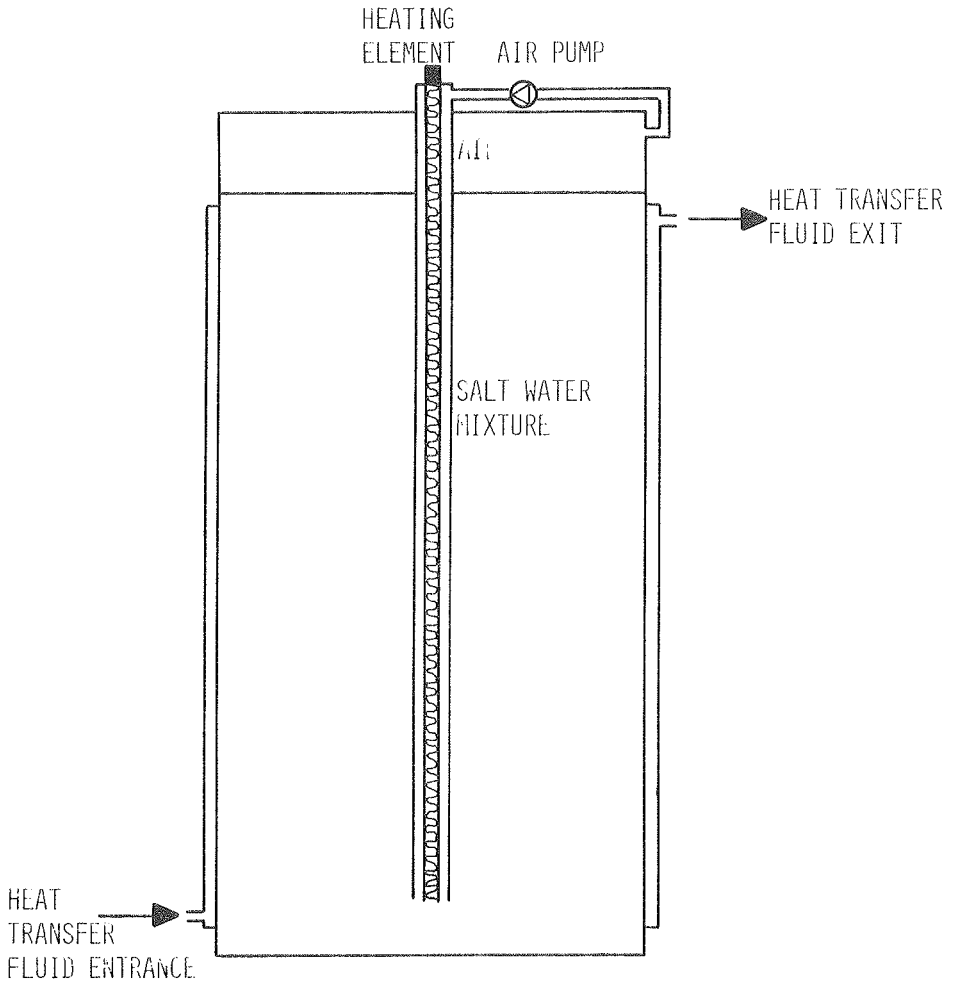


Figure 9 . Schematical illustration of the storage, where air circulation is used as stirring. The direction of the heat transfer fluid is upwards corresponding to a cooling.

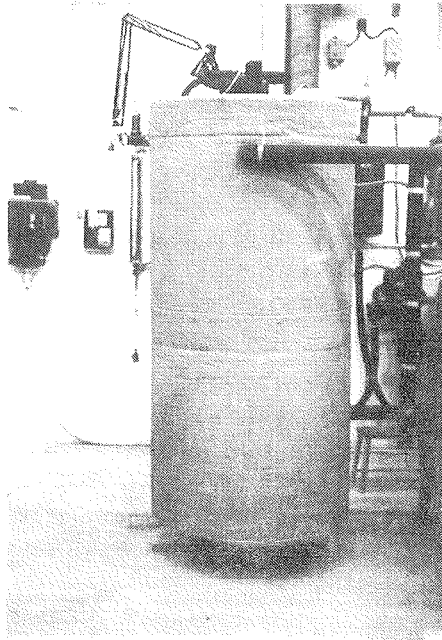


Figure 10. The 500 l storage tank with the air pump situated in the top of the container.

$$\epsilon = \frac{T_{out} - T_{in}}{T_s - T_{in}}$$

T_{in} is the temperature of the oil entering the storage, T_{out} is the temperature of the oil leaving the storage, and T_s is the heat storage medium temperature.

Further the heating power removed from or transferred to the storage per $^{\circ}\text{C}$ temperature difference between the storage medium and the heat transfer fluid was measured for an unbroken heating/cooling cycle.

2.4.2 Measurements with the storage using air circulation as the stirring

The measurements of the storage capacity were carried out in the same way as already described in [1]. The only difference is that water is used as the heat transfer fluid instead of the Gilotherm D12 oil. Therefore the density and specific heat of water are used in the calculations instead of the values for the mineral oil. The thermal loss from the container was measured to be $3(T_s - T_a) W$. T_s and T_a are the temperatures of the storage medium respectively the ambient air, and the measurement is in good agreement with the theoretical calculations.

Also for this storage the effectiveness of the heat exchanger from the heat transfer fluid to the storage medium and reversely was measured and found from:

$$\epsilon = \frac{T_{out} - T_{in}}{T_s - T_{in}}$$

T_{in} is the temperature of the water entering the mantle, T_{out} is the temperature of the water leaving the mantle and T_s is the temperature of the heat storage medium.

The heating power removed from or transferred to the storage per $^{\circ}\text{C}$ temperature difference between the storage medium and the heat transfer fluid was measured too for an unbroken heating/cooling cycle.

2.5 Results

2.5.1 Storage with oil as heat transfer fluid

2.5.1.1 Emulsion problems

As described in [1] small scale experiments with the storage system were carried out without formation of a layer of emulsion between oil layer and salt water mixture. Therefore the problems which occurred in this full scale storage were quite unexpected. The problem was that insufficient separation between the oil layer and the salt water mixture occurred. An increasing layer of emulsion consisting of oil and salt water mixture was formed when the oil flow velocity was not limited to a small amount. Therefore the oil flow velocity had to be limited to a relatively small amount resulting in a too small heat transfer capacity, that is: The temperature differences must be too large in order to transfer the heat to and from the storage.

Therefore this emulsion problem had to be solved before testing of the storage could take place. How the problem was solved is described in the following by the chemical consultant Erik Pedersen.

The sodium sulfate was a technical product with specified maximum amounts of impurities, the main constituent of which could be sodium formate ($< 0.5\%$).

Small scale experiments with the technical product showed that it contained a slowly soluble soap-like constituent. Elemental analyses of carbon in the bulk material showed a content of less than 0.1% , however. Experiments showed that sodium formate added to a pure mixture caused no troubles.

We tentatively assumed that the product contained small amounts of large negatively charged ions, well known from soaps to be very effective emulsifiers. The trouble-causing material could be effectively removed only after three recrystallizations of the technical product. This procedure, however, would be tedious for the nearly two tons of material in the heat storage system.

2.5.1.1.1 Experimental

Addition of small amounts of quaternary ammonium salts to the salt/water/oil emulsions was shown to increase the rate of separation into two layers. The salts investigated ranged in molecular size and shape from the small tetramethylammonium to the larger tetrabutylammonium and cetyltrimethylammonium salts. The small ones were almost without effect, and for the long chain molecules like cetyltrimethylammonium salts the optimum concentrations were very critical, at too high concentrations they themselves behaved as emulsifiers. The only satisfactory salt was tetrabutylammonium hydrogensulfate. Its effect increased up to a concentration of 50 mg per 100 g of emulsion, where the rate of separation was increased ten-fold. The effect was roughly linear in concentration. At higher concentrations the effect was not increased.

2.5.1.1.2 Discussion

On the basis of our experiments on a small scale we therefore proposed to add 500 g of tetrabutylammonium hydrogensulfate (the total amount readily available in Denmark at that time, cost approximately DKr 1000 per kg). This was later shown to increase the rate separation by a factor of approx. five as expected.

The chemistry behind this is based on a solvent extraction effect. Salts containing large cations (positive) as well as salts containing large anions (negative) are often quite soluble in water provided that the counter ions are small. Salts where both ions are large are usually sparingly soluble in water and more soluble in nonpolar liquids such as oils. This is caused by ion pair formation in these solvents.

The addition of tetrabutylammonium ions to the emulsions therefore caused the large emulsifying anions to be extracted into the oil, and their emulsifying effect was quenched by ion pair formation.

The application of such quaternary ammonium salts in heat storage systems can be considered quite harmless.

2.5.1.2 Measurements

Having solved the emulsion problem, 35 heating/cooling cycles were carried out.

The extra water principle worked in such a way that no decrease in the storage capacity of the salt water mixture during these 35 heating/cooling cycles was observed. The results of the measurements are given in table 1, where also the theoretically calculated storage capacities found in [1] are given. There is good agreement between theory and measurements. Figure 11 shows the measured heat content.

Since the maximum of supercooling was 3°C , supercooling is not a serious problem. The start solidification temperature of the sodium sulfate mixture varied from 31.3°C to 31.8°C , while the theoretical start solidification temperature is 32.2°C .

No emulsion problems occurred after the addition of the special salt to the storage.

The pipe system in which the oil is conducted to the heat storage worked on the whole as planned, and the heat transfer capacity to and from the storage had reasonably large amounts except for cooling at low temperatures. For a typical unbroken heating/cooling cycle the heat transfer capacities are given by means of the effectiveness of the heat exchange between salt water mixture and oil inside the container, ϵ and the heat transfer power per $^{\circ}\text{C}$ temperature difference between oil and salt water mixture in table 2. Figure 12 shows the heat transfer capacity for an unbroken heating/cooling cycle. ϵ is defined by the structure of the inside of the storage and the temperature difference between oil entering the heat storage and the heat storage. ϵ is independent of the oil flow velocity and is almost always equal to 1.00 while heating even for great amounts of temperature differences between oil entering the heat storage and the heat storage. While cooling, ϵ is equal to 1.00 as long as solidification does not occur. When solidification starts, ϵ decreases since the salt hydrate crystals have poor thermal conductivity. The oil flow velocity decreases as solidification

heating/cooling	temperature interval °C	storage capacity		<u>measured</u> <u>calculated</u>
		measured Wh	calculated Wh	
cooling	34.9 - 31.0	27910	29040	0.96
heating	31.0 - 41.8	40850	40170	1.02
cooling	36.8 - 29.2	57220	55310	1.03
heating	29.2 - 39.2	55860	59180	0.94
cooling	39.2 - 26.1	82490	82240	1.00
heating	26.1 - 39.7	89270	83040	1.08
cooling	36.3 - 27.3	67650	70130	0.96
heating	27.3 - 40.4	72190	76740	0.94
cooling	39.2 - 28.9	64390	61980	1.04
heating	28.9 - 34.6	53740	54560	0.98
cooling	34.6 - 30.8	35570	31770	1.12
heating	30.7 - 42.5	43950	46070	0.95
cooling	40.4 - 28.0	77840	71700	1.09
heating	28.0 - 40.6	72340	72020	1.00
cooling	39.5 - 29.8	55060	53180	1.04
heating	29.8 - 45.1	61980	62220	1.00
cooling	36.8 - 31.1	32700	30450	1.07
heating	31.1 - 35.4	26350	28190	0.93
cooling	35.4 - 29.5	48590	49890	0.97
heating	29.5 - 47.3	70760	69100	1.02
cooling	41.6 - 30.4	49910	48930	1.02
heating	30.3 - 34.4	37670	38680	0.97
cooling	34.4 - 25.2	76820	79160	0.97
heating	25.2 - 42.0	88220	91420	0.96
cooling	42.0 - 30.1	52740	53550	0.98
heating	30.1 - 32.5	37790	38560	0.98
cooling	34.9 - 29.5	48140	49080	0.98
heating	29.3 - 34.9	51950	51190	1.01
cooling	34.4 - 26.5	70870	72180	0.98
heating	26.5 - 49.1	95420	95910	0.99
cooling	49.1 - 29.4	73840	73110	1.01
heating	29.0 - 48.7	74340	76440	0.97
cooling	48.7 - 28.0	84690	85110	1.00
heating	28.0 - 43.1	75600	76060	0.99
cooling	42.0 - 29.1	68010	66480	1.02
heating	29.0 - 49.7	79200	78060	1.01
cooling	45.1 - 28.5	73200	75420	0.97
heating	28.4 - 36.2	60750	62070	0.98
cooling	47.3 - 27.6	88120	85770	1.03
heating	27.6 - 38.2	70390	71070	0.99
cooling	37.8 - 31.7	20900	20620	1.01
heating	31.5 - 43.0	32590	33130	0.98
cooling	39.2 - 26.0	81470	82790	0.98
heating	26.0 - 43.9	87180	90380	0.96
cooling	44.3 - 27.2	81800	83760	0.98
heating	27.2 - 47.4	86320	88770	0.97

Table 1a. Measured storage capacity of the 1500 l Na₂SO₄ salt water mixture storage.

heating/cooling	temperature interval °C	storage capacity		<u>measured</u> <u>calculated</u>
		measured	calculated	
		Wh	Wh	
cooling	43.9 - 25.5	96010	93040	1.03
heating	25.5 - 44.0	88940	93200	0.95
cooling	44.0 - 26.8	83580	85880	0.97
heating	26.8 - 35.4	74270	72000	1.03
cooling	35.4 - 24.9	79330	82260	0.96
heating	24.9 - 45.8	99590	99040	1.01
cooling	45.8 - 28.3	76880	77970	0.99
heating	28.3 - 35.8	60490	61810	0.98
cooling	35.8 - 25.8	80240	78390	1.02
heating	25.8 - 46.3	94690	95340	0.99
cooling	42.5 - 27.0	79460	82150	0.97
heating	27.0 - 43.5	83500	83770	1.00
cooling	41.3 - 29.1	63990	63570	1.01
heating	29.0 - 48.7	74760	76440	0.98
cooling	44.0 - 26.3	88240	88820	0.99
heating	26.3 - 48.0	92680	95280	0.97
cooling	48.0 - 27.0	91510	91040	1.01
heating	27.0 - 49.4	93740	93300	1.00
cooling	44.8 - 25.1	94720	96460	0.98
heating	25.1 - 47.3	103030	100500	1.03
cooling	47.3 - 26.3	95000	94150	1.01
heating	26.3 - 38.2	78880	79450	0.99
cooling	38.2 - 28.1	65120	67360	0.97
heating	28.1 - 51.3	90020	88520	1.02

Table 1b. Measured storage capacity of the 1500 l Na₂SO₄ salt water mixture storage.

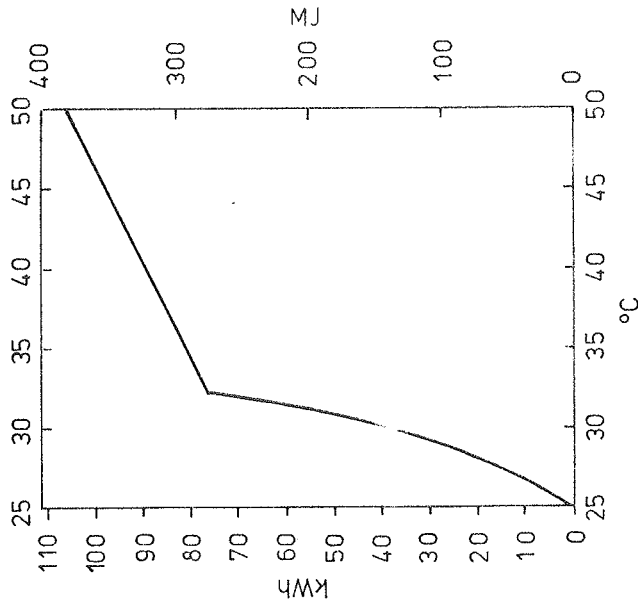


Figure 11. Heat content of the 1500 l storage versus storage temperature.

