Testing of an Industrial PCM Heat Storage Prototype Using Adipic Acid-Graphite

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Abstract. A prototype of an industrial PCM heat storage has been built and tested. The module is designed for use in an industrial steam system. The module has a storage capacity of 4 kWh (14 MJ) and a power of about 8 kW, allowing for charge and discharge times of 30 min. As PCM, adipic acid has been used (melting temperature 150 °C), that was mixed with expanded graphite to enhance the effective thermal conductivity. For conductivity improvement, 12% of graphite was found to be sufficient. The study concludes that the module can deliver the required thermal power and storage capacity and shows a stable performance.

Keywords: PCM · Industry · Heat storage · Adipic acid · Graphite

1 Introduction

In the EU industry, over 8000 PJ is used for heating. About a third of the energy is used to run processes with temperatures under 250 °C, often using process steam at 150–250 °C. Reducing the corresponding fossil energy use can be realized with high temperature heat pumps using renewable electricity to produce steam, together with heat storage to buffer fluctuating heat streams, particularly related to batch processes. PCM (Phase Change Material) can store a large amount of heat in a small temperature interval around the melting temperature, making it very interesting for industrial heat storage, particularly in steam systems. However, obtaining sufficient thermal power and stable performance are critical issues. The present paper reports the final results of the FlexSteam project, carried out at TNO, aiming to develop cost-effective PCM-heat storage technology as key-component for a sustainable industry. The project consortium consisted of TNO, Blueterra, Bronswerk Heat Transfer, Tata Steel, DOW and Royal Cosun.

2 Development History

The aim of the project is the development of cost-effective PCM-heat storage technology as key-component for a sustainable industry. Since most of the industrial heat use below 250 °C is in the form of process steam, e.g. for applications in the food industry, paper

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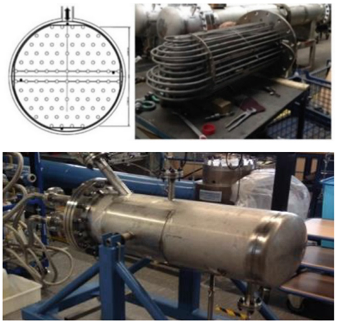

Fig. 1. Initial PCM heat storage prototype (PCM applied at shell side).

industry and chemical industry, the project focuses on integration of the storage in an industrial steam system. Therefore, it should be possible to charge the storage with excess process steam, and discharge it by converting boiler feedwater to steam.

Typical industrial applications require relatively short-term storage, resulting in relatively high specific power. Also, high reliability and low payback times are key requirements. To meet the targets of high reliability and low payback times, the choice was made to focus on conventional technology for the heat exchanger, for which a shell-and-tube heat exchangers was selected, being the default technology for industrial heat exchange, due to simple and robust design.

Next, the choice has to be made whether to apply the PCM at the shell side or at the tube side in the heat exchanger. Initially, the choice was made to apply the PCM at the shell-side, in order to maximize the specific storage capacity. This resulted in the storage prototype shown in Fig. 1. More information on this project can be found in [1, 2].

However, this turned out to have a number of disadvantages. First of all, the concept was difficult to scale up. Next, possible leakage in the PCM part would disable the whole storage. Furthermore, specific power was found to be relatively low, requiring better thermal design and higher PCM conductivity. Also, it was found that 'inert zones' occurred in the PCM storage, where the PCM could not fully melt or solidify due to limited charging and discharging time. And finally, the hydraulic connection of all the tubes (see the number of hydraulic connections in Fig. 1 top right!) added substantially to the cost.

Therefore, in the present Flexsteam project, the choice was made to invert the design; the PCM was placed in the tubes and the heat transfer medium flows around it on the shell side. In this way, the upscaling is much more straightforward (adding more tubes), possible leakage would disable one tube but not the whole storage, only one hydraulic connection would be needed for the flow (since the PCM-filled tubes do not require hydraulic connection) and it would be relatively easy to ensure full charging and discharging of the tubes, making more efficient use of the available storage capacity.

