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Energilagring i aluminiums faseovergang

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Energy storage in aluminum phase transition

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Institute of Technology
Cooling and heat pump technology
The technology park
Kongsvang Allé 29
8000 Aarhus C

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Authors:
Benjamin Zühlsdorf, Danish Technological Institute
Lasse Søe, Danish Technological Institute Lars
Reinholdt, Danish Technological Institute.
Henrik Kjeldsen, Institute of Technology Brian
Elmegaard, DTU Mechanics Bjarti Thomsen,
Umhvørvisstovan Peter Badstue Jensen,
Aalborg CSP A / S

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1. Project details

Project title	Energy storage in aluminum phase transition
Project ID	12204
Support program	PSO 2014-1
Project manager (company / institution)	**Institute of Technology** Kongsvang Allé 29 8000 Aarhus C CVR 56976116 Contact: Lasse Søe, las@teknologisk.dk
Project partners	**Aalborg CSP A / S** Hjulmagervej 55 9000 Aalborg CVR 21142042 Contact: Peter Badstue Jensen, pbj@aalborgcsp.com **Verdo Produktion A / S** Agerskellet 7 8920 Randers NV CVR 25481984 Contact: Henrik Bøgh Nielsen, heni@verdo.dk **DTU Mechanics, Department of Mechanical Technology** Nils Koppels Allé 110 2800 Kgs. Lyngby CVR 30060946 Contact: Brian Elmegaard, be@mek.dtu.dk **STØTEK A / S** Aage Grams Vej 1 6500 Vojens CVR 10783445 Contact: Per Høegh, p.hoegh@stotek.dk

	Umhvørvisstovan Traðagøta 38 - Postboks 2048 FO-165 Argir Faroe Islands CVR 405388 Contact person: Bjarti Thomsen, bjartiT@us.fo
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2. Brief description of the project's goals and results

English

The increasing share of electricity produced by means of renewables, eg windturbines and solarpanels, having a fluctuating output is expected to cause big balancing problems in the existing power grid. This might be solved by implementing large-scale electricity storage. This study looks into integrating thermal high temperature energy storages into existing steam power plants. As heat storage material (AlSi12), 88% aluminum and 12% silicon has been analyzed. The aluminum will work as phase change material (PCM), and it is available at a comparably low cost, and due to high energy density it is found space efficient. The highest application potential was found to be the heat demand for evapora tion and superheating of the steam used to run the steam power plants. The study indicates that the water preheating should be realized by the available molten salt technology.
Small-scale experiments confirmed AlSi12's general suitability as PCM. It was concluded that storages with AlSi12 as PCM can be realized, while constructive challenges might arise if short discharging times are required.

Dansk

The increasing share of electricity produced using renewable energy sources such as wind turbines and solar panels, can result in balancing problems around electricity production and consumption in the existing electricity grid. Large-scale energy storage may be the solution. In the present project, the integration of thermal high-temperature energy storage facilities in existing steam power plants has been analyzed. An alloy of 88% aluminum and 12% silicon (AlSi12) has been investigated and found suitable as phase change material (PCM). AlSi12 is commercially available and is comparable in price to more traditional materials used for thermal energy storage. The high energy density of aluminum means that the physical size of the layer can be reduced considerably compared to normal energy stores. The greatest application potential has been shown to be for the evaporation and superheating process of the steam that drives the turbines at the steam power plants. The analysis also indicates that preheating of the water involved in the steaming process can advantageously be done using the already available liquid salt technology. Small-scale experiments have confirmed the general suitability of AlSi12 as a storage medium. A warehouse with AlSi12 can be constructed, but design challenges can arise if a rapid discharge is required.

3. Project summary

Better utilization of the varying electricity production from renewable energy sources such as wind turbines and solar cells are becoming increasingly important, as the amount of energy from these sources constitutes an ever-increasing part of the danish energy supply. This leads to an increasing need for an active matching of energy production and consumption. Electric storage in smaller capacities and shorter time can be handled by e.g. batteries, while technologies for storing large amounts of energy are still lacking. This is expected to create a large demand for high capacity energy storage to stabilize the electricity supply in Denmark. This need is already seen in other countries with less stable electricity networks.

The efficiency of the conversion electricity> storage> electricity ("power to power") can be expressed as *round trip efficiency,* which is desired as high as possible. The technology that has been investigated in this project is based on storing electricity as heat at a high temperature. The selected storage temperature of approx. 600 ° C matches the temperature levels used today in the thermal steam-based cogeneration plants in Denmark. The storage temperature thus allows the same high efficiency to be achieved when converting back from heat to electricity. The high-temperature storage technology can contribute to maintaining the steam-based power plants and their great flexibility in a future Danish energy system, where electricity production will primarily be based on renewable energy sources.

The project work is based on the use of a Phase Changing Material (PCM). So far, R&D activities in high-temperature storage have been primarily concentrated on different types of molten salt, which are based on temperature change rather than on phase shifts. The latter is already used today in Concentrated Solar Power (CSP) plants.

In the present project, the suitability of a metal as a phase-shifting material has been investigated. Storage in metals has several advantages over salts:

- Significantly better thermal conductivity (x 100)
- High energy density
- High temperature at phase change
- Ideal for electricity production (aluminum melts at 660 ° C)
- Stability: Congruent melting, no subcooling and low thermal expansion.

Tailor-made PCM materials with special thermal properties can be made by carefully selecting the right metal or the right alloy composition. The temperature working range when discharging the storage is very high, which ensures a more efficient conversion of the stored heat to electricity (ie a better *round* trip efficiency) compared to most existing heat storage technologies.

3.1. Results

Storage media

In the project, possible storage media have been analyzed, and an alloy of 88% aluminum and 12% silicon has been chosen as the phase-shifting material. The phase transition from solid to liquid material takes place at approx. 577 ° C, which is within the temperature range often used in conventional power plant steam turbines. The heat can thus be used for the production of electricity (via steam turbine) and district heating.

In the project, a test plant has been designed and built for the purpose of providing the thermal and mechanical data required to be able to build an energy storage based on phase-changing aluminum.

• A smaller furnace was used to assess the stability of the alloy in cyclic phase shifts. • A larger furnace was designed and used to study the hardness around melt the point.

No changes in the thermophysical properties of the material were observed due to the cyclic melt solidification experiments. Furthermore, it could be stated that the phase transition was very sharp - ie. there was no temperature slip - and that the alloy showed some plastic properties just below the melting point. Both experiments thus confirmed the suitability of the alloy as a phase-shifting material for high-temperature energy storage.

Application potential

As mentioned above, the idea is to use the high-temperature heat storage in combination with conventional steam power plants. This will probably result in lower investment costs due to the possibility of using existing plants and infrastructure, just as it will be possible to maintain central plants and their stabilizing effect on the electricity grid.

The liquid salt technology, which is known from *concentrated solar* power plants (CSP), is a technology with the same purpose and is already commercially available. As a starting point, this technology was therefore used to evaluate the idea of using the metal alloy as a phase-shifting storage medium. The analysis showed that the investment cost of the storage medium AlSi12 itself is comparable to the medium used in connection with the salt technology. When using the AlSi12 aluminum alloy, the size of the bearing is significantly reduced and all the way down to 25% compared to if liquid salt is used. The biggest difference, however, is that the aluminum alloy provides heat at a constantly high temperature, while liquid salt is cooled in the discharge process.

The high temperature is an advantage if heat is required at a constant high temperature, but the high temperature also entails a number of design challenges. In power plant processes, lower temperatures are required in the heating process (sensitive heating of water), while evaporation and superheating (possibly the multi-stage superheating) require heat at high temperature. The greatest potential was therefore found by using a combination of liquid salt and AlSi12, where the heating process takes place using liquid salt, while the evaporation and superheating process takes place with energy from the AlSi12 high-temperature storage. In this combination, it is also possible to realize for the steaming directly in the warehouse without a secondary medium.

Recommendations for construction of heat storage

A final design of the heat storage can only be determined when the application and boundary conditions are known. However, on the basis of experience from the literature and from the experiments carried out, some aspects that are relevant to the construction of a heat storage could be deduced. One important design parameter is the area of the heat transfer surface in relation to the volume of storage medium, as this parameter defines how fast the storage can be discharged. A larger heat exchanger area enables faster discharge processes, but is nevertheless associated with design challenges and higher investment costs. In addition, different constructions of the enclosure have been discussed. There can be e.g. a steel container is used if it is coated on the inside and insulated from the outside. The container must also be designed so that the storage medium can expand, which can be solved by having a "free" surface on the storage medium (an unfilled container). The cavity between the "free" surface of the storage medium and the container wall must - to avoid corrosion / oxidation of the storage medium -
filled with a blank gas.

3.2. Expected utilization of project results

The project has aimed to investigate the application potential of a phase-shifting metal for high-temperature heat storage as well as to assess the possibility of realizing large-scale storage based on this technology.

The above results show that there is a potential for use if the alloy is used in combination with liquid salt. In this combination, the aluminum alloy is used to reduce the disadvantages of liquid salt by covering the heat / energy requirement at high temperatures, while liquid salt is used to cover the heat requirement at lower temperatures, as otherwise there would be structural challenges associated with the metallurgy. In this application, the metal storage is thus used as a supplement to the liquid salt technology instead of replacing the technology completely. Thus, the design challenges are moderate and it is expected that it will be possible to design such a warehouse for the purpose described. However, a definitive conclusion requires a large-scale demonstration plant that can be used to shed more light on the loads on the warehouse and the dynamics of large-scale warehouses.

It can be concluded that a heat storage with AlSi12 as phase-changing material - in combination with a liquid salt storage - can ensure that the central CHP plants can be maintained and used to smooth the electricity production from the renewable energy sources and thereby contribute to a stable electricity grid. .

4. Project goals

The need for energy storage is significantly more pronounced in connection with the increased use of solar and wind energy. One possible solution, which in principle has great potential, is to use phase-shifting high-temperature bearings, which are characterized by utilizing the ignited heat in connection with phase-shifting (liquid ÿ solid) to store energy.

Storage in phase-shifting materials (PCM) has several advantages over more traditional storage in non-phase-shifting materials. This is especially true for metallic phase-shifting materials. First, the energy density is high: in an aluminum-based warehouse, it will be 1 MJ / L - 1.5 MJ / L, which is comparable to the energy density of the much more expensive lithium batteries. Secondly, the energy quality is relatively good due to the high melting point of the metal (approx. 600 ° C for aluminum alloys). Thirdly, the price (DKK / MJ) is only a fraction of what it is for battery-based storage, which can therefore not be expected to be used for storing large amounts of electricity for a longer period of time.

The idea of the project has been to investigate the storage of electrical energy by melting aluminum and subsequently extracting the energy again during solidification as heat at high temperature (500 ° C - 600 ° C). Aluminum is chosen as it suits the temperatures used in modern thermal steam-based power plants, and thus can be assumed to be able to achieve the same high efficiency when converting back from heat to electricity. This also allows you to use already existing power plants, which makes the establishment costs lower.

The structure and overall content of the project are:

- Analysis of possible materials such as PCM in combination with steam power plants
- Analysis of application potential
- Design proposals for full-scale realization
- Comparison with alternatives.

4.1. PCM materials in combination with steam power plants

4.1.1. Selection of PCM material

There are many factors that play into the choice of the most suitable phase-shifting material for a high-temperature energy storage:

The phase transition must take place at a suitable temperature. If the temperature is too low, the thermal energy can not be utilized so efficiently - especially in connection with electricity production. If the temperature is too high, it can present material challenges in connection with the construction of the warehouse. In addition, one must be aware that charging / filling the warehouse requires an overtemperature - e.g. 600 ° C hot steam to charge a storage with phase transition at 576 ° C. Finally, it is an advantage if commercially available equipment ("standard equipment") is available to convert the stored thermal energy into electrical energy. There are many choices among inorganic salts and metals, whereas organic compounds are usually more limited in relation to the maximum possible temperature.

The energy density should be high. This can be achieved if the heat of fusion is large. In general, there is a connection between the melting point and the heat of fusion, and therefore a phase-shifting high-temperature energy storage will almost automatically have a high energy density. For a bearing based on an aluminum alloy, the energy density will be of the same order of magnitude as for a lithium battery.

Thermal conductivity must be good. The thermal conductivity limits how quickly and easily the heat can be drawn out of the storage. If it is small, it is difficult / expensive to pull a large effect out of the warehouse, just as filling takes longer. Metals generally have high thermal conductivity.

Chemical stability is important so that the bearing does not change properties during the operating period. Unlike many salts, the metal alloys are generally stable - even at high temperatures. However, there are two points of attention: 1) Liquid metal reacts with solid metal, and therefore a PCM container must be coated with a protective surface. 2) Liquid metal reacts with the oxygen in the air, which means that a chemically inert shielding gas (argon or nitrogen) must be used.

The thermal expansion around the melting point should be small. This aspect also favors metals over salts.

The price should be kept as low as possible. Here it is important to be aware of the total cost in relation to the practical utility of a warehouse - e.g. via a cost-benefit-ana lyse.

Kensisarin [1] has analyzed a large number of possible materials to investigate their suitability for phase-shifting high-temperature energy storage. An important conclusion is that salts have a number of inappropriate properties. Among other things. they have a low thermal conductivity, they are chemically corrosive, have a large volume change upon melting, a tendency to significant subcooling and - in some cases - a high cost. Metals generally do not have these properties and are therefore often competitive despite a slightly lower energy density.

In a study of different phase-shifting materials for storing thermal energy at high temperature (> 420 ° C) from solar panels, Khare et al. [2] focused on commercial grade and eutectic metal alloys. The advantage of using a eutectic mixture is that its melting point is well defined and therefore has less tendency to fractionate / stratify. The study examines factors such as energy density, storage capacity as well as life cycle energy and CO2 costs. It is stated that the eutectic doctors ring 88Al-12Si (88% aluminum and 12% silicon, melting point = 576 ° C) and 60Al-34Mg 6Zn (melting point = 443 ° C) as well as the metals Al (661 ° C) and Mg (648 ° C) are suitable as storage media for a phase-shifting energy storage. In particular, 88Al-12Si is distinguished by a suitable melting point, the lowest cost, the smallest thermal expansion and a very high energy density. Pure aluminum (commercial grade) is number two in relation to costs etc. and will be the obvious choice if it turns out in terms of design to be an advantage with a higher melting point.

Kotzé et al. [3] has collected data for a large number of metal alloys with a melting point between approx. 350 and 950 ° C, which can be seen in Figure 4.1. As above, the eutectic alloy 88Al-12Si is highlighted. In this context, it should be mentioned that Li et al. [4] investigated the hypereutectic alloy 83Al-17Si. 1200 melts and solidifications were made by varying the temperature between 480 ° C and ~ 640 ° C over a period of 100 minutes. A slight reduction in the heat of fusion was observed (-4.1 ° C; no measurement uncertainty is indicated) together with microstructural changes, but no change in the initial temperature of melting (liquidus point, 577 ° C) is seen.

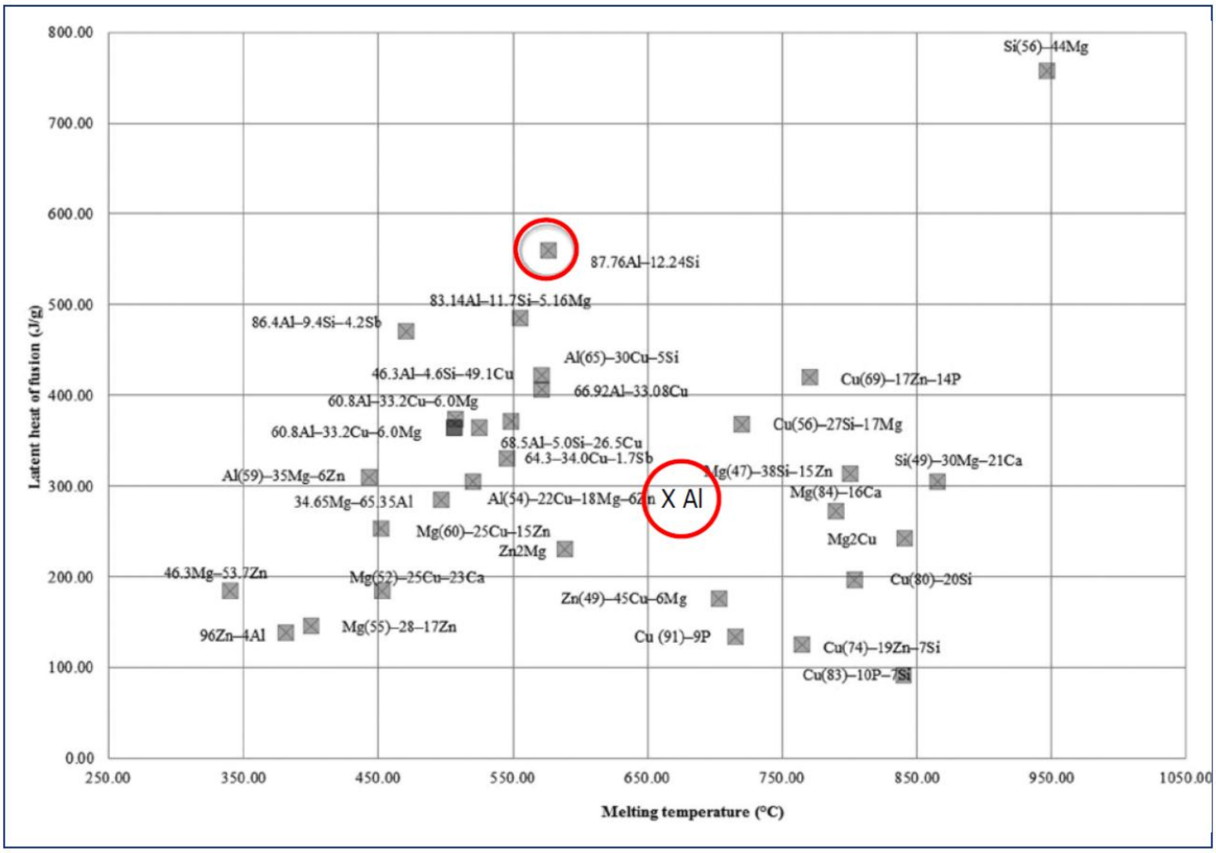

Figure 4.1: Melting heat and temperatures for different metal alloys. Kotzé et al. [3].

In conclusion, the eutectic alloy 88Al-12Si is recommended for the following reasons:

Melting point 576 ° C allows the production of steam for efficient turbines.
Therefore, it is possible to achieve a relatively good efficiency in the conversion of stored thermal energy into electricity.
2. The specific heat of fusion is high compared to similar alloys. In other words, the storage capacity will be large - measured in relation to weight. Alternatively, it can be said that the warehouse will be cheaper if the storage capacity is maintained.
The mixture is eutectic, which means that the melting point is well defined and that there will probably be no problems with fractionation / stratification.
4. The thermal expansion associated with melting is relatively small.
5. Thermal conductivity is good.

The alloy is widely used for casting and is therefore relatively inexpensive and available in large quantities.

4.1.2. Al-Si12 as storage media

In an international context, a number of studies and test experiments have been carried out aimed at building up aluminum-based phase-shifting energy storage facilities. Some of the most important are mentioned in the following. In a remarkable study, Kotzé et al. [5] made a principle sketch for an aluminum-based storage unit as well as performed simulation of the unit and test experiments. The study provides far from a complete recipe for building such a warehouse, but clearly highlights a number of the most important issues. Moha et al. [6] reviews the status (2017) of high temperature energy storage and discusses both salts and metals. They highlight the following advantages of metal bearings: High thermal conductivity, high energy density, low vapor pressure and good thermal stability. It has been made
stability test of phase-shifting AlSi12 (aluminum mixed with 12% silicon) in small capsules [7] and of Al-34% Mg-6% Zn [8], but only the results of AlSi12 are presented below.

Table 4.1: Thermophysical properties of AlSi12 close to melting point. See [1], [9].