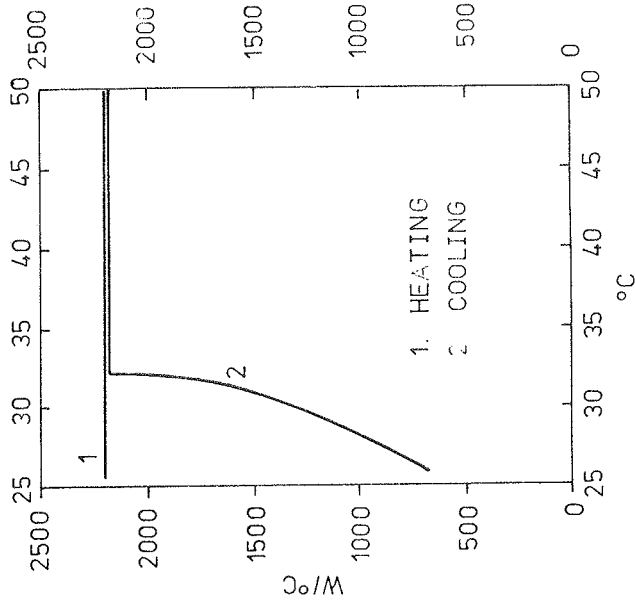


Figure 12. Heat transfer power per °C temperature difference between oil and salt water mixture for an unbroken heating/cooling cycle versus storage temperature.

HEATING	COOLING				HEATING/COOLING
	STORAGE TEMPERATURE °C	TRANSFERRED HEAT POWER kW	FLOW VELOCITY l/min	EFFECTIVENESS OF HEAT EXCHANGE OIL/SALT WATER	HEAT TRANSFER POWER PER TEMPERATURE DIFFERENCE BETWEEN OIL AND SALT WATER MIXTURE W/°C
HEATING	25	15	43	0.99	2200
	26	15	43	0.99	2200
	27	15	43	0.99	2200
	28	15	43	0.99	2200
	29	15	43	0.99	2200
	30	15	43	0.99	2200
	31	15	43	0.99	2200
	32	15	43	0.99	2200
	35	15	43	0.99	2200
	40	15	43	0.99	2200
	45	15	43	0.99	2200
	25	4	14	0.90	600
	26	4	17	0.90	700
	27	4	19	0.90	800
	28	4	22	0.94	1000
	29	4	24	0.94	1100
COOLING	30	4	29	0.94	1300
	31	4	33	0.94	1500
	32	4	43	1.00	2200
	35	4	43	1.00	2200
	40	4	43	1.00	2200
	45	4	43	1.00	2200

Table 2 . Heat transfer capacities for the heat storage during an unbroken heating/cooling cycle.

takes place. This is caused by formation of solid salt hydrate crystals in some of the nozzles. This in connection with the decrease of ϵ results in a decrease in the heat transfer power per $^{\circ}\text{C}$ temperature difference between oil and salt water mixture as solidification takes place. This is a serious problem, which has to be solved, before a practical use of the storage in a solar heating system can take place, see section 4.3. Therefore the oil inlet system must be designed in such a way that the oil flow velocity always should have approximately the same amount regardless of the progress of the solidification. The heat transfer capacity is largely dependent on the design of the inlet system, and for other designs than the one used here, the heat transfer capacity would be different.

Concerning the long term stability of the storage tank the following observations were made. No larger changes in the inside of the storage tank were noticed after 5 months of experiments. The inside surface treatment had no weak points, and the copper pipe system through which the oil was conducted to the storage had not been attacked. The only part of the storage which had been slightly attacked during the experiments was the outlet system for the oil. Here steel was used in connection with a copper plate, and this resulted in corrosion of the copper. Therefore it must be recommended only to use either steel or copper inside the storage.

2.5.2 Storage with air circulation as the stirring

The heat transfer fluid was water, and the flow velocity through the mantle was fixed to 9 l/min. The direction of the heat transfer fluid through the mantle could both be upwards and downwards, so that any positive effects on the heat transfer capacity produced by natural convection in the mantle could be utilized. For cooling the heat transfer fluid in the mantle is heated, that is the natural direction through the mantle is upwards. For heating the direction is downwards. Therefore these directions were used in the experiments.

The experiments existing of 26 heating/cooling cycles were carried out without any problems. The extra water principle also worked in an excellent way in this storage type. No decrease in the storage capacity of the salt water mixture during the experiments was observed. The results of the measurements are given in table 3, where also the theoretically calculated storage capacities found in [1] are given. Also for this storage good agreement between theory and measurements was observed. Figure 13 shows the measured heat content.

The maximum of supercooling was 3°C , and the start solidification temperature varied from 31.0°C to 31.5°C , while the theoretical start solidification temperature is 32.2°C .

The air circulation worked as planned, and the heating element situated in the pipe was not used, since no salt hydrate crystals prevented the circulation of air, not even after a long period without air circulation at low temperatures.

The heat transfer capacity to and from the storage had for practical use in a solar heating system a reasonably large amount, see section 4.3. The heat transfer power per $^{\circ}\text{C}$ temperature difference between the heat transfer fluid and the salt water mixture is dependent on the conditions of the experiment. Under practical circumstances as a part of a solar heating system the conditions are changing continuously. For a single example with a power input of 7000 W and a power outtake of 2000 W the heat transfer power per $^{\circ}\text{C}$ temperature difference between the heat transfer fluid and the salt water mixture is shown in figure 14 for an unbroken heating/cooling cycle as a function of the mean temperature of the heat transfer fluid in the mantle. The decrease in the heat transfer capacity for cooling at low temperatures is caused by the formation of a layer of solid salt hydrate crystals with poor thermal conductivity on the container wall. As soon as heating is started the heat transfer capacity increases, because the crystals situated on the wall melt, and the wall is in contact with the liquid phase resulting in increased heat transfer capacity due to natural and forced convection.

heating/cooling	temperature interval	storage capacity		<u>measured</u> <u>calculated</u>
		measured	calculated	
	°C	Wh	Wh	
cooling	42.5 - 26.1	25740	26340	0.98
heating	26.1 - 41.4	25770	25920	0.99
cooling	49.6 - 28.5	24930	25370	0.98
heating	28.5 - 47.9	24950	24460	1.02
cooling	48.5 - 23.5	34430	33460	1.03
heating	23.5 - 47.5	34770	32920	1.06
cooling	47.5 - 22.2	36400	35080	1.04
heating	21.6 - 47.1	34450	34860	0.99
cooling	47.1 - 21.3	34950	35190	0.99
heating	21.3 - 47.2	35840	35240	1.02
cooling	47.2 - 20.5	35210	36010	0.98
heating	20.5 - 47.3	35740	36060	0.99
cooling	47.3 - 26.9	27490	27660	0.99
heating	26.9 - 47.7	28010	27880	1.00
cooling	47.7 - 27.0	27990	27680	1.01
heating	27.0 - 47.9	28110	27790	1.01
cooling	47.9 - 26.9	27220	27990	0.97
heating	26.9 - 47.7	27480	27880	0.99
cooling	47.7 - 20.2	36110	36730	0.98
heating	20.2 - 46.8	37290	36250	1.03
cooling	46.8 - 20.5	34800	35790	0.97
heating	20.5 - 50.2	35110	37620	0.93
cooling	50.2 - 23.7	33800	34130	0.99
heating	23.7 - 50.4	35160	34290	1.03
cooling	50.4 - 23.7	34850	34290	1.02
heating	23.7 - 50.0	34020	34080	1.00
cooling	50.0 - 23.4	34000	34390	0.99
heating	23.7 - 50.0	34720	34080	1.02
cooling	50.0 - 23.4	33990	34390	0.99
heating	23.4 - 49.9	32870	34330	0.96
cooling	49.9 - 23.4	34840	34330	1.01
heating	23.4 - 50.0	32970	34390	0.96
cooling	50.0 - 23.4	33850	34390	0.98
heating	23.4 - 50.0	34830	34390	1.01
cooling	50.0 - 23.0	33750	34880	0.97
heating	23.0 - 49.8	34020	34770	0.98
cooling	49.8 - 23.0	35040	34770	1.01
heating	23.0 - 49.8	33630	34770	0.97
cooling	49.8 - 23.2	33720	34540	0.98
heating	23.2 - 50.0	33520	34650	0.97
cooling	50.0 - 29.2	23990	23660	1.01
heating	29.2 - 43.8	19760	20320	0.97
cooling	43.8 - 24.0	30980	30300	1.02
heating	24.0 - 47.2	32340	32130	1.01
cooling	47.2 - 24.5	31730	31490	1.01
heating	24.5 - 42.0	29420	28700	1.03
cooling	42.0 - 26.1	27080	26240	1.03
heating	26.1 - 61.4	33970	36680	0.93
cooling	61.4 - 28.0	32710	32930	0.99
heating	28.0 - 48.0	25830	25720	1.00
cooling	41.0 - 26.0	26010	25870	1.01
heating	26.0 - 42.5	25910	26670	0.97

Table 3. Storage capacity of the 500 l Na₂SO₄ salt water mixture storage.

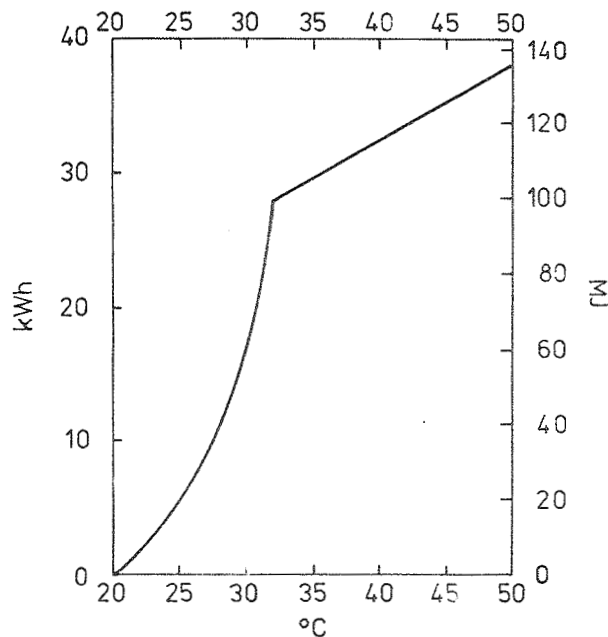


Figure 13.

Heat content of the 500 l storage versus temperature.

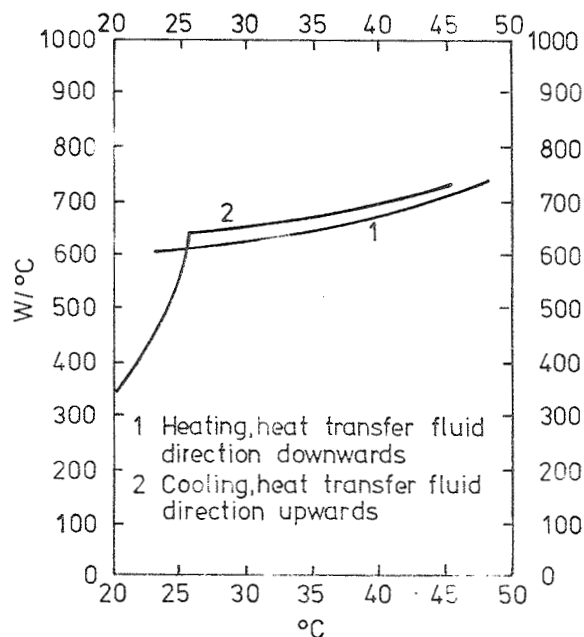


Figure 14.

Heat transfer power per $^{\circ}\text{C}$ temperature difference between the heat transfer fluid and the salt water mixture for an unbroken heating/cooling cycle versus the mean temperature of the heat transfer fluid.

Power input: 7000 W

Power outtake: 2000 W

Heat fluid velocity: 91/min.

The heat transfer capacity will for other amounts of heating power transferred to and from the storage be different, but the difference will not be of important magnitude.

No sign of changes due to age was observed during or after the experiments.

2.6 Conclusion

Two full scale storage types, both making use of the extra water principle, were examined, and both types worked stably during repeated heating/cooling cycles. The storage type with oil as the heat transfer fluid caused more problems than the mantle storage. Also concerning the heat transfer capacity and the cost of investment the mantle storage type seems favourable compared to the type making use of oil as heat transfer fluid.

3. THE PERFORMANCE OF SOLAR HEATING SYSTEMS WITH A SALT WATER MIXTURE STORAGE AND WITH A HOT WATER STORAGE

3.1 Aim

The aim of the calculations is to compare salt water mixture storages making use of the extra water principle and a mineral oil as the heat transfer fluid with a traditional hot water storage as part of a solar heating system in a one family house.

3.2 Storage

In the calculations two different storage types were taken into consideration:

The first storage type is a salt water mixture storage making use of the extra water principle with a mineral oil as the heat transfer fluid conducted through a pipe to the bottom of the container and through a nozzle system to the salt water mixture. Due to density differences the oil forms a layer at the top of the heat storage container. This oil layer is assumed to make up 2% of the storage volume. The remaining 98% of the storage volume is filled with the salt water mixture.

The heat transfer fluid in the heat supplying systems and in the solar collector system is water, and a heat exchanger separates the mineral oil from collector fluid and the fluid in the heat supplying systems. This heat exchanger is assumed to have a capacity of $89 \text{ W/}^{\circ}\text{C m}^2$ collector area. The heat transfer in the oil flow per degree centigrade temperature difference between oil entering and leaving the storage is assumed to be $69 \text{ W/}^{\circ}\text{C m}^2$ collector area. The effectiveness of the heat exchange between the oil and the salt water mixture inside the storage container is assumed to be 0.75, that is for heating:

$$\frac{T_{in} - T_{out}}{T_{in} - T_s} = 0.75$$

and for cooling:

$$\frac{T_{out} - T_{in}}{T_s - T_{in}} = 0.75$$

T_{in} is the temperature of the oil entering the storage, T_{out} the temperature of the oil leaving the heat storage, and T_s is the temperature of the salt water mixture.

Two different salt water mixtures with the heat of fusion situated in different temperature intervals were calculated: A Na_2SO_4 water mixture where the fraction of anhydrous salt in the salt water mixture based on weight is 0.33, and a NaCH_3COO water mixture where the fraction of anhydrous salt in the salt water mixture based on weight is 0.58. The first-mentioned has the heat of fusion situated at low temperatures, while the last-mentioned has the heat of fusion situated at high temperatures. The storage capacity of these storages is given in figure 15.

The other storage type which was calculated is a traditional hot water storage, in which a heat exchanger spiral is placed to separate the solar collector fluid from the storage medium. The solar collector system fluid is water, and for this storage type the storage material itself is used in the heat supplying systems. The heat exchanger spiral is assumed to have a heat transfer capacity of $60 \text{ W/}^\circ\text{C m}^2$ collector area. The heat capacity of a hot water storage is shown in figure 15, where the heat capacity of the salt water mixture storages is shown.

For both storage types the shape of the storage container is cylindrical with a height equal to twice the diameter. All storages are assumed insulated with 10 cm of mineral wool and placed in a room at 20°C .

