

A pinch of salt

Dr Dmitry Sergeev an Application Scientist from Netzsch on seasoning energy storage with salt to provide a more efficient energy transition.



Ashlim concentrated solar power plant with capacity of 121 MW in Israel

Salts and salt systems fulfill a wide range of applications in various industries and everyday life, for example in food preservation and flavouring, pharmaceuticals and medicine, agriculture and horticulture, water treatment, as well as the large amount of salts that are used in industrial sectors such as the chemical industry, metallurgy, nuclear and solar energy.

Specialist salt applications can be found in molten carbonate fuel cells, high-temperature batteries, die-casting processes with lost salt cores, production of ceramics, glasses, and powerful permanent magnets and energy efficient lighting devices. Such a wide field of salt system applications is possible due to the variety of compositions available.

Salts are formed by the combination of positive and negative ions and can be created from different elements and anions, leading to a various range of properties and behaviours. Depending on the composition of salts (e.g., Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- , F^- , Cl^- , Br^- , I^- , CO_3^{2-} , SO_4^{2-} , etc.), the different application temperature ranges can significantly vary, with some starting from temperatures below 0°C (salt hydrides) and going up to $1,500^\circ\text{C}$.

The term 'molten salts' is associated with the application of salt systems in the energy sector, especially in nuclear power plants, which use molten salts as a coolant for solid fuel or as a fuel itself. In this case, fluorides and chlorides of alkaline, alkali earths and actinides are used, due to their melting behaviour and thermal stability in the operating temperature range.

As a coolant or heat transfer fluid (HTF), molten salts have relatively high heat capacity and low viscosity and can be easily pumped through pipelines and heat exchangers with less resistance, which also minimises energy loss and pressure drops in the system.

Similar technology was later adopted for concentrated solar power (CSP) plants. CSP plants are one of the most

promising renewable technologies that play a major role in solving the world's present and future electricity problems. The main operation principle of CSP plants is concentrating solar radiation on a receiver, where temperatures can exceed $1,000^\circ\text{C}$, reaching up to $1,500^\circ\text{C}$ or more, and transferring this energy to a heat transfer medium.

The thermal energy is used for generating electricity and parallel stored in thermal energy storage. This energy can also be used for heating and other industrial processes such as water desalination, enhanced oil recovery, food processing, chemical production, mineral processing or also for hydrogen production.

CSP plants should be considered in combination with photovoltaics and wind turbines, because they offer the possibility of continuous electricity feed into the grid, independent of daily cyclical fluctuations in solar radiation intensity, through the integration of thermal storage systems. The primary goal of further development of CSP plants is to reduce costs of produced electrical energy and improve the reliability and lifetime of materials in related subsystems.

Did you know?

As of 2019, the total installed capacity of concentrated solar power (CSP) plants worldwide was approximately 6.2GW. In comparison, the installed capacity of photovoltaic (PV) systems at that time was around 585GW. This indicates, that CSP represents only about 1% of the installed capacity of PV.

Source: Helioscsp. *The Concentrated Solar Power industry has become increasingly diverse*



Thermal energy storage

Thermal energy storage technologies have been known since ancient Greece, such as furnaces for heating homes. The main purpose of these devices is to accumulate energy during heating or cooling processes to use it when required, for example at night.

Nowadays, thermal storage is used in a wide range of applications with different temperature ranges – as cold storage for refrigerators and heat storage for solar-assisted heating for buildings (0-100°C), industrial processes (100-300°C) and high-temperature storage for power plants (300-1,000°C). Development of thermal energy storage technology as well as of suitable materials has accelerated significantly during the last decade, due to high demand for renewable energy integration into the electrical grid.

Currently, sensible thermal energy storage (TES) is used in CSPs, which helps to maintain operating conditions at night and during fluctuations. The operating principle of these devices is based on the heat capacity of molten salts.

The energy density of sensible TES is dependent on the amount of storage material and its temperature range. For example, to maintain the operating conditions of a CSP at 50MW for eight hours, 28,500t of SolarSalt – one of the most well-known mixtures of 40% mol KNO_3 -60% NaNO_3 – are required with a solar-field temperature difference of 100°C. (see image left). The main limitation for storage materials is the thermal stability. For example, SolarSalt will be used usually below 565°C.