Characteristic	*Value*	*Unit*
Specific heat capacity, fixed: ()	1,038	J / (g · K)
Specific heat capacity, liquid: ()	1.741	J / (g · K)
Melting temperature:	576	° C
Specific heat of fusion,:	560	J / g
Density:	2.70	g / cm 3
Thermal conductivity:	160	W / (m · K)

To supplement the literature study, test measurements have been performed to map practical aspects of the thermophysical properties. As can be seen from the above discussion, the eutectic alloy 88Al-12Si is an obvious candidate as a storage medium in a thermally high temperature energy storage. It has therefore been selected for the test measurements.

4.1.2.1. Analysis of properties in cyclic melt-solidification tests

The principle behind the test experiments is to subject the studied sample of AlSi12 (= 88Al-12Si) to repeated heating and cooling so that the sample alternately solidifies and melts.
During the process, the temperature in the sample and the added heat output are measured. This makes it possible to see if there are any changes in the alloy. This chapter contains a brief summary of the cyclic melt and solidification tests, while a detailed test description is included as an appendix in Chapter 8.

Test setup

A photograph of a principle sketch of the test setup is shown in Figure 4.2 and Figure 4.3. Thus, 293 g of AlSi12 have been used in the experiment, which is enclosed in a crucible of high-density graphite. Dig len is placed in a quartz tube that is closed with an airtight flange at the top. To avoid oxidation of the phase-shifting material, the quartz tube has been evacuated of air before heating and filled with an inert shielding gas (argon). A quartz tube in the middle of the set-up is used to measure the center temperature of the phase-changing material.

Figure 4.2: Photo of test furnace with melting cell. In the middle is a quartz tube with a thermal sensor and a connection to argon shielding gas. The melting cell itself with the phase-shifting material (AlSi12) is not visible.

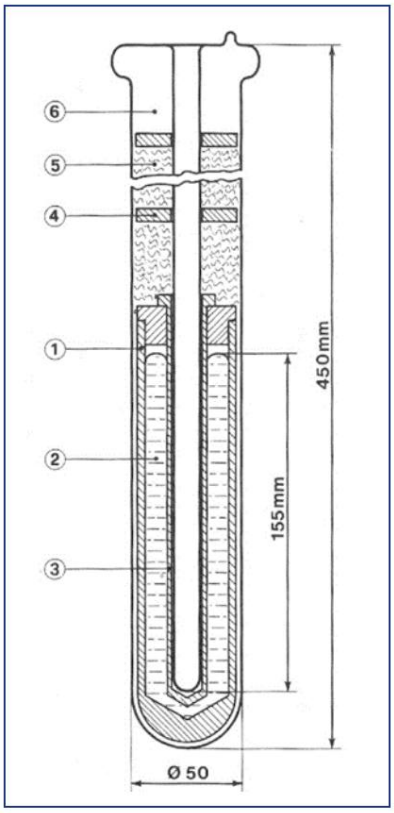

Figure 4.3: Principle sketch for the structure of the melting cell. See text. The figures indicate the following: 1) Graphite crucible, 2) metal, 3) quartz well for thermal sensor, 4) graphite heat shield, 5) insulating quartz wool, 6) argon shielding gas. The stated dimensions are approximate.

The measurements were performed by controlling the temperature of the test furnace around the melting point of the phase-shifting AlSi12 alloy (approx. 576 ° C). During the measurements, in addition to the oven's set point temperature and control value, the oven's electrical heat output (measured as a percentage of max.) And the temperature in the phase-changing AlSi12 have been registered. The mentioned parameters are logged with a time interval of approx. 5 seconds.

A typical temperature sequence is shown in Figure 4.4 and consists of the following phases:

1. Extra heating, = 586 ° C (+11 ° C in relation to "Liquid phase stabilization" (point 2.), 0 - 1.5 hours)

Liquid phase stabilization, 3. = 575 ° C (1.5 - 5 hours)
Solidification, = 567 ° C (5 - 15 hours)
4. Extra cooling, 16.5 = 556 ° C (-11 ° C in relation to "Solid phase stabilization" (point 5.), 15 - hours)
5. Stabilization in solid phase, = 567 ° C (16.5 - 20 hours)
Melting, = 576 ° C (20 - 30 hours).

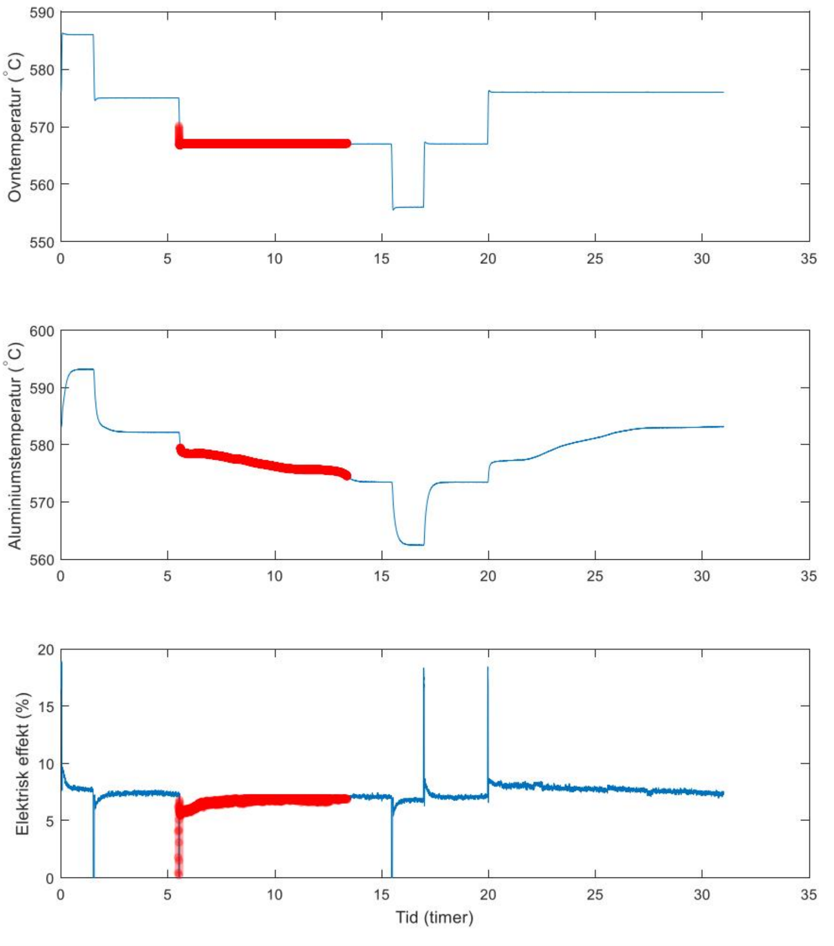

Figure 4.4: A typical measuring cycle of approx. 30 hours with solidification (5 - 14 hours, marked in red) followed by melting (20 - 30 hours). Top: oven temperature (set point); middle: the measured temperature in the phase-shifting aluminum; bottom: the oven's electric was meeffekt.

Test results

During the test run, the above cycle was run 111 times, and various characteristic properties were measured to examine whether there are changes due to the cyclic loads. Figure 4.5 shows the temperature profile of the center temperature for all 111 measures
ger.

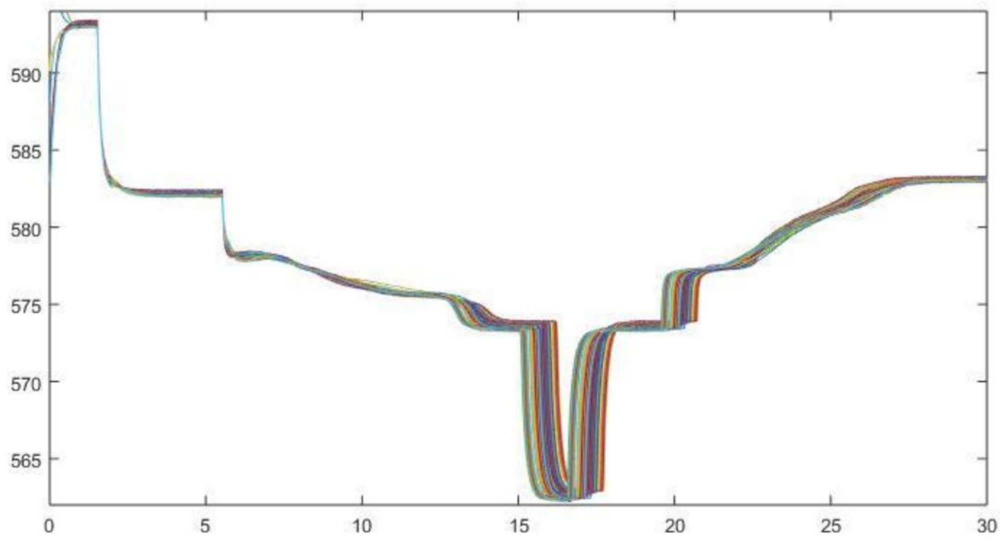

Figure 4.5: Measurement of the temperature in the middle of the crucible (in ° C) as a function of time (in hours). The figure shows all 111 measurements made according to the standard temperature sequence described in Chapter 8.1.

The following properties were analyzed in detail:

- Temperature course
- Solidification time
- Undercooling

Solidification point
Slope of melting curve.

A detailed analysis of the results is attached in the appendix. Overall, it can be stated that the analyzed properties did not show any variations / tendencies during the experimental studies. Thus, it can be concluded that AlSi12 has no properties, which means that it can not be used as storage media.

Conclusions

Measurements and analyzes of over one hundred solidifications and melts of a crucible with phase-changing AlSi12 have been carried out. The purpose of the test work was to find out whether the examined material was suitable as a storage medium in a phase-changing high-temperature energy storage.

The measurements are controlled according to a fixed temperature sequence. During the measurements, the temperature of the test furnace and crucible with phase-changing AlSi12 and added power are registered. The analysis has examined parameters such as solidification time, subcooling, solidification point and slope of melting curve.

The conclusion is that all the melting and solidification curves generally follow the same course, and there are only minor variations at the level of detail. It can therefore be concluded that there is no evidence that significant material chemical changes have taken place and the ter mophysical properties are thus unchanged. This means that the AlSi12 alloy studied is suitable as a storage medium in a phase-shifting high-temperature energy storage.

4.1.2.2. Analysis of properties close to the melting point

With a view to upscaling the warehouse, it was relevant to investigate the possible mechanical forces that can arise in connection with. volume change at phase shift. Upon solidification it disappears AlSi12 ca. 6%, which can immediately be assumed to affect the warehouse walls and possibly in efforts with unacceptably large forces, which in the long run can lead to damage directly or due to exhaustion. On the other hand, it can be assumed that the firmness decreases as the melting and thus the volume increase increases. The shrinkage from the melting point to room temperature is approx. 1%, which is not expected to pose a risk of injury, as the brine dish will only be cooled slightly below the solidification point. It is further known from molding techniques [10] that AlSi12 exhibits certain plastic properties immediately after solidification.

To prove this and transfer it to the use as a storage medium, a special furnace was designed and built.

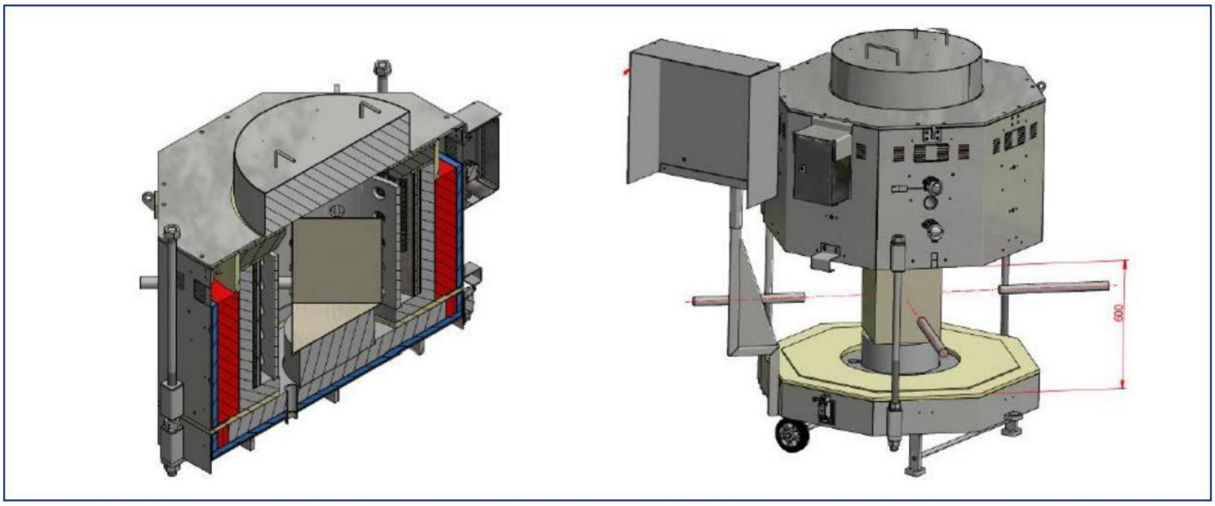

Figure 4.6: 3D model of the special furnace from Støtek.

Test setup

The oven is sized and divided into two parts with a separate bottom section. Figure 4.6 shows a 3D model of the special furnace, and Figure 4.7 shows the installation at the Danish Technological Institute.

The bottom of the oven is fitted with three pipe connection flanges to be able to control the cooling of the oven. There are extra-mounted pipe connections on four of the sides for measuring points for thermometers on the aluminum workpiece. In addition, there is a thermoceramic molded tube with holes to be able to control the air circulation between the heating elements. The heating elements are specially designed and adapted to the oven.

The control is manufactured at the request of the Danish Technological Institute with various heating and cooling programs in order to be able to perform the most optimal tests.

The oven was started up in a four-day procedure in which the temperature was gradually increased to dry out the oven and avoid thermal stresses. Then, aluminum ingots were melted in the furnace and the temperature gauge was installed. Figure 4.8 shows the crucible with aluminum bars in the melting furnace - directly after the bars were inserted into the furnace.

Figure 4.7: The special oven from Støtek to melting experiments.

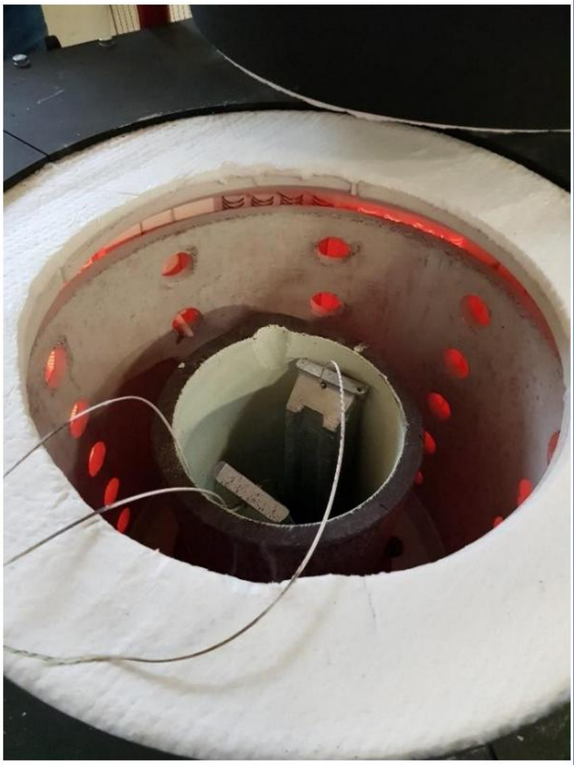

Figure 4.8: Opened special furnace from Støtek with crucible and aluminum bars at the start of melting.

The crucible was made of silicon carbide with a coating on the inside. The coating was pigmented grease and was cured in the oven. Two type K temperature gauges with jacket were used for additional temperature measurement.

In melting experiments, two bars of 3.12 kg AlSi12 each were used. This corresponds to a storage capacity in the phase transition (without superheating or subcooling of the metal) of:

$$6.24 \text{ kg ÿ } 560 \frac{\text{kJ}}{\text{kg}} = 3494 \text{ kJ} = 0.97 \text{ kWh}. \quad (1)$$

To test the construction and nature of the alloy around the melting point, the temperature was varied between 550 ° C and 590 ° C. Near the melting point, temperature ranges were chosen smaller. After the metal temperature had stabilized at one point, the furnace was opened and hardness was qualitatively tested with a pointed rod.

Results and conclusions

The alloy showed a very sharp transition from liquid to solid phase. The physical nature of the alloy was relatively hard just below the melting point and changed only to a very limited extent upon further cooling. Figure 4.9 shows the metal surface after pressure tests at 570 ° C. It is seen that there are some small marks in the surface from the experiment with the pointed rod. However, it was not possible to penetrate the surface or deform the metal
to a greater extent.

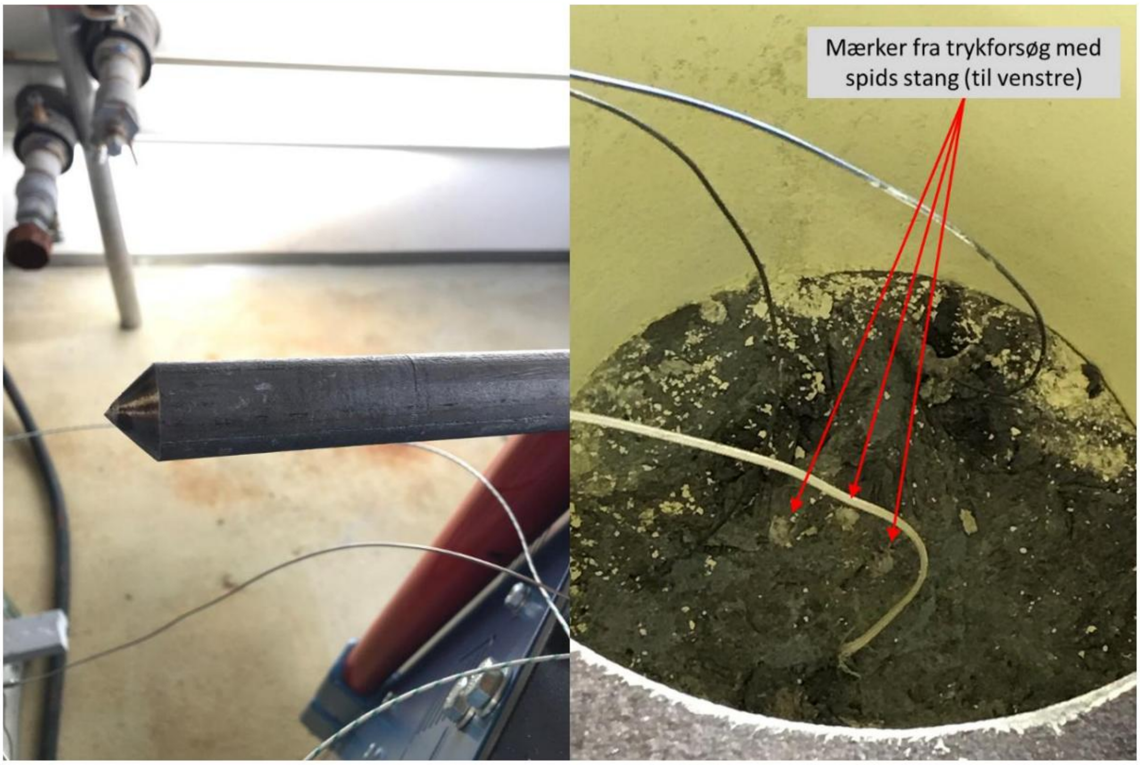

Figure 4.9: Photos from the crucible with aluminum (right) and pointed rod, which was used to test the consistency of aluminum at 570 ° C.

Directly above the melting point, the metal was completely liquid. The dynamic course of the phase transition itself did not prove possible to examine in sufficient detail with the test set-up to substantiate the thesis of the softness / plasticity of the volume increase during melting.