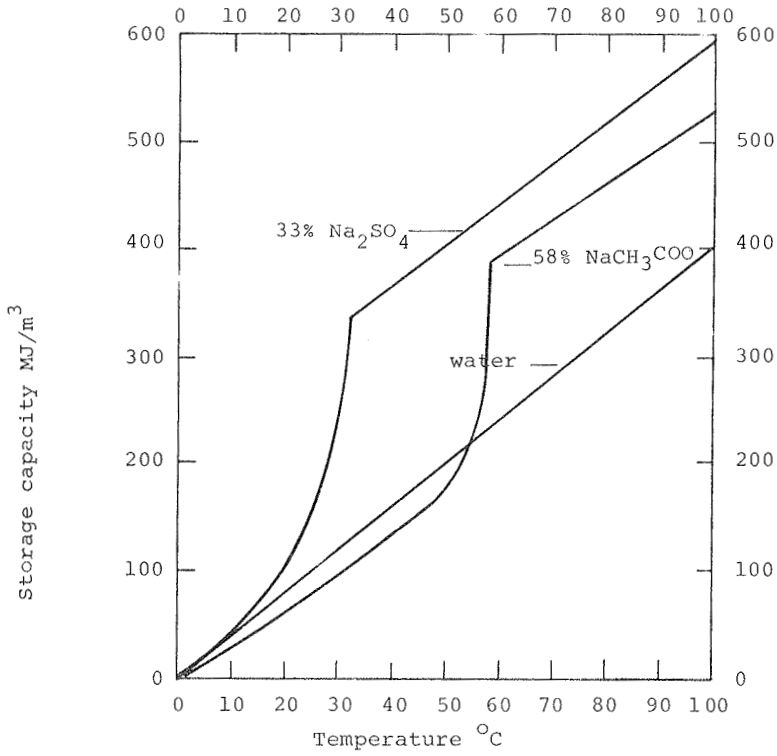


Figure 15. Storage capacity of the three different storages.

3.3 Solar Collector

Both a single glazed and a double glazed flat-plate solar collector were calculated. With a reasonable assumption the efficiency η of such collectors can be found by the equation:

$$\eta = \eta_0 - U \cdot (T_{fi} - T_a) / I$$

where T_{fi} is the fluid inlet temperature ($^{\circ}\text{C}$)

T_a is the ambient temperature ($^{\circ}\text{C}$)

I is the solar radiation on the solar collector (W/m^2)

η_0 is the solar collector efficiency for a fluid inlet temperature equal to the ambient temp.

U is the heat loss coefficient for the solar collector ($\text{W/m}^2 \text{ } ^{\circ}\text{C}$)

The quantity of U depends first and foremost on the number of glass covers and on the fluid temperature. With a reasonable assumption U can be found from these formula for typical liquid flat-plate solar collectors:

$$U = \begin{cases} 5.90 + 0.03 \cdot T_{fi} & \text{W/m}^2 \text{ } ^{\circ}\text{C} \text{ for single glazed collector} \\ 3.30 + 0.02 \cdot T_{fi} & \text{W/m}^2 \text{ } ^{\circ}\text{C} \text{ for double glazed collector} \end{cases}$$

η_0 depends first and foremost on the angle of incidence i , the number of glass covers and the design of the solar collector. With a reasonable assumption η_0 can be found from these formula for typical solar collectors:

For a single glazed solar collector:

$$\eta_0 = \begin{cases} 0.75 & \text{for } i < 50^{\circ} \\ 0.75 - 0.75 \cdot \frac{i-50^{\circ}}{40^{\circ}} & \text{for } i \geq 50^{\circ} \end{cases}$$

For a double glazed solar collector:

$$\eta_0 = \begin{cases} 0.70 & \text{for } i < 50^{\circ} \\ 0.70 - 0.70 \cdot \frac{i-50^{\circ}}{40^{\circ}} & \text{for } i \geq 50^{\circ} \end{cases}$$

For a single example with $I = 750 \text{ W/m}^2$ and $T_a = 10^\circ\text{C}$ and for an angle of incidence less than 50° , the efficiencies of the solar collectors which were calculated are given as functions of the fluid inlet temperature in figure 16. The single glazed collector has a greater efficiency than the double glazed collector for small fluid inlet temperatures, in return it decreases more rapidly for increasing inlet temperature.

3.4 Solar Heating System

The solar heating system which was calculated is schematically shown in figures 17 and 18 for the two different storage types. The solar heating system can supply both space heating and hot water supply with heat.

If the temperature of the water in the 200 l hot water tank is not high enough, that is 45°C when the water is tapped, an auxiliary energy source will rise the temperature to this level. The temperature of the water entering the hot water tank is assumed to be 10°C , and the daily tap water amount is assumed to be 250 l. The hot water tank is cylindrical, insulated with 10 cm of mineral wool and placed in a room at 20°C .

If the temperature is not high enough to give out the space heating power which is needed in the house, an auxiliary energy source will give the rest of the power. That is: only a fraction of the heat demand is supplied by the solar heating system.

The solar collectors are facing south, and the collector tilt from vertical is 25° , which is about the optimum tilt angle under Danish conditions.

3.5 Building Type

In order to cover almost all Danish single family houses three differently insulated houses were calculated. The houses are one-family houses with 120 m^2 of floor area and with three different standards of insula-

Solar collector efficiency for small angles of incidence:

single glazed collector: $\eta = 0.75 - (5.90 + 0.03 T_{fi})(T_{fi} - T_a)/I$

double glazed collector: $\eta = 0.70 - (3.30 + 0.02 T_{fi})(T_{fi} - T_a)/I$

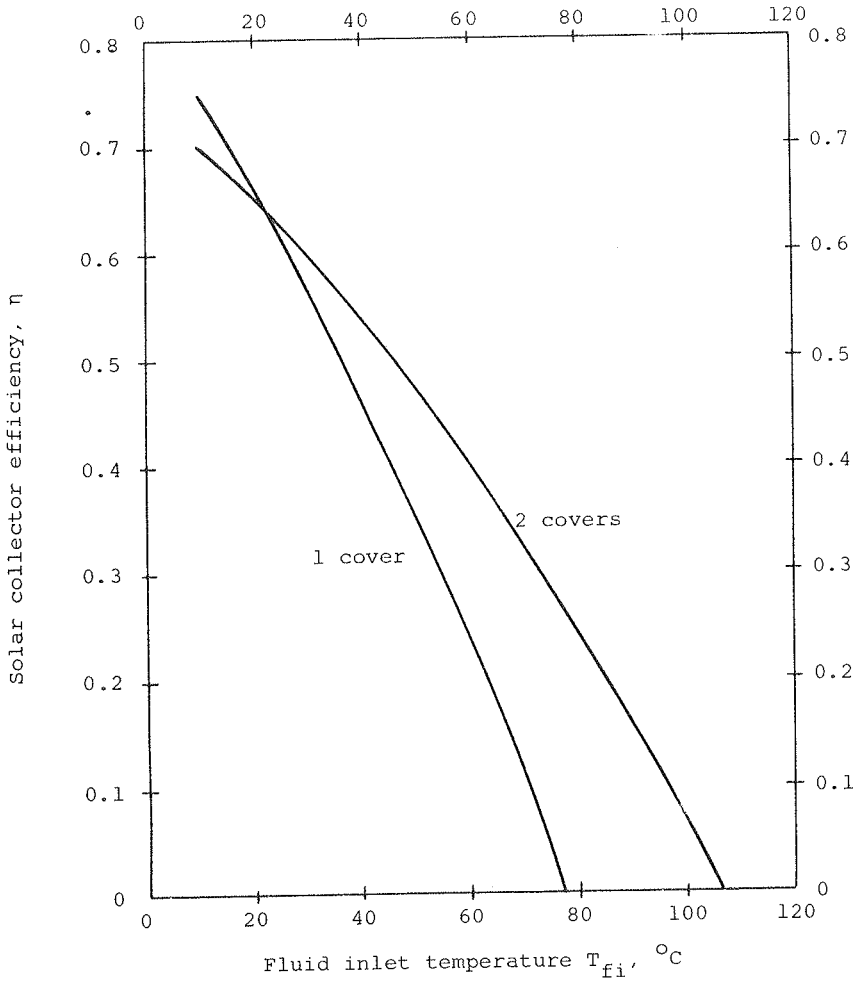


Figure 16. Solar collector efficiency as a function of the fluid inlet temperature with $I = 750 \text{ W/m}^2$ and $T_a = 10^{\circ}\text{C}$ for small angles of incidence.

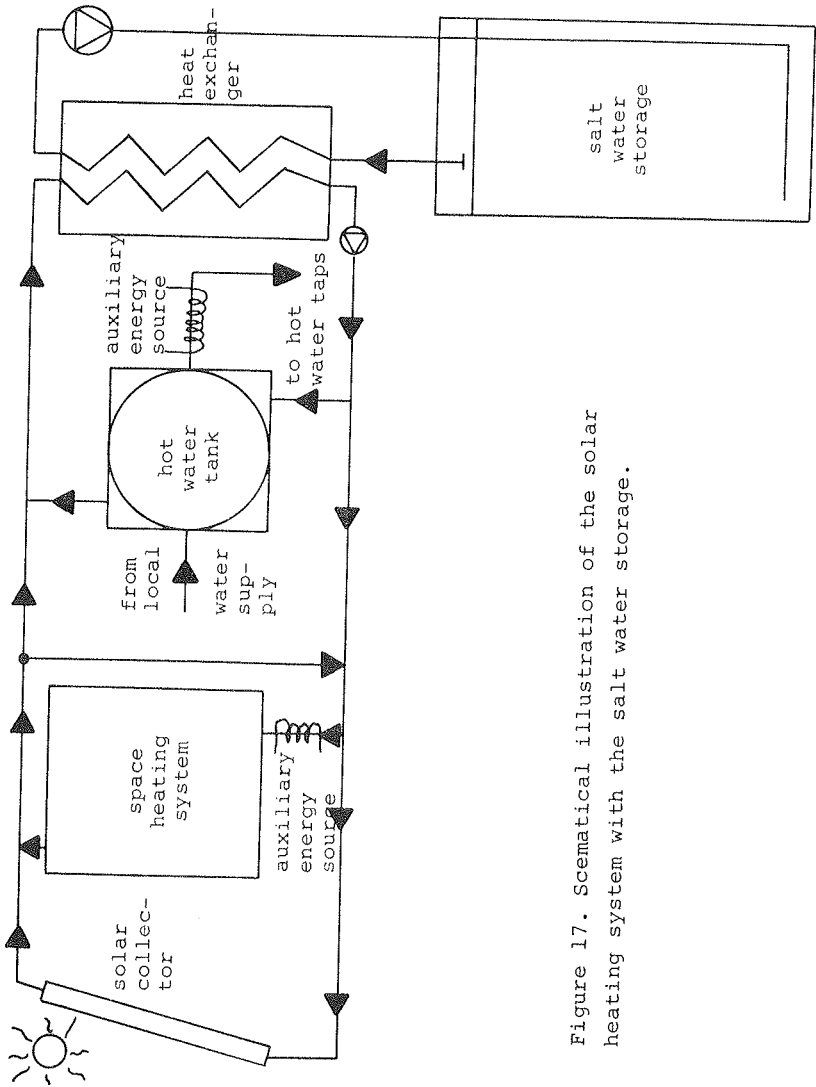


Figure 17. Schematic illustration of the solar heating system with the salt water storage.

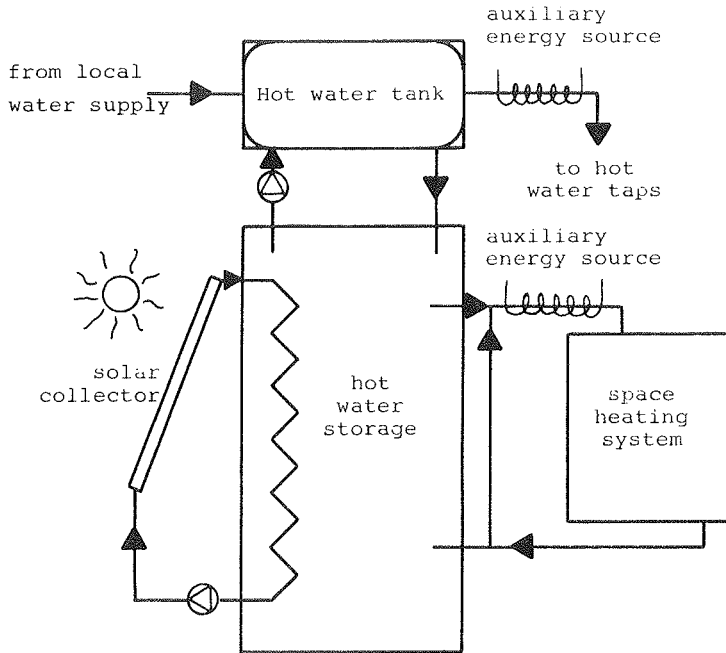


Figure 18. Schematical illustration of the solar heating system with the hot water storage.

tion. House 1 is insulated as a typical house from the beginning of this decade, house 2 is insulated according to the Danish Building Codes, and house 3 is an extremely well-insulated house. The energy quantities used for the different houses are given in table 4.

House number	Building heat loss, W/°C		Dimensioning heat loss, Q _{dimen.} W	Total heat demand for space heat. in the Ref. Year, kWh
	Trans-mission	Venti-lation	(20°C indoor, -12°C outdoor)	
1	229	68	9500	23700
2	150	41	6100	14000
3	86	30	3700	6200

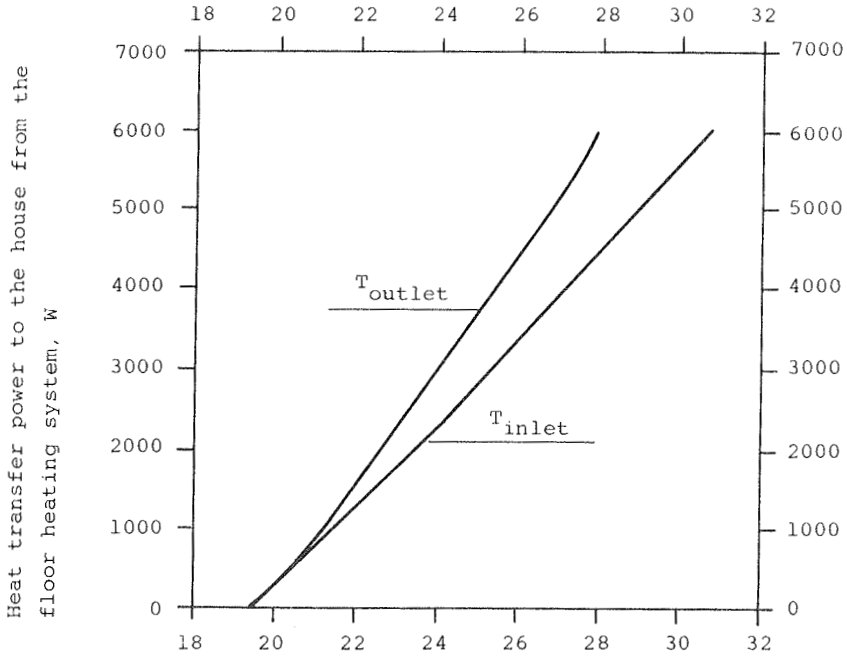
Table 4. The energy quantities for the 3 houses used.

As previously mentioned the amount of hot water supply was fixed to 250 l per day, heated from 10°C to 45°C. This gives an amount of heat requirement for hot water supply during the year of 3650 kWh for each house.

3.6 Space Heating System

Three different space heating systems were calculated, that is space heating systems demanding low, medium and high feed water temperatures from the heat storage.