To achieve higher energy conversion rates of CSP plants, the concepts with higher operation temperature are considered. From this point of view, molten salts with different kinds of anions – chlorides, carbonates, sulfates and fluorides – are in focus for further investigation.

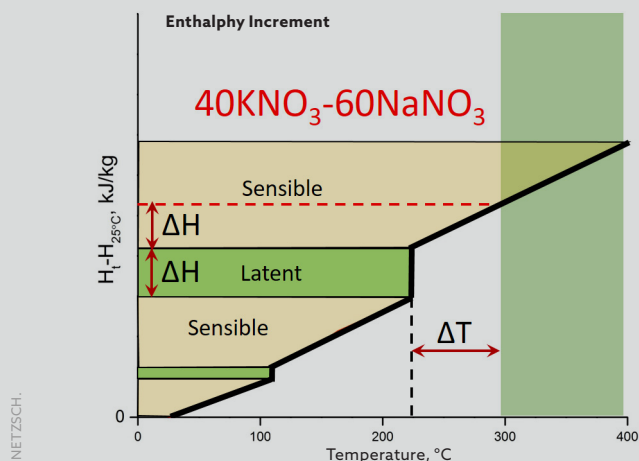
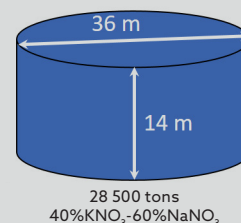
These salts have higher thermal stability range, but at the same time they have also higher melting temperatures and will be used mainly as phase-change materials.

Heat transfer fluids will be considered supercritical, such as supercritical carbon dioxide (sCO_2), which can be integrated in the sCO_2 -Brayton cycle for the optimal power cycle for achieving higher thermo-electric conversion efficiency. With this increased efficiency, it is necessary to increase the capacity of the energy storage itself. One of the most efficient ways is to use the latent heat of phase transitions, e.g. liquid-solid or solid-solid. In this case, the same amount of energy can be stored in a temperature interval of 1°C as in 75°C in the case of the sensible mode of the SolarSalt (see image below).

Therefore the use of TES in two modes (sensible + latent) can be twice or more as efficient as using a sensible mode alone. In addition, salts can also be used as thermochemical storage through reversible chemical reactions, such as the decomposition of Ca(OH)_2 or CaCO_3 . For the proper design and modelling of heat exchangers and other equipment, it is necessary to have reliable and validated dataset of thermophysical properties of salt mixtures.

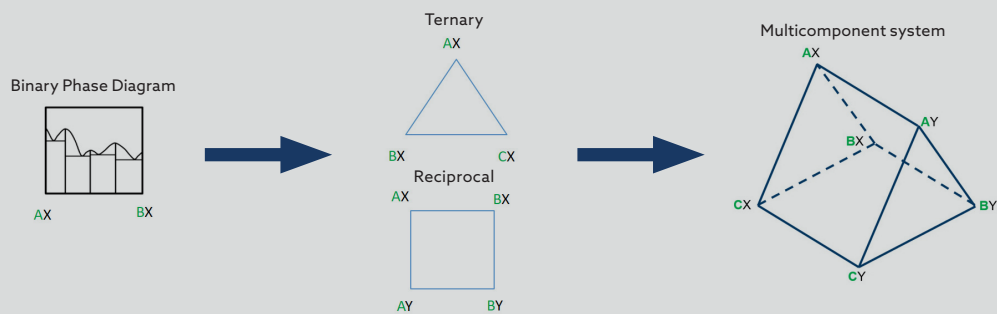
Below: Parameters of sensible thermal energy storage with SolarSalt

Sensible Thermal Energy Storage	
Solar-Field Inlet Temp:	290°C
Solar-Field Outlet Temp:	390°C
Solar-Field Temp Difference:	100°C



Feature

Right: Schematic representation of binary, ternary, reciprocal and multicomponent systems