4.2. Analysis of application potential

Energy can be stored in different forms and for different purposes. Energy can, for example, be stored as electrical energy, mechanical energy, chemical energy or thermal energy. Depending on the application, each technology has advantages and disadvantages. The application defines, for example, with what type of energy - e.g. electricity or heat - the storage is charged and what type of energy is to be produced during the discharge - e.g. electricity, heat or a chemical product. In addition, the application defines how many cycles (charges and discharges) are to be ridden and how long the energy is to be stored.

In the present project, an application is analyzed where electricity is to be stored from fluctuating renewable electricity sources - e.g. wind or sun - when there is a surplus of electricity in the grid, and until there is a need for electricity - e.g. in phases with a little wind and sun.

For this purpose, there are different technologies that have different properties. Batteries, for example, have a high efficiency and can react quickly, but they are relatively expensive. *Pumped hydro storage* also has a high efficiency, but is associated with areas with special geographical features. Thermal electric bearings are characterized by the fact that they can be realized on a large scale and are independent of geographical areas. In addition, investment costs for thermal storage are relatively low compared to other technologies. While the transformation from electricity to thermal energy can be realized without loss, the system efficiency is limited by the efficiency from heat to electricity.

The technology that has been investigated in this project used a high temperature PCM material (aluminum or the alloy AlSi12), as the high temperature increases the efficiency of the transformation from heat to electricity. In addition, this technology allows the warehouse to be integrated directly into existing steam power plants, resulting in high efficiencies and less investment.

The technology that is commercially available and most similar to the technology studied is a liquid salt storage. Liquid salt technology is known from *concentrated solar power plants* (CSP), where liquid salt is heated from the sun and stored in large tanks in order to operate an ordinary steam power plant when a need for electricity arises [11].

To get an idea of how competitive it is to use aluminum or AlSi12 as a storage medium for large-scale storage, the technology is compared with the commercially available technology that uses liquid salt.

The following chapters highlight the possibilities of integrating aluminum or AlSi12 into different steam power plants, after which stock dimensions and investment costs are assessed and compared with liquid salt technology. This is followed by a chapter which discusses the potential of the technology in the Danish and Faroese energy systems.

4.2.1. Integration of high-temperature heat storage with existing power plants

A high-temperature heat storage with phase-changing aluminum as storage material is intended to be directly included as a heat source for an existing power plant. This is reminiscent of a Pumped Heat Electricity Storage configuration (PHES), which, however, means that a heat pump is used for storage - not just direct electric heating. Aluminum melts at 660 ° C, while the melting point of alloys is in the range around this temperature and lower. This fits well with the temperature at turbine inlets in steam power plants, and with that an aluminum storage and other storage with the same temperature can potentially be integrated directly with an existing power plant.

This has been analyzed using an existing model of a larger Danish power plant, the Aved ear plant Block 1 (AVV1), which is a combined heat and power plant that was commissioned in 1991 and which has an electrical power of 250 MW in condensing operation at full boiler load. The electrical efficiency is 42%. In back pressure operation, 212 MW of electricity and 330 MJ / s of district heating are produced for the Copenhagen district heating system. The plant's boiler delivers steam at 240 bar / 540 ° C, which is reheated to 540 ° C after the high-pressure turbine. The process of the plant is illustrated in Figure 4.10.

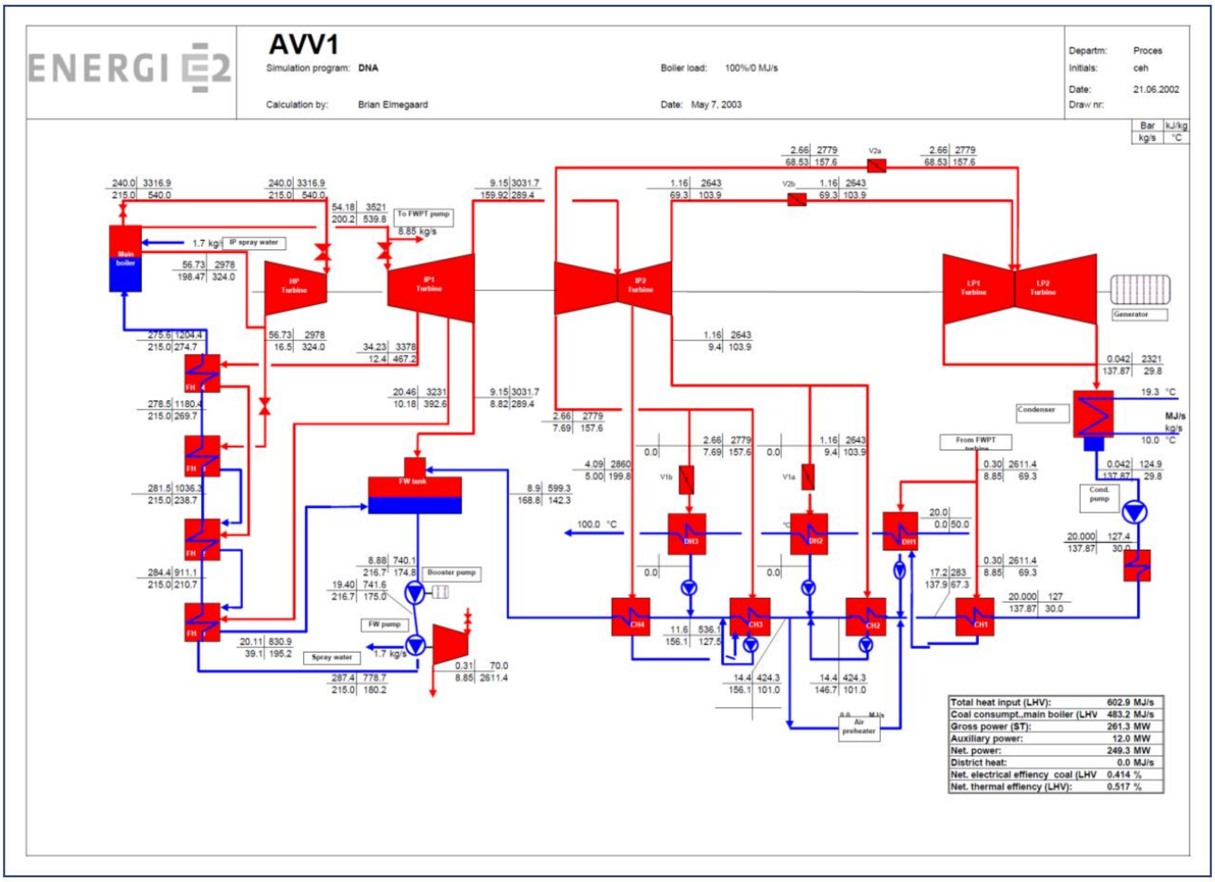

Figure 4.10: Process diagram for Avedøreværket Block 1 [12].

These are the valves indicated by V1a, V1b, V2A and V2b, which are used to switch the operation between condensation and back pressure operation. With these and varying firing, the operating range illustrated in Figure 4.11 is achieved. The figure is taken from [12], in which a complete thermodynamics

The model of the plant has been developed and modeled throughout the operating area. The model is implemented in the simulation tool DNA and includes all main components of the plant with characteristics for the entire operating area. This includes, among other things, heat transfer conditions in heat exchangers as well as turbine and pump operation. The turbines in particular have an influence on the process, which is modeled using turbine constants, which describe the relationship between mass flow and inlet and outlet pressures for each turbine. In addition, the gait temperature is included in the context.

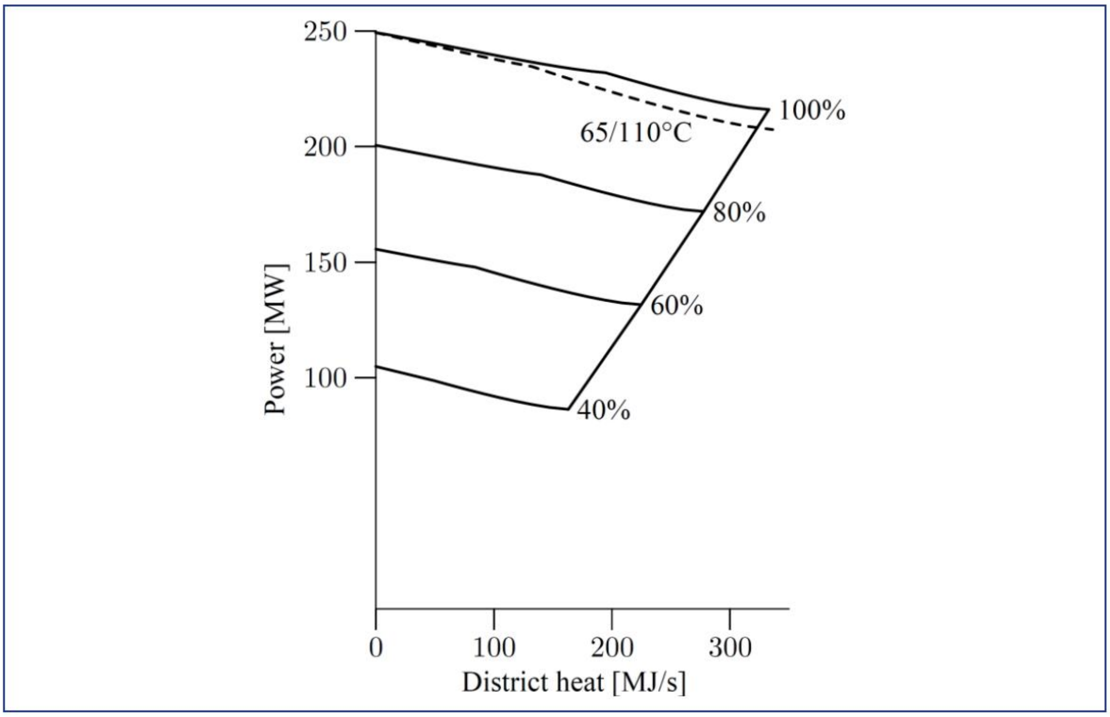

Figure 4.11: PQ diagram for AVV1 [12].

During operation of the aluminum warehouse - and other warehouses - the energy content of the warehouse will fall during discharge, where steam is produced. Depending on the characteristics of the storage and the heat transfer ratio between storage media and steam, the temperature reached by the steam may drop. This is a different behavior than for usual processes, where an attempt is made to maintain the turbine inlet temperature for the sake of the efficiency of the plant. The effect of lowered turbine inlet temperature for the model of AVV1 has been investigated to gain insight into the efficiency that a warehouse integrated with this plant will be able to achieve.

Figure 4.12 shows the steam mass flow for full boiler load at varying turbine inlet temperature. The flow is increased at a lower inlet temperature, as the same heat flow must be transferred to the steam. It is also seen that the relationship is apparently linear. Mass flow but is the same for both back pressure and condensation operation.

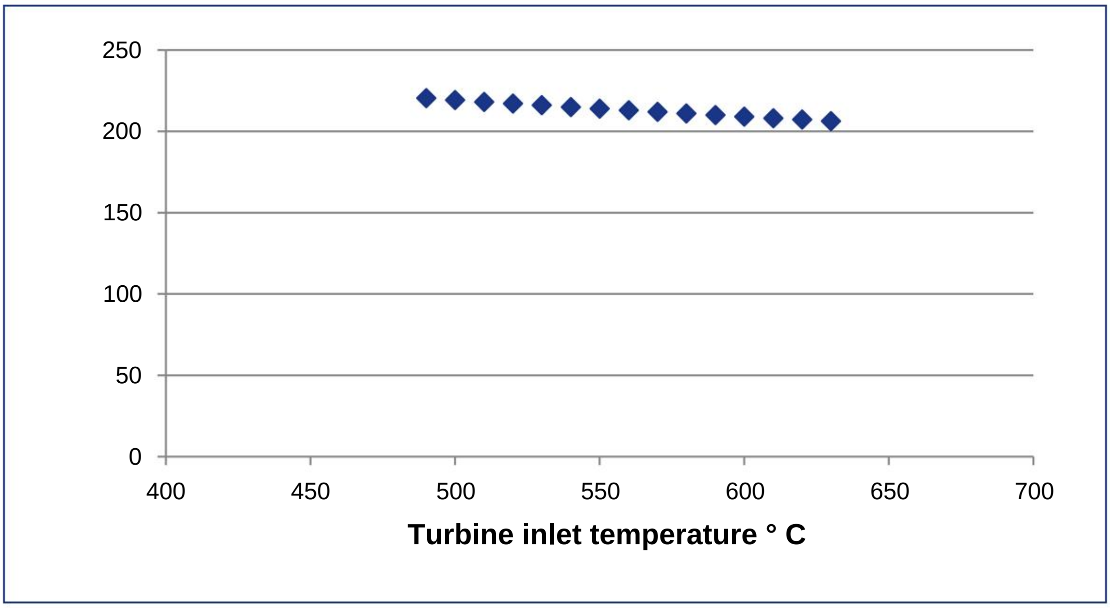

Figure 4.12: Steam mass flow at changed turbine inlet temperature.

Figure 4.13 illustrates the significance of the electricity effect. This also shows an approximate linear relationship, where the effect decreases at lower inlet temperature. The figure also illustrates the difference between the electrical performance of the two modes of operation.

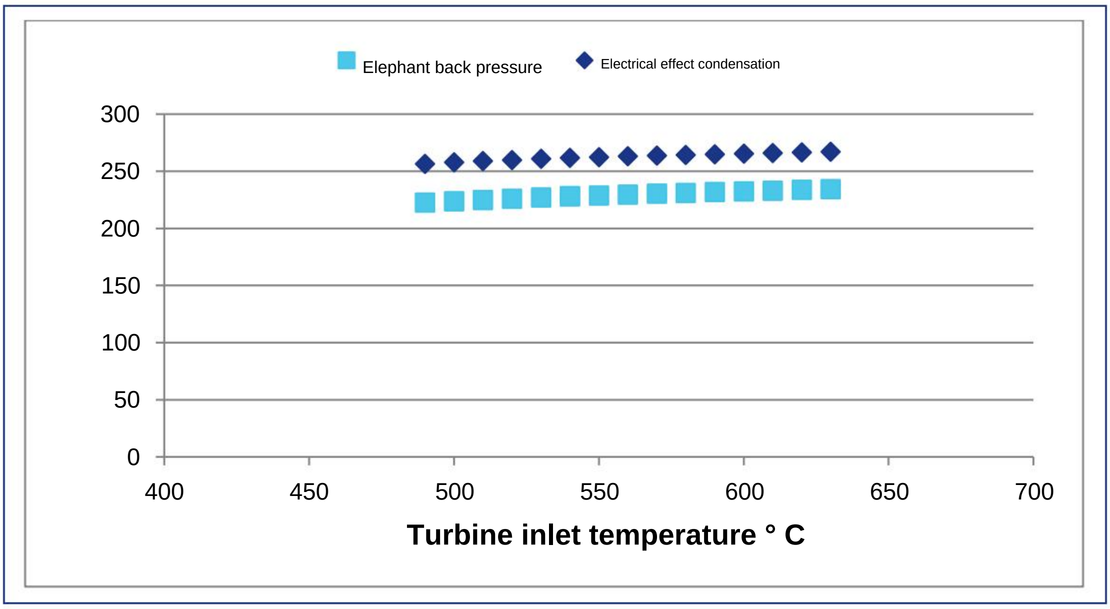

Figure 4.13: Power output at changed turbine inlet temperature.

The relationship between electrical efficiency in the two modes of operation and thermal efficiency in back pressure operation is illustrated in Figure 4.14. Here it is seen that the electrical efficiency will decrease by about 1 percentage point if the turbine inlet temperature drops to 490 ° C. This corresponds to a decrease in electricity output of 2%, which will directly influence the overall storage efficiency from electricity to electricity in a direct electricity storage operation.

The analysis thus shows that there will be a significant advantage in achieving constant operating conditions for integration between warehouse and plant, and that the electricity-to-electricity efficiency will be affected by a decrease in steam temperature.

At the varying operating points, no conditions have been found in the process, which gives rise to concern that the plant will not function technically at lower steam temperatures.

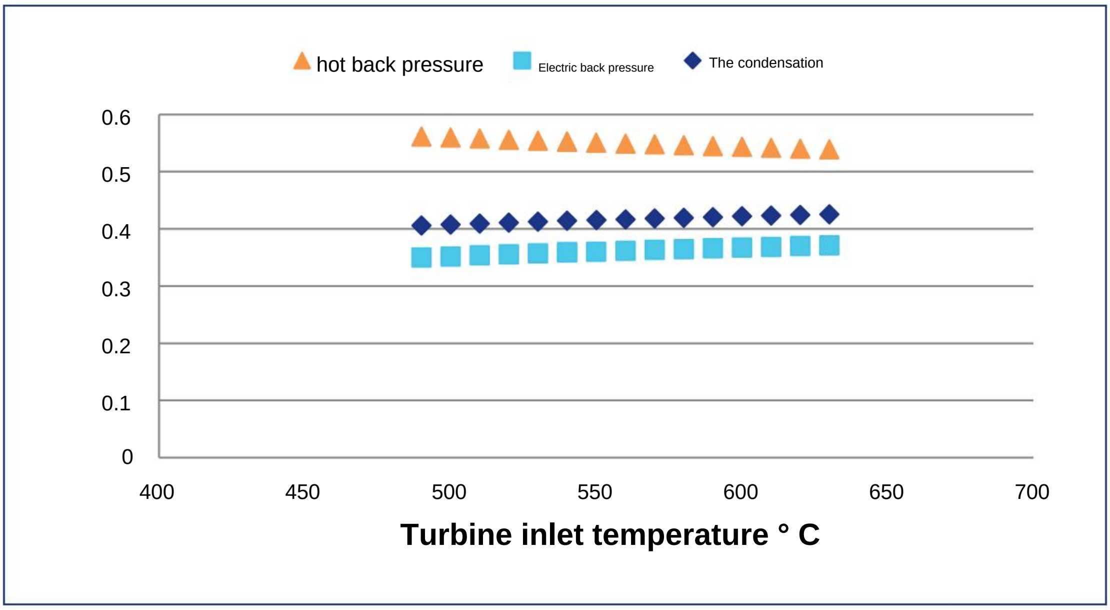

Figure 4.14: Electricity and heating efficiency at changed turbine inlet temperature.

Since the technology has proven suitable for a complicated back-pressure CHP plant such as the Avedøre power plant, smaller technically complex power plants will also be able to make use of the technology. For example, this applies to processes in back-pressure plants such as Verdo's plants in Randers, which are expected to have a similar characteristic at lower turbine inlet temperatures.

4.2.2. Overall estimates of inventory size and costn ger for the storage medium

A liquid salt storage, such as used in *concentrated solar power plants* is the most similar storage technology that is commercially available. In order to get an impression of AlSi12's competitiveness in comparison with liquid salt, an analysis has been made of overall parameters such as stock size and cost of the storage medium.

4.2.2.1. The size of necessary stock

The physical size of the storage is determined by the properties of the storage medium such as density and heat of fusion and by power plant requirements such as efficiency from heat to electricity, electrical performance and the desired storage time. Figure 4.15 shows the relationship between the physical storage size and the thermal and electrical storage capacity. In addition, an example of a power plant with a capacity of 100 MW of electricity is shown, which requires a storage capacity equivalent to 72 hours. In this case, a storage size of about 43,000 m3 is required . Calculations behind the diagram are based on an efficiency from heat to electricity of 40% and assume that only heat from the phase transition is used. That is, aluminum is not cooled below the melting point or heated above the melting point during the storage cycle.