The first space heating system was a floor heating system which utilizes the heat content of the heat storage situated at low temperatures. For a floor heating system it is a reasonable assumption that 5% of the heat taken from the heat storage to the space heating system is lost to the ground. The flow in the floor heating system is of the amount 2 m³/h. The assumed heat transfer power from the floor heating system to the house as a function of the inlet and the outlet temperature of the fluid is given in figure 19. Only small temperatures are necessary to transfer a large amount of power to the house.



Temperature of inlet and outlet fluid in the floor heating system, °C.

Figure 19 . Heat transfer power to the house from the floor heating system as a function of the inlet and outlet fluid temperature.

The two other heating systems which were calculated require higher temperatures of the fluid in the heating system in order to transfer the heat to the house. Therefore the NaCH_3COO salt water mixture storage is used as the salt storage for these heating systems. The radiators are dimensioned so that the dimensioning heat loss of the house, $Q_{\text{dimensioning}}$ with the unit W, can be transferred to the house by means of the radiators, when the inlet and outlet fluid temperatures in the heating system, $T_{\text{inlet dimensioning}}$ and $T_{\text{outlet dim.}}$, are 60°C and 40°C , respectively 90°C and 70°C , corresponding to typical heating systems. The formula which are used in these calculations are found by means of the theory described in [2]. The formula used are:

$$T_{\text{inlet}} = T_{\text{indoor}} + \frac{Q}{M} \left(\frac{1}{\exp\left(\frac{Q}{M} \left(\frac{a}{Q}\right) - 1.3\right) - 1} + 1 \right)$$

$$T_{\text{outlet}} = T_{\text{inlet}} - \frac{Q}{M}$$

where T_{inlet} is the temperature of the fluid entering the heating system which is necessary in order to transfer the required space heating power

T_{indoor} is the indoor temperature which is assumed to be 20°C

T_{outlet} is the temperature of the fluid leaving the heating system

Q is the required space heating power (W)

M is the flow factor ($\text{W}/^\circ\text{C}$) in the heating system which is found from the dimensioning conditions:

$$M = \frac{Q_{\text{dimensioning}}}{T_{\text{inlet dim.}} - T_{\text{outlet dim.}}}$$

a is a constant also found from the dimensioning conditions:

$$a = \frac{Q_{\text{dimensioning}}}{\frac{T_{\text{inlet dim.}} - T_{\text{outlet dim.}}}{\ln \frac{T_{\text{inlet dim.}} - T_{\text{indoor}}}{T_{\text{outlet dim.}} - T_{\text{indoor}}}} \cdot 1.3$$

For these two heating systems the necessary temperatures of the fluid on the heating system are of course depending on the required heating power, but also on the dimensioning heat loss, that is the grade of insulation of the house.

3.7 Method of Calculating the Performance of the Solar Heating System

A computer program was developed to simulate the solar heating system. On the basis of the data in the Reference Year [3] the direct and diffuse solar radiation is calculated hourly. The diffuse radiation is the sum of the radiation from the sky and the reflected radiation from the area in front of the solar collector. These data are used to calculate the amount of useful solar energy which is circulated from the solar collector to the heat storage hourly.

The heat balance for the heat storage is calculated every hour. The three parts in the heat balance are: the useful solar energy from the solar collector, the heat for the supplying systems, i.e. the heat for hot water supply and for space heating supply, and the heat loss from the heat storage container to the environment. The heat taken from the heat storage to the heat supplying systems is found by the temperature of the heat storage, the required inlet and outlet fluid temperatures of the heating system, the temperature of the hot water tank and the efficiencies of the heat exchangers used in the system.

The temperature of the heat storage is calculated on the basis of the actual amount of heat in the storage, which is found from the above mentioned heat balance.

For every hour during the year the heat balance for the heat storage, the temperature of the heat storage and the amounts of heat which are taken from the heat storage to the heat supplying systems are calculated. These quantities are summed up for the year, and the solar fraction, i.e. the fraction of the total yearly heat requirement which is received from the solar heating system, is calculated.

3.8 Results

The results of the calculations are shown by means of figures in this section. The solar collector area varied from 10 m^2 to 80 m^2 , and the storage volume varied from 0.1 m^3 to 10 m^3 .

As an example of the presentation of the results let us look at figure 20, where the solar fraction is given as a function of the storage volume for different collector areas and different storage types for house number 3, the extremely well insulated house with a floor heating system and a single glazed collector. The salt water storage used in this example is the sodium sulfate water storage. For small collector areas the salt storage is not much better than the water storage. For increasing collector area the difference in the performance for the two storage types increases. With a constant collector area and solar fraction the volume for a water storage will be 2 to 3 times as big as for a salt water storage if the collector area is not too small. The results for a double glazed collector are shown in figure 21, the conditions here are the same as for a single glazed collector.

For a constant collector area of 50 m^2 the results of the same example are shown in figure 22. The salt water storage in connection with a single glazed collector gives approximately the same result as a water storage in connection with a double glazed collector. To give a better comparison between the salt water storage and water storage than

Total heat requirement for space heating in the reference year: 6200 kWh

Total heat requirement for hot water supply during the year: 3650 kWh

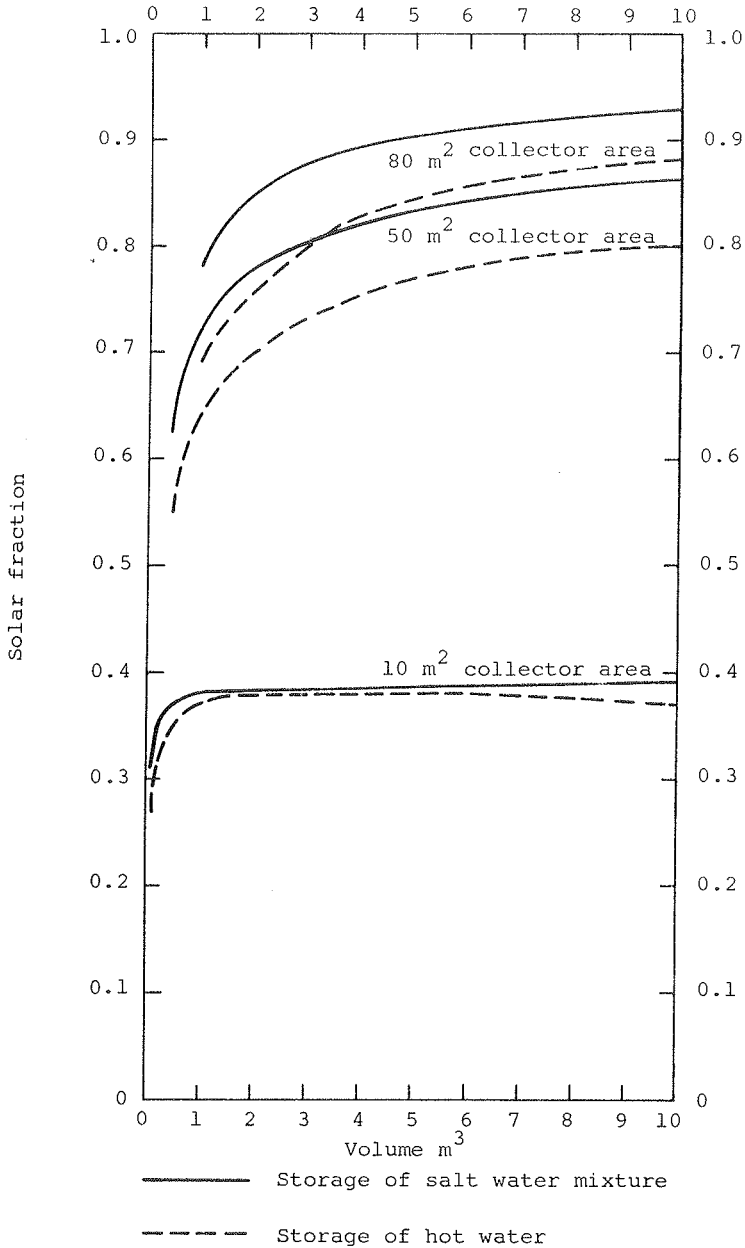


Figure 20. Solar fraction as a function of the storage volume for different single glazed collector areas and storage types. The heating system is a floor heating system.

Total heat requirement for space heating in the reference year: 6200 kWh

Total heat requirement for hot water supply during the year: 3650 kWh

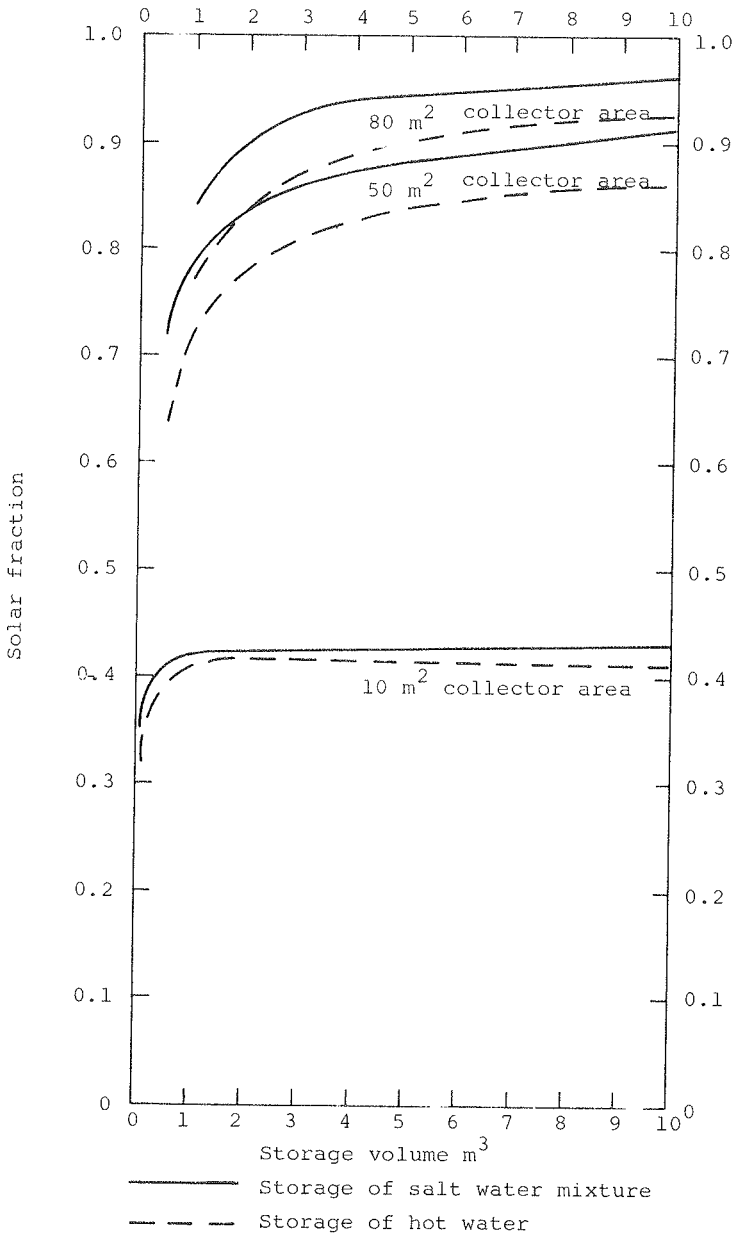


Figure 21 Solar fraction as a function of the storage volume for different double glazed collector areas and storage types. The heating system is a floor heating system.

Total heat requirement for space heating in the reference year: 6200 kWh

Total heat requirement for hot water supply during the year: 3650 kWh

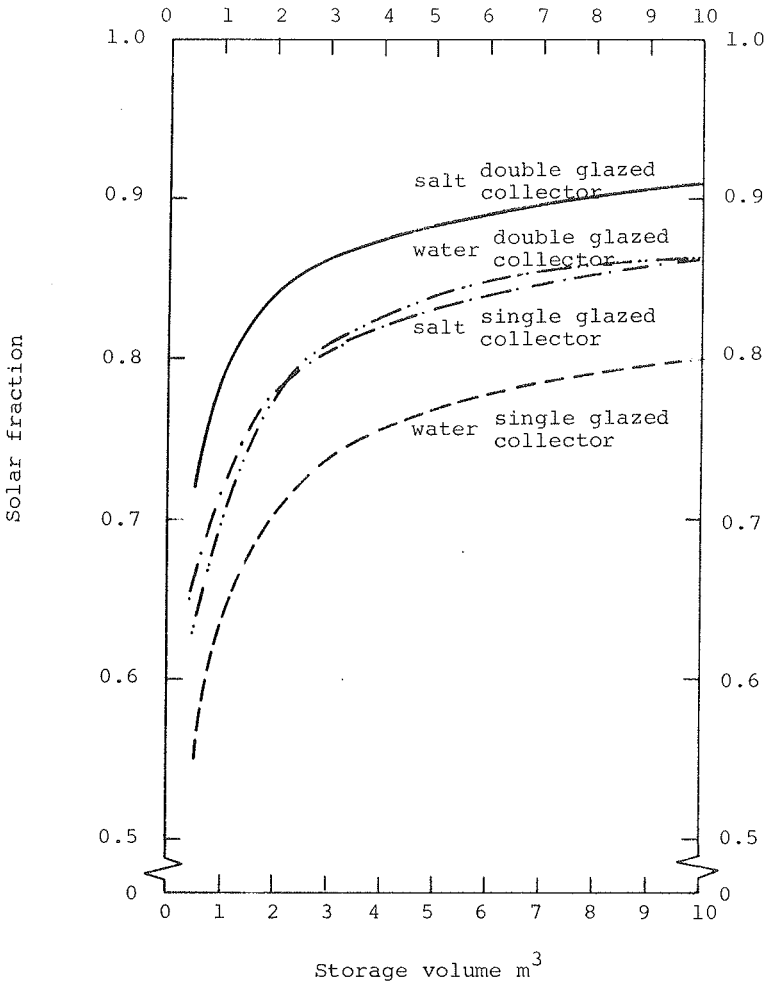


Figure 22 . Solar fraction as a function of the storage volume with the collector area of $50 m^2$.

The heating system is a floor heating system.

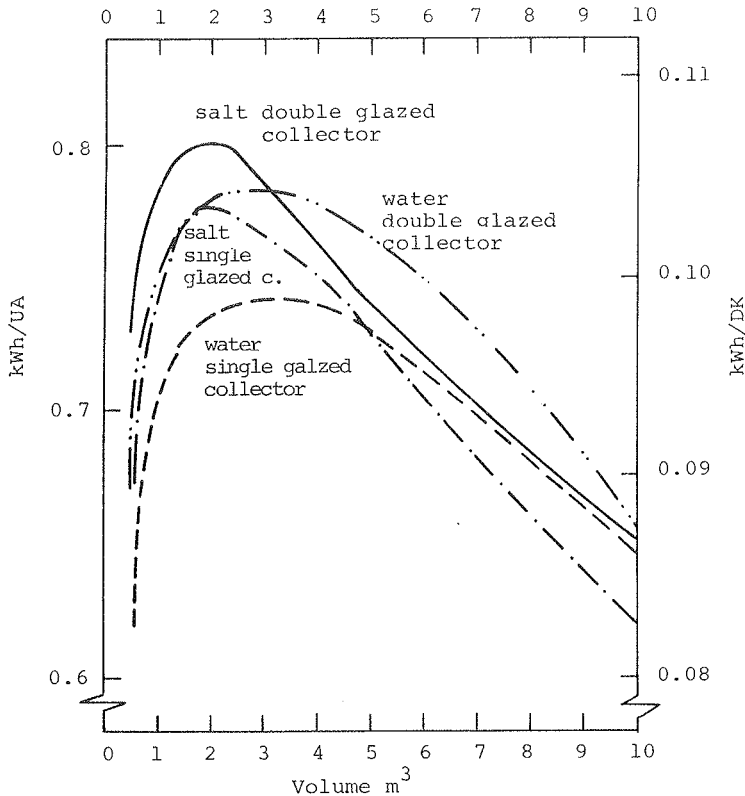
given in figures 20, 21 and 22, the utilized yearly solar energy per cost of investment of the solar heating system can be compared for the different storages. This is done with the constant solar collector area of 50 m^2 , and the results are given in figure 23, where the prices used are also given. The maximum of each curve gives the best volume of the storage. The difference between the different storage systems is small, but a salt water storage in connection with a double glazed collector seems with the used assumptions to be a little better than the other solutions. The best volume for the salt storage is about half of the best volume for the hot water storage. No costs of required house volume for the storage are calculated in this example, so the advantage of using the salt storage can be greater than calculated here.

