Introduction

The Thermal Energy Storage (TES) is defined as the temporary storage of thermal energy at high or low temperatures. As most of the renewable energy sources (solar, wind, ...) are intermittently available, the target of TES is to improve performances of energy systems with a smoother supply and an increased reliability.

Three main types of thermal energy storage have to be considered (Figure 1):
- Storage of sensible heat
- Storage of latent heat
- Storage of thermochemical heat

For each TES mode, various types of transformations or reactions are available and are well known. This application note will demonstrate how the thermal analysis and calorimetric methods are used to investigate the different TES techniques and to characterize the materials (solid and liquid) used in the corresponding processes.

Sensible heat

When heating or cooling a liquid or a solid without changing phase, the method is called sensible energy storage. The sensible heat of a substance corresponds to the amount of energy required to raise or cool the temperature of the material on a given temperature range. This sensible heat is related to the heat capacity $C_p$ of the material and is related to the following relation between $T_1$ and $T_2$:

$$Q = m \int_{T_1}^{T_2} C_p \, dT$$

Sensys DSC

(-120°C to 830°C)
The calorimetric technique is the ideal technique for measuring the heat capacity of a material. The DSC signal for a given sample at a temperature $T$ is equal to:

$$\frac{dq}{dt} = mC_p \frac{dT}{dt}$$

where
- $dq/dt$ is the DSC signal
- $dT/dt$ is the temperature scanning rate

The first DSC technique for measuring the heat capacity is called the continuous heating (or cooling) mode (Figure 2). A linear heating rate is applied between $T_1$ and $T_2$. The $A_s$ deviation corresponding to the DSC signal of the sample is corrected from the $A_b$ deviation corresponding to the DSC signal of the blank curve (obtained with two empty crucibles).

The second DSC technique, called the step heating (or cooling) mode is based on the application of an incremental temperature (Figure 3). In that case the $C_p$ determination is related to the integration of the DSC signal on a given temperature increase, according to the following relation:

$$\int_{T_1}^{T_2} \frac{dq}{dt} \, dt = m \int_{T_1}^{T_2} C_p \frac{dT}{dt} \, dt$$

giving

$$Q_{1}^{T_{2}} = mC_{p} \Delta T$$

The $Q_s$ area corresponding to the sample curve is corrected from the $Q_b$ corresponding to the blank curve (with two empty crucibles). In that case a mean $C_p$ value is measured for the given temperature range.
According to the type of material (solid or liquid), the range of temperature to be investigated, SETARAM provides calorimeters and DSC’s to work from -196°C up to 1600°C for Cp determination. The following table gives a list of the different calorimetric devices with their range of temperature, the Cp mode that can be applied, the volume available for the sample, the expected accuracy (for more information on the Cp drop technique see technical note TN 680)

<table>
<thead>
<tr>
<th>Calorimeter/DSC</th>
<th>Temperature (°C)</th>
<th>Continuous</th>
<th>Cp mode</th>
<th>Drop</th>
<th>Sample type</th>
<th>Volume (cm³)</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC 131</td>
<td>-170</td>
<td>0.05</td>
<td>Solid, liquid</td>
<td>0.3</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensys</td>
<td>-120</td>
<td>0.45</td>
<td>solid, liquid</td>
<td>12.5</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MicroDSC</td>
<td>20</td>
<td>Good</td>
<td>solid, liquid</td>
<td>0.3</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labsys</td>
<td>1600</td>
<td>0.45</td>
<td>solid, liquid</td>
<td>12.5</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT2-15</td>
<td>-196</td>
<td>Good</td>
<td>solid, liquid</td>
<td>0.45 (DSC)</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C80</td>
<td>300</td>
<td>High</td>
<td>solid, liquid</td>
<td>5 (drop)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MHTC</td>
<td>1500</td>
<td>Good</td>
<td>solid</td>
<td>0.45 (DSC)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Setaram calorimeters and DSC’s for Cp determination
Latent heat

All pure substances are found under three different states: solid, liquid and vapour. To go from one state to another, addition or removal of heat is required. The heat that causes these changes is called latent heat. Latent heat does not affect the temperature of a substance as this temperature will remain constant during the whole process of transformation (Figure 4).

Latent heat is mainly coming from melting or crystallization, vaporisation or condensation. The use of the latent heat of a material allows to bring a significant increase in the capacity of thermal energy storage as seen on Figure 5.

Phase Change Materials (PCM’s) with large latent heat are substances that are used according to different ranges of temperature:
- For low temperature range (less than 100°C), mostly organic materials such as paraffins, fatty acids and salt hydrates
- For medium temperature range (less than 200°C), organic materials such as sugar alcohols (erythritol)
- For higher temperature (above 200°C), inorganic salt materials such as nitrates, hydroxides, chlorides, carbonates, fluorides

Gas hydrates (especially CO$_2$ hydrates) are also used for their large heat of formation and dissociation.