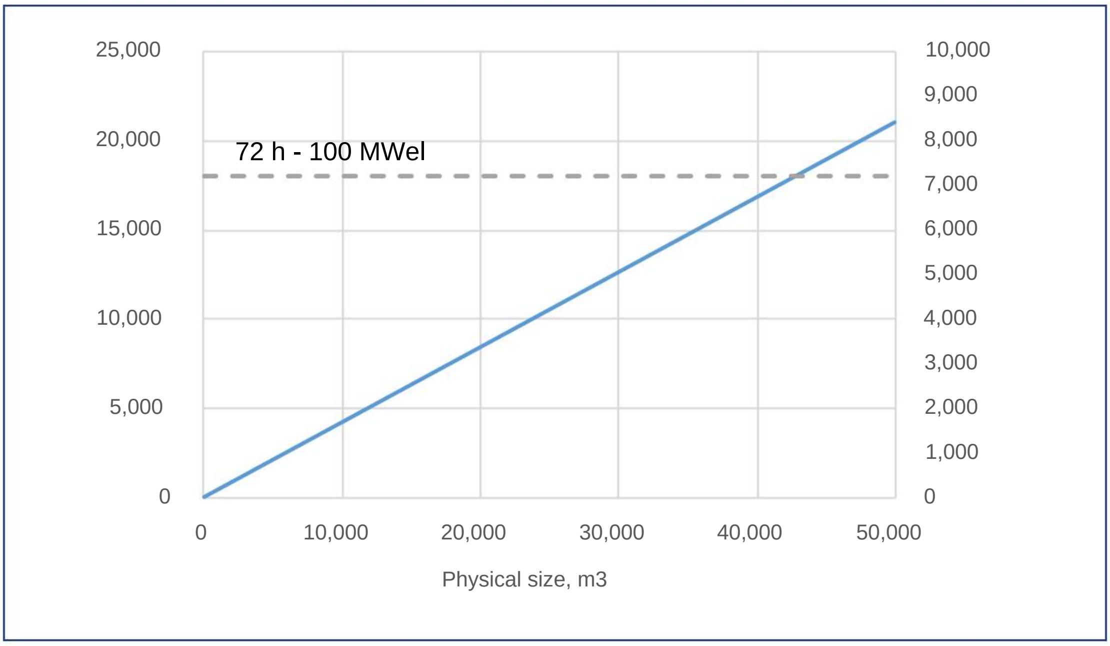

Figure 4.15: Storage capacity depending on physical storage size based on a heat of fusion of 560 kJ / kg, a density of 2700 kg / m3 and a power plant efficiency from thermal to electric of 40%.

The AlSi12 alloy can store 560 kJ / kg x 2700 kg / m3 = 1512 MJ / m3 . Liquid salt can store 1.3 KJ / kgK x (565 ° C - 270 ° C) x 1900 kg / m3 = 783 MJ / m3 . In addition, two tanks of the same size are required for liquid salt at two different temperatures (270 ° C and 565 ° C), as the heat is stored as sensitive heat instead of as latent heat as in a PCM.

4.2.2.2. Assessment of investment costs in stock media

The analyzed storage technology can be considered as an alternative storage technology to the commercially developed technology that uses liquid salt. This section compares the cost of storage media with liquid salt technology.

Specific storage media costs are calculated based on the storage media's heat capacity and price.

Costs for aluminum are calculated as:

$$\frac{1355 \frac{€}{kg}}{540 \frac{kJ}{kg}} = 3.70 \frac{€}{kJ}. \quad (2)$$

Costs for liquid salt are calculated as:

$$\frac{900\ \frac{€}{kg}}{1.3\ \frac{kJ}{kg\ K}\ ÿ\ (565\ ÿ - 270\ ÿ)} = 2.34\ \frac{€}{kJ}. \qquad (3)$$

The specific cost indicates that the storage medium liquid salt is about 33% cheaper than AlSi12. However, the costs are of such a size that it is easy to compensate for the price difference through benefits in other plant components - such as heat exchanger or container.

4.2.3. The potential for electrical storage

The Danish electricity grid is characterized by great robustness with strong international connections.

In contrast, the Faroese network is quite weak, with no connections to other countries and with a very strong expansion of especially wind power.

The challenges and thus the opportunities in the two regions are therefore different, which is illustrated in the following.

4.2.3.1. Denmark

Denmark has an electricity grid with a large proportion of fluctuating renewable energy sources - e.g. wind and sun. Wind power had a capacity of 5460 MW in 2017, which corresponds to 38% of the total electricity capacity [13]. In 2017, the share of renewable energy in the electricity supply was 64%, while 43% came from wind [13]. However, Denmark still has a large capacity of thermal power plants, just as strong international connections are able to compensate for variations in the electricity grid.

This situation means that the market potential for energy storage in the current Danish system is limited. However, it is expected that there will be a need for large-scale storage as the use of renewable energy expands.

It is believed that a technology is promising if the technology is able to store electricity at low cost and to stabilize the electricity grid just like thermal power plants today.

Both requirements are met by the analyzed technology. A heat storage with metal such as PCM could be integrated into existing power plants, while the existing power plant and the entire infrastructure can be maintained. Thus, the technology has the potential to become cost-effective, while maintaining the stabilizing performance of thermal power plants.

In this project, a final design of the system was not determined and thus a reliable assessment of investment costs could not be concluded. However, the above comparison with liquid salt technology suggests that storage in aluminum has the potential to become an economically competitive supplement.

4.2.3.2. Faroe Islands

The Faroe Islands, with its 51,000 inhabitants, are isolated in the Northeast Atlantic.

Modern society has a relatively high energy demand, which is mainly covered by imported oil. On the islands, there is broad agreement that renewable energy sources must be expanded significantly, so that you become less dependent on imported oil and at the same time get a 'green' profile.

Almost half of the imported oil is used for the operation of fishing vessels and other sea transport. It is difficult in the short term to spot any alternative to replacing this oil.

The situation is different with the other half of oil consumption, which is used for electricity production, land transport (cars) and heating. Here are alternatives so that oil can be phased out:

1. Electricity can be produced from water, wind and solar energy.
2. Petrol and diesel cars can be replaced by electric cars.

Heating can be moved from oil burner to various types of heat pumps and other electric heating.

The goal has been for this restructuring to be completed by 2030.

The Faroe Islands have no cable connection to the outside world, and all electricity must therefore be produced locally. Electricity consumption has risen to just over 300 GWh per year in recent years - half is produced from hydropower and wind power, and the other half comes from oil. When transport and heating are moved from oil to electricity, electricity consumption is almost doubled. Renewable energy sources must therefore be greatly expanded to replace the current electricity production from oil and the increased consumption for transport and heating.

Hydropower has been used in the Faroe Islands since 1921 and was the mainstay of electricity production in the first half of the last century. The best sites have been taken into use, and environmental considerations speak against a significant expansion of hydropower.

The Faroe Islands are one of the world's most suitable locations for wind power, as many accessible localities have an average wind speed of over 10 m / s. With the last wind farm, which came into operation in 2014, the total wind power tripled and is now 18 MW. More wind power is on offer, and more wind farms will come into operation in the coming years. It is expected that the wind force will be approx. tenfold by 2030. Wind power is the cheapest form of production, and it pays to expand it until there is a 30-40% surplus in relation to electricity production.
This profit will come at unpredictable times, but can be used for flexible consumption such as. a heat storage.

The Faroe Islands are located at 62 ° N, and the possibility of electricity production from solar energy is therefore not timeless. Production from water and wind energy is greatest in winter, and at this time of year oil consumption for electricity production is minimal. Oil consumption is greatest in summer, when less water and wind energy is available. Solar energy can therefore prove to be crucial in avoiding oil in the summer.

In a future electricity system, which is largely based on fluctuating energy sources such as wind and solar, energy storage will become a necessity. It is possible to expand the existing hydropower system with *pumped hydro* storage facilities, so that excess fluctuating wind and solar energy can be stored as water in high-lying reservoirs and be available for electricity production when there is a shortage of energy. However, sites for *pumped hydro storage* are limited and the technology requires large investments. Environmental considerations can also become a constraint.

One option is to store energy in large amounts of hot water. This is known from Danish district heating installations, where water in large dams is heated in the summer, and where water is used throughout the winter. With this technique, however, it is not possible to produce electricity as needed, and the technique will therefore have limited interest in the Faroe Islands.

A high-temperature energy storage, where the energy can be released both as electricity and heat, will be extremely valuable for the future Faroese electricity system.

4.3. Definition of recommendations for constructive realization

The previous chapters show that there is some potential for using the AlSi12 alloy as a phase change material (PCM), and suggest that the technology has the potential to become an alternative technology to e.g. liquid salt as a storage medium. However, there are a number of challenges associated with using AlSi12 with regard to the design of the warehouse. This chapter therefore sheds light on various possibilities for integrating stocks in steam power plants as well highlights challenges in possible constructions of heat storage tank.

4.3.1. Integration in steam power plants

Figure 4.16 shows how the aluminum storage can be included as a direct replacement for a steam boiler. When replacing a steam-producing boiler with an aluminum storage, the storage must be able to take up space in the already established feedwater circuit. In this way, the already established infrastructure around electricity and heat production can be reused, which will create some economic benefits. By implementing the aluminum storage as a direct replacement for a boiler, some complications arise around the large temperature differences that will arise. Power plants with district heating production (DH) will normally operate with feedwater return around 50 ºC - 60 ºC, and at this temperature the feedwater will enter the aluminum storage, which is 577 ° C for AlSi12 or 660 ° C for pure aluminum. This will result in thermal stresses that the material must be able to absorb without leakage or component damage. Challenges due to thermal stresses are expected to result in more complex constructions and thus also higher costs.

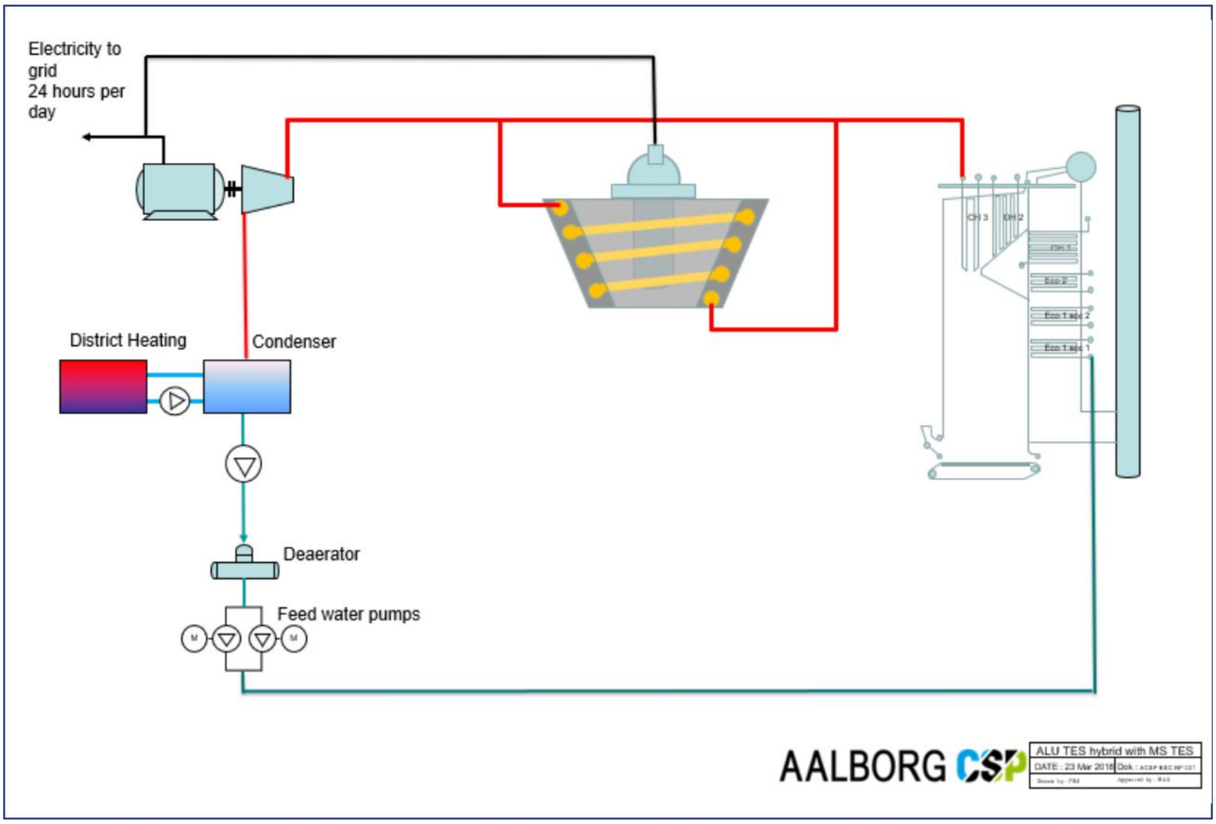

Figure 4.16: Aluminum bearing in single loop layout.

Therefore, a solution has also been looked at, where the aluminum bearing is combined with a see customer circle. By using a secondary circuit, it is possible to gradually heat the feed water through a *steam generating system* (SGS) [14], which means that a smaller temperature difference is created in the aluminum storage. When using a two-circuit system, a *high thermal fluid* (HTF) must be used for heat transfer in the primary circuit. It is not possible to circulate the molten aluminum because it must not come into contact with the steel structure and therefore another material must be used which can be operated at temperatures up to 660 ° C. Therefore, it is recommended to use molten salt (Molten Salt, (MS)), which has proven to be able to operate at higher temperatures without complications. However, challenges may arise in this form of configuration, as it is not possible to require yellower production.

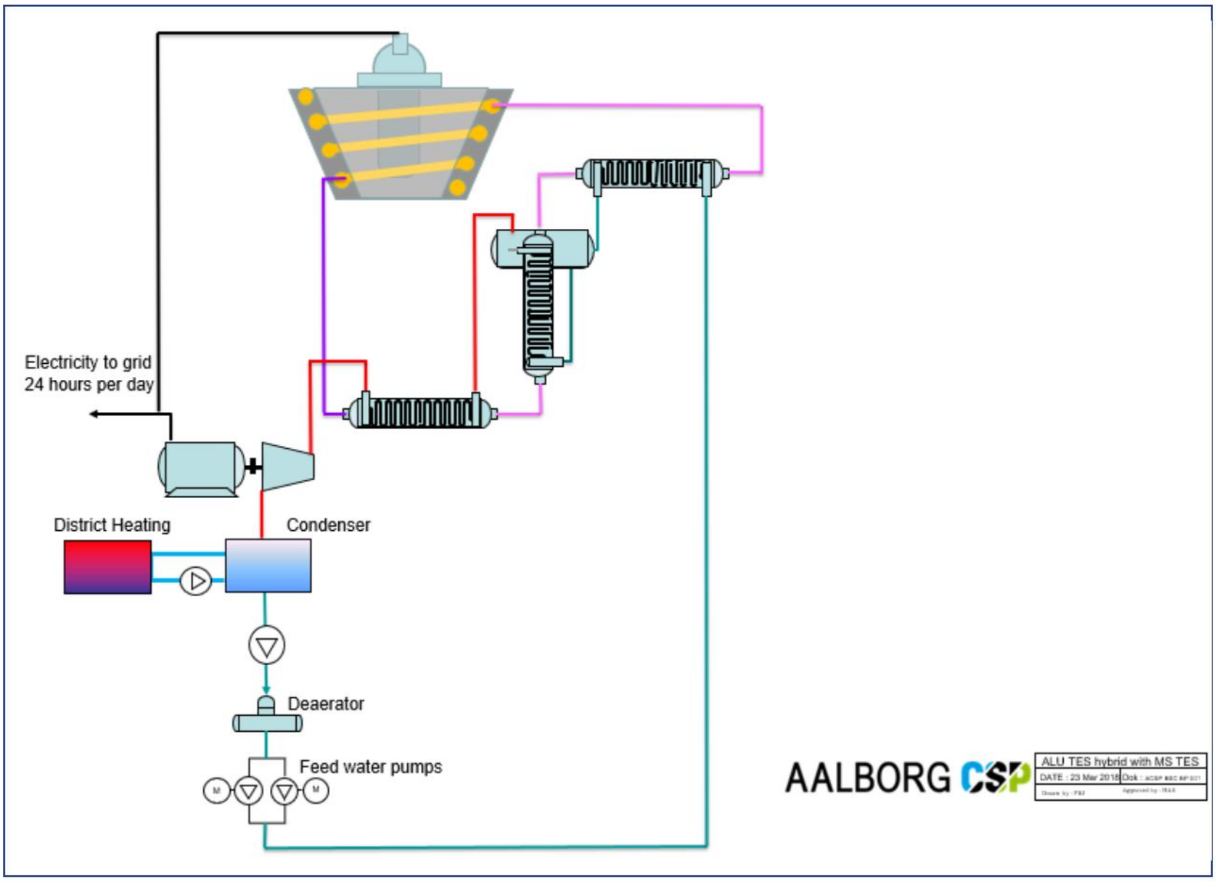

Figure 4.17: Aluminum bearing in double loop layout.

In order to design a system with maximum utilization of the renewable energy sources, the aluminum storage can advantageously be included in a hybrid system combined with an MS storage and a *Steam Generation System* (SGS), as it is known from integrated CSP systems. The MS system is designed with a two-tank system consisting of a cold (270 ° C) and a hot (565 ° C) tank. The cold MS is pumped through an electric heater, which uses excess electricity from wind and solar energy on the grid to heat the MS. Here, the hot salt is stored until there is a lack of production from renewable energy sources, and pumped through the integrated SGS. Here, the energy is transferred to the feedwater circuit for steam production (545 ° C), which is passed on through the aluminum storage, where the steam is boosted up to 557 ° C. The increased steam quality ensures maximum utilization of the combined district heating and electricity production.

The advantage of using a hybrid plant is that the steam enters the aluminum storage at the evaporation temperature instead of at the feedwater return of about 50 ° C. This reduces thermal stresses in the material and ensures a reliable and leak-free operation.

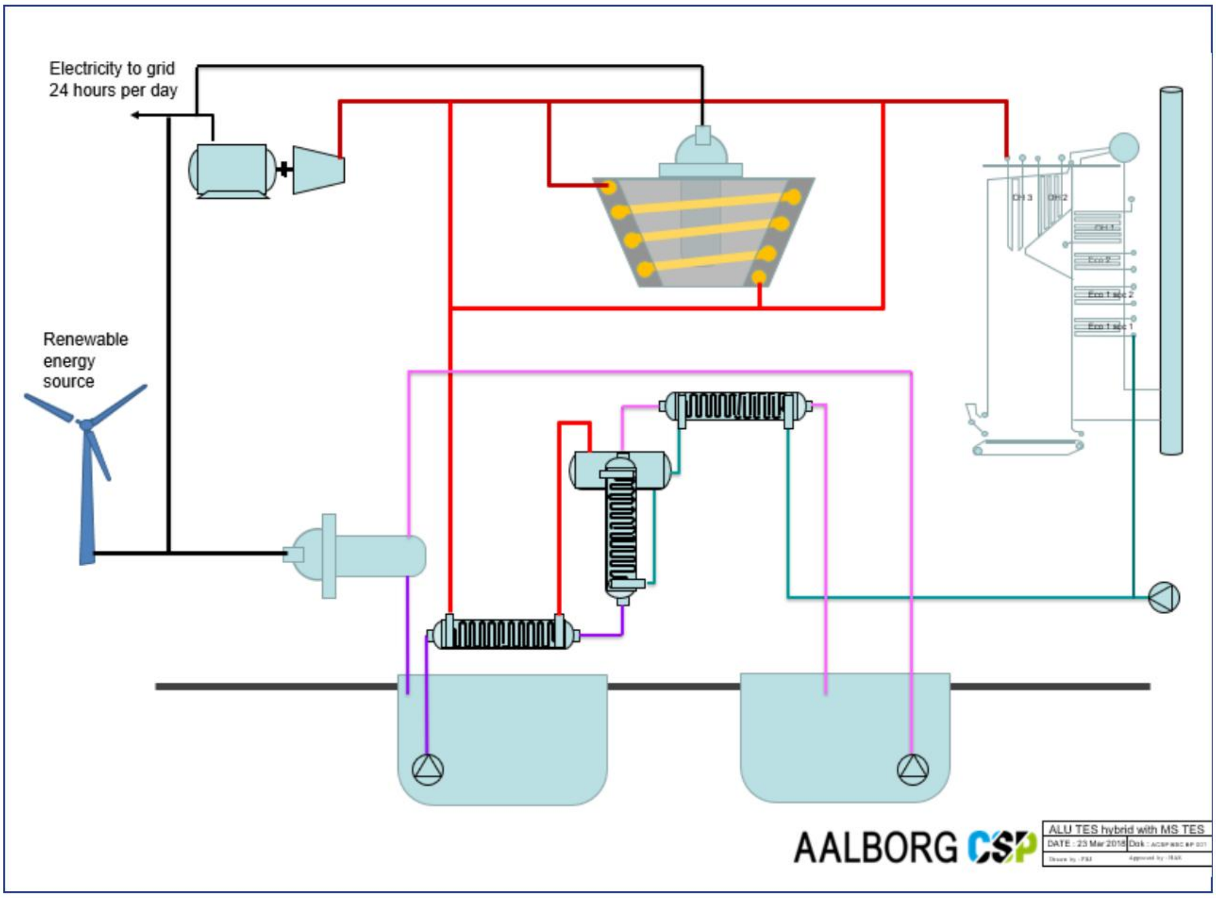

Figure 4.18: System layout with combination of liquid salt and aluminum as storage medium.