Well seasoned

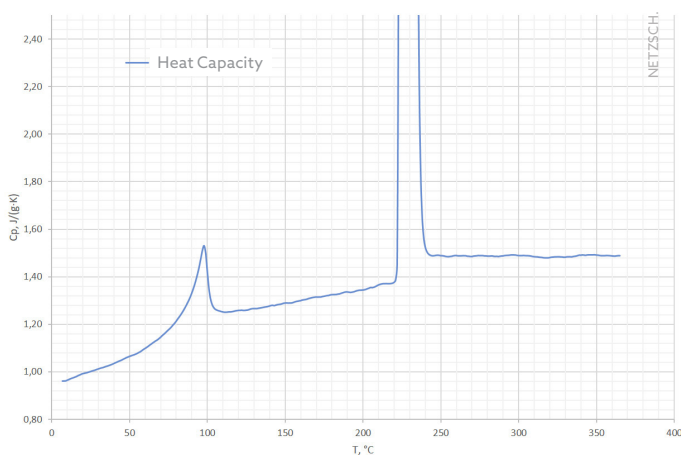
When selecting a suitable salt mixture, various requirements should be considered – high-energy density, high-thermal conductivity, low viscosity, thermal stability, low corrosion and low price to name a few. To be able to vary these parameters, a consistent and verified thermodynamic database containing multicomponent salt and metal systems should be developed.

Multicomponent systems can be represented as a combination of three, four or even more components. Typically, by mixing two compounds in different proportions, the melting behaviour will be changed accordingly – this is especially sought after if it is possible to decrease the melting temperature of initial components. This melting behaviour can be represented with a binary phase diagram. Phase diagrams help visualise the melting and solidification processes at different temperatures and compositions (see image above).

By considering multicomponent systems, the variation of possible compositions increases exponentially. Therefore, application of mathematical methods is necessary for solving such complex tasks. One of a suitable and well-established approach for such calculations is the Calculation of Phase Diagrams (CALPHAD) method. In the frame of this method, the available experimental data should be collected and critically analysed. In the case of missing or insufficient experimental data, the important properties have to be studied using various methods of thermophysical and thermochemical analyses.

The accuracy of thermodynamic properties of pure compounds is critical for the overall reliability of thermodynamic databases. Thermodynamic properties, such as enthalpy, entropy, Gibbs energy, heat capacity, and phase equilibria, must be carefully determined and critically assessed from experimental measurements. Ideally, data from multiple sources and studies are compared and validated to ensure accuracy and consistency.

Below: Measurement of the specific heat capacity of a 50% mol NaNO_3 -50% KNO_3 mixture measured in NETZSCH application laboratory



Thermal analysis

For valid and reliable thermodynamic and thermophysical properties, it is necessary to rely on multiple independent techniques to ensure the data obtained is accurate and consistent.

One of the main experimental techniques for the determination of phase diagrams is differential thermal analysis, which allows the determination of phase transition temperatures (structural changes, melting, crystallisation, solid solution) of different mixtures/compositions.

Phase changing materials (PCM)/HTF materials should have a vapour pressure as low as possible in the working temperature range to reduce potential contamination problems. In addition, a chemical decomposition of components can follow a change of the composition and the thermochemical properties of the PCM/HTF. Therefore, knowledge of the thermal stability, vapour pressure and gas phase composition is important.

This information can be obtained with thermogravimetry and evolved gas analysis, such as Fourier-transform infrared spectroscopy, mass spectrometry and gas chromatography. To determine the energy density of storage materials, the use of a differential scanning calorimetry (DSC) can be applied. The heat capacity of solid and liquid phases, as well as enthalpy of phase transitions, can be obtained (see image on lower left hand side). The DSC method makes it possible to observe the change in heat capacity during the heating of the sample *in situ*, and it enables the observation of kinetic effects by using different heating rates.

In addition to thermodynamic properties – thermal expansion, thermal conductivity and viscosity are also important characteristics that significantly influence the behaviour and performance of PCM/HTF materials. Understanding and measuring these properties are essential for design engineering. These properties can be obtained by using dilatometry, thermomechanical analysis, laser flash analysis, rotational and capillary rheometry.

However, it is not enough to use just one experimental method. In most cases, suitable crucible materials for the experimental studies must be found and experimental procedures must be established, taking into account the reactivity and volatility of the systems under examination.

Therefore, for each type of salt, the experimental conditions should be determined and evaluated. The experimental results obtained should then be critically evaluated or compared with known values. This is possible by using thermodynamic modelling, which considers different properties of the system and combines them in one comprehensive thermodynamic database.

Therefore, the combination of experimental data, computational techniques and predictive models is critical for advancing our understanding of materials and their behaviour under different conditions. Also see *Materials World*, June 2023, for an article on the importance of the field of experimental thermodynamics in materials science at bit.ly/3Xlvnq.