The above mentioned results from house number 3 in connection with a floor heating system are representative for the results obtained in the analysis which was carried out. Therefore only a few other results will be given in this careful way, and the rest of the results will be given in a few figures where the differences in the performance of the solar heating systems for the different storage types are made plain.

Figures 24 and 25 show the solar fraction as a function of the storage volume for different collector areas for both NaCH_3COO water storages and hot water storages for the solar heating system with a single respectively a double glazed collector. The total heat requirement for space heating and hot water supply during the year is 17650 kWh, and the heating system is demanding medium temperatures. The salt storage seems to be somewhat less favourable in this example than in the above mentioned example, probably caused by the unfavourable melting point for the salt in connection with the demanded temperatures in the heating system, but apart from this point the results in this example are analogous with the results in the above mentioned example.

Total heat requirement for space heating in the reference year: 6200 kWh

Total heat requirement for hot water supply during the year: 3650 kWh



Costs used:

Tank:	350 UA/m ³	
single glazed collector	150 UA/m ²	
double glazed collector	160 UA/m ²	
salt	50 UA/m ³	storage
heat exchanger oil	30 UA/m ³	storage
insulation	30 UA/m ³	insulation
heat exchanger, circulation pump, connecting pipes etc. for salt storage	1500 UA	
heat exchanger, circulation pump, connectin pipes etc. for water storage	1100 UA	
required house volume	0 UA/m ²	basement storage

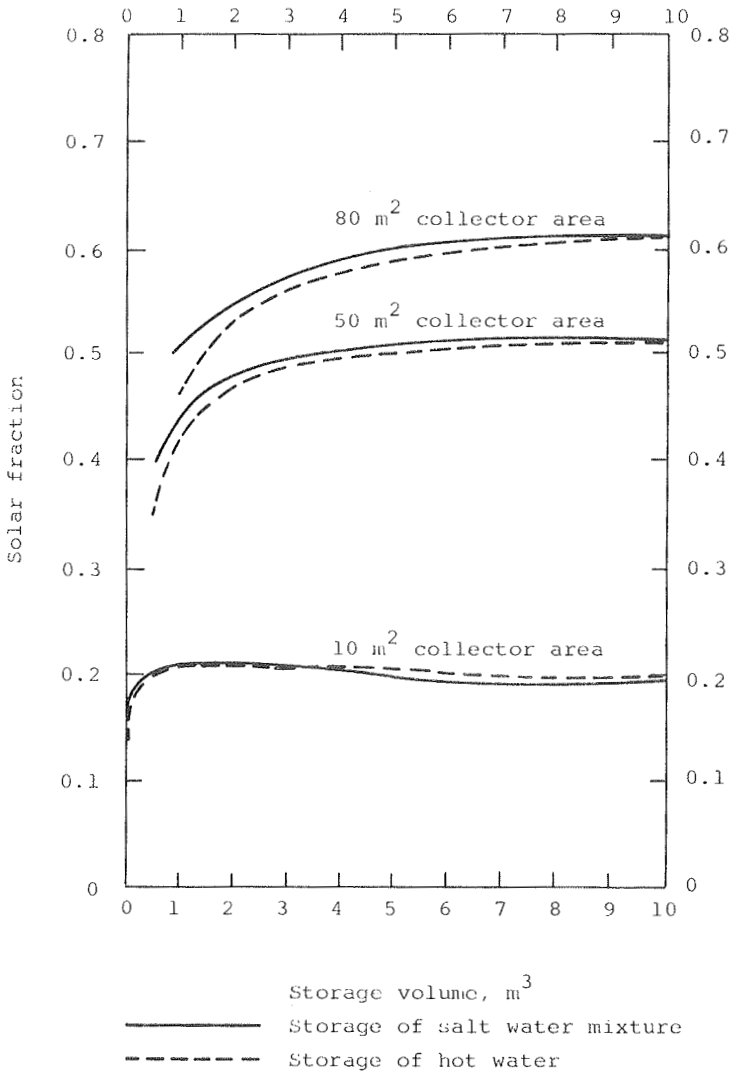
FIGURE 23. Utilized yearly solar energy per cost of investment as a function of the storage volume with the collector area of 50m².

1 U.A. = 7.5 DK

The heating system is a floor heating system.

Total heat requirement for space heating in the reference year: 14.000 kWh

Total heat requirement for hot water supply during the year: 3.650 kWh

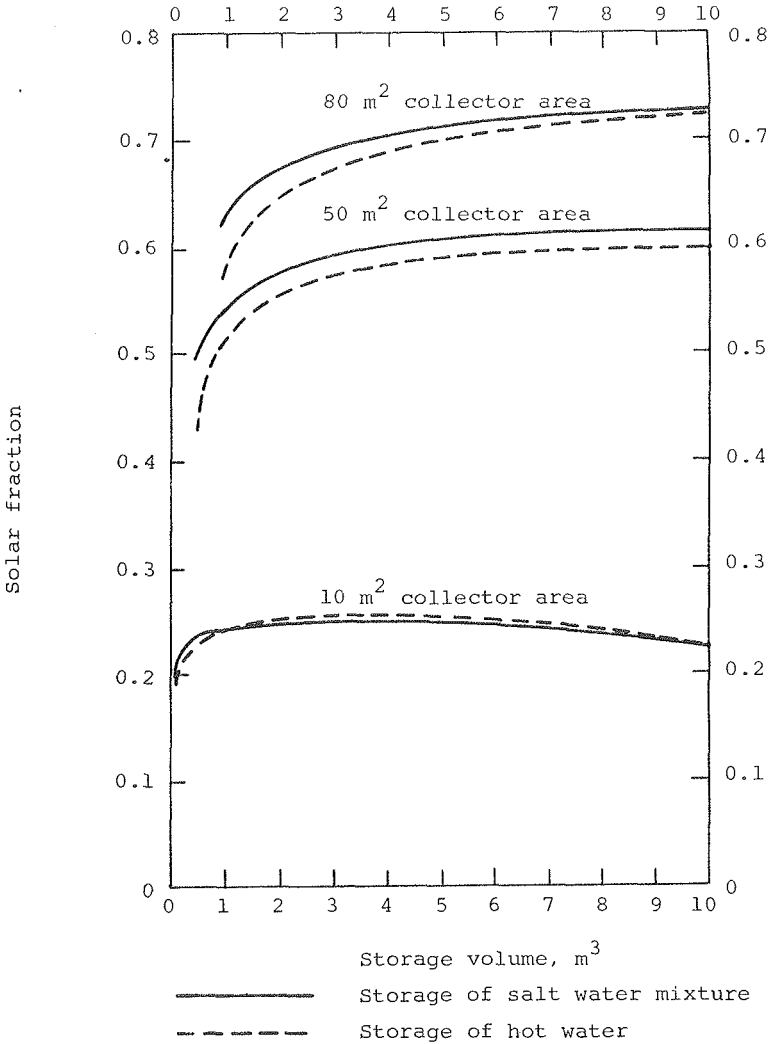


Solar fraction as a function of the storage volume for different single glazed collector areas and storage types. The heating system is demanding medium temperatures.

Figure 24

Total heat requirement for space heating in the reference year: 14.000 kWh

Total heat requirement for hot water supply during the year: 3.650 kWh



Solar fraction as a function of the storage volume for different double glazed collector areas and storage types. The heating system is demanding medium temperatures.

Figure 25

Total heat requirement for space heating in the reference year: 23.700 kWh

Total heat requirement for hot water supply during the year: 3.650 kWh

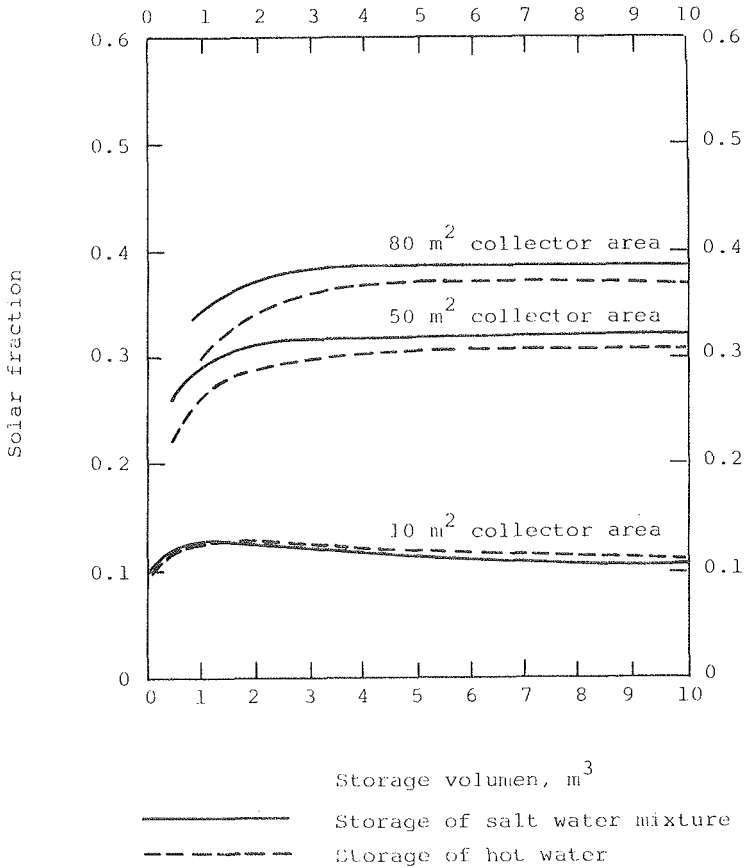


Figure 26 . Solar fraction as a function of the storage volume for different single glazed collector areas and storage types. The heating system is demanding high temperatures.

Figures 26 and 27 show the same as figures 24 and 25 for another example, the house with 27350 kWh/year as the total heat requirement for space heating and hot water supply with a heating system demanding high temperatures. The salt water mixture used in this example is also the sodium acetate water mixture, and the results are quite analogous with the results obtained for the other houses and heating systems.

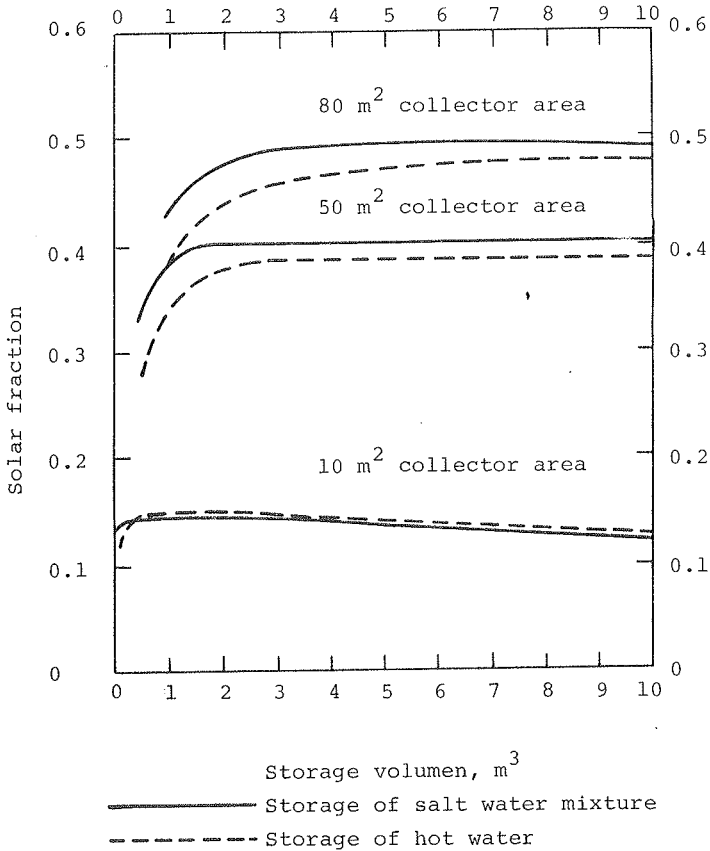
The best volume of the heat storage can be found by means of the method illustrated in figures 22 and 23. The result obtained from the example in these figures was that the volume of the salt storage should be approximately the half of the volume of the hot water storage. For a single example the influence of the volume of the salt water storage on the performance is shown in figure 28. The utilized yearly solar energy per m^2 collector area is shown as a function of the collector area for different storage types and storage volumes. The dotted line corresponds to a hot water storage having a volume of 0.1 m^3 per m^2 collector area, which in Denmark is about the best volume of the water storage and a widespread rule-of-thumb for solar heating system engineers. Besides the curve for the water storage, 3 different curves for the salt water storage corresponding to 0.01, 0.05 and 0.1 m^3 per m^2 collector area are given. The utilized yearly solar energy per collector area decreases at increasing collector area. The utilized yearly solar energy per collector area increases at increasing volume of the salt water storage. Curves 2 and 3 are almost identical, that is: the increase of the performance of the solar heating system for increasing storage volume almost stops when the storage volume has reached a certain amount, which for the salt storage is about $0.05 \text{ m}^3/\text{m}^2$ collector area, and for the hot water storage about $0.1 \text{ m}^3/\text{m}^2$ collector area. Therefore these storage volume/collector area rates were selected and used in the presentation of the rest of the results from the analysis.

These selected rates are also in reasonable good agreement with the results found in the example in figure 23.

The influence of the heating system in connection with the influence of the storage type is illustrated in figure 29 for an example with a double glazed collector and the house which has a total yearly heat demand of 17650 kWh. Three different heating systems demanding low, medium and high temperatures were investigated, and also here the utilized yearly solar energy per m^2 collector decreases at increasing collector area. The performance of the solar heating system increases for heating systems demanding decreasing feed water temperature. There seems to be no other difference between a salt storage and a water storage than that the volume of the water storage is the double of the volume of the salt water mixture storage, since the curves for the water storage and salt storage almost are identical. The heating system has no influence on the choice of storage type.

The influence of the house, that is the influence of the total heat requirement in connection with the influence of the storage type on the thermal performance of the solar heating system, is illustrated in figure 30 for an example with a floor heating system and a double glazed solar collector. Also here the utilized yearly solar energy per m^2 collector decreases at increasing collector area. The utilized yearly solar energy per m^2 collector increases for increasing yearly requirement for space heating and hot water supply. That is: the greater the heating demand, the better the performance of the solar heating system. The curves for the salt storage and the water storage are almost identical, that is: the performance is about the same both for a solar heating system having a salt water mixture storage and for a solar heating system having a water storage, when the volume of the salt water storage is half of the volume of the water storage. It is also seen that the total heat requirement per year has no influence on the choice of storage type.

Total heat requirement for space heating in the reference year: 23.700 kW
Total heat requirement for hot water supply during the year: 3.650 kW



Solar fraction as a function of the storage volume for different double glazed collector areas and storage types. The heating system is demanding high temperatures.

