Thermal Analysis and Calorimetry applied to Thermal Energy Storage (TES)

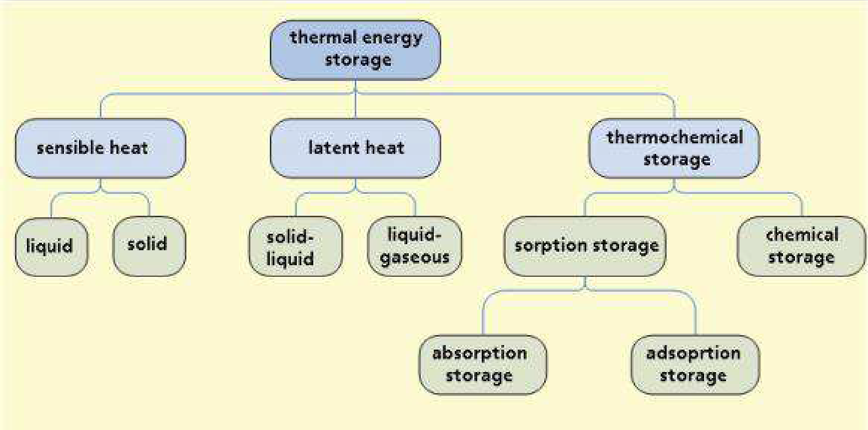
INTRODUCTION

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 only intermittently available, the purpose of TES is to improve the performance of these energy systems by smoothing out the supply and therefore making them more reliable.

Three main types of thermal energy storage are considered (Figure 1):

- Storage of sensible heat
- Storage of latent heat
- Storage of thermochemical heat

For each type of TES, there are various types of transformations and reactions. This application note will demonstrate how thermal analysis and calorimetric methods can be used to investigate the different TES techniques by characterizing the materials (solid and liquid) used in the processes.



Sensible heat

Energy can be stored by heating or cooling a liquid or a solid without changing its phase. This 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 dependent on the heat capacity, Cp, of the material and is also dependent on the following relation between T1 and T2:

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

Calorimetry 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

One DSC technique for measuring heat capacity is called the continuous heating (or cooling) mode (Figure 2). A linear heating rate is applied between T1 and T2. The curve, As, which corresponds to the DSC signal of the sample is corrected using the curve, Ab, which corresponds to the DSC signal of a blank curve (obtained using two empty crucibles).

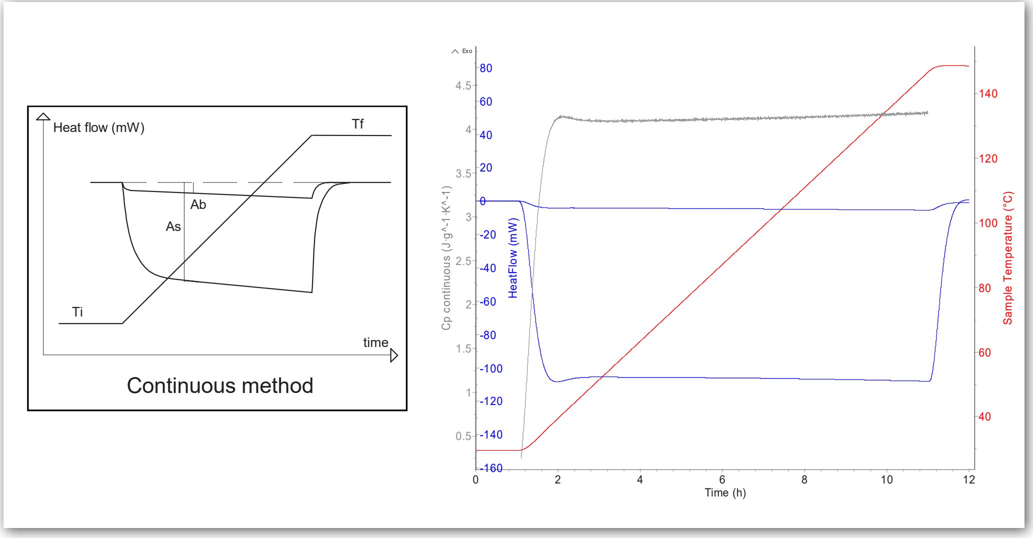


Figure 2: Cp determination using the continuous heating mode

Another DSC technique for measuring Cp is called the step heating (or cooling) mode. An incremental temperature profile is applied (Figure 3). In this case the Cp determination corresponds to the integration of the DSC curve over a given temperature increase, according to the following relation:

$$\int_{T_1}^{T_2}\frac{dq}{dt}dt = m\int_{T_1}^{T_2}Cp\frac{dT}{dt}dt \qquad \text{which yields} \qquad (Q)_{T_1}^{T_2} = m\overline{Cp}\Delta T$$