Aluminum itself will have a constant temperature during melting and solidification. This offers potential for optimizing the steam process for better integration with a constant temperature heat source - for example at several reheating steps, which will be able to optimize the efficiency under certain conditions.

Therefore, one could also think of a system where the heating is realized with liquid salt, and the evaporation and superheating - possibly also the multi-stage superheating - is realized with aluminum storage.

4.3.2. Media for heat transfer

4.3.2.1. Charging

The aluminum bearing can be designed to charge in one of the following ways:

Direct electrification, where electricity is added to the aluminum and the resistance in the metal causes it to heat up and melt. This is implemented with electric heaters integrated in the aluminum storage, where the heat thereby migrates out into the storage from the heat sources.

Integrated heat exchangers in the aluminum storage, where a secondary liquid heats up the aluminum storage. This process will also take place from the heat exchangers and out into the warehouse.

Direct electrification, however, turns out to be the obvious choice if the purpose of the warehouse is electrical storage.

4.3.2.2. Discharge

The basic idea behind a high temperature thermal storage is to convert the thermal energy (with relatively low energy quality) to mechanical / electrical energy (high energy quality) by producing high temperature steam and utilizing it in efficient steam turbines. It is therefore obvious that an efficient method must be developed to extract the thermal energy from the storage. Below, it is briefly touched on how the energy can be extracted from a high-temperature energy storage based on phase-shifting metals.

Direct transfer. By direct transfer is meant that the thermal energy is transferred directly from the metal storage to the steam (via an appropriate separation). To simplify the discussion, only the overheating of the steam is considered here, but there are several alternative methods for the steam production itself. The disadvantage of this method is that the energy transfer is relatively inefficient, and therefore a relatively extensive construction is required into the phase-shifting metal storage. In addition, a ceramic protective layer is required between the steam line and the liquid metal. The big advantage is that there is no need for an expensive intermediary. Therefore, the solution is probably the most optimal purely economical.

Transfer via gas. This solution is characterized by a secondary circuit that transports the thermal energy from the storage to a heat exchanger, where it is then transferred to the steam. It is assumed that an inert gas is used - e.g. Ar, He or Nÿ. These gases do not react with the liquid metal, and therefore a physical separation is not necessary, which could potentially give rise to a simpler construction. In turn, a heat exchanger is needed to transfer the thermal energy to the steam. So there are both advantages and disadvantages in relation to the direct transfer to the steam.

Transfer via liquid metal. Primary refrigeration circuits based on liquid metal were developed in the decades after 1950 for use in nuclear power plants in the United States. The knowledge thus obtained is published in the "Sodium-NaK Engineering Handbook" [15]. It is possible to use sodium (Na, in English: Sodium), but as the melting point is 97.8 ° C, there is a risk of it solidifying in the pipes when shutting down. Therefore, it is advantageous to use a eutectic mixture of Na (22%) and K ("Potassium", 78%), which is liquid from -12.8 ° C to 785 ° C. Together with steam and other gases, NaK has a very high density and a good thermal conductivity. Therefore, a circuit based on NaK as the primary heat transfer means will be able to transport very large amounts of thermal energy compared to a gas circuit of similar size.

A significant disadvantage associated with using liquid metals such as Na and NaK, is the risk of fire, as both Na and - to a greater extent - K react with both the oxygen in the air and the water. The necessary safety precautions may be disproportionately costly.

The great potential that NaK has as a heat transfer agent has led several people for cutting groups, [16], [17], to propose using NaK as a heat transfer agent in connection with solar panels (Concentrated Solar Power (CSP)). A fire in the sodium circuit of a CSP test facility in the 1980s (see discussion and references in [16]) underscores the importance of effective safety measures.

4.3.3. Heat transfer to and from the warehouse with secondary media

When discharging the storage, the steam must be charged. This can be done by letting the steam or a secondary liquid flow through heat exchangers (possibly pipes) in the aluminum storage. When using a secondary liquid in the storage, the heat must be transferred in another heat exchanger to the steam. Both in connection with charging and discharging, it is important to consider the ter modynamic properties of aluminum when changing phases from solid form to liquid form - and vice versa. Table 4.2 shows the most important thermodynamic properties for aluminum in the area around phase change - approx. 660 ° C.

Table 4.2: Thermophysical properties of aluminum.

Characteristic	*Solid at 659 ° C*	*Melting point 660 ° C*	*Liquid at 661 ° C*
Specific heat capacity, kJ / kgK	1,277	-	1,125
Fusion heat, kJ / kg	-	321	-
Conductivity, kJ / m2K	211.6	-	0.905
Density, kg / m3	2550	-	2377

It can be seen from Table 4.2 that the fusion heat contains approx. 250 times more energy than the specific heat capacity for both solid and liquid form. This means that in order to obtain the same amount of energy from 1 kg of aluminum on cooling as at the phase change, the cooling must be at 250 ° C, or 250 kg of aluminum, cooled by 1 degree, must be used to achieve the same amount of energy as the phase transition of 1 kg of aluminum contains.

The conductivity, which is a measure of how well / quickly the energy is transported through the material, is for aluminum in solid form of 211.6 kJ / m2K, whereas in liquid form it is 0.905 kJ / m2K. This means that the charge during discharge, where the aluminum goes from liquid to solid form, can transfer 233 times more energy on 1 m2 surface than during charging, where the aluminum goes from solid form to liquid, as there will be molten aluminum during charging

between the source and the solid aluminum, while on discharge there will be a solidified layer of aluminum between the heat transfer surfaces and the molten aluminum.

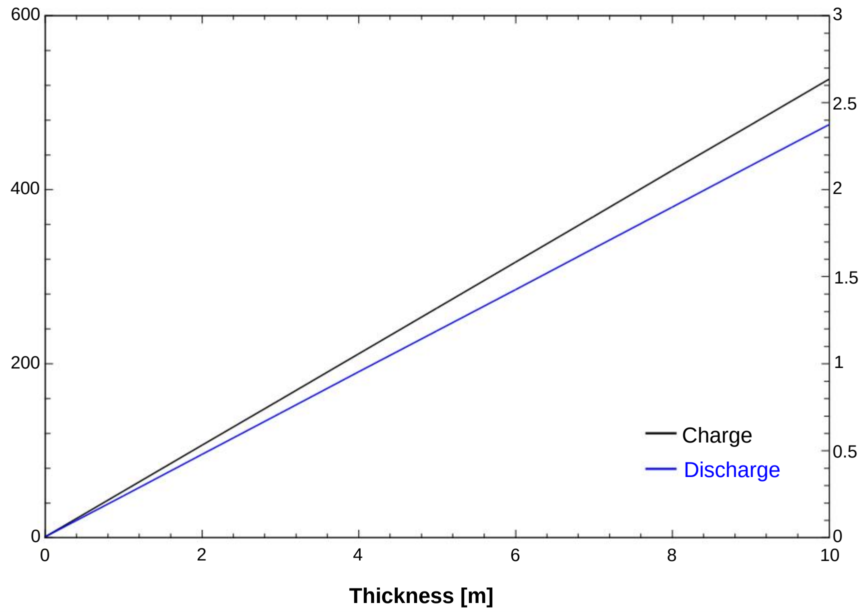

Figure 4.19: Heat exchanger area required to move 1 MW of energy through a given thickness of the storage during charging and discharging.

Figure 4.19 shows the heat exchanger areas required at resp. charging and discharging if 1 MW is to be moved through a given thickness of the bearing, which will correspond to the distance from the heat exchanger to the front of the solidifying or melting aluminum.

The discharge of the aluminum bearing will probably have to be done using a secondary liquid, as the requirements for materials by introducing high-pressure steam directly into the exchangers in the bearing will most likely lead to high costs and great complexity. A secondary medium that could be suitable for the purpose is an alloy of Sodium and Potassium called NaK, which in the right mixing percentage is liquid between -11 ° C to 785 ° C. NaK is also used for cooling nuclear reactors and is therefore a well-known technology for moving energy. The heat is transferred from the aluminum storage at a constant temperature at the phase transition, where NaK is heated. The transfer between NaK and steam takes place by heating the steam and cooling NaK - ie with temperature slip on both streams. It has been investigated what such a heat exchange between NaK and steam will look like when used to transfer the heat from the aluminum storage to the steam turbines. Figure 4.20 and Figure 4.21 show what the temperature profile of NaK and steam looks like in the heat exchange at steam pressure of resp. 270 bar and 58 bar. The pressures are the same as in the boiler and the general manager at Avedøreværket block 1 and have been chosen on this basis.

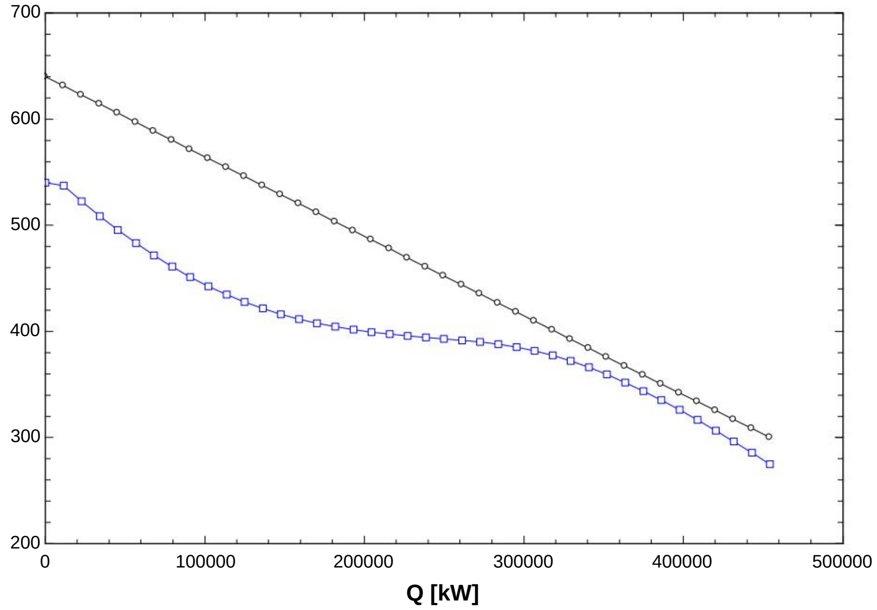

Figure 4.20: TQ diagram of heat exchange between NaK and 270 bar steam.

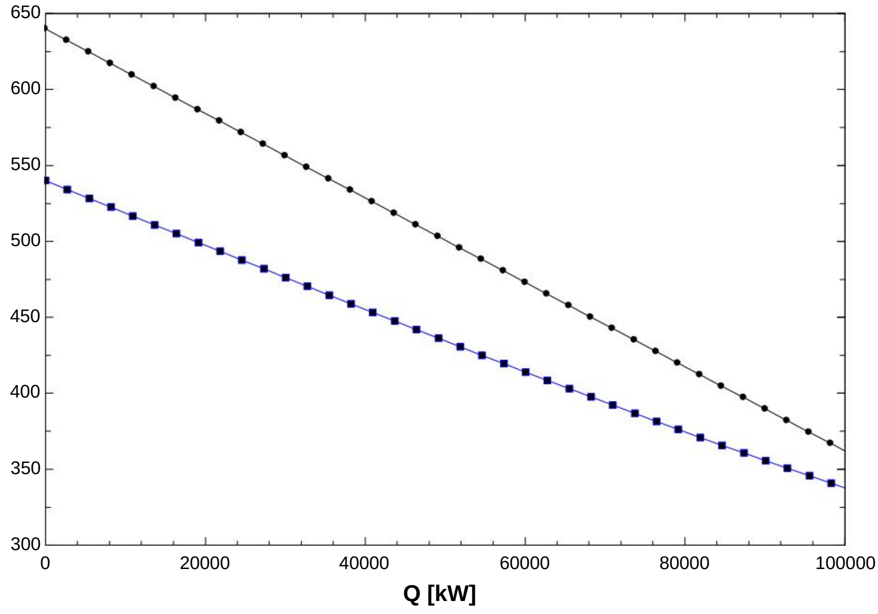

Figure 4.21: TQ diagram of heat exchange between NaK and 58 bar steam in reheating units.

It is seen that NaK has an almost linear relationship between temperature and transferred energy. The steam, on the other hand, changes the temperature profile depending on the pressure. As can be seen from Figure 4.20 and Figure 4.21, the steam has an almost linear relationship between temperature and transferred energy at "low" pressure, whereas the temperature profile of the steam changes characteristics during heating from 290 ° C to 540 ° C at a pressure of 270 bar, as it enters as water and condenses in the heat exchanger. However, both temperature profiles must be said to match satisfactorily from these initial studies.

It will be possible to make an aluminum bearing that can discharge quickly to a secondary medium, as the conductivity during discharge is very high compared to the conductivity during charging. When using the same heat exchanger, this must either be oversized for the discharge or undersized for the charge if the same technology is to be used for both charging and discharging. It should therefore be considered whether it is possible to use two different technologies for discharging and charging - possibly. heaters or electrification by charging, as these technologies are efficient and may be easier to integrate than heat exchangers. In relation to finding secondary media to move the heat from the warehouse to the steam, there are several options, but NaK has proven to have a good profile for steam pressure and temperatures that correspond to the steam used at Avedøreværket block 1.

4.3.4. Construction of container and heat exchanger

The preceding chapters indicate that there is some potential associated with using AlSi12 as a storage medium compared to liquid salt. Especially if there is a need for heat at a constant high temperature - such as in steam power plants with multi-stage heating. However, the literature study has shown that there is a lack of experience with the construction of a heat storage with AlSi12 as storage medium on a large scale. It has not been part of this project to build a large-scale warehouse, but some aspects have been found that are relevant in relation to the construction of a large-scale warehouse.

Encapsulation

A challenge associated with phase-shifting high-temperature energy storage based on aluminum is that liquid metals react chemically with solid metals. Therefore, one can e.g. do not use stainless steel for encapsulation. One possible solution is to use high density graphite. This solution is used e.g. in connection with calibration of temperature in so-called fixed points (solidification, melting or triple points), but unfortunately it is an expensive solution.

A cheaper alternative to encapsulation is ceramic materials. Fukahori et al. [18] has investigated the resistance of four possible ceramic materials to five phase-shifting materials: Aluminum and three Al / Si alloys. Their study shows that AlÿOÿ, AlN and SiÿNÿ do not react with the liquid metal alloys and are therefore suitable. In contrast, SiC and SiO2 react chemically with the liquid alloys and are therefore not suitable.

To ensure mechanical strength, a layered construction of the enclosure will probably be necessary:

In the interior, there must be a layer that is chemically resistant to the phase-shifting metal alloy.

Next, a metal layer is proposed to give the structure strength.

3. Additional layers may be required to ensure additional strength and insulation.

Among the three suitable candidates mentioned above, AlN and SiÿNÿ have a better thermal conductivity than AlÿOÿ, which is an advantage if it is also used on the surface for the wire transfer. However, this is not necessarily crucial if the ceramic protective layer is relatively thin.

Physical dimensions

With regard to the construction, it is important to get a sense of how large a heat exchanger area should be per cubic meter of storage medium. It is assumed that the charging of the storage can be realized by distributing electric heaters in the storage so that the melting process takes place in a satisfactory manner. However, it is expected that a limiting aspect will instead be the heat exchanger area required to transfer the heat to evaporating water while the discharge process is taking place. One cubic meter of AlSi12 can store heat quantity *Q* = 560 kJ / kg x 2700 kg / m3 = 1512 MJ / m3 = 0.42 MWh / m3 . The time charging to discharge the storage, ie to draw 0.42 MWh out of a cubic meter of storage media, depends crucially on the heat flux if the heat exchanger is designed to discharge. could transfer 0.1 MW, it takes about 4 hours to discharge the warehouse. But if the heat exchanger is designed for larger heat fluxes - for example 1 MW - the storage can be discharged

24 minutes.

$$\text{stock} = ÿ_0^{\text{discharge}} (ÿ\ \text{discharge}) = ÿ_0^{\text{discharge}} (ÿ) \quad . \qquad (4)$$

The relationship between the heat flux discharge and the parameters describing the heat exchanger is shown in equation 4. The heat exchanger is defined by its surface *A* and its heat transfer coefficient U. The heat transfer coefficient depends on the heat transfer from the surface to the steam but also on the distance from the liquid aluminum to the heat transfer surface. This distance changes as the aluminum met begins to solidify. If the heat exchanger is designed with a larger heat exchanger area, the distance to the surface is smaller, just as the transition *coefficient U* is smaller.

Both aspects contribute to possible larger heat fluxes and thus to a faster discharge process. On the other hand, a greater density of the heat exchanger area in the storage medium means a greater challenge in terms of construction as well as increased investment. The temperature difference *ÿT* also has an influence, since larger differences contribute to faster discharge processes.

It can therefore be concluded that the heat storage can be designed with different degrees of heat exchanger area per volume of storage media, and that the design will define the maximum speeds for the discharge process. A more challenging design with a larger investment enables faster discharge processes, while a simpler design increases the discharge time. The final design of the heat storage and heat exchanger area can therefore only be determined once the application has been completely defined and the required discharge rates have been determined. Figure 4.22 and Figure 4.23 show possible constructions with a low and a high degree of heat exchanger area per volume of storage medium.

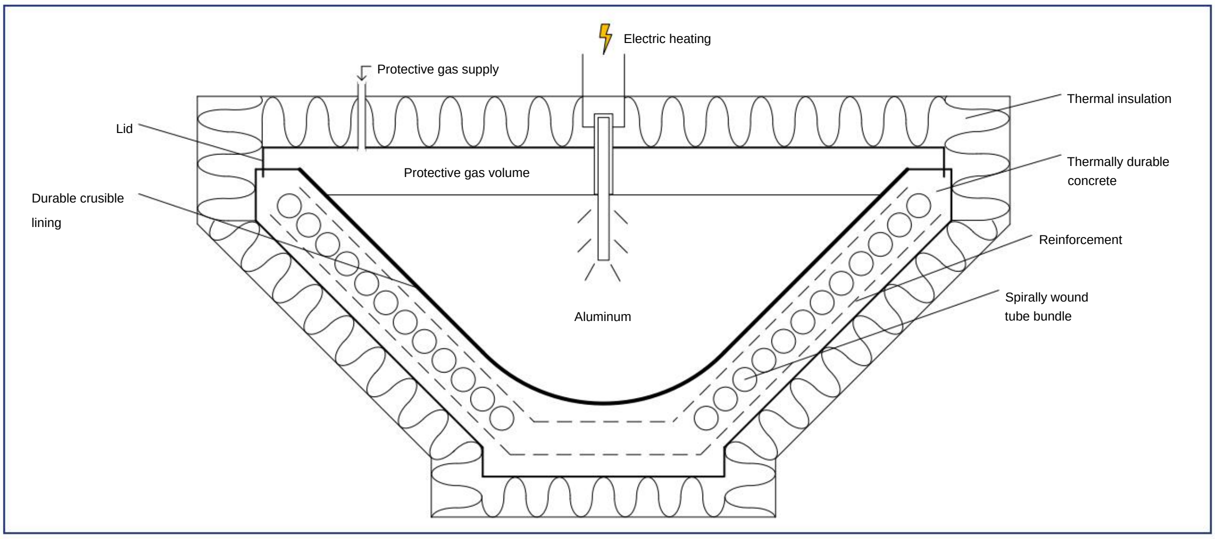

Figure 4.22: Principle sketch of possible design of aluminum storage with a low degree of heat exchanger area per volume of storage medium.

