EXPERIMENTAL STUDIES ON SEASONAL HEAT STORAGE BASED ON STABLE SUPERCOOLING OF A SODIUM ACETATE WATER MIXTURE

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1. Introduction

Theoretical studies have shown that a 36 m² solar heating system can fully cover the yearly heat demand of a low energy house in Denmark if the solar heating system is based on a 6000 l seasonal heat storage with a sodium acetate water mixture supercooling in a stable way. The heat storage is divided into a number of separate modules.

The heat storage concept is based on the advantage of stable supercooling to achieve a partly heat loss free heat storage. If a sodium acetate water mixture, which has a melting point of 58°C, has been fully melted, it can cool down in its liquid phase to the surrounding temperature and still preserve the latent heat related to the heat of fusion. The heat storage can be left in this state with no heat loss until a heat demand occurs, in which case solidification is activated, the heat of fusion is released, and the heat storage temperature increases almost immediately to the melting point.

The investigations of a seasonal heat storage module described in this paper are carried out within the IEA Task 42 project "Compact Thermal Energy Storage: Material Development and System Integration".

2. Investigated seasonal heat storage module

A flat laboratory heat storage module described by Furbo et al. (2010) is investigated experimentally. Figure 1 shows a schematic sketch of the heat storage module with approximated dimensions in mm. The module is filled with 305 kg salt water mixture consisting of 58% (weight%) sodium acetate and 42% (weight%) water. The volume of the salt water mixture is about 234 l. The salt water mixture is used, since it supercools in a stable way. Investigations by Furbo (1978) have shown that a salt water mixture of 58% NaCH₃COO and 42% water can be used in tanks made from steel without a risk of corrosion. The module material is therefore steel and the wall thickness is 2 mm. Both the lower and upper surfaces of the flat module can be used as heat transfer areas for heat transfer to and from the module.

Two different heat transfer methods for the heat storage module are investigated. Water is for both methods used as heat transfer fluid. For the first heat transfer method, water can be pumped through two copper absorbers placed below and above the module as shown in figure 2. Heat is transferred from/to the salt water mixture, to/from the upper or lower module surface, the copper absorber and the water flowing through the absorber. Wooden slats are placed above and below the absorber strips in such a way that there will be thermal contact between the absorber fins and the module surfaces. A paste with a good thermal conductivity is placed between the copper absorbers and the upper and lower surfaces of the heat storage module. The construction is insulated with 100 mm mineral wool.



Fig. 1: Principle sketch of heat storage module with two holes used to fill in the salt water mixture.



1: Wooden slats. 2: Salt water mixture in steel module. 3 & 9: Copper pipes. 4 & 8: Absorber fin. 5: Mineral wool. 6: Bottom of module. 7: Paste with good thermal conductivity.

Fig. 2: Principle sketch of heat storage module with absorber heat transfer system and insulation.

Figure 3 shows photos of the heat storage module investigated by means of the first heat transfer method. Thermocouples for measurements of the module surface temperatures are placed both on the upper and lower surfaces of the heat storage module.

Figure 4 shows photos of the heat storage module using the second heat transfer method. The heat storage module is placed in a stainless steel container with small separate rooms for water below and above the module. Silicone pipes are attached to the upper and lower surfaces of the module in such a way, that water pumped through the separate rooms will flow through the rooms in a serpentine way, guided by the silicon pipes. The water will therefore flow through the lower room in direct contact with all parts of the lower module surface, and water will flow through the upper room in direct contact with all parts of the upper module surface. Heat is transferred from/to the salt water mixture, to/from the upper or lower module surface and the water flowing through the upper or lower room.

The flat module is placed with a small tilt from horizontal. A small brass tank shown in figure 5 is in good thermal contact attached to the outer surface of the side of the module. This brass tank, which has a pressure of 5 bar, can be filled with liquid CO_2 from a pressure container. The boiling point of the CO_2 in the brass tank is thus -78°C. As described by Furbo et al. (2010), the solidification of the salt water mixture can be started by cooling down a small part of the supercooled salt water mixture to -16°C by boiling a small amount of CO_2 in the small brass tank.