Still, it is important to reduce the number of tubes, to reduce the effort in filling and handling of the tubes and therefor the cost of the design. Therefore, the thermal conductivity of the PCM should be increased, allowing for fewer but larger diameter tubes.

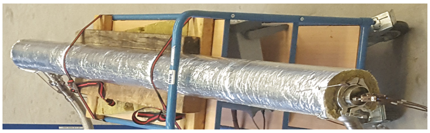

Fig. 2. Tube-in-tube configuration, with PCM-graphite discs in the inner tube.

First tests were carried out on graphite plate impregnated with PCM RT70 (Rubitherm) and stacked in 1m tubes, that could be cooled or heated via a tube-in-tube construction, with the PCM in the inner tube the power was increased from 20 W/kg_PCM for the old configuration to 130 W/kg_PCM for the new configuration, which was ascribed to the increase in effective thermal conductivity resulting from the addition of the graphite.

However, it was also concluded that on solidification, the contact between the PCM-graphite matrix and the wall was suboptimal, possibly due to some shrinkage of the PCM-graphite composite, while the graphite matrix would prevent effective adhering of the solidified PCM to the wall (as would have occurred without the graphite). In addition, the filling of the tubes with impregnated PCM-graphite discs was labor intensive. Therefore, it was decided to develop another filling strategy.

Finally, also more materials development was needed. The initial tests described above were carried out with paraffin RT70 and $MgCl_2.6H_2O$ as PCM. However, the melting temperature of these materials was rather low for industrial applications (respectively 70 °C and 116 °C) and in addition, $MgCl_2.6H_2O$ had significant corrosion issues. Therefore another PCM had to be found. Initially, tests were carried out with D-Mannitol (melting temperature 167 °C) [3]. Unfortunately, this material turned out to be very sensitive to oxidation and repeatedly degradation of the material was observed. Therefore, a new PCM had to be chosen, and a new graphite/PCM composite material had to be developed. From the literature, adipic acid was selected for further testing. Adipic acid melts at 150 °C, was reported to be relatively stable and is a low cost material since it is produced industrially on large scale for the production of nylon 66.

3 Materials Testing

3.1 DSC Testing

First, pure adipic acid was subjected to thermal cycling in a DSC. The results are shown in Fig. 3a. As can be seen, the material shows virtually no degradation over 98 cycles. Conveniently, supercooling was very small, showing fast solidification at only a few degrees below the melting point.

After the cycling, the DSC cup was opened, as shown in Fig. 4. The adipic acid in the cup shows no browning or discoloration that would be indicative of degradation of the material.

Next, a mixture of adipic acid with 20%wt graphite was tested over 46 cycles, as shown in Fig. 4. For the graphite, GFG75 ($D_{50} = 75\ \mu m$) was selected. Also in this case, no discernible degradation was observed. In addition, the supercooling effect completely

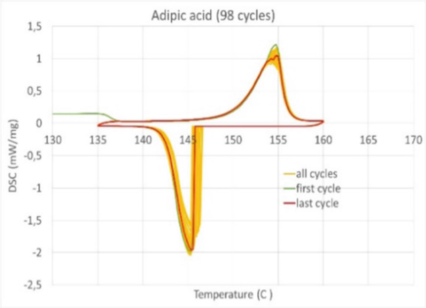

Fig. 3. DSC results on pure adipic acid, 98 cycles.

Fig. 4. DSC cup with pure adipic acid, opened after 98 cycles.

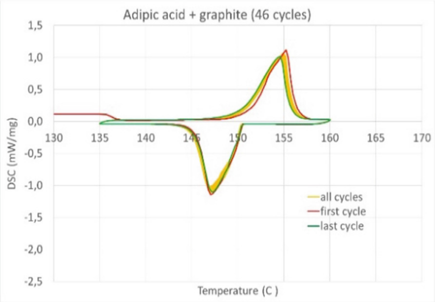

Fig. 5. DSC results on adipic acid with 20% GFG75, 46 cycles.

disappears; the onset temperature for solidification is identical to the onset of melting. It is concluded that adipic acid with graphite forms a stable PCM with no supercooling.

