Development of an Active High Temperature PCM Storage Concept with Coated Heat Exchanger Plates

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Abstract

Feasibility of the concept of an innovative high temperature latent heat storage with active scraper mechanism to enhanced discharge heat flow was demonstrated in 2016, showing advantages of the active over the passive concept. However, parasitic power for the movement of the scrapers was high due to abrasion on the bearings for the scraper slide. A new scraper mechanism, where the mounting was changed from central slide to a portal frame, was designed and tested, showing some reduction in parasitic power, however, not in the expected range.

Therefore, investigation was redirected to focus on improved performance through non-stick coating of the heat exchanger plate, to eliminate or diminish adhesion of the salt on the heat exchanger surface. Various coatings were tested. Initial results with self-made coatings led to a glass coating of Polyox Borosilicate, in which the adhesion of the sodium nitrate salt was so low, that the salt was easily removed with a sharp-edged scraper. Further investigations focused on commercially available coatings for high temperature applications. Initial oven-tests showed easy spalling of the salt from the coatings. A test rig was built, to be able to test samples directly in a bath of nitrate salts, with cooling of the surface inside the molten salt, representing a more realistic test environment. Under these conditions, adhesion mechanisms were very different from the initial test results and no satisfactory result was obtained, the solidified salt was firmly attached to all coatings, same as to the non-coated plate.

Keywords: latent heat storage, PCM, high temperature, non-stick coating, active, power-to-heat, process heat.

1. Introduction

A major challenge of latent heat storages is the unfavorable characteristic within the discharging process, due to the insufficient heat transfer between the liquid storage medium and the heat transfer fluid, caused by low thermal conductivity of the storage media and the increase of the solid layer on the heat exchanger surface during discharge process. Active concepts (Zipf et al., 2013), (Pointner et al., 2014), (Nepustil et al., 2016) have the potential for a steady discharge heat flow and even for separation of capacity and power in future designs (Laing-Nepustil et al., 2015).

Another important issue for our future energy system is coping with fluctuation in electricity generation. Here, power-to-heat options with latent heat storage will provide flexibility at high exergy level (Laing et al., 2015). For this application, efficient and cost effective electrical charging of high temperature storage is an important issue.

The application fields for high temperature PCM storage are in industrial processes and power plants, with storage temperatures up to 350 °C. Known organic non-stick coatings have low temperature resistance up to approx. 250 °C, therefore research focuses on inorganic coatings.

2. Description of Concept

An innovative active concept for latent heat storage was developed, using flat plate heat exchanger and moving linear scrapers to keep the thickness of the solidified PCM constant after initial discharging. Proof of concept was successful, however, parasitic power was quite high. A re-design of the scraper mechanism was done to reduce parasitics. The re-designed linear scraper mechanism is shown in Fig. 1. The mounting is changed from a central slide to a portal frame, supported by four ball bearings. Two bearings each are guided in a track on each sides of the

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storage. For exact positioning in relation to the cooling plates, two bearings each are mounted in the middle of the traversal trusses, and guided along the middle track. The cooling plates are also fixed by this support frame, in order to avoid the relative movement due to thermal expansion, to keep the gap between scraper and cooling plate constant. The support frame is fixed to the storage containment, so the cooling plates can be fixed to the containment bottom without risking relative movement. The number of scrapers is doubled and they are fixed to the traversal trusses. By doubling the number of scrapers, each scraper will only move along half of the cooling plate length. This in turn allows for more variations on scraper velocity and momentum. The scrapers have a telescope mechanism and a radial form at the lower tip. When the solid layer, caused by heat losses through the bottom of the containment, reaches the lower tip of the scraper, it can move upwards, reducing the momentum from sliding along the solid layer noteworthy.

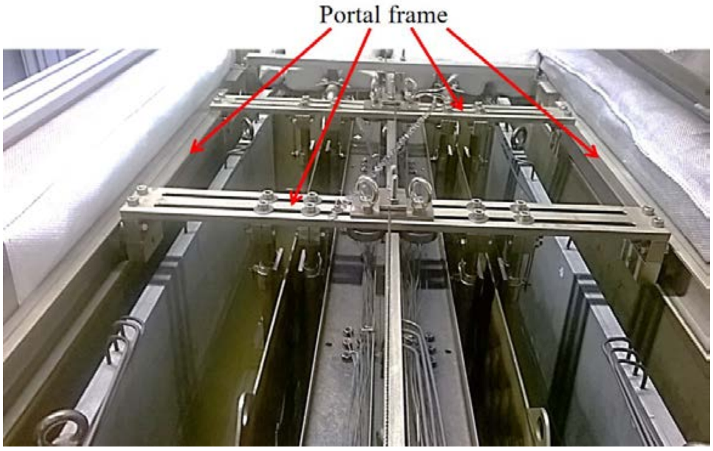

Fig. 1: Re-design of linear scraper mechanism with a portal support frame

Test results with the new scraper mechanism showed only a reduction of scraper parasitics of about 20-30%, which was not satisfying.