Fig. 3: Photos of the heat storage module with a copper absorber used for the heat transfer.





Fig. 4: Photos of the heat storage module with silicone pipes attached to the upper surface.



Fig. 5: Brass tank with CO₂ used for starting the solidification.

3. Tests of seasonal heat storage module

The heat storage module has been tested in a laboratory heat storage test facility for the two heat transfer methods described in section 2. The module has been charged through the bottom surface of the module and discharged through the top surface. The module has also been tested in periods without charge and discharge. The activation of solidification of the supercooled salt water mixture by boiling CO_2 at the outer surface of the module has been tested. Finally, charge and discharge tests through both the bottom and top surfaces of the module have been carried out for the module for the heat transfer method using the copper absorbers by the heat transfer.

The module was investigated through a period of about 1 year. The results and experience of the investigations are summarized in sections 3.1, 3.2 and 3.3.

3.1 Supercooling and solidification start method for supercooled salt water mixture

The investigations showed that the salt water mixture supercools if all the salt hydrate crystals of the heat storage module are melted during the charge period. If the whole volume of the salt water mixture is not heated to a minimum temperature of 64° C for a period of at least one day, the supercooling will not be stable.

The solidification start method using boiling CO_2 in good thermal contact with the outer surface of the heat storage module is reliable. The solidification started in all cases about 1 minute after the liquid CO_2 entered into the brass tank. However, it must be mentioned that the placement of the brass tank with the liquid CO_2 is of vital importance for the suitability of the method. The solidification start method does not work if the brass tank is placed at the very bottom of the tilted module. The reason is most likely that phase separation takes place in the heat storage module in such a way that anhydrous salt is placed at the very bottom of the tilted module and a non saturated salt water solution is placed in the upper part of the tilted module. A strong cooling of the anhydrous salt at the bottom of the module caused by the boiling CO_2 will not start the solidification, because the anhydrous salt at the bottom of the module is not in contact with the water, which should be used to form the salt hydrate crystals.

3.2 Heat content of heat storage module and reliability

The tests showed that the measured heat content of the heat storage module is as high as the theoretically calculated heat content of the heat storage module. For instance, for the heat transfer method using the absorbers, the measured heat content for the module is about 38 kWh in the temperature interval from 25°C to 82°C. This corresponds reasonably well to the theoretically calculated heat content of the 305 kg salt water mixture, the 90 kg steel of the heat storage module, the 26 kg copper of the absorbers and of the 4.6 kg water in the absorbers: 34.8 + 0.7 + 0.2 + 0.3 = 36 kWh.

Based on the good agreement between the measured and the calculated heat content of the heat storage module, it is concluded that only a small part of the salt water mixture does not take part in the phase change due to the phase separation problem mentioned in section 3.1.

It should also be mentioned that during the whole measuring period there are no signs of problems with reliability or durability.

3.3 Heat exchange capacity rate

Theoretical calculations by Schultz and Furbo (2007) have shown that the heat exchange capacity rates both for charge and discharge of a seasonal heat storage module for solar heating systems fully covering the yearly heat demand of low energy buildings must be around 500 W/K. The tested heat storage module has an approximate volume of 234 l, corresponding to about half the volume of a suitable heat storage module for a real seasonal heat storage. It is therefore estimated that the heat exchange capacity rate for the investigated heat storage module must be around 250 W/K.

Figures 6, 8 and 10 show measured temperatures and figures 7, 9 and 11 shows measured heat exchange capacity rates for charge and discharge periods for the heat storage module using the heat transfer method with the absorbers. Figure 6 shows inlet and outlet temperatures for the water flowing through the lower absorber as well as temperatures for the upper surface of the heat storage module during a charge period where heat is only transferred from the lower absorber to the heat storage module. The volume flow rate of the water flowing through the absorber is 6.2 l/min. Figure 7 shows the heat exchange capacity rate during the same charge period. The heat exchange capacity rate is determined with the assumption that the measured mean temperature of the upper surface of the heat storage module is equal to the temperature of the salt water mixture.