Figure 27

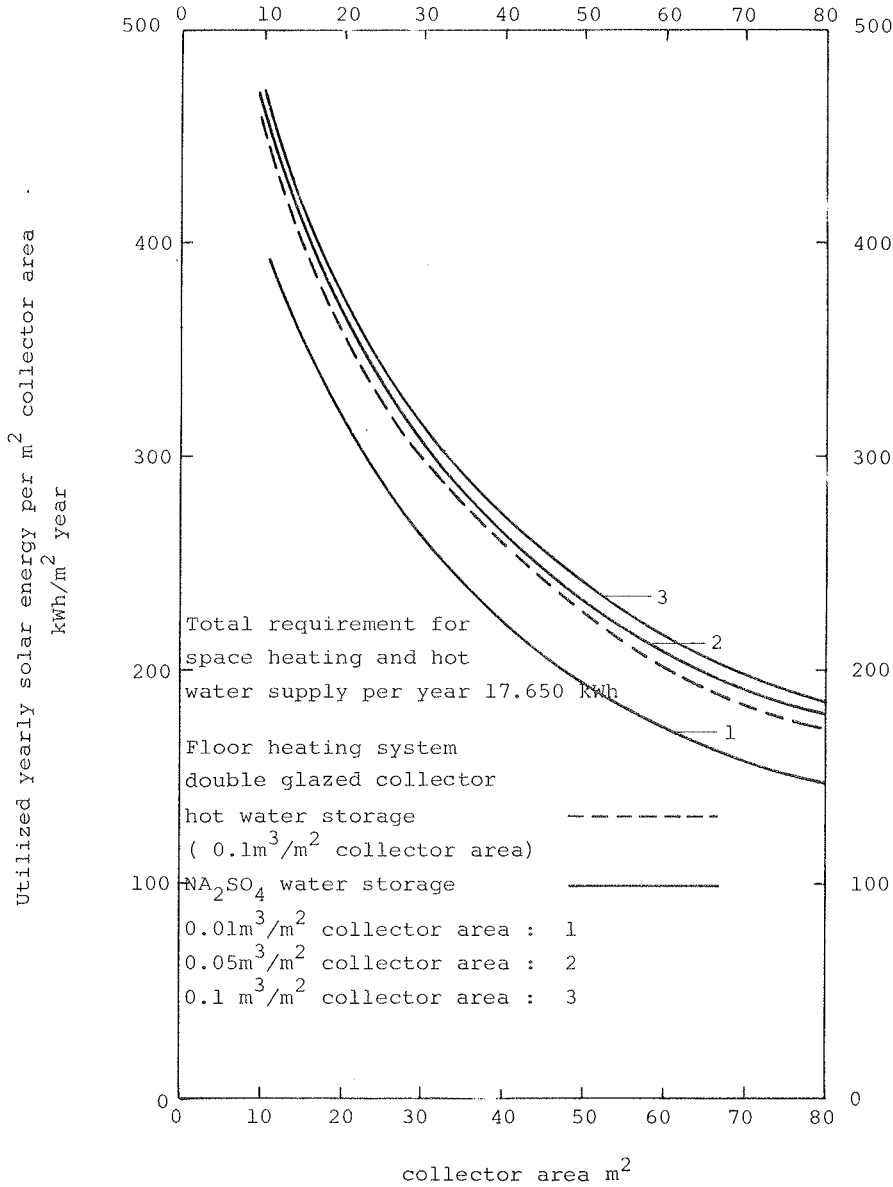


Figure 28. Utilized yearly solar energy per m^2 collector area as a function of the collector area for different storages.

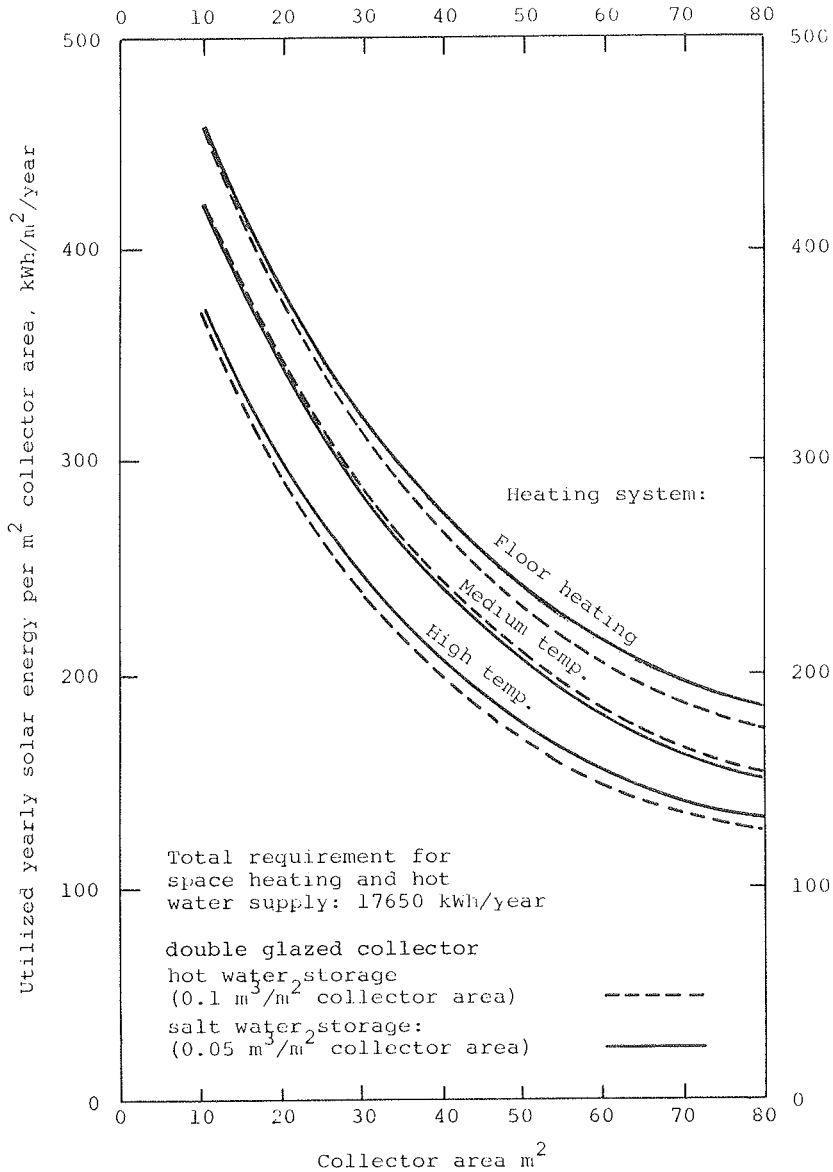


Figure 29. Utilized yearly solar energy per m^2 collector area as a function of the collector area for different heating systems and storage types.

These were some of the results found from the analysis, and the conclusion is that the volume of the salt water storage should be about half the volume of the water storage. No differences in the thermal performance of the solar heating system should be expected due to change of storage type. Accordingly the interesting question is: For which collector areas is the salt storage economically more favourable than the hot water storage? This of course depends on the costs of the water storage, the salt storage, the solar collector and the required house volume for the storage. For the example used in figure 30 the utilized yearly solar energy per cost of investment is given as a function of the collector area in figure 31 with the costs given in the figure. The maximum of each curve gives the best collector area concerning the optimum of the utilized yearly solar energy per cost of investment. The solar heating systems are most advantageous for houses with large total heat demands. Due to higher initial costs of the salt storage the water storage system is more favourable than the salt storage system for small collector areas, in the example collector areas less than 30 m^2 . For collector areas larger than 30 m^2 the salt storage becomes more favourable than the water storage. The results of course depend on the used costs. With other costs the results will be different.

The point of intersection, that is the collector area where the salt and water storage system give the same utilized solar energy per cost of investment, is found for a single example in figure 32. The costs of the parts of the solar heating system are given in the first column. The black line gives the collector area where the salt and the water storage system give the same utilized solar energy per cost of investment with the costs given in the column for the reference system. This collector area is 25 m^2 . The variations in the mentioned collector area are shown for variations in one of the price factors, while the rest of these factors have the

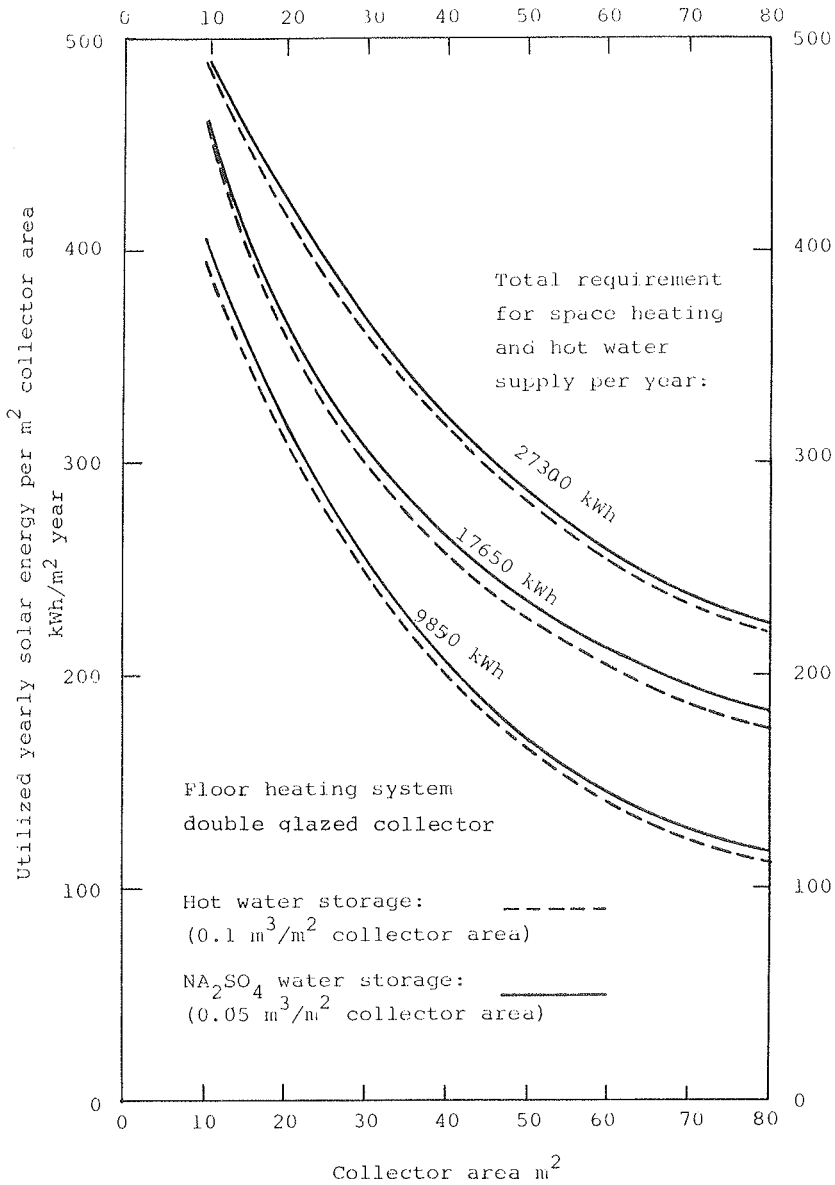
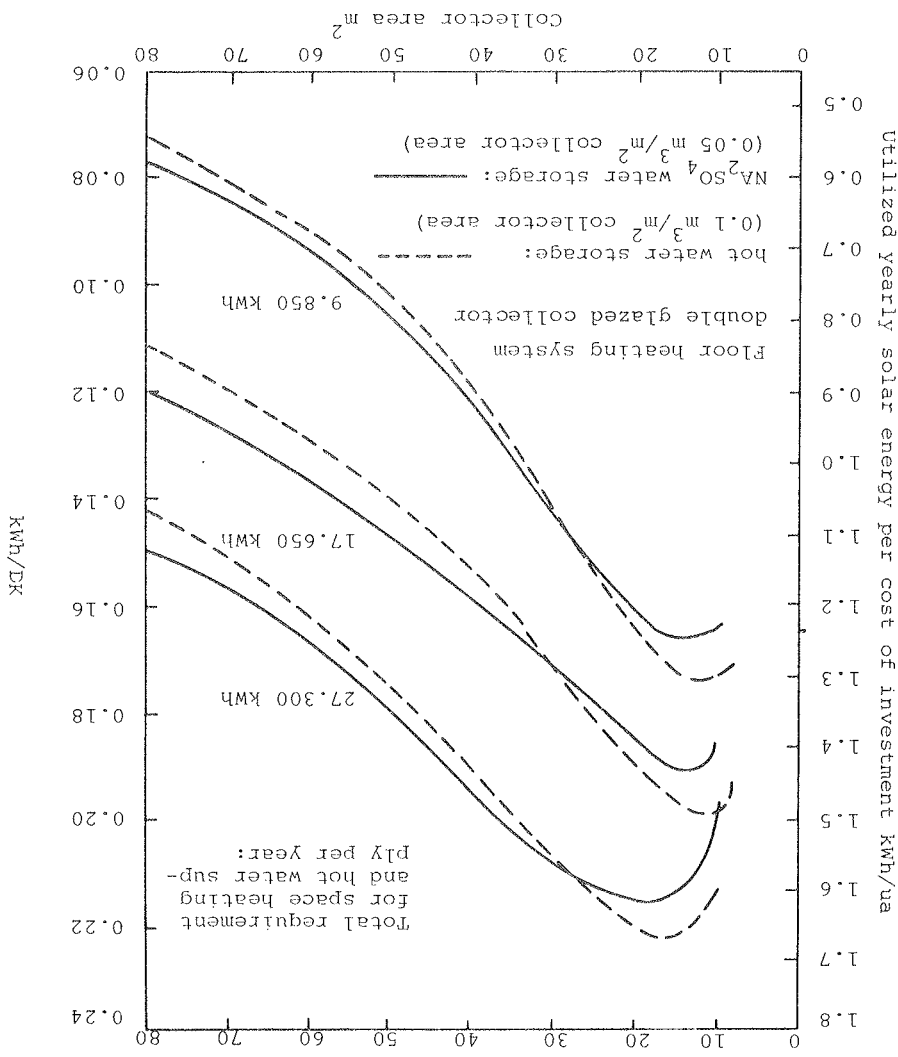


Figure 30 . Utilized yearly solar energy per m^2 collector area as a function of the collector area for different heating demands and storage types.