Finally, the DSC peaks are integrated to determine the change in melting enthalpy of the material over the different cycles. The result is shown in Fig. 6 for the pure adipic acid and in Fig. 7 for the adipic acid with graphite. For both materials, a very stable performance can be seen in both melting and solidification enthalpy and melting and solidification temperature. For the samples, melting enthalpy and solidification enthalpy are identical. For the pure sample, a value of 250 kJ/kg is found, and for the sample with 20% GFG75 this is lowered to 210 kJ/kg, corresponding to the lower fraction of PCM in the composite sample. Furthermore, in the pure sample, a temperature difference of

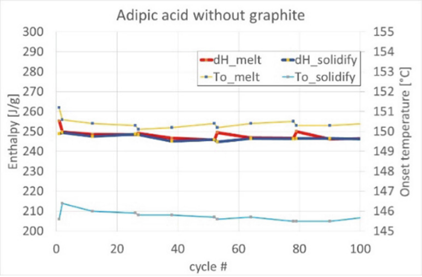

Fig. 6. Melting enthalpy adipic acid pure, 98 cycles, (b) with 20% GFG75, 46 cycles.

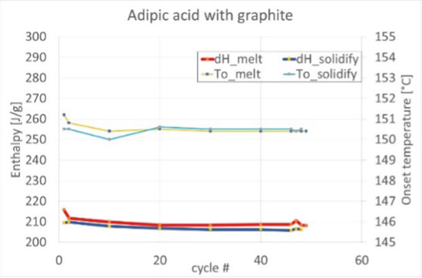

Fig. 7. Melting enthalpy adipic acid with 20% GFG75, 46 cycles

5 °C can be observed between melting and solidification, that is reduced to less than 0.5 °C for the composite sample with graphite.

3.2 Thermal Conductivity Testing

Having checked that the adipic acid with and without graphite both have a stable performance as PCM, also the increase in conductivity should be checked. The adipic acid composite is pressed into tablets, whose thermal conductivity is measured by LFA. As shown in Fig. 8, the thermal conductivity of the solid samples increases from about 0.85 W/mK without graphite to 3.4 W/mK for 10% graphite and 5 W/mK for 20% graphite (measured in the direction of pressing).

However, filling the tubes with pressed tablets was cumbersome (= costly) and contact with the wall was found to be suboptimal. Therefore, as an alternative, a mixture of graphite and adipic acid was molten and poured into the tube. This resulted in a graphite concentration of about 15%. Figure 10 shows the measured conductivity for samples taken from the top and the bottom of the PCM/graphite composite, to check homogeneity over the sample. As can be seen, thermal conductivity was similar as for the pressed samples (in the direction of the pressing) and a homogeneous thermal conductivity was obtained.

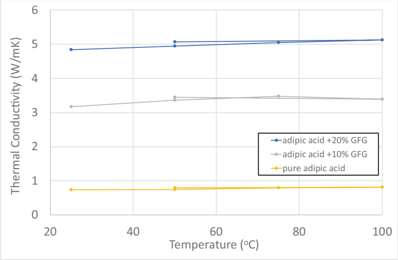

Fig. 8. Thermal conductivity Adipic acid + GFG75, measured in pressing direction.

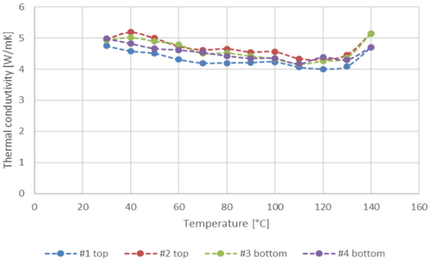

Fig. 9. Thermal conductivity of solidified molten mixture of 85% Adipic acid + 15% GFG75.