Charge through bottom surface - 6.2 l/min

Fig. 6: Measured inlet and outlet temperatures for water flowing through the lower absorber with a volume flow rate of 6.2 l/min and 9 temperatures at the upper surface of the module during a charge period through the bottom surface.



Fig. 7: Measured heat exchange capacity rate for a charge period with water flowing through the lower absorber with a volume flow rate of 6.2 l/min.

The heat exchange capacity rate during the charge period is about 40-60 W/K, which is about a factor of 5 too low.

Figure 8 shows inlet and outlet temperatures for the water flowing through the upper absorber as well as temperatures for the lower surface of the heat storage module during a discharge period where heat is only transferred from the heat storage module to the upper absorber. The volume flow rate of the water flowing through the absorber is 4.2 l/min and the salt water mixture is in liquid phase, that is: The salt water mixture is supercooled for the last part of the discharge. Figure 9 shows the heat exchange capacity rate during the same discharge period. The heat exchange capacity rate is determined with the assumption that the measured mean temperature of the lower surface of the heat storage module is equal to the temperature of the salt water mixture.



Fig. 8: Measured inlet and outlet temperatures for water flowing through the upper absorber with a volume flow rate of 4.2 l/min and 9 temperatures at the lower surface of the module during a discharge period through the upper surface. The salt water mixture is in the liquid phase.



Fig. 9: Measured heat exchange capacity rate for a discharge period with water flowing through the upper absorber with a volume flow rate of 4.2 l/min and with the salt water mixture in the liquid phase.

The heat exchange capacity rate during the discharge period is about 15-45 W/K, which is about a factor of 8 too low.

Figure 10 shows inlet and outlet temperatures for the water flowing through the upper absorber as well as temperatures for the lower surface of the heat storage module during a discharge period, where heat is only transferred from the heat storage module to the upper absorber. The volume flow rate of the water flowing through the absorber is 7.4 l/min, and the solidification of the salt water mixture is started in the beginning of the discharge. Figure 11 shows the heat exchange capacity rate during the same discharge period. The heat exchange capacity rate is determined with the assumption that the measured mean temperature of the lower surface of the heat storage module is equal to the temperature of the salt water mixture.



Fig. 10: Measured inlet and outlet temperatures for water flowing through the upper absorber with a volume flow rate of 7.4 l/min and 9 temperatures at the lower surface of the module during a discharge period through the upper surface. The solidification of the salt water mixture is activated in the start of the discharge.



Fig. 11: Measured heat exchange capacity rate for a discharge period with water flowing through the upper absorber with a volume flow rate of 7.4 l/min and with solidification of the salt water mixture.

The heat exchange capacity rate during the discharge period is about 10-30 W/K, which is about a factor of 12 too low.

It is concluded that the heat exchange capacity rates are too low, as long as only one absorber is used during charge and discharge.

Measurements showed that the heat exchange capacity rates both for charge and for discharge are increased by using both the lower and the upper absorber during charge and discharge. However, the heat exchange capacity rates are still far too low. For instance, for the discharge with the solidifying salt water mixture, the heat exchange capacity rate is a factor of 6 too low, even if both absorbers are used.

Most likely, the main reason for the poor heat exchange capacity rate is a poor thermal contact between the flat absorbers below and above the heat storage module and the surfaces of the module. The poor thermal contact is caused by the balloon effect of the heat storage module illustrated in figure 12. The density of the salt water mixture is a strong function of the temperature and whether the mixture is in the liquid or solid phase. The higher the temperature, the lower the density is. The module is schematically shown at a low (left) and a high (right) temperature in figure 12. The expansion of the salt water mixture at high temperatures will result in a balloon shape of the steel module. It is obvious that flat absorbers placed below and above the module will have a decreased thermal contact with the module surfaces at high temperatures, resulting in decreased heat exchange capacity rates.



Fig. 12: Schematic sketch of heat storage module at a low temperature (left) and a high temperature (right).