COSTS USED:

- tank: 350 ua/m²
- double glazed collector: 160 ua/m²
- heat exchanger oil: 50 ua/m³
- insulation: 30 ua/m³
- heat exchanger, circulation: 30 ua/m³
- pump, connecting pipes etc. 1500 ua
- for salt storage
- heat exchanger, circulation: 1100 ua
- pump connecting pipes etc.
- for water storage
- required house volume: 1 ua/m²
- 0 ua/m² basement storage
- 1 ua = 7.5 DK

Figure 31. Utilized yearly solar energy per cost of investment for different heating demands and storages as a function of the collector area.

collector area where salt and water storage solar heating systems gives the same utilized solar energy per cost of investment

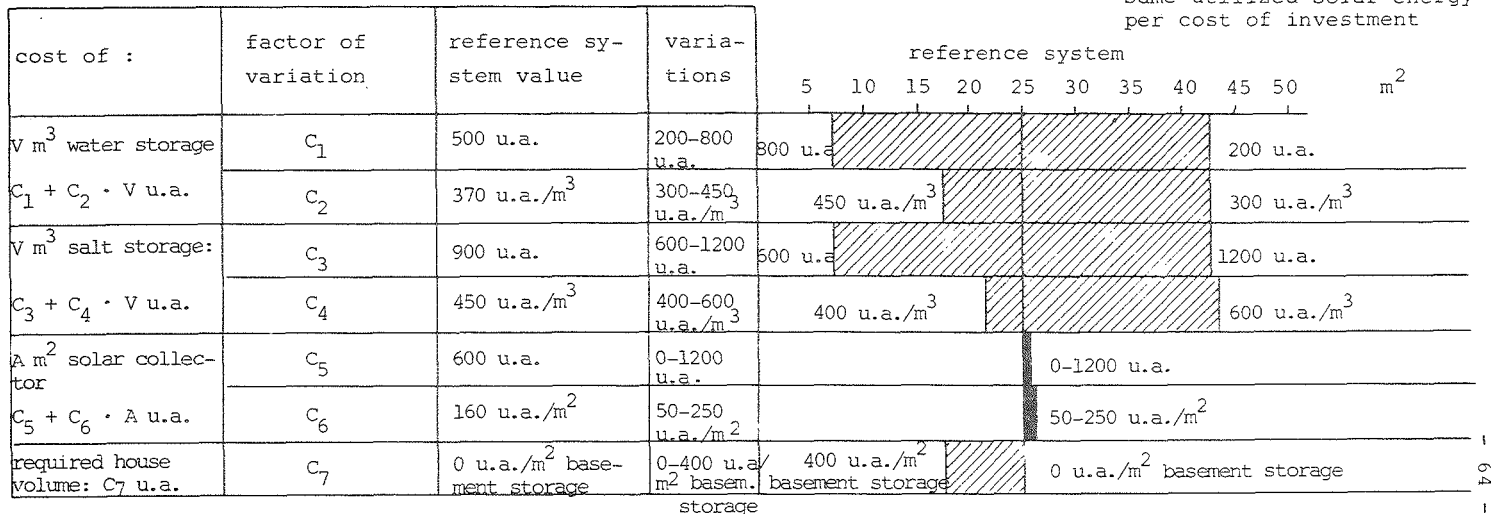


Figure 32 . Solar collector area where the solar heating system gives the same utilized yearly solar energy per cost of investment for a salt storage and a water storage as a function of variations in the used costs.

Used assumptions :

Total requirement for space heating and hot water supply per year : 17.650 kWh
 floor heating system
 double glazed collector

volume of hot water storage : 0.1 m³/m² collector area

volume of Na₂SO₄ - water storage : 0.05 m³/m² collector area

reference system values. Only for collector areas larger than the area found in this figure, salt water mixture storages are favourable compared with hot water storages. If the price of the $V \text{ m}^3$ water storage is for instance $200 + 370 V \text{ u.a.}$, and the other prices are as given in the reference system, the collector area has to be as large as 42 m^2 , before the salt storage is as favourable as the water storage, and for collector areas larger than 42 m^2 the salt water mixture storage is favourable compared with the hot water storage. Variations in the solar collector costs have no influence on the point of intersection, while variations in the costs of the storages have great influence on the point of intersection. The cost of the basement storage has also influence on the point of intersection, although not as much as the costs of the storages. The considerations lead to the conclusion that salt storage only will be economically comparable or favourable to water storage for large solar collector systems.

3.9 Conclusion

The conclusion of the analysis is that the volume of a salt water mixture storage should have half the volume of a water storage. No essential difference in the thermal performance of the solar heating system appears with change of storage type from water storage to salt water mixture storage. Economically, considerations show that only for large solar heating systems the salt storage will be favourable.

4. CONSIDERATIONS CONCERNING CONSTRUCTION OF A HEAT OF FUSION STORAGE UNIT

4.1 Storage Material

Storage material candidates in heat of fusion storages are inorganic congruently melting salt hydrates, incongruently melting salt hydrates where phase separation is avoided, organic compounds, and organic and inorganic eutectic mixtures. This project deals with incongruently melting salt hydrates, and further an investigation of some organic compounds as heat storage materials was carried out.

As a rule the organic compounds have small densities compared with the inorganic salt hydrates, resulting in a small storage density per unit volume. This makes the salt hydrates favourable as heat storage materials.

In [1] the selection of salt hydrates for heat storage materials is described. In addition to this a search for organic compounds was carried out. Some of the most promising organic compounds from this search were investigated more carefully in this project in order to find the heat storage capacity of these materials. The investigation was carried out by the chemical consultant Erik Pedersen, and his report covering this subject is given in the following.

4.1.1 Enthalpies of Ethylene Carbonate, Tetraethylammonium Chloride Tetrahydrate, Stearic Acid, and Benzyl Stearate in the Temperature Range 0-90°C

Experimental:

The enthalpies were determined by application of a calorimeter consisting of a silvered and vacuum insulated dewar system equipped with a mechanical stirrer, thermocouple sensor, and heating element. The internal volume was 150 ml. The stirrer was made of 2 x 0.2 mm stainless steel tubing in order to keep the heat leaks low. The

thermocouple was a Ni-Cr/Ni element having a sensitivity of $41 \mu\text{V K}^{-1}$. The temperature was recorded on a Varian 10" strip chart recorder having a linearity of 0.2%. The heating element was made of a ribbon of "Kanthal" alloy in direct contact with the content of the calorimeter. The power was obtained from a voltage stabilized dc supply.

The calibration was performed by application of 100 g of water. The thermal capacity of the system was found to be 88 J K^{-1} in the range $0-90^\circ\text{C}$. The heat leak was measured for every 10°C in this range, and appropriate corrections for this were made in all measurements. Corrections were also made for the heat produced by stirring; these were negligible for liquids and only small for solid samples. The rate of stirring and the power applied were set at values giving the best compromise between the problem of obtaining temperature equilibrium in solid samples and the problem of correcting for heat leaks. For solid samples we applied approximately 3 W and 18 W for liquids.

The samples were pure grade products obtained from Fluka except for the benzyl stearate which was obtained by reacting equal amounts of benzyl alcohol and stearoyl chloride and recrystallizing the product from toluene. Samples corresponding to 100 ml at 25°C were applied.

Results:

The calculated enthalpies per unit of volume are shown in Figures 33-36. At temperatures below the melting points temperature equilibrium was a problem due to the low thermal conductivities of the samples. The two curves in these ranges in the figures indicate estimated uncertainties. Also indicated in the figures are the values for water (dashed lines). We observed some corrosion of the heating element in liquid tetraethylammonium chloride tetrahydrate. The rate was dependent on the voltage

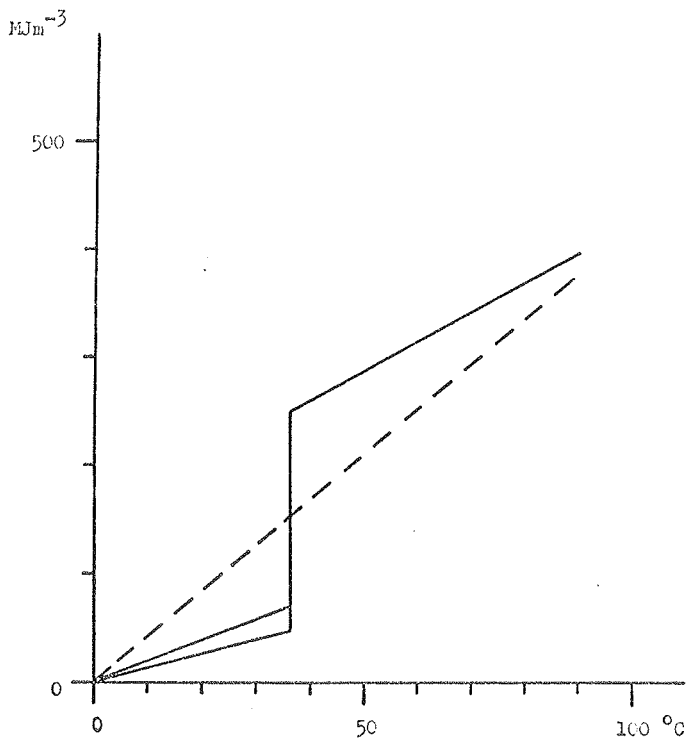


Fig. 33. Enthalpy of ethylene carbonate, $\text{C}_3\text{H}_4\text{O}_3$.

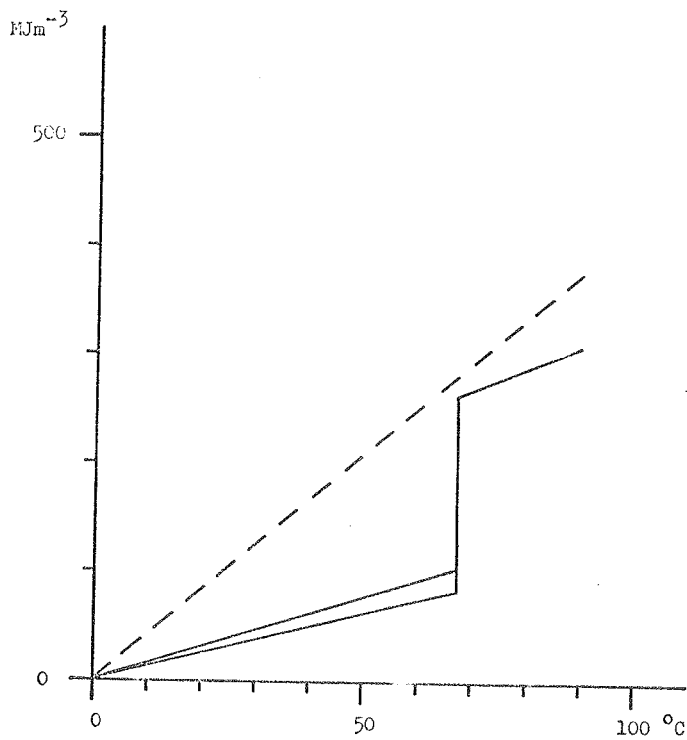


Fig. 34. Enthalpy of stearic acid, $C_{17}H_{35}COOH$.

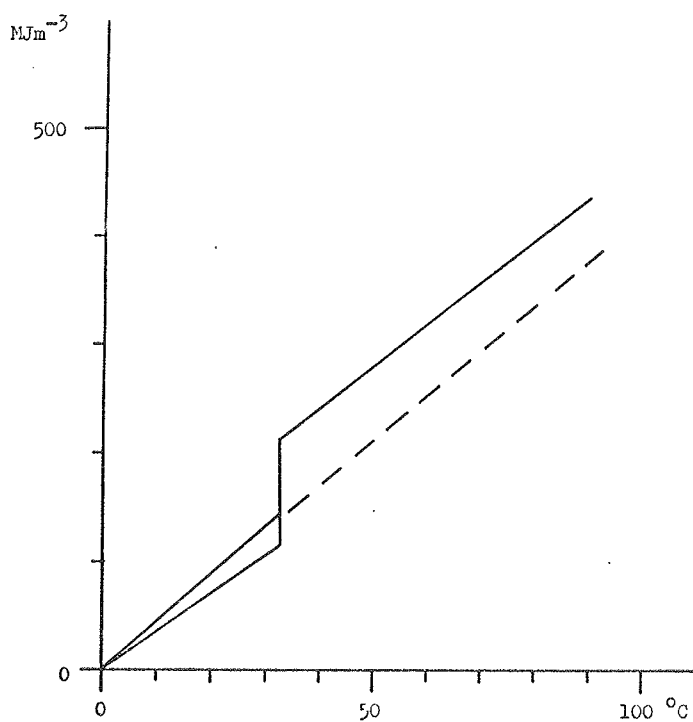


Fig. 35. Enthalpy of tetraethylammonium chloride tetrahydrate, $(C_2H_5)_4NCl \cdot 4H_2O$.

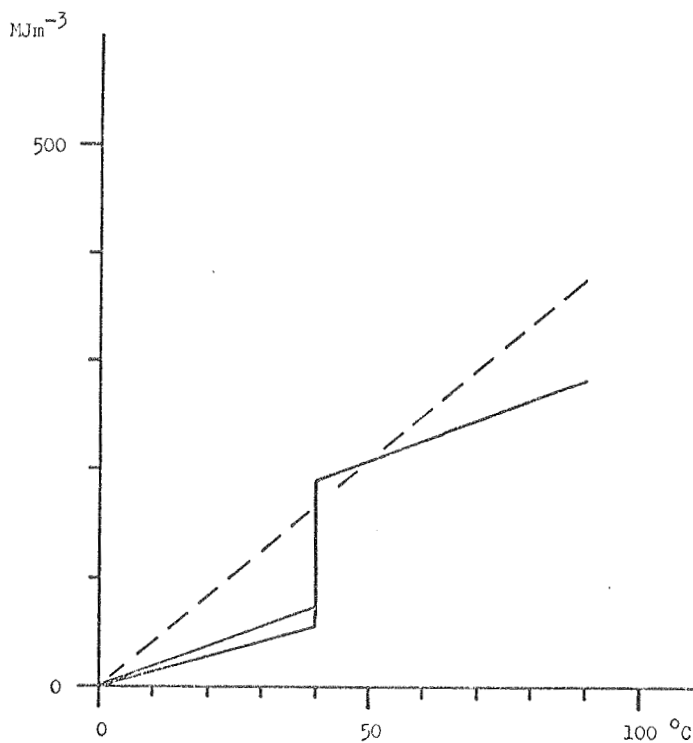


Fig. 36. Enthalpy of benzyl stearate, $\text{C}_{17}\text{H}_{35}\text{COOCH}_2\text{C}_6\text{H}_5$.

across the element. The resultant changes in resistance were considered in our calculations. The changes in volume observed in the temperature range were approximately 5% for all samples. Congruent melting was observed. We found the following densities of the samples at 25°C: Ethylene carbonate 1.32, tetraethylammonium chloride tetrahydrate 1.00, stearic acid 0.85, benzyl stearate 0.90, all in g ml⁻¹.

The prices of the investigated organic compounds will be somewhat higher than the prices of the inorganic salt hydrates. For stearic acid for instance 650 u.a./t for 20 t delivery.

4.2 Stability of the Heat Storage

The heat storage material itself obviously must be stable.

If a salt hydrate is used the melting must either be congruent, or phase separation must be avoided if the melting is incongruent. This phase separation can for instance be avoided by means of microencapsulation, rotation or vibrant stirring of the storage material, but also by means of the extra water principle.

Further the container material in connection with the storage material must be stable at the temperatures by which the storage is operating. This could lead to limitations in the choice of both container material and storage material. For some of the most promising salt water mixtures making use of the extra water principle found in [1], experiments were carried out in order to elucidate the problems concerning the use of such salt water mixtures as storage materials in containers of unprotected steel and copper. The experiments were carried out by the Danish Corrosion Centre and are described in the following by Ebbe Rislund and Finn Yding.

4.2.1 Corrosion of Steel and Copper in Salt Hydrates of Na₂SO₄, Na₂CO₃, Na₂HPO₄ and NaCH₃COO

Background:

Salt hydrates may be used for storage of heat in solar heating systems instead of water in order to store more

heat in a smaller volume. A detailed description is given in [1]. The salt hydrate is kept in a tank where heat exchange is accomplished by bubbling oil from the solar collector through the salt hydrate. The storage tank may be filled completely and supplied with a closed expansion tank for the oil, thus limiting the oxygen supply to very small amounts. It must be equipped with a heating element for melting the hydrates after idle periods.

If possible the tank would be made of unprotected steel and the heating element of copper. The experiments described here aim to show if this will give any corrosion problems under less ideal conditions, that is without restriction of the oxygen supply.

Experimental:

Corrosion of steel and copper coupons was measured in beakers, stagnant and with free access of air, except for two layers of plast balls to decrease evaporation. The amount of salt hydrate was 2 l, and in each beaker 6 coupons of 50 x 80 x 1 mm were placed.