To be suitable for energy storage, a PCM has to possess the following specifications:
- a large phase change enthalpy
- a phase change temperature adapted to a given energy storage
- a reproducible phase change
- a limited subcooling

All these parameters are measured via the calorimetric technique. The calorimeters and DSC’s described in Table 1 that are able to investigate solid and liquid materials can apply for the determination of latent heat. However, there are significant differences in terms of sample volume and temperature scanning rate. The choice of these two parameters is of high importance in the thermal investigation of PCM’s.

DSC 131 evo
(-170°C / 700°C)
An example is given with the investigation of a sample of plaster containing PCM. Approximately 50 mg of sample is analyzed with the DSC 131, a standard plate DSC, into a closed aluminum crucible (100µL) at a heating rate of 3°C/min between -5°C and 45°C (Figure 6). The material shows a very good melting/crystallization reversibility in term of temperature range and enthalpy (25.1 J.g⁻¹) that is perfectly adequate for its use as a TES substance.

\[ Q = 25.1 \text{ J.g}^{-1} \]

Figure 6: Melting and crystallization of a plaster containing PCM and cross-section of the DSC131 detector

However the plate DSC detector has some major drawbacks for the investigation of PCM’s:
- as the calorimetric detection is performed through the bottom of the crucible, the amount of sample to be investigated is small. In case of experimentations on non homogeneous materials, the accuracy will be very poor.
- in order to get a reasonable calorimetric signal, according to the small amount of sample, it is needed to work with scanning rates higher than 1°C/min. Such a scanning rate is quite far from the variations of temperature that are measured during the real thermal energy storage and also far from the thermodynamically stable conditions.

The solution is to use larger amounts of sample and very low scanning rates. These specifications are offered by the Calvet type calorimeters and MicroDSC. With a calorimetric design, the sample contained in the vessel is fully surrounded by the detector. The C80 and MicroDSC detectors are shown on Figure 7. Such a detector is adapted for the investigation of sample volume equal to 1 cm³. The high calorimetric sensitivity and stability allow the use of scanning rates as low as 0.001°C.min⁻¹ or 0.6°C.hour⁻¹ !

An example is given with the analysis of an homogeneous blend of polyolefins encapsulated in polymer beads with the MicroDSC7. The sample mass is 390 mg corresponding to about 10 beads. The sample is heated from -20°C to 50°C followed by cooling from 50°C to -20°C at 1°C.min⁻¹ and then at 0.04 °C.min⁻¹ in order to measure the influence of the scanning rate on the hysteresis (Figure 8). By lowering the scanning rate, the hysteresis is considerably reduced and sharper peaks of melting and crystallization are obtained.

Figure 7: Cross-section of the C80 (top) and MicroDSC (bottom) detector

µDSC7 Evo
-45°C/120°C

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The enthalpy variation of the tested PCM seen on Figure 9 clearly shows the influence of the scanning rate for the definition of the correct temperature range for an appropriated thermal energy storage.

Calorimetry also offers the possibility to work on large amounts of materials as seen on Figure 10. A mass of 10 grams of hydrated ferric chloride FeCl$_3$·6H$_2$O is investigated with the C80 calorimeter at a low scanning rate (0.1°C.min$^{-1}$). The material is tightly encapsulated in a glass ampoule that is introduced in the calorimetric vessel. This encapsulation will prevent any evaporation or contamination between the sample and the metallic vessel. The ferric chloride provides a large melting heat between 30°C and 47°C. The corresponding integral curve, including the heat capacity of the material and its melting enthalpy, provides the capacity of thermal energy storage for such a material.
**Formation and dissociation of CO₂ hydrates (High Pressure MicroDSC)**

High Pressure Calorimetry has proved to be a valuable technique in the investigation of gas hydrate formation and dissociation, especially in the case of CO₂ hydrates. The formation and dissociation of CO₂ hydrates evolve a significant enthalpy value that is interesting for thermal energy storage. The formation of the hydrates requires a pressure of CO₂ around 20 bar and a low temperature.

A High Pressure vessel is used for such an experimentation (Figure 11). The vessel is connected to a high pressure gas panel to monitor the gas pressure and is introduced in the HP MicroDSC7 (Figure 12). For the test, water is introduced in the vessel and a pressure of 20 bar CO₂ is applied on the solution.

A sample of 269.51mg of 10wt% THF solution in water is cooled down to -20°C to form the gas hydrate. Then the sample is reheated at 1°C.min⁻¹ to dissociate the hydrate. In the case of the formation of CO₂ hydrate, it is needed to firstly proceed to a cycling (successive heating and cooling) in order to obtain an hydrate accumulation.