The heat exchange capacity rates for the heat storage module using the heat transfer method with water in direct contact with the module surfaces are investigated by Fan et al. (2011). The heat exchange capacity rates are determined for charge periods with heat transfer from water flowing through the room below the heat storage module to the heat storage module and for discharge periods with heat transfer from the heat storage module to water flowing through the room above the heat storage module.

The investigations show that the heat exchange capacity rates for the heat transfer method with water in direct contact with the module surfaces are higher than the heat exchange capacity rates for the heat transfer method using the absorbers. However, the heat exchange capacity rates are about a factor of 3 too low, both

for charge and discharge periods. Further, it is estimated, that if the heat is transferred both by means of water flowing through the upper and the lower room, the heat exchange capacity rates will still be a factor of 1.5 too low for charge periods and for discharge periods.

Based on the investigations, it is therefore concluded, that the heat transfer areas for the heat storage module are too small.

4. Small scale tests on the height of heat storage modules

Small scale experiments with a salt water mixture consisting of 58% NaCH₃COO and 42% water are carried out with the aim to elucidate if the height of the salt water mixture in a heat storage module will result in phase separation problems during a long heat storage period.

The salt water mixture is placed in small glass containers with heights of the salt water mixture of 3 cm, 5 cm and 8 cm. The glasses are heated to 80°C. After this heating period the glasses are placed in a room with an air temperature of about 20°C for 1 month. Figure 13 shows photos of the supercooled salt water mixture in the three glasses. The solidification of the supercooled salt water mixture was initiated after 1 month by cooling the glasses in a freezer to a temperature below -16°C. After that the glasses are placed in a room at an ambient temperature of about 20°C. The glass with the salt water mixture height of 8 cm contain a small liquid volume, while none of the other two glasses contain any visible liquid volume after the solidification. This experiment indicates that phase separation problems will appear if the salt water mixture height is 8 cm, and that phase separation problems will not appear as long as the height is not higher than 5 cm, at least for a heat storage period of 1 month.

A similar experiment with a 6 months heat storage period is ongoing.



Fig. 13: Photos of glasses with 3 different heights of supercooled salt water mixture.

5. Improved design of seasonal heat storage module

The investigations showed that the heat storage module works satisfactorily with regard to heat storage capacity, stable supercooling, activation of solidification and reliability. The investigations also showed that the heat exchange capacity rate to and from the heat storage module is too low, and that the heat transfer areas of the heat storage module are too small.

Further, preliminary small scale investigations indicate that phase separation problems will not decrease the durability of the heat storage module as long as the height of the module is not larger than 5 cm.

Based on the investigations, a new 300 l flat heat storage module with increased heat transfer areas will be constructed. The heat storage module material will be steel, and the thickness of all steel walls will be 2 mm. The height of the salt water mixture in the heat storage module will be 5 cm, and there will be rooms with vertical heights of 2 mm above and below the salt water tank. Water can be pumped through the rooms in a serpentine way, and heat can be transferred to and from the salt water mixture from and to the water flowing through both rooms.

The heat storage module will be tested in the laboratory during the winter 2011-2012. It is hoped that the heat storage module will have good thermal characteristics inclusive sufficiently high heat exchange capacity rates.

6. Conclusions

Experimental investigations of a 234 l seasonal heat storage module based on a salt water mixture consisting of 58% NaCH₃COO and 42% water as heat storage material have been carried out. The salt water mixture has a melting point of 58°C.

The investigations showed that the salt water mixture will supercool in a stable way if all salt hydrate crystals in the heat storage module are melted during the charge period, that a method to activate solidification of the supercooled salt water mixture using boiling CO_2 in a small tank attached to the outer surface of the heat storage module is reliable, that the heat content of the heat storage module is as high as theoretically calculated, and that the durability of the heat storage module is good. The investigations also showed that the heat exchange capacity rate to and from the heat storage module is too low, and that heat transfer areas of the heat storage module are too small.

Based on the investigations, a new 3001 flat heat storage module with increased heat transfer areas will be constructed. It is hoped that the new heat storage module will have good thermal characteristics inclusive sufficiently high heat exchange capacity rates.

7. References

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