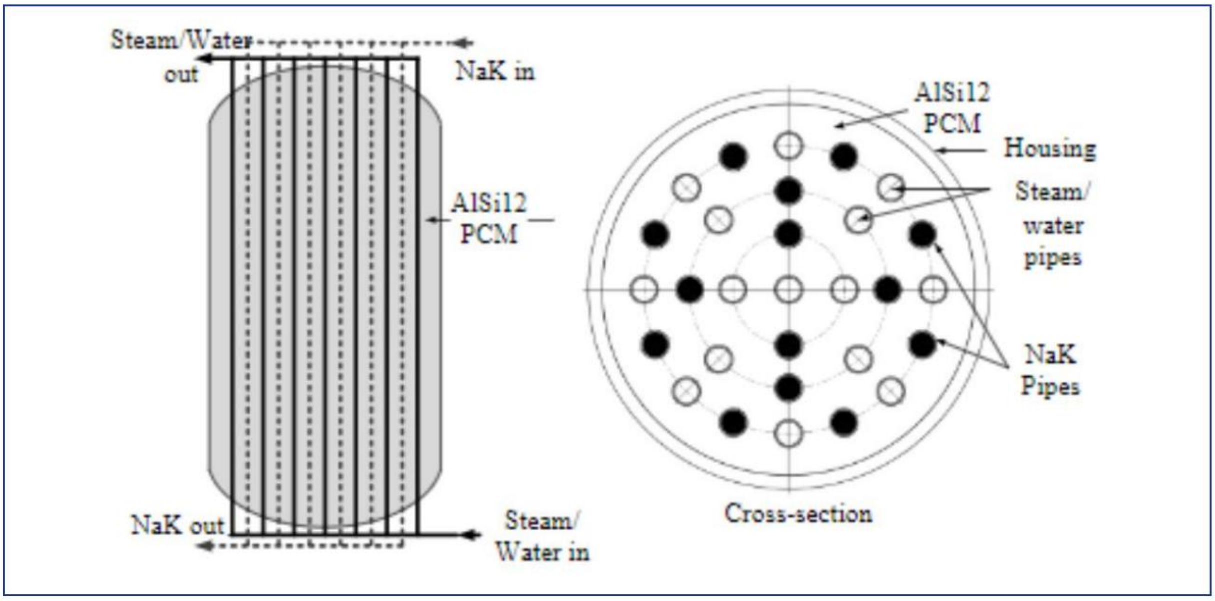

Figure 4.23: Principle sketch of possible design of aluminum storage with a high degree of heat exchanger area per volume of storage medium [5].

Expansion of storage medium

It was found that the volume of AlSi12 decreases by about 6% upon solidification. The change in volume can in principle result in challenges with the construction in the form of mechanical loads on the material. Therefore, it is recommended to construct the warehouse with an open side to enable an unobstructed volume change in the solidification process. The open side must not be filled with air because the oxygen in the air will result in corrosion of the storage medium, which could affect the properties of the storage medium in the long term. A nearby solution could be to fill the volume with a blank gas to avoid corrosion. An example where used blank gas for this purpose is found in Chapter 8, where the cyclic melting and solidification experiments ments with the small oven are described.

If a construction with pipes for heat transfer is chosen in the middle of the storage medium, see e.g. Figure 4.23, there is a risk that the pipelines will be exposed to special loads through volume changes - especially during the solidification process. This relationship can only be investigated by a demonstration experiment on a larger scale than carried out in this project.
However, the experiments with the special furnace from Støtek and the literature on casting technology [10] indicate that deformation of the storage medium is to some extent plastic. This means that the storage medium will adapt to e.g. pipelines through the solidification process, which will keep the load on the pipelines to a limited extent. In addition, the construction can be left in such a way that a part of the storage medium becomes liquid all the time, which under supports the possibility of plastic deformation. As mentioned, this study can only be done after the use and construction have been finally determined.

Insulation

Large-scale high-temperature energy storage is necessarily linked to the issue of insulation. A study of the technical possibilities has shown that there are commercially available technologies that are known from other high-temperature processes - for example foundries or other thermal storage. A proposal from a possible supplier - Skamol A / S -
showed that the heat loss to the surroundings can be reduced to about 250 W / m2 to 300 W / m2 by using a 4-layer insulation system with a thickness of 200 mm in total. This is equivalent to about halving the heat loss compared to a conventional 2-layer insulation with conventional materials.

Conclusion

It can be concluded that the construction of one energy store using AlSi12 is another aluminum-based alloy or a pure aluminum such as PCM, can in principle be made. The final construction depends on the application-specific requirements and can therefore only be determined when the application and all boundary conditions are known. It can also be concluded that the construction is associated with some engineering challenges, which can become especially challenging when fast discharge processes are required. However, a slower discharge will make it possible to choose an easier construction, which also means lower investment costs.

5. Project results and dissemination of results

5.1. Results

In the project, it has been investigated which media are suitable as storage medium in combination with steam power plants, and pure aluminum as well as the alloy of 88% aluminum and 12% silicon (AlSi12) have both been identified as suitable candidates. Pure aluminum has a higher melting temperature, which can give a higher efficiency, but is at the same time significantly more expensive. AlSi12 gives a slightly lower efficiency because the melting temperature is at 577 ° C, but is still significantly cheaper. It is therefore recommended to choose AlSi12 as the storage medium instead of pure aluminum.

AlSi12 has been studied for its properties as a storage medium. Cyclic tests have shown that the properties remain constant through more than one hundred melting and solidification processes. In addition, the properties of AlSi12 have been tested on a slightly larger scale, and the tests have shown that there is a sharp transition in the phase transition - ie. no temperature slip
While the hardness of the alloy was to some extent plastic just below the melting point.

Overall, it was found that the potential is greatest if the PCM storage with AlSi12 is used when there is a need for heat at a constant high temperature. This is required for example for evaporation and (multi-stage) superheating. The heating process - ie. the heating of the liquid up to the evaporation temperature - must, however, be covered by liquid salt, which is an already fully developed and commercially available technology, as the use of the aluminum alloy can result in greater design challenges.

AlSi12 also has the advantage that only about 25% is required compared to the physical one
size of the storage tank compared to the size required when using liquid salt.

The analysis of the most important aspects for the construction of the heat storage has shown that there are some challenges in relation to the construction. But the analysis has also indicated that these challenges can in principle be solved. Possibilities for coatings of surfaces have been demonstrated to protect the steel structure from chemical reactions with the storage medium as well as an option to use blank gas to avoid corrosion of the storage medium. An analysis of the various constructions has shown that the size ratio between the heat transfer area and the storage volume will determine possible velocities for drawing heat / energy out of the storage. One
larger surface area in relation to the storage volume enables faster unloading processes of the warehouse, but this is also associated with greater challenges in relation to the construction as well as higher investment costs.

5.2. Dissemination of results

In addition to the present professional reporting to EUDP, the project results have been disseminated on several occasions - including:

- Conference on Advanced Energy Storage, Danish Technological Institute, 2017.
- Conference on Advanced Energy Storage, Danish Technological Institute, 2018.
- Cooling and Heat Pump Forum 2019.
- On the Danish Technological Institute's website.
- Presentation at international annex meetings and workshops in connection with the project 'Danish participation in IEA ECES Annex 30 Thermal Energy Storage'.

6. Application of project results

The project's results are based on contributions from the various project partners - contributions that have been continuously communicated to the entire project group. In addition, inputs have been obtained from possible suppliers of specific plant components, and the results have also been discussed with companies and institutes, which can see a relevance in the project.

The project partners in particular got a good feel for a possible utilization of the technology. Verdo A / S and Umhvørvisstovan concluded that there is a certain application potential for the technology - especially in steam power plants with a heat demand at a constant high temperature.

Aalborg CSP A / S has been included as a possible supplier and specialist with experience in similar technologies - especially liquid salt storage. Aalborg CSP A / S sees a potential for the technology in combination with their own and already developed technology based on liquid salt. Aalborg CSP emphasizes, however, that the efforts to solve design challenges in connection with an aluminum-based heat storage are still significant, and that the advantages compared to their already existing technology, which uses liquid salt, are limited in certain applications that require heat at constant high temperature.

7. Conclusion and perspective

The purpose of the project has been to investigate the possibility and potential of using aluminum or an aluminum alloy as a phase-shifting material (PCM) for energy storage in combination with steam power plants. This combination is characterized by limited investment costs, as the warehouse can be implemented in existing steam cogeneration plants, and the technology is therefore expected to be usable to increase the use of fluctuating renewable electricity sources.

In the project is an alloy of 88% aluminum and 12% silicon (AlSi12), which is identified as a suitable medium for the purpose. AlSi12 has a melting point at 577 ° C and has shown stable properties in cyclic melt solidification experiments, enabling a combination with conventional steam power plants.

A significant challenge in relation to the construction of the storage arises in connection with relatively large temperature differences between the storage medium (aluminum) and the liquid heating (water) before evaporation. The greatest potential for use was found in a solution where the AlSi12 storage is used for evaporation and superheating, while the late sible water heating is done using liquid salt as storage medium. With this solution, the challenges associated with the construction of the warehouse are moderate, just as there is a good utilization of the heat stored in the phase transition of AlSi12. In the combination, the salt storage will have to contain approx. 40% and the aluminum bearing approx. 60% of the total energy amount for water heating, evaporation and superheating.

However, in order to be able to assess the potential for use definitively, a detailed study of the technology is required - especially in relation to the construction and in relation to the combination with a liquid salt storage and a steam power plant. In order to investigate possible constructions in more detail, the use and boundary conditions must be determined. After this, it will be possible to assess the investment costs and to examine loads, operating conditions and further aspects in a demonstration plant.

8. Appendix

8.1. Testing of AlSi12 in cyclic melting and solidification processes

The Danish Technological Institute has previously studied methods for determining the energy content of phase-shifting stocks using models [19] and test experiments [20], [21]. The experiments described in this report involve a smaller melting cell containing the AlSi12 aluminum alloy. This alloy excels for the purpose at a melting point of approx. 576 ° C and high value (greater than the value for pure aluminum) for the specific heat of fusion [3].

To supplement the literature study, test measurements have been performed to map practical aspects of the thermophysical properties. As can be seen from the above discussion, the eutectic alloy 88Al-12Si is an obvious candidate as a storage medium in a thermally high temperature energy storage. It has therefore been selected for the test measurements.

Table 8.1: The content (cf. data sheet) of various substances in the phase change alloy studied: Al-Si12 / EN AC-4220

Element	*Nominal content,% by weight (permissible range)*
Eel	87.75 (balance)
Cu	0.009 (0 - 0.05)
Fairy	0.37 (0 - 0.55)
Mn	0.021 (0 - 0.35)
Si	11.8 (10.50 - 13.50)
Ten	0.025 (0 - 0.15)
Zn	0.024 (0 - 0.10)
Others	(0 - 0.015)

Figure 8.1: Photo of test furnace with melting cell. In the middle is a quartz tube with a thermal sensor and a connection to argon shielding gas. The melting cell itself with the phase-shifting material (AlSi12) is not visible, but is shown in Figure 8.3.

An important difference between typical laboratory measurements and large-scale energy storage lies in the purity of the materials being studied. The material consumption for laboratory measurements is typically very limited, and therefore it is possible to use metal alloys of high purity. On the other hand, it will typically be necessary to use industrial alloys for an actual single layer bearing to keep costs down. Therefore, in order to create better comparability, an ordinary casting alloy has been used in the experiments described here. The content of the mixture is described in Table 8.1.

The principle behind the test experiments is to subject the studied sample of AlSi12 (= 88Al-12Si) to repeated heating and cooling so that the sample alternately solidifies and melts.
During the process, the temperature in the sample and the added heat output are measured. This makes it possible to see if there are any changes in the alloy.

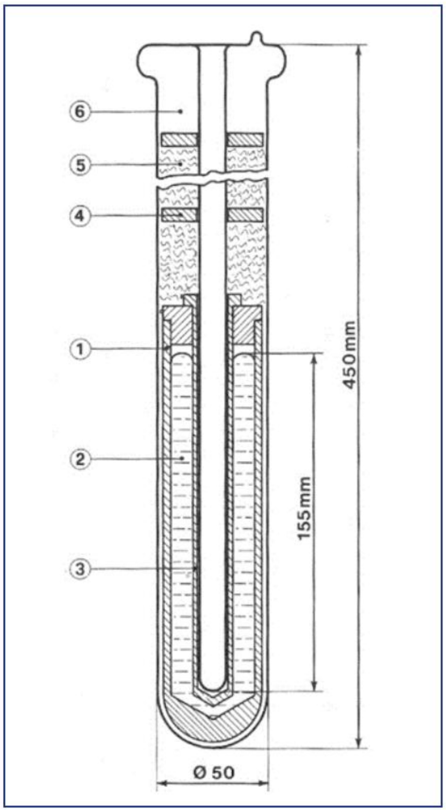

Figure 8.2: Principle sketch for the structure of the melting cell. See text. The figures indicate the following: 1) Graphite crucible, 2) metal, 3) quartz well for thermal sensor, 4) graphite heat shield, 5) insulating quartz wool, 6) argon shielding gas. The stated goals are about trained.

Figure 8.3: Crucible with AlSi12 and enclosing quartz tubes.

It should be mentioned that powder was used for the experiments. This proved to be inappropriate. To prevent the sample material from reacting with the oxygen in the air, it was necessary to pump the air around the sample away and replace it with shielding gas (argon) before starting the heating. In practice, it proved impossible to pump the air away from the powder - despite great care - without the powder being dispersed. During the subsequent heating, the dispersed powder reacted with the enclosing quartz tube (see below), so the tube was damaged and had to be replaced.

8.1.1. Set-up for testing alloys

The test setup is shown in Figure 8.1, Figure 8.2 [22] and Figure 8.3. Thus, 293 g of AlSi12 have been used in the experiment, which is enclosed in a crucible of high-density graphite. The crucible is located in a quartz tube that is closed with an airtight flange at the top. To avoid oxidation of the phase-shifting material, the quartz tube has been evacuated of air before heating and filled with an inert shielding gas (argon). A quartz tube in the middle of the set-up is used to measure the center temperature of the phase-changing material.

8.1.2. Calibration of thermocouple

The temperature in the middle of the melting cell is measured with a thermocouple type S. Thermal voltage from the thermocouple is measured and converted to temperature with a *Fluke 1586A Super-DAQ Precision Temperature Scanner.* The calibration of the thermocouple is performed at three temperature fixation points:

1) Freezing point of tin (231,928 ° C)
2) Zinc freezing point (419,527 ° C)
3) Aluminum solidification point (660,323 ° C).

The temperature is calculated from the measured thermal voltage, and then the deviation to the fixed points is calculated, see [23]. The calibration results are shown in Figure 8.4. The results seen later in the report are all corrected for the observed deviation. In Table 8.2 , an uncertainty budget has been prepared for the thermocouple. It is seen that the expanded uncertainty (= 2) is 0.37 ° C.

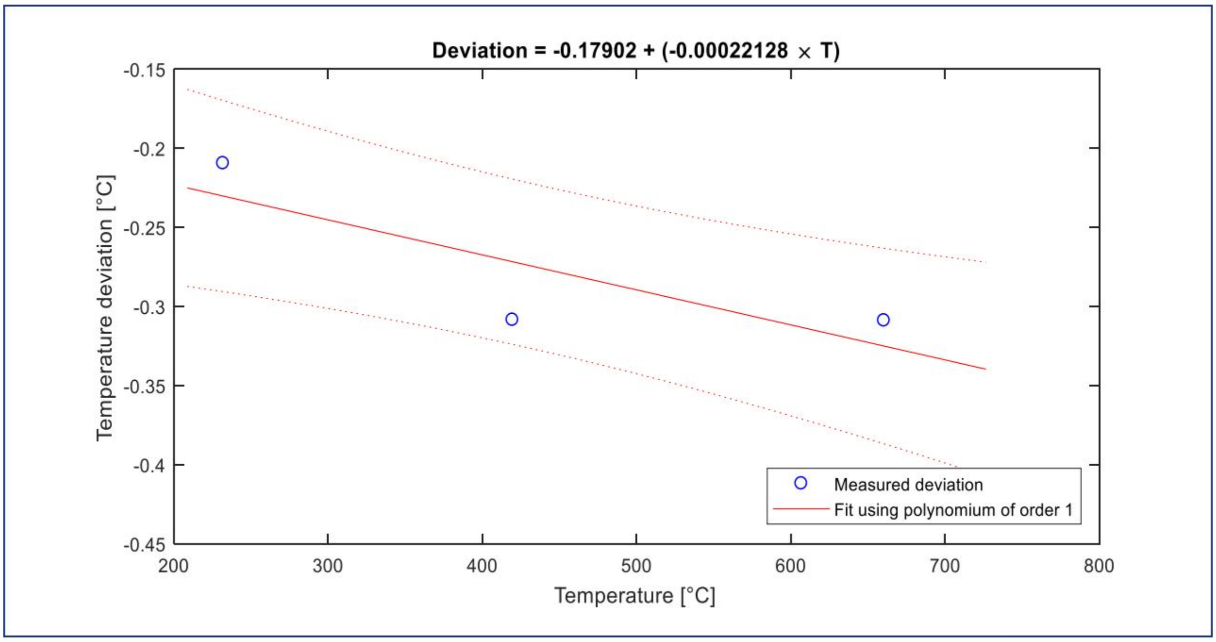

Figure 8.4: Calibration data for the reference thermocouple used. The graph shows the temperature deviation as a function of temperature. Blue circles: Calibration data; Red solid line: Used fit; Red dotted lines: Standard uncertainty of fit.

Table 8.2: Uncertainty budget for the thermocouple located in the middle of the phase-shifting AlSi12 alloy. All uncertainty contributions are stated in ° C. As can be seen, the total expanded uncertainty is 0.37 degrees Celsius (given for = corresponding to a confidence interval of about ,95%).

	Contribution (° C) Distribution Divisor	*u*
Operation	*0.1000* uniform normal uniform 0.3000 1.2500 normal	0.058
Calibration	normal 0.0676 normal 0.25 3.46	0.087
Hysteresis and inhomogeneity	3.46	0.058
Inverse IEC584 conversion	1.00	0.000
Regression	1.00	0.068
Zero point compensation	2.00	0.125
Total standard uncertainty		**0.185**
Expanded uncertainty		**0.37**

8.1.3. Measurement sequences

The measurements were performed by controlling the temperature of the test furnace around the melting point of the phase-shifting AlSi12 alloy (approx. 576 ° C). During the measurements, in addition to the oven's set point temperature and control value, the oven's electrical heat output (measured as a percentage of max.) And the temperature in the phase-changing AlSi12 have been registered. The mentioned parameters are logged with a time interval of approx. 5 seconds.

A typical temperature sequence is shown in Figure 8.5 and consists of the following phases:

1. Extra heating, = 586 ° C (+11 ° C in relation to "Liquid phase stabilization" (point 2.), 0 - 1.5 hours)

Liquid phase stabilization, 3. = 575 ° C (1.5 - 5 hours)
Solidification, = 567 ° C (5 - 15 hours)
4. Extra cooling, 16.5 = 556 ° C (-11 ° C in relation to "Solid phase stabilization" (point 5.), 15 - hours)
5. Stabilization in solid phase, = 567 ° C (16.5 - 20 hours)
Melting, = 576 ° C (20 - 30 hours).

The solidification phase is marked in red in the figure. A total of 111 similar measurements have been made. In addition, a number of measurements have been made with various other temperatures kvenser.