4 salt hydrates were examined at both room temperature and at 80°C:

Na_2SO_4 , conc. 33%

Na_2CO_3 , conc. 33%

Na_2HPO_4 , conc. 27%

NaCH_3COO , conc. 58%

The solutions were prepared at 60°C, using ordinary tap water (total hardness 22°dH, Cl^- 33 ppm, pH 7.3). At 80°C the hydrates remained in solution, whereas at room temperature there was little or no free water between the salt hydrate crystals.

Unalloyed steel and copper, both of normal commercial grade, were used for test coupons. For each salt hydrate at each temperature 3 beakers were prepared containing:

- five vertically placed steel coupons and one steel coupon lying at the bottom
- three copper and two steel coupons, vertically placed, and one steel coupon lying at the bottom
- three couples of steel and copper coupons, vertically placed and connected by a steel bolt with a distance between steel and copper of 1 cm obtained by a plastic spacer.

Vertically placed coupons were fastened by a plastic wire through a small hole in the coupon. On the galvanic couples the wire was fastened around the plastic spacer.

Before exposure the coupons were cleaned and weighed. They were inspected regularly during the 22 days of exposure, after which they were removed and inspected before and after cleaning. All coupons were reweighed after cleaning.

Results:

The test results are given in table 5. They include calculated average corrosion rate, inspection for pitting and discolouration of the solutions.

Sodium sulphate, Na_2SO_4 , gave corrosion of steel both when cold and hot, and there was a significant increase in attack when the steel was connected to copper. The corrosion rates were low, but there was a strong tendency to localized corrosion in the hot solutions at edges and especially at crevices. Copper was not attacked. The sulphate solutions were quickly discoloured by rust.

Sodium carbonate, Na_2CO_3 , did - as expected - not attack steel, but gave some corrosion of copper. The test results show a tendency to increased corrosion of copper when coupled to steel in hot solutions. The hot carbonate solutions were discoloured by copper corrosion products.

Table 5. Test Results.

Solution, Temperature	Corrosion rate mm/year	Pitting, discolou- ration	Steel coupons	Copper present to copper	Steel coupons connected to copper	Copper coupons with steel present	Copper coupons connected to steel	Pitting, discolou- ration	Copper coupons connected
Na_2SO_4	r.t.	3-6	a	2-6	a	6-8	<1	a	a
33%	80°C	5-6	p, a	5-8	sp, a	10-16	<1-2,5	a	a
Na_2CO_3	r.t.	<1	<1	<1	b	<1	1-3	<1-3	b
33%	80°C	<1	<1	<1	b	<1	1,5-2	4-5	b
Na_2HPO_4	r.t.	<1	<1	<1	b	1,5-2,5	sp, b	2-8	b
27%	80°C	9-18	10-16	<1	b	1,5-2,5	sp, b	50-55	b
NaCH_3COO	r.t.	<1	<1	<1	b	<1	sp	<1	b
58%	80°C	<1	<1	<1	b	<1	sp, b	9-10	b
								9-10	

sp = slight pitting of steel at wire connections and edges, or under plastic discs, <0,1 mm 22 days
 p = pitting of steel at wire connections and edges, or under plastic discs, 0,1-0,2 mm / 22 days
 a = solution discoloured by rust

b = solution coloured blue by copper corrosion products

Disodium phosphate, Na_2HPO_4 , did not attack steel when cold, but gave some corrosion when hot. Freely exposed copper was slightly attacked, but coupling to steel gave a significant galvanic effect and high corrosion rates of copper, especially in hot solutions which were discoloured by copper corrosion products. There was a slight pitting tendency of steel when coupled to copper.

Sodium acetate, NaCH_3COO , did not cause corrosion of steel, except for a slight pitting tendency when coupled to copper. The hot solutions gave some attack of copper but without galvanic effects, and the hot solutions were discoloured by copper corrosion products.

Presence of copper without metallic contact to steel did not in any case affect the corrosion of steel.

There was no difference in corrosion of vertically and horizontally placed steel coupons, and corrosion following the lines of the salt hydrate crystals in the cold solutions was not observed.

Conclusion:

For heat storage tanks the following conclusions may be drawn from the test results:

1. Na_2SO_4 should not be used without complete prevention of oxygen access, as it causes some corrosion of steel with tendency to localized corrosion, especially at crevices. If oxygen is excluded no or very little corrosion would be expected, but crevice corrosion may still cause trouble.
2. Na_2CO_3 can be used safely in steel tanks. The tendency to accelerated corrosion of copper when coupled to steel may be critical for a copper heating element in a steel tank (large cathode-anode area), and steel is recommended for the heating element.

3. Na_2HPO_4 can be used in steel tanks, but prevention of oxygen access is recommended. Heating elements should be made of steel and not of copper, as there is a strong increase in corrosion of copper when coupled to steel. Also, coupling to copper seems to give a tendency to pitting of steel.
4. NaCH_3COO can be used in tanks made from steel and copper. However, there is a slight attack of copper in hot solutions, and coupling between copper and steel seems to give a tendency to pitting of steel. It is therefore recommended to use steel also for the heating element.

In these conclusions it is assumed that the heat exchanging oil does not alter the corrosivity of the solutions.

The galvanic effects mentioned above may of course be prevented by preventing metallic contact between copper and steel.

Tanks made of unprotected steel should be filled completely with salt hydrate and oil to prevent corrosion in vapour filled spaces.

4.3 Heat transfer capacity for the storage

In order to elucidate the importance of the amount of the heat transfer capacity to and from the storage calculations with the same assumptions as in section 3 were carried out with different heat transfer capacities. The results of these calculations are given in figure 37 and 38 for a single example. In figure 37 the utilized yearly solar energy per m^2 collector area is given as a function of the collector area for different heat transfer capacities from the storage to the heating systems. The utilized yearly solar energy per m^2 collector area increases at increasing heat transfer capacity. The increase in the performance of

the solar heating system almost stops when the heat transfer capacity has reached a certain amount, about $30 \text{ W/}^{\circ}\text{C m}^2$ collector area. In figure 38 the utilized yearly solar energy per m^2 collector area is given as a function of the collector area for different heat transfer capacities from the solar collector to the storage. Also here the utilized yearly solar energy per m^2 collector area increases at increasing heat transfer capacity. The increase in the performance of the solar heating system almost stops when the heat transfer capacity has reached a certain amount, about $40 \text{ W/}^{\circ}\text{C}$ collector area.

If therefore the amount of heat transfer capacity for cooling and heating is $30 \text{ W/}^{\circ}\text{C m}^2$ collector area respectively $40 \text{ W/}^{\circ}\text{C m}^2$ collector area, no essential increase in the performance is obtained by increasing the heat transfer capacity.

Two different heat transfer methods for the heat storage were examined in the experimental phase of the project. In the first method oil in direct contact with the storage medium was used. In the second method heat transfer through the surface area of the container was used. For both methods the heat transfer capacity for an unbroken heating/cooling cycle was measured.

The two examined heat storage volumes were 1500 l and 500 l, corresponding to 30 m^2 respectively 10 m^2 collector area.

For the 1500 l storage a sufficient amount of heat transfer capacity is $900 \text{ W/}^{\circ}\text{C}$ and $1200 \text{ W/}^{\circ}\text{C}$ for cooling respectively heating. For cooling at low temperatures the measured heat transfer capacities, see figure 12, therefore are too small. The oil inlet system must therefore be designed in such a way that the oil flow velocity does not decrease as solidification takes place.

For the 500 l storage a sufficient amount of heat transfer capacity is $300 \text{ W/}^{\circ}\text{C}$ and $400 \text{ W/}^{\circ}\text{C}$ for cooling respectively heating. Therefore no heat transfer problems exist for this storage type, see figure 14.

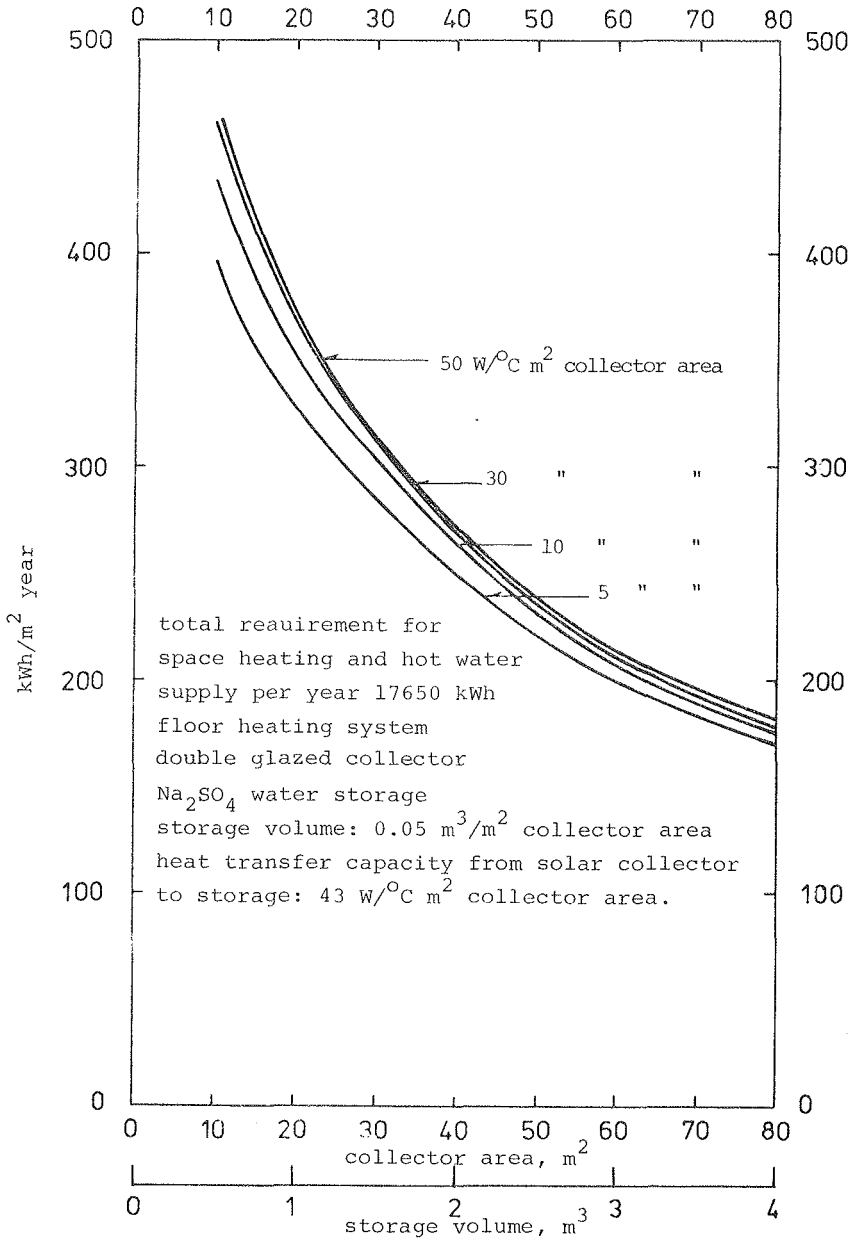


Figure 37. Utilized yearly solar energy per m^2 collector area as a function of the collector area for different heat transfer capacities from the storage to the heating systems.

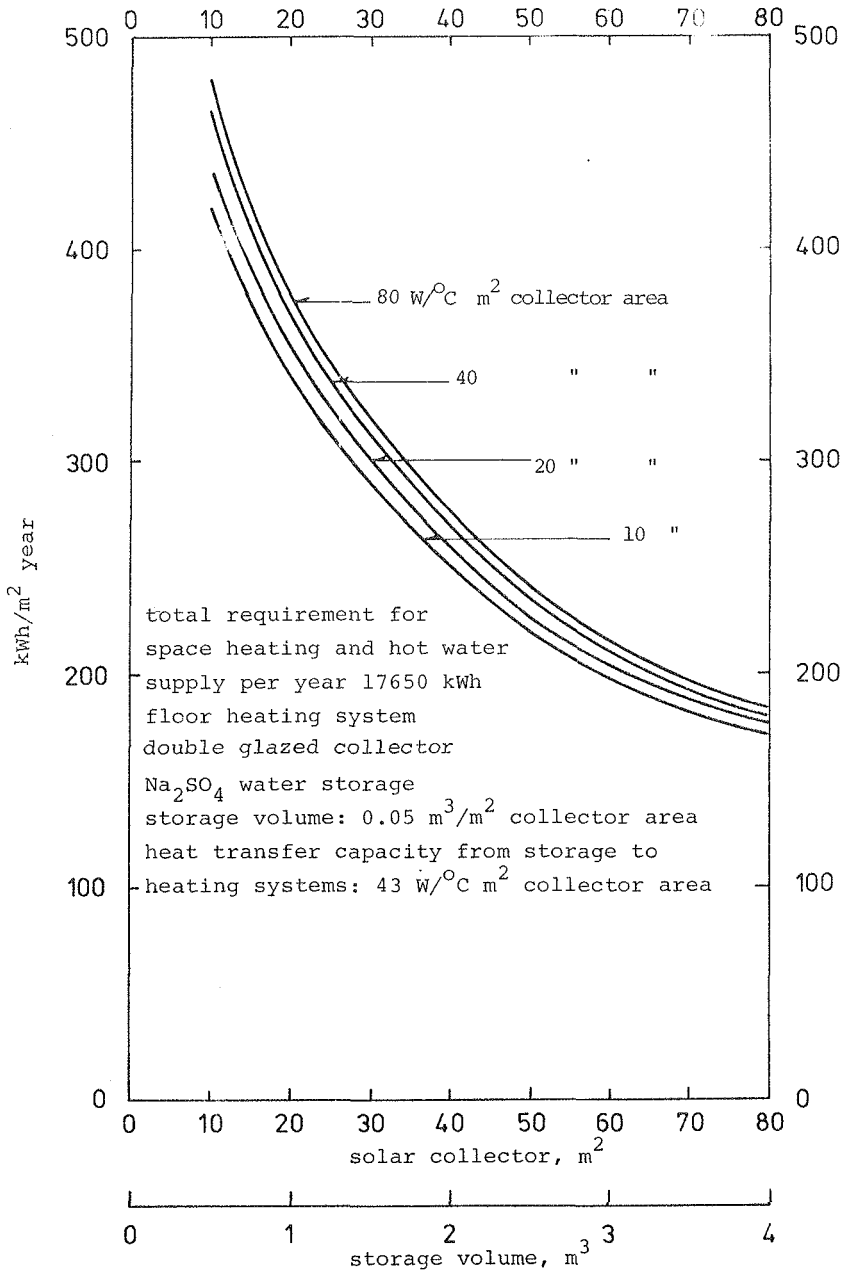


Figure 38. Utilized yearly solar energy per m^2 collector area as a function of the collector area for different heat capacities from the solar collector to the storage.

5. CONCLUSION

Two different full scale storage types both making use of the extra water principle have been examined by means of experiments. There was no decrease in the performance of the storages after several heating/cooling cycles, and the storages worked as a whole as planned. There seems to be no technical problems which cannot be overcome concerning obtaining a stable and reliable heat storage making use of the extra water principle.

Heat storages making use of the extra water principle and, as heat transfer fluid, a heat transfer oil in direct contact with the storage medium were compared with hot water storages as part of solar heating systems by means of computer calculations. The conclusion of these calculations was that the volume of the salt water mixture storage should be about half the volume of the water storage. Economically, heat of fusion storages will only be favourable in solar heating systems larger than a certain amount, which of course depends of the actual prices of the different heat storages.

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