Another aim for the second generation design of the active latent heat storage is to combine the electrical heating with the cooling plate for power-to-heat applications. With this, the amount of components and material inside the storage can be minimized, while maximizing the available heat exchanger surface. The same heat exchanger surface can be used for charging and discharging (Nepustil et al., 2016). A promising solution offers thick film technology. With this PTC (positive temperature coefficient) technology any geometry of heater surface can be printed on a metal substrate. The heating layers are electrically insulated with further layers of film coating. As the layer thickness is less than 50 micro meters, thermal resistance is very low. The printed layer is very robust and not sensitive to breakage or thermal shock. When printing thick film heaters onto the heat exchanger plates, it is obvious that one might implement the outer layer as a non-stick coating to reduce adhesion of the solidified salt on the heat exchanger plate.

As test results with the re-designed scraper mechanism are still not satisfying, further development is focused on the investigation of non-stick coating for the heat exchanger plates, independently from the thick film heater development.

3. Non-Stick Heat Exchanger Surface

The aim is, to develop a high-temperature-resistant non-stick coating for the heat exchanger inside the phase change storage. With such a coating, it is expected that during discharge of the storage, the adhesion between the crystalized PCM and the heat exchanger will be so low that the solidified PCM will be easily removed from the heat exchanger plate by some moving mechanism, resulting in constant high heat flux.

3.1 First coating tests

Different methods were tested to create a non-stick coated surface (Patsoh, 2017). A nano-scale coarse structure helps to minimize the contact surface between coating and Nitrate salt. As a result, interfacial tension between salt and coated surface is reduced. This non-stick property is above all due to the layer thickness and the undulating surface morphology of the coating. Promising results were obtained with borosilicate glass powder, mixed in a binder of polyethylene oxide and demineralized water (Polyox Borosilicate), applied on etched surface of stainless steel (Fig. 2). The samples were dried for 5 minutes at ambient temperature and then heated up in the furnace to 950 °C.

To test adhesion of sodium nitrate on the coated surface, a vessel with sodium nitrate was heated in the furnace to 350 °C. The sample plate was also heated up to 315 °C. Then the sample was immersed into the molten salt several times, with approx. 6 seconds at ambient air in between for crystallization. When the solid layer reached about 3 mm, it was tried to remove the slat layer from the plate by pushing with a sharp-edged scraper on the salt.

Fig. 2: Sample with Polyox Borosilicate glass coating with an applied layer of Sodium nitrate (left) and after salt was removed (right). (Patsoh, 2017)

With this manual method of applying the coating, layer thickness was uneven and reproducibility was difficult. However, it looks like a promising option, especially as on the thick film heaters, a thin layer of glass material is applied as an overglaze.

3.2 Commercial Coatings

Since there are different non-stick coatings already existing in the market, however, very few for high temperature applications, the next step was to test some of them, which have temperature stability of at least 260 °C. Therefore, eutectic mixture of sodium/potassium nitrate with a melting point of 222 °C is used for adhesion tests.

The tested sample plates and the selected coatings are listed in Tab. 1. For the tests, samples of stainless steel with a size of 150 mm by 100 mm by 2 mm were coated on one side. A non-coated stainless steel plate is used as a reference.

Tab. 1: List of sample plates investigated

Coating trade name	Supplier	Max. application temperature	Base material
None			Stainless Steel V4A
PFA Ruby-Red®	Hüni GmbH + Co. KG, Germany	260 °C	X5CrNi18-10
PFA 7152	Hüni GmbH + Co. KG, Germany	260 °C	X5CrNi18-10
ChemCoat 1501F	Impreglon Surface Technology Group, Aalberts Industries, Germany	260 °C	X2CrNiMo17-12-2
DURAQUARZ®	acs Coating Systems GmbH, Germany	400 °C	X5CrNi18-10
DURAPEK®	acs Coating Systems GmbH, Germany	280 °C	X6Cr17

Fig. 3 shows first wetting tests with water, dropped on the coated surface (left side) and the uncoated sample (right side). The clear result is, that all the coatings to be tested are less wetted than the uncoated steel plate.