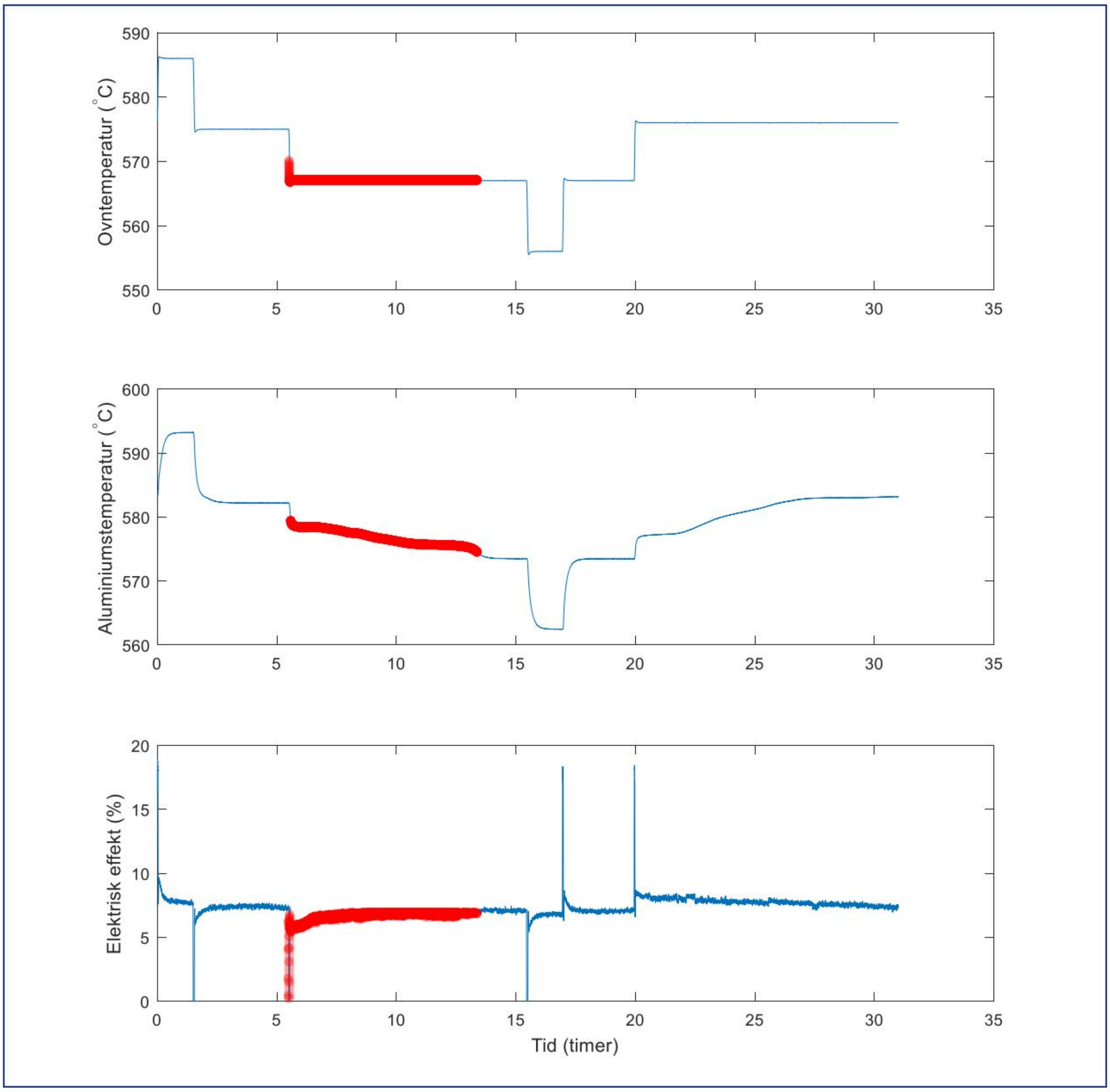

Figure 8.5: A typical measuring cycle of approx. 30 hours with solidification (5 - 14 hours, marked in red) followed by melting (20 - 30 hours). Top: oven temperature (set point); middle: the measured temperature in the phase-shifting aluminum; bottom: the oven's electric var meeffekt.

8.1.4. Thermophysical description

It is natural to define the capacity of a phase-shifting storage as the energy that can be released during solidification. As solidification and filling in practice are associated with a change in temperature, a contribution from sensitive heat is also included - ie. the capacity will be:

= () ÿ (- $_0$) + () ÿ ($_1$ -) + ÿ . (5)

Here () and () are the heat capacity of the storage in resp. solid and liquid state, the melting point, is the specific heat of fusion, and of course, that 0 and 1 defines the temperatures at which the storage is resp. empty and full, is the mass of the phase-shifting material. That is $_0$ < and 1 >.

The degree of filling reflects how much energy is stored in relation to the capacity, and can therefore be indicated by:

= () ÿ (-) + ÿ / () ÿ (-) + () ÿ (-) + ÿ %, (6)

where indicates the fraction of the stock that has been melted and ÿ. If> corresponding result: , is it

= () ÿ (-) + () ÿ (-) + ÿ / () ÿ (-) + () ÿ (-) + ÿ %. (7)

This corresponds to the storage being empty (= 0%) when the temperature is 0 and the phase-shifting material is in solid form. The storage is full (= 100%) when the temperature is 1 and the phase-shifting material is in liquid form1 .

The degree of filling ("stock condition") can be determined in several different ways, as sketched quite earlier. An obvious method is to keep track of supplied and delivered energy by measuring the added net effect, . Using this and the definition in equation (711) we get:

= ÿ $_0$ / () ÿ (- $_0$) + () ÿ ($_1$ -) + ÿ ÿ 100% + $_0$. (8)

Note that the constant $_0$ is included. It is necessary to have a well-defined time when the stock filling degree is 0 . starting point. In the integral $_0$ Eg. is = 0, to = $_0$ indicates if the warehouse is empty, ie. = $_0$ $_0$.

The most robust procedure for obtaining a well-defined starting point is the following: First, the storage is stabilized at a certain temperature that is clear above or below the melting point, so that the phase state of the storage (solid or liquid) is well defined. The temperature of the storage is then recorded and the degree of filling is determined by equation (7). $_0$

[1] Note that> 100% is achieved for> 1 and correspondingly <0% for < $_0$.

In this case studied, the applied thermal power is most accurately determined by measuring the temperature gradient between furnaces ( ) and the phase-shifting AlSi12 ():

= =ÿ ÿ = ÿ (- + ÿ). (9)

Here the proportionality constants and the offset ÿ are added, where the latter i.a. is an expression of ambient heat loss and calibration. In practice, both can be easily determined from the measurements.

The degree of filling can now be determined directly from the measurements as:

= ÿ ÿ ÿ 0 / () ÿ (- 0) + () ÿ (1 -) + ÿ ÿ 100% + 0 . (10)

If the temperatures are close to the melting point, by far the largest part of the stored energy will be due to the heat of fusion, whereas the contribution that relates to was the degree of filling the mechapacity disregarded. It is therefore true that ÿ is equal to the fraction of the phase-shifting material which is in (sensitive heat) can be molten form. Therefore can

determined with good accuracy from equation (10):

= ÿ = ÿ ÿ 0 / () ÿ (- 0) + () ÿ (1 -) + ÿ . (11)

8.1.5. Results of tests

Over a hundred solidifications and melts have been made, and the main results are summarized below. Figure 8.6 shows the 111 measurement series performed according to the standard temperature sequence described in section 8.1.3. For comparison, Figure 8.7 shows the first four measurement series and Figure 8.8 the last four. An immediate consideration of the plotted data shows that the curves generally follow the same course. However, there are some minor variations between the different curves at the level of detail. But as can be seen in the following, these are mainly due to the temperature control of the oven. The immediate conclusion is therefore that the AlSi12 alloy studied is thermochemically stable and thus suitable for use as a storage medium in a phase-shifting high-temperature energy storage.

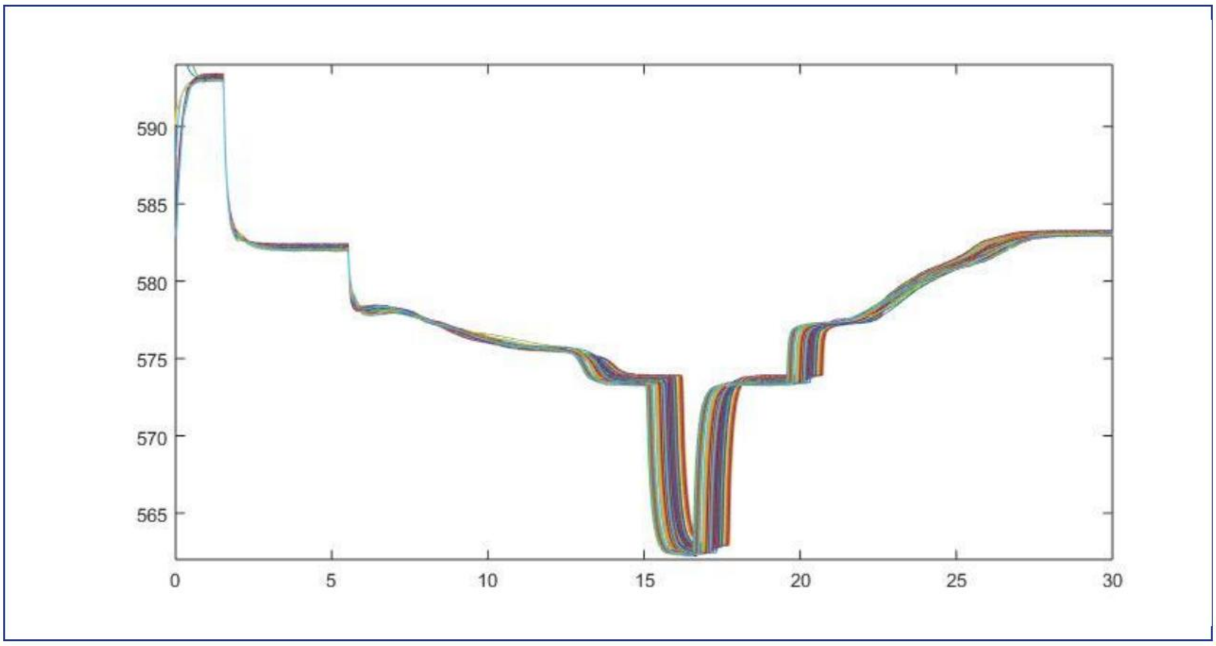

Figure 8.6: Measurement of the temperature in the middle of the crucible (in ° C) as a function of time (in hours). The figure shows all 111 measurements made after the standard temperature sequence is described know in section 88.1.3.

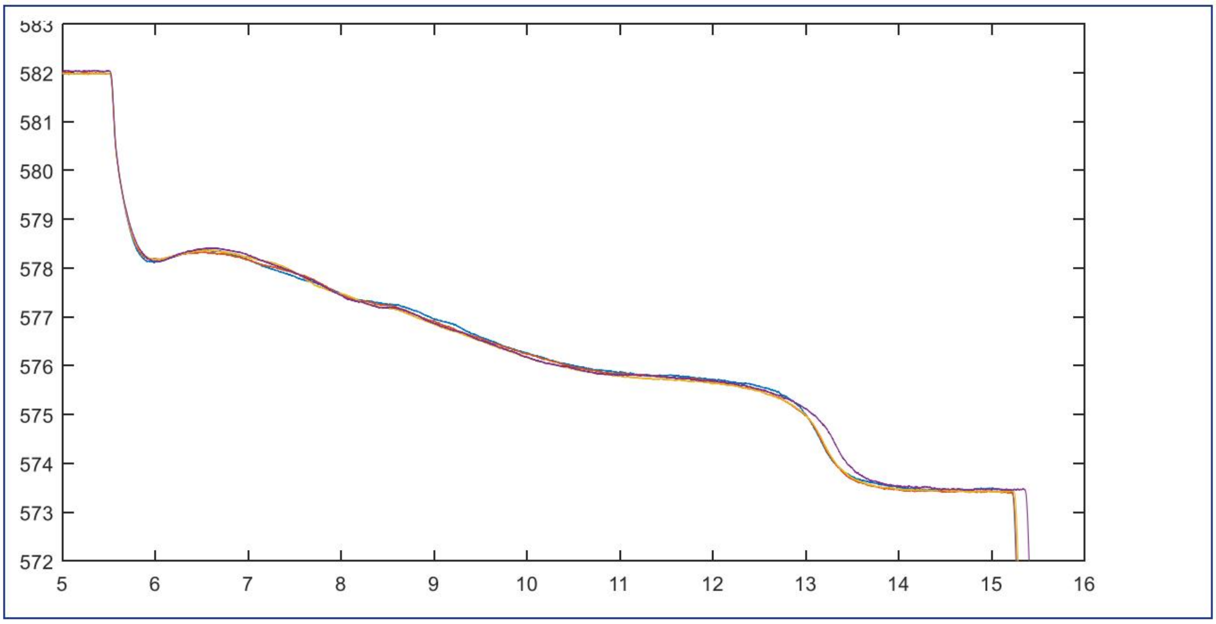

Figure 8.7: Measurement of the center temperature in the middle of the crucible with aluminum as a function of time. The figure shows the result of the first four solidifications. The entire temperature sequence for the measurement is shown in Figure 8.5. Subcooling is seen at the start of solidification (approx. Six hours). The solidification is fully completed about 13 - 14 hours after start, and there is a small difference in the solidification time for the different curves.

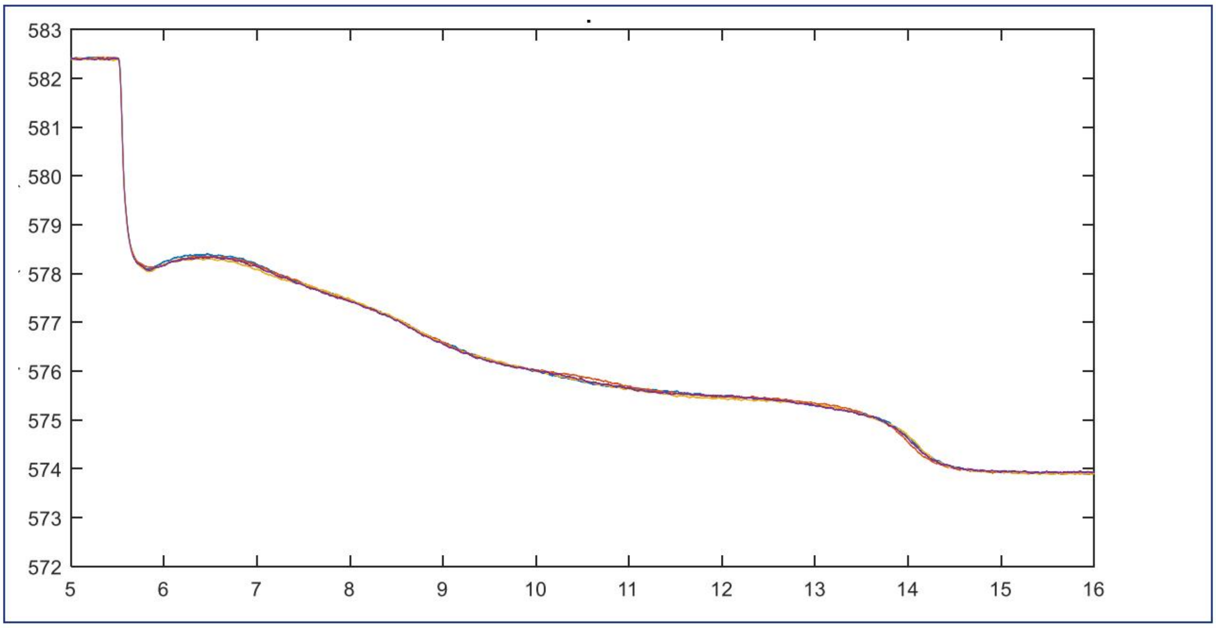

Figure 8.8: Similarly Figure 8.7, but for the last four solidifications.

In the following, the curves in Figure 8.6 will be analyzed in detail, and parameters such as solidification time, subcooling, solidification point and inclination of the melting curve will be examined in detail.

8.1.5.1. Solidification time

As an example of primary measurement results, Figure 8.7 shows the temperature profile of the four first solidifications. The solidification begins after approx. 5.5 hours, by lowering the oven temperature abruptly (see Figure 8.5). As a result, a relatively rapid cooling is first seen - corresponding to the emission of sensitive heat. Then aluminum co-cools at approx. 6.0 hours, after which the solidification begins. During the solidification process itself, the temperature changes only slightly and slowly, gradually decreasing. The end of the solidification process is clearly marked by a rapid drop in temperature.

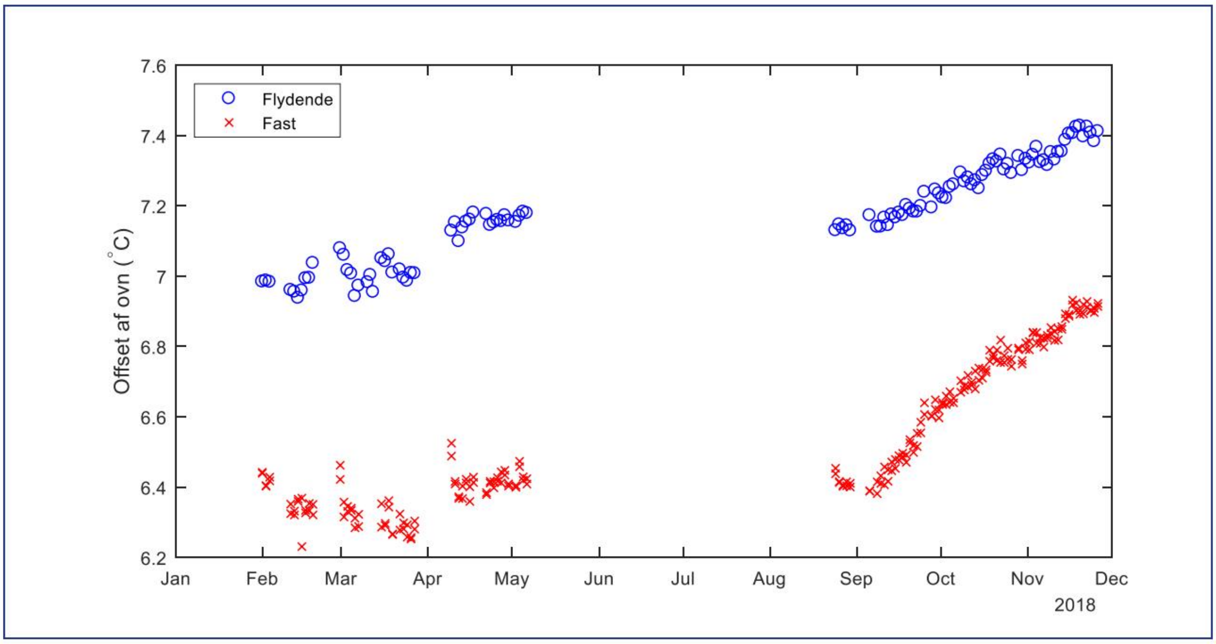

Figure 8.9: Difference between the measured temperature in the phase-changing material and that of The "setpoint" under stable conditions (ie observed[12] the oven) - the temporal evolution as a function of the measurement time. evolution is probably due to a slow change in the properties of the thermocouple which controls the furnace.

It is interesting to note that there is a small difference in the solidification time, which is reflected in the fact that the transition from solidification to cooling (after approx. 13 - 14 hours) is shifted. This could immediately indicate that there have been some chemical changes in the phase-shifting AlSi12 alloy, but a closer analysis (see below) shows that it can rather be linked to the furnace control. For comparison, the last four solidifications (out of 111) are shown in Figure 8.8, and as can be seen, there is no significant difference between these.