The area ,Qs, corresponds to the sample curve and is corrected using the area, Qb, which corresponds to the blank curve (using two empty crucibles). In this method, a mean Cp value is measured for the given temperature range.

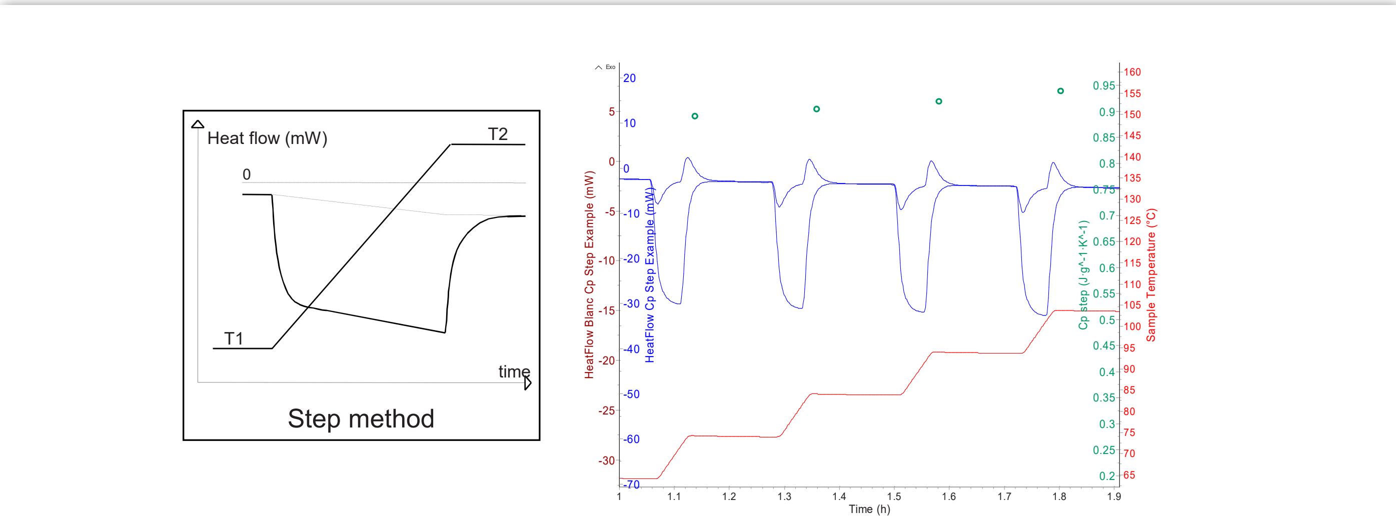


Figure 3: Cp determination using the step heating mode

According to the type of material (solid or liquid), and the temperature range of interest, SETARAM provides calorimeters and DSC's that work from -196°C up to 1600°C for Cp determination. The following table gives a list of the different calorimetric devices with their temperature range, the Cp mode that can be applied, the available sample volume, and the expected accuracy (for more information on the Cp drop technique see technical note TN 680).

Calorimeter/ DSC	Temperature (°C)		Cp mode			Sample type	Volume
	Min	Max	Continuous	Step	Drop		(cm³)
SETLINE DSC	-170	700	🟪	🟪		Solid, liquid	0.05
CALVET PRO	-120	830	🟪	🟪		solid, liquid	0.3
MICROCALVET	-45	120	🟪	🟪		solid, liquid	1
THEMYS ONE	20	1600	🟪	🟪		solid	0.3
CALVET CRYO	-196	200	🟪	🟪		solid, liquid	12.5
CALVET	20	300	🟪	🟪		solid, liquid	12.5
CALVET DC	20	1500	🟪	🟪	🟪	