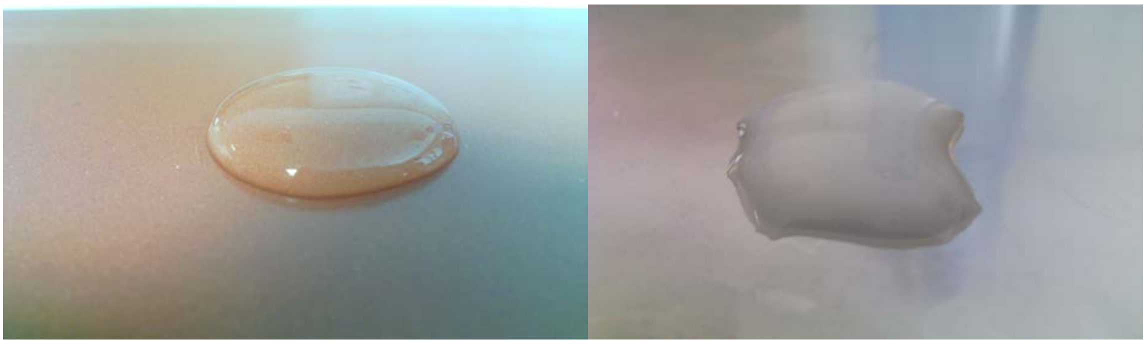

Fig. 3: Water drop on PFA Ruby Red (left) and uncoated steel plate (right).

Fig. 4 shows wetting tests with the eutectic salt mixture. Left side shows a crystallized salt drop on the ChemCoat sample and right side on the uncoated steel plate. The eutectic salt mixture showed high contact angles on all surfaces, including the non-coated stainless steel.

Fig. 4: Crystallized salt drop on ChemCoat (left) and uncoated steel plate (right).

For better understanding, whether the salt is easier to be scratched away from the different coatings, the following experimental setup was built up (Fig. 5): The different samples were heated up in the oven to 240 °C. Molten salt-mixture (54% KNO_3 and 46%$NaNO_3$) with the same temperature was dropped onto the samples. Then the oven was switch off to let the samples slowly cool down over night. On the next morning it was tested, whether the salt is easier to be scratched away from the coated samples than from the uncoated steel plate. No difference was observed between the coated samples and even the uncoated steel plate; the salt could be removed easily with the finger from all samples.

Fig. 5: Testing plates in the oven, wetted with molten salt.

Fig. 6: Test to remove crystallized salt from Ruby Red with hammer and chisel

When the samples are cooled down to ambient temperature, of course there is a strong influence of the different thermal expansion coefficients, which might support the salt to flake off. Therefore, the next step was to observe, whether there is a difference, when sample and salt are not cooled down completely before trying to scratch it away, to minimize the influence of the different thermal expansion coefficients. This setup is also much closer to real application conditions. After applying the molten salt onto the samples, the oven temperature was regulated to 200 °C and the plates were kept for about three hours in the oven. After this time, the plates were fixed in a bench vise and the salt was removed by a chisel and a hammer (see Fig. 6). In order to protect the coating from the sharp chisel, the tool itself was covered with a piece of plastic. It was observed that the adhesion between salt and sample was slightly higher than in the previous test with cold samples, but the salt could also be removed in a flake. Only on the Duraquarz coating, the salt stuck even a bit harder than on the uncoated steel.

Overall, these qualitative pretests showed no satisfying results, as there are many external influences which are hard to eliminate. Therefore, the samples were tested under realistic environment, immersed in molten salt and cooled on the uncoated side in a specially designed test rig.

3.3 Testing under realistic environment

A test rig was built up, to compare different coatings regarding their non-stick properties and behaviour in the molten salt under realistic conditions. The rig includes an aluminum element with a W-shaped channel for cooling the plates with an air-flow and a mechanism to manually scratch the crystallized salt away (Fig. 7). On each side of the cooling plate, a test sample plate can be attached. The construction is fixed in a stainless steel containment, filled with 22 kg eutectic mixture of sodium/potassium nitrate. To melt the salt, two heating elements are attached to the walls of the containment. The molten salt containment is inserted in a well-insulated containment, to minimize side effects. Two thermocouples are attached between the test sample and cooling plate on each side (Fig. 8).