To analyze the oven's control, the difference between the oven's own temperature measurement and the calibrated temperature measurement made in the middle of the crucible has been compared under stable conditions - ie. at the end of the stabilization phases included in the measurement sequences (see section 8.1.3). The result of this analysis is shown in Figure 8.9, and from the data shown, several conclusions can be drawn. First, there is a significant difference ("offset") of 6 - 7 degrees Celsius between the reference temperature measured in the crucible and the temperature measurement made with the oven's own thermocouple. Secondly, this is the difference depending on the state form of the phase-shifting AlSi12 alloy. Third, it is seen that the difference is time dependent. The first two aspects are irrelevant to the analysis, but this is not the case with the third. In particular, the significant increase seen for the solid (the red x's in the figure) will mean that the temperature of the furnace (for the same setting) will rise slowly and thus approach the solidification point with the result that the temperature gradient between furnaces and crucible decreases. The expected consequences are, that the thermal effect applied to the crucible will decrease, and thus the solidification time will increase, which is also the case (see below).

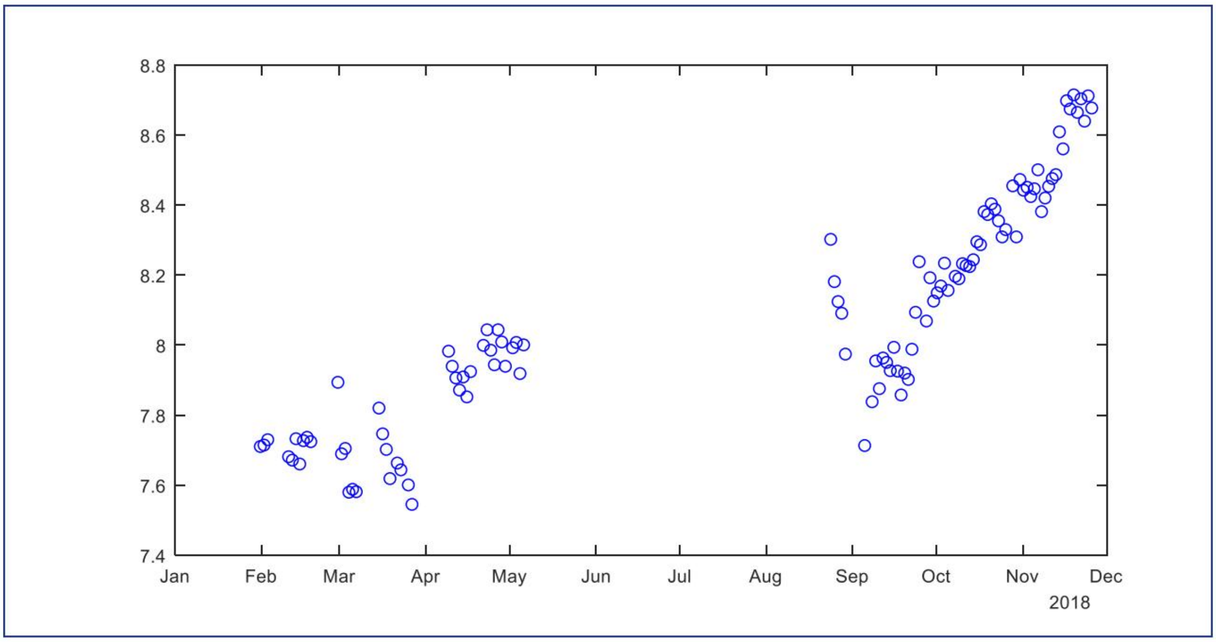

Figure 8.10: Clotting time in hours for 111 clotting sequences shown as a function of the date of execution of the measurement.

The solidification time for all 111 measurements is shown in Figure 8.10. As mentioned, the solidification time depends on the temperature of the furnace and on the properties of the phase-changing alloy. As observed above, the observed change in solidification time can be linked to the long-term change in oven temperature shown in Figure 8.9. In other words, there are no clear signs of material-chemical changes in the phase-shifting alloy.

8.1.5.2. Melted fraction of material

In order to go more in depth with the characterization of solidification and melting curves, it is necessary to determine how large a part of the phase-shifting material is on resp. solid and liquid state form. For this purpose, the methodology specified in section 8.1.3 is used.

In particular, it should be mentioned that equation (11) is used to calculate the molten (i.e., floating) fraction of the phase-shifting material. The analysis takes place in the following steps:

1. First, calculate the capacity of the , using equation (5) and the thermophysical warehouse, parameters in Table 8.3. The temperature $_0$ (corresponding to "empty" energy storage) and parameters ("full" storage) are selected as the melting temperature ± 3 K:
   1 a. Empty $_0$ = 576 ÿ3 = 573 ° C
   storage: b. Full $_0$ = 576 + 3 = 579 ° C.
2. ÿ storage: determined from measurements where the temperature is kept constant over a long period.
3. Proportionality constant is calculated by studying the energy balance during an emptying of the warehouse. More specifically, equation (7) is used to calculate the degree of filling before and after the fillings, and then isolated by rewriting equation (10).

4. It is now possible to calculate the size of the molten fraction of phase-shifting uses, cf. equation (11). AlSi12, taking approximation ÿ

For all 111 solidification sequences, the above method has been used to calculate the fraction of molten AlSi12 as a function of time. It is therefore possible to draw graphs,
which shows the temperature versus the size of this fraction. As a concrete example, this is shown for the first four measurement sequences in Figure 8.11.

Table 8.3: Thermophysical properties of AlSi12. See [1], [9].

Characteristic	Unit	Value
Specific heat capacity, fixed: ()	J / (g · K)	1,038
Specific heat capacity, liquid: ()	J / (g · K)	1,741
Melting temperature:	° C	576
Specific heat of fusion,:	J /	560
Density:	gg / cm3	2.70
Thermal conductivity:	W / (m · K)	160

The approximation in point 4. corresponds to disregarding the sensitive heat in relation to the heat of fusion. The magnitude of the corresponding error can be calculated as:

$$\frac{() ÿ (- () ÿ \quad _0) + () ÿ (-) \quad _1 -)}{(-) + () ÿ (\quad _0 \quad\quad _1 + ÿ} = 0.015. \quad (12)$$

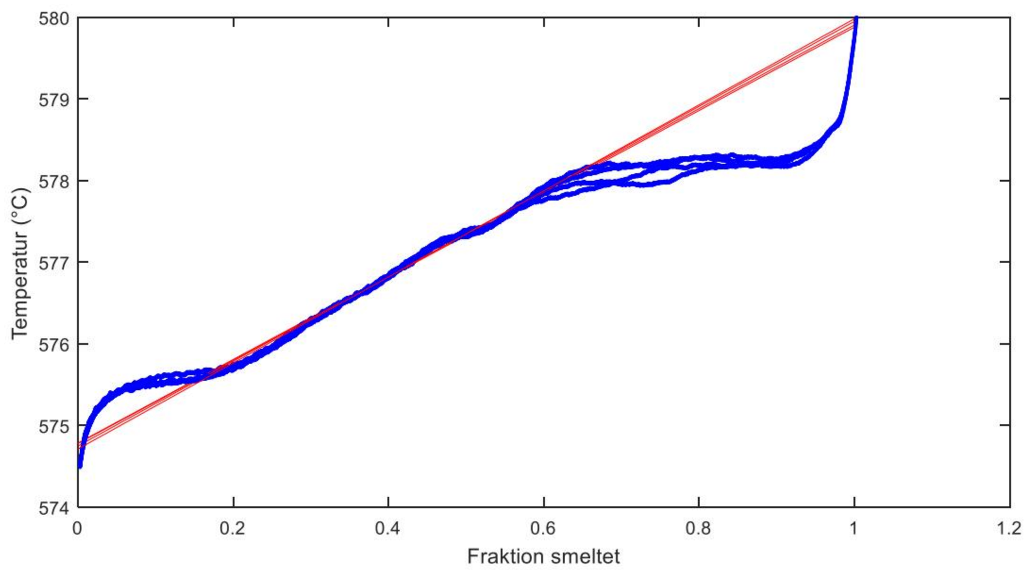

Figure 8.11: The course of the solidification curves from Figure 8.7 rewritten to show the temperature as a function of the size of the molten fraction of phase-shifting AlSi12. Blue curves: measured data; Red lines: linear regression. The effect of subcooling is clearly visible on the right. The "bump" in the blue curves on the left (at ÿ 0.1) is due to an inaccuracy in the analysis method. See text.

The error is thus only 1.5%, which is of no significance in the present context. A larger error occurs because the assumption in equation (9) that the applied thermal power is proportional to the temperature gradient is only approximately correct for the overall system. In particular, it should be noted that, as can be seen in Figure 8.11, a smaller bump occurs around ÿ 0.1. A similar error (with opposite sign) is expected around the onset of solidification, but can not be observed due to the subcooling.

8.1.5.3. Analysis of subcooling, etc.

In the section above, it is calculated how large a part of the phase-shifting AlSi12 has been melted. The calculation makes it relatively straightforward to carry out a closer examination of subcooling, etc.

Therefore, a linear regression of the temperature during solidification has been performed as a function of the fraction of molten AlSi12 - as shown in Figure 8.11 for the first four measurement sequences. The regression is only based on data in the range 0.3 <<0.6 - corresponding to 30 - 60% molten AlSi12 (the middle, flat part of the curves).

The subcooling is determined as the largest distance between the linear regression and the measurements. This method has been chosen to have a clear and easily determined quantitative measure of the subcooling. The results for all 111 solidification sequences are shown in Figure 8.12.

Two interesting observations can be made immediately from the data shown. First, there is a significant variation in the subcooling between the different measurements - sometimes even within a relatively short time interval. Therefore, a certain spread in the size of subcooling can be expected between the individual measurement sequences for an energy storage. Second, a significant increase in subcooling can be seen from August to December (2018). By comparing with Figure 8.9, it can be seen that the control of the oven shows the same trend. Thus, this observed increase may be linked to the control of the furnace, but it is also possible that the impurities are concentrated (eg in the surface layer),
so that the degree of purity of the phase-shifting AlSi12 alloy is increased.

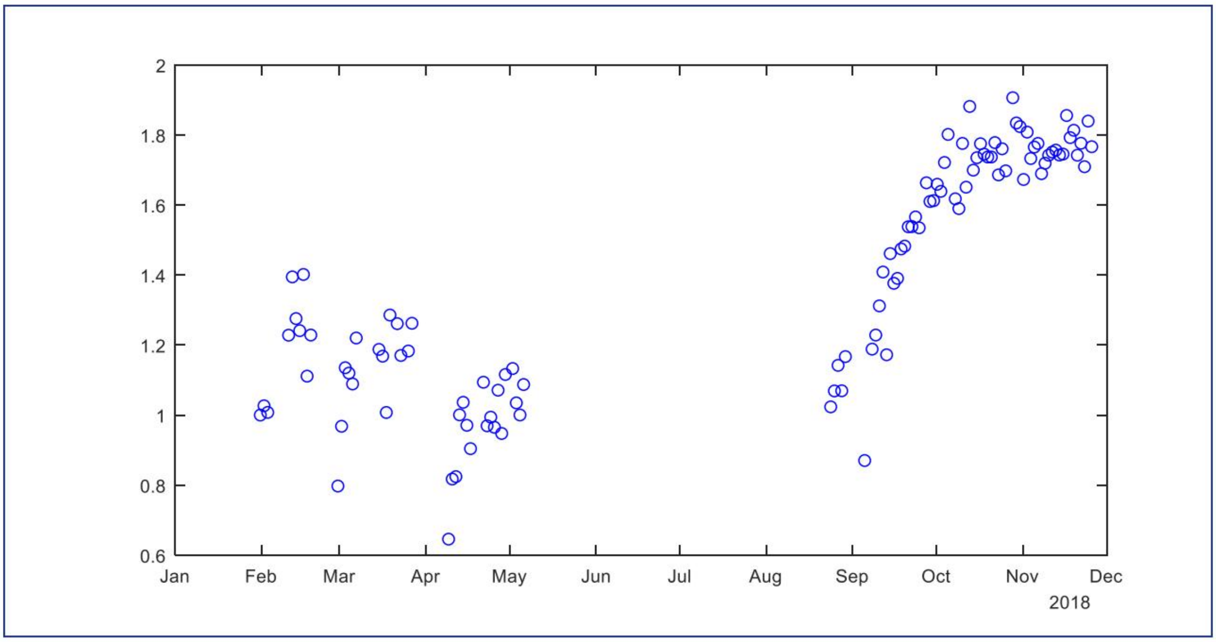

Figure 8.12: The subcooling (in degrees Celsius) as a function of date for all 111 measurement sequences.

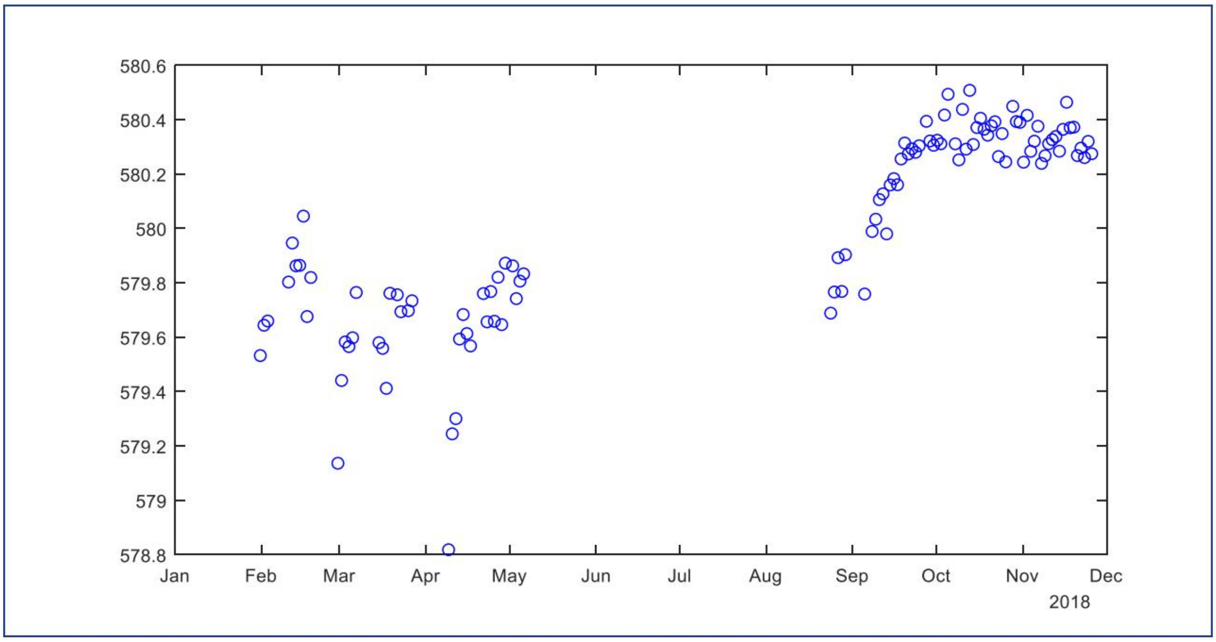

Figure 8.13: The solidus point - ie. the temperature at which solidification begins. It is determined as the intersection between the linear regression (red line in Figure 8.11) and = 1.

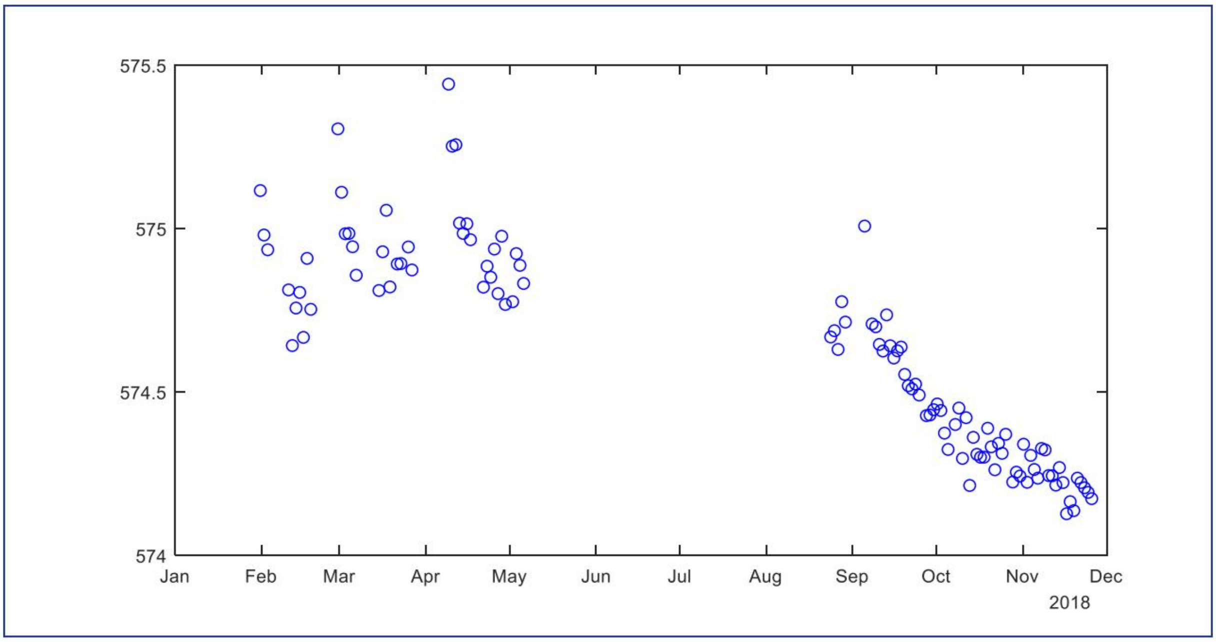

Figure 8.14: The temperature at which the solidification is completed. It is determined as the intersection between the linear regression (red line in Figure 8.11) and = 0.

The start and end temperatures for the solidification process are shown in resp. Figure 8.14 and Figure 8.13. It can be observed that the solidification typically starts around 580 ° C and ends around 575 ° C. Here, too, the change in the control of the furnace can be observed.

8.1.6. Energy density

As can be seen from the above, the energy density of a phase change stock is mainly determined by the specific heat of fusion,. It is possible to give an estimate of the magnitude of the latter parameter on the basis of the measurements performed. In short, the method involves keeping an eye on the energy accounts during solidifications and melts. This requires i.a. 1) measurement of the temperature of the AlSi12 alloy, 2) measurement of the applied power to the furnace and 3) a determination of the energy loss to the surroundings. Most details about the determination have been reported previously [22], and it was determined that the heat of fusion for the phase-shifting AlSi12 was:

$$= \quad \pm\% \; ÿ \quad . \qquad (13)$$

An abnormal unit of measurement has been used here - more precisely as (percentage of the oven's maximum power) × (second). According to the oven manual, the maximum power = 2 kW, and the mass of the AlSi12 alloy tested is = 293 g.

$$= \frac{}{100\%} \quad \frac{1}{} = \frac{12700\%}{100\%} \text{ ÿ } 2000 \text{ J / s ÿ } \frac{1}{\text{g. } 293 \text{ g}} = 867 \text{ J / } \qquad (14)$$

This is only a relatively rough estimate, and the provision is therefore judged to be in accordance with the value given in Table 8.3, = 560 J / g.

8.1.7. Conclusion on test measurements

Measurements and analyzes of over one hundred solidifications and melts of a crucible with phase-changing AlSi12 have been carried out. The purpose of the test work was to find out whether the examined material was suitable as a storage medium in a phase-changing high-temperature energy storage.

The measurements are controlled according to a fixed temperature sequence. During the measurements, the temperature of the test furnace and crucible with phase-changing AlSi12 and added power are registered. The analysis has examined parameters such as solidification time, subcooling, solidification point and slope of melting curve.

The conclusion is that all the melting and solidification curves generally follow the same course, and there are only minor variations at the level of detail. It can therefore be concluded that there is no evidence that significant material chemical changes have taken place and the ter mophysical properties are thus unchanged. This means that the studied AlSi12 alloy
is suitable as a storage medium in a phase-shifting high-temperature energy storage.

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