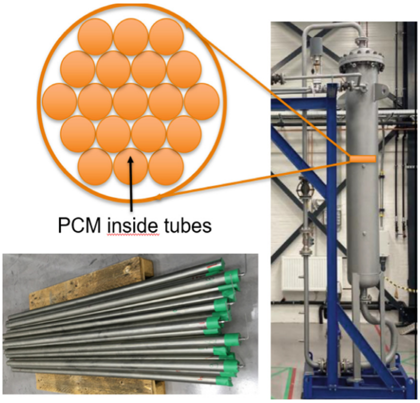

Fig. 10. PCM heat storage (bottom left): tubes before positioning in the heat storage, (top left) top view of tube arrangement, (right) storage.

4 Thermal Storage Design

The thermal storage, designed and built by Bronswerk Heat Transfer, is shown in Fig. 10. The vessel contains 19 tubes (see top view at the left), each of 2 m length and 51 mm outer diameter. The tubes are filled with 3.5 kg of a PCM composite each. In the photo of the tubes, note the connections in some caps for the thermocouple inserts.

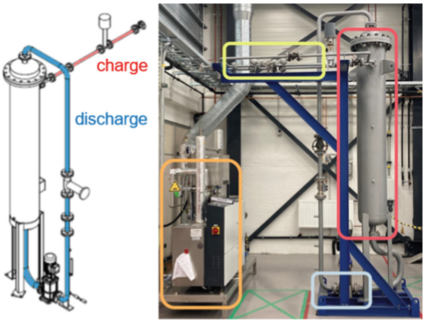

Fig. 11. Charging / discharging system (a) yellow: steam supply/discharge, (b) orange: steam generator, (c) blue: recycling pump and feedwater connection, (d) red: PCM storage

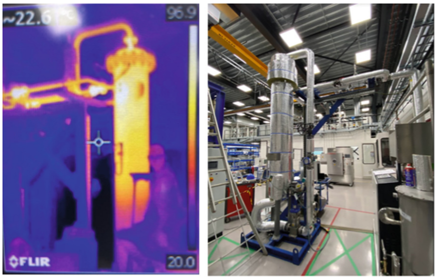

Fig. 12. (a) IR photo of storage during steam charging, (b) after insulation.

Figure 11 shows the system layout to which the storage is connected. For charging, the prototype is connected to a steam generator. The supplied steam causes an almost uniform heating of the storage, as can be observed in Fig. 12a, showing an IR photo of the storage during charging.

On discharging, the tubes are wetted by a falling water film coming from the header at the top of the vessel. This film is partially evaporated to produce ~ 135ºC steam. The non-evaporated fraction of the water film arriving at the bottom of the tank is collected and pumped again towards the header at the top (excess water flow is used to ensure optimal wetting of the tubes). The released steam is condensed with cold water in the condenser of the steam generator. Note the multiple tubes in the yellow frame in Fig. 11; this construction was made to have the steam flow always in the same direction through the pressure difference sensor, used to measure the flow on both charging and discharging. (However, in the end, it was found that this way of measuring the flow was not very reliable and a better value could be obtained by measuring the change in water volume in the condensate tank to establish the generated steam flow.) And finally, the heat storage was insulated, as shown below in Fig. 12b.

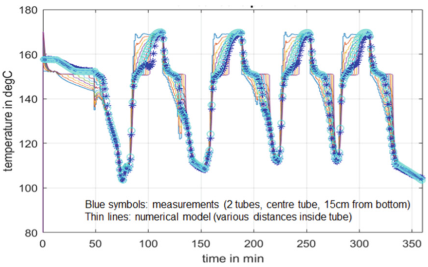

Fig. 13. Temperature in PCM during charge-discharge cycles.