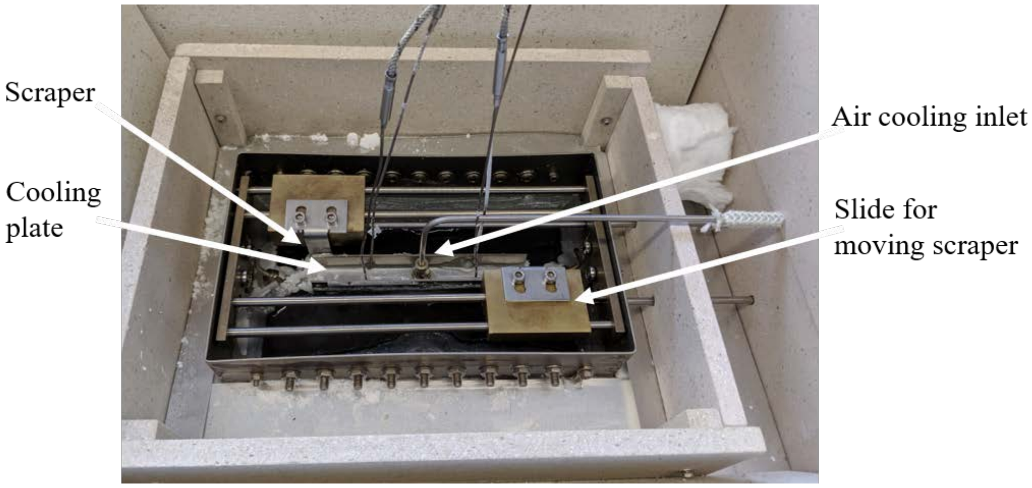

Fig. 7: Test rig for investigation of high temperature non-stick coatings in nitrate salts

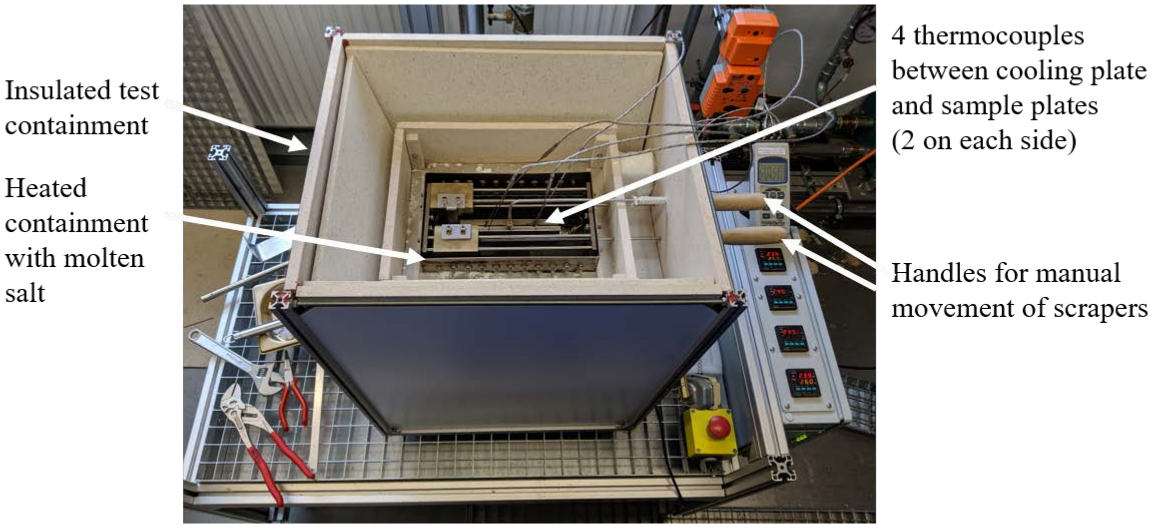

Fig. 8: Test rig for investigation of high temperature non-stick coatings in nitrate salts

The process of testing remains same as above: The salt is melt by the integrated heating elements. Then two plates are inserted into the salt and fixed to the cooling element. One of the plates is always the uncoated stainless steel as reference. Then the cooling process is started. As soon as the temperature falls to 230 °C, the scraping process is started. According to the tact of an acoustic signal, the scraper is moved manually, until the resistance gets too high and the scraper is unable to be moved anymore.

3.2 Results and Discussion

None of the samples showed a non-stick behavior. The salt stuck to the surface and the scraper only scratched salt from the solidified salt layer. From the qualitative testing, no significant differences between the uncoated reference sample and the different coated samples could be observed.