The figure 13 shows the decrease of the free water melting peak (0 to 10°C) with the successive cycles and the appearance of a CO₂/THF co-hydrate melting peak (10°C to 17.5°C) and of the CO₂ hydrate melting peak (17.5°C to 20°C). After 28 cycles (Figure 14), free water melting peak disappeared in favor of the co-clathrate and the hydrate dissociation.
The cycle number 5 was used to perform a mathematical separation (Marquard routine fitting assymetric Gaussian peaks) on the three underlying peaks to have a clear separation of the contribution due to free water, the THF/CO₂ co-hydrate and the CO₂ hydrate (Figure 15).

From the peak separation it is possible to evaluate the heat of melting of the CO₂ hydrate that is equal to 12.18 J.g⁻¹ of solution, i.e. 13.56 J.g⁻¹ of water.

The comparison with literature value of the heat of dissociation of CO₂ hydrate (ΔHdiss= 500.11 J.g⁻¹ H₂O ) allows determining a ratio of hydrate formation of 2.7%. after 5 cycles.

The same calculation can be applied to each cycle.

Figure 15: Separation of the thermal contributions of the melting of free water, CO₂/THF co-hydrate, and CO₂ hydrate for heating cycle 5
Thermochemical heat

For thermochemical energy storage, the principle is to use the heat that is evolved during the following reversible reaction:

\[ A \text{ (solid)} \leftrightarrow B \text{ (solid)} + C \text{ (gas)} \]

This type of reaction based on the adsorption (exothermic)/desorption (endothermic) process is achieved with different types of sorbents:
- Silicates, silica gels, silica aerogels, ordered mesoporous silicates (MCM, SBA)
- Zeolites
- Metal aluminophosphates
- Metal Oxide Frameworks MOF’s
- Composites : salts + sorbates such as water, methanol, ethanol, ammonia

The calorimetric and thermogravimetric techniques have been used for many years to investigate such adsorption/desorption reactions. Different methods can apply for such experiments:
- the TG-DSC method
- the calorimetric method

- The TG-DSC method
The TG-DSC method has the main advantage of measuring the capacity of adsorption (desorption) in term of mass and enthalpy on the same sorbent material.
In the case of interaction with water, a relative humidity generator has to be connected to the TG-DSC instrument.

![Figure 16: Cross section of Sensys TG-DSC and picture of Wetsys relative humidity generator with a RH profile](image)
The Sensys TG-DSC is especially very well adapted for the investigation of adsorption/desorption in humid atmosphere (Figure 16). This system combines the performance of a symmetrical balance and the high sensitivity of a Calvet type DSC. Combined with a Wetsys relative humidity generator, it is possible to investigate the sorption process according to the relative humidity as seen on figure 17 for silicagel.

The following experimental conditions are selected:
- Silica gel initially activated by heating to 165°C to evacuate humidity
- Temperature of the adsorption test: 25°C
- Sweeping of wet air (50 ml.min⁻¹)
- 10 hours under different RH: 10%, 20%, 60% and 80%

![Figure 17: TG-DSC curves for the adsorption of water on silica gel at different RH](image)

The TG-DSC curves provide the mass increase due to water adsorption and the corresponding exothermic heat that define the heat storage capacity for such a material at a given temperature.

Calorimetry is another method for the investigation of the adsorption/desorption process. With the C80 calorimeter (see cross section of the detector on figure 7), a gas flow vessel is available to introduce a vapour on a dry sample at a given temperature. An example is given with the adsorption of water vapour on a zeolite at 24°C under different water vapour pressures (Figure 18).

The zeolite is initially activated during 6 hours at 312°C under vacuum. The gas flow calorimetric vessel, containing the activated zeolite, is connected to a gas line coming from the water vapour generator. This generator is designed to work under reduced pressure of vapour. For the test, two vapour pressures are investigated: 4.58 mmHg and 9.20 mmHg.

The heat storage capacity is obtained versus the vapour pressure. According to the type of zeolite, this value can largely be different.
The same type of gas flow calorimetric vessel is also very useful to follow the thermochemical heat storage relative to the sorption behavior of salt mixtures, and especially composites made of porous materials impregnated with hygroscopic salt hydrates. The exothermic reaction provide a high heat storage capacity. For the desorption process, a limited temperature up to 130°C is only needed.

Figure 19 gives an example of the use of the gas flow vessel of the C80 calorimeter for the measurement of the hydration of an attapulgite granulate impregnated with different salt mixtures (MgSO$_4$, MgCl$_2$). The partial substitution of MgSO$_4$ by MgCl$_2$ results in a higher heat of adsorption.

Figure 19: Hydration of attapulgite granulate impregnated with different salt mixtures at 30°C and 85%RH (from K. Posern and C. Kaps, Thermochimica Acta, 502 (2010) 73-76)