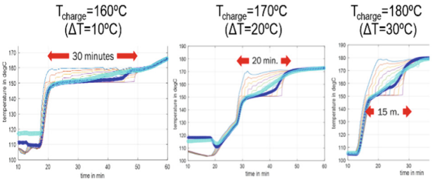

Fig. 14. Temperature in PCM during charge-discharge cycles for different charging temperatures.

5 Storage Testing

Next, the storage was tested. First, 3 charge-discharge cycles were carried out, as shown in Fig. 13. The 2 different symbols in the figure correspond to 2 different tubes, representing the PCM temperature in the center of each tube, 15 cm from the bottom. The lines correspond to modelling results for the PCM temperature (for more information on the model, see [4]). The model indicates the temperature for different locations at fixed intervals between the surface and the center of the tube. In principle, the experimental results (symbols) should correspond to the innermost line of the modelling (representing the center), but in practice the thermocouples are probably not exactly positioned in the center, allowing for small deviations. Overall, a very good match can be observed, as well as a stable performance.

Finally, the storage was tested for different charge temperatures; in three different tests, steam of 160 °C, 170 °C and 180 °C was used to charge the storage. Considering the melting temperature of 150 °C, this resulted in a temperature difference for the charging of 10 °C, 20 °C and 30 °C. As expected, the increasing temperature difference resulted in shorter charging times. However, this is not a linear dependency, which is related to the fact that at higher charging temperature, not only the heat transfer increases, but the sensible heat content and the heat losses as well.

From the measurements, it was concluded that he PCM heat storage has a total storage capacity of about 10 kWh over the temperature range 130 °C-170 °C, of which 4 kWh is related to the melting heat of the PCM, the remaining 6 kWh being related to sensible heat in the PCM, vessel and water in the storage prototype. From the amount of condensed steam, the average power could be determined. This was found to be in the range of 20–40 kW (depending on the temperature difference used for charging and discharging).

The average roundtrip efficiency was found to be about 80% for 1 h cycles. The relatively large heat loss of ~ 2 kW (for charging at 160 °C) is related to the relatively small size of the storage and the correspondingly relatively large loss area (larger storages have lower loss area per volume), as well as the duration of the charging-storage-discharging cycle. It is expected that upscaling the storage and shorter cycles will increase the storage efficiency (e.g. to 90%).

6 Conclusions and Further Work

From the presented results, the following conclusions can be drawn:

- A shell-and-tube PCM heat storage design with PCM in the tubes is an effective concept for building a reliable heat storage with sufficient power for industrial heating applications.
- Adipic acid as PCM material shows good chemical stability, almost no supercooling and melts around 150 °C.
- Addition of graphite to adipic acid increases the thermal conductivity to values needed for 1 h cycles charging and discharging.

Regarding future work, the focus will be on expanding the range of stable PCM's to cover a larger temperature range 130–300 °C, the testing of these PCM's for longer cyclic stability > 100 cycles and the development of an industrial pilot for PCM thermal storage in steam utilities, e.g. for the food industry, paper industry, chemical industry or other industrial steam users.

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References

1. H.A. Zondag, A.J. Marina, S.F. Smeding, H.S.K. Subramanian, R. de Boer, J. van der Kamp (2019), Experimental results on PCM heat storage with graphite conductivity enhancement, proceedings IRES Conference 2019.
2. H.A. Zondag, R. de Boer, S.F. Smeding, J. van der Kamp (2018), Performance analysis of industrial PCM heat storage lab prototype, Journal of Energy Storage 18, pp. 402-413.
3. H.A. Zondag, G.J. Herder, M. van der Pal, S.F. Smeding, G. Elzinga, R de Boer, (2020), Development of an Industrial Heat Storage Using High-Temperature PCM-Graphite Composites, proceedings IRES Conference 2020.
4. M. van der Pal, K. Ingenwepelt and R. de Boer (2022), Development of a latent heat storage for industrial application, HPC 2021 (postponed to 2022).