Fig. 9 to Fig. 13 show the coated samples after tests in the test rig. About 80 % of the sample plate was immersed in the salt. All samples show a sliding track just above the immersed part, which is due to cooling effects on the top of the test rig, where salt solidifies around the scraper mechanism, forming an increasing salt crust (Fig. 14). This salt crust is eventually leading to a blocking of the scraper mechanism.

The two PFA coatings, PFA Ruby Red (Fig. 9) and PFA 7152 (Fig. 10), are ripped off at some points by the load along the sliding line. Here the coating is foil-like.

On the ChemCoat 1501F sample (Fig. 11), the coating was damaged through mechanical load in the top side.

The Duraquarz coated sample (Fig. 12) was damaged through handling with pliers. The Durapek coating (Fig. 13) showed the highest mechanical resistance and showed no relevant marks.

Fig. 9: PFA Ruby Red. Sliding track just below the upper bore holes, damage of the coating on the right side of the sliding track.

Fig. 10: PFA 7152. Sliding track just below the upper bore holes, damage of the coating on the left side and on the right bore hole of the sliding track.

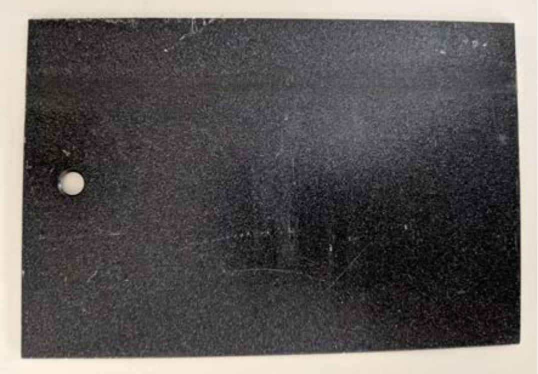

Fig. 11: ChemCoat 1501F. Sliding track below the upper edge visible.

Fig. 12: Duraquarz, damaged on the top side through handling with pliers.

Fig. 13: Durapek, hardly damaged, sliding track slightly visible.

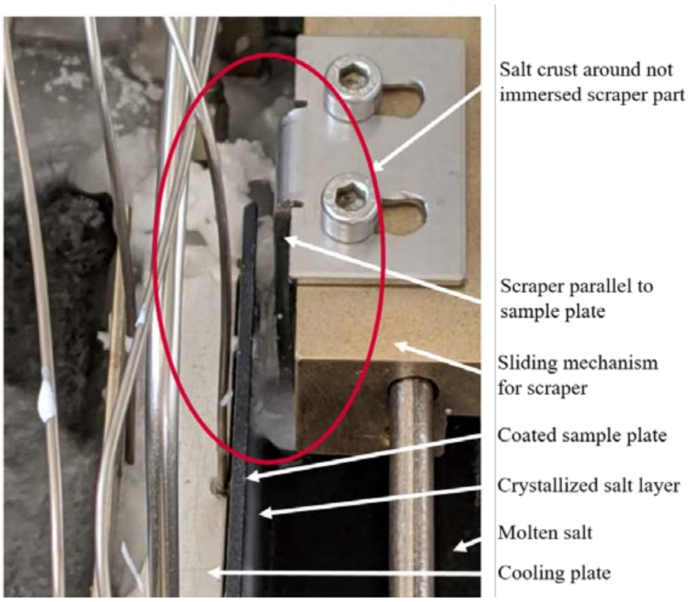

Fig. 14: Salt crust around not immersed scraper part, causing a blocking of the scraper mechanism

4. Conclusions

There is a strong influence of cooling mechanism and temperature on the spalling of the salt from coated and uncoated sample plates. This is due to internal forces caused by the different thermal expansion coefficients, but the presence of oxygen might also be of influence (v. Wartenberg, 2007).

All wetting and adhesion test with drops of molten salt on the sample plates or dipping of samples in molten salt are not representative for the latent heat storage application. Therefore, oven tests are not sufficient for adhesion tests in latent heat applications.

Investigation of wetting and adhesion between nitrate salts and cooling plates needs a realistic test environment, like the test rig described.

Fully immersed samples in nitrate salt showed no spalling behavior of the salt from the coated samples. Also with mechanical load from the scraper, the solid salt layer could not be removed from the cooling plate, only salt was scraped off from the solid/liquid interface. In the qualitative testing described, no difference between coated and uncoated surfaces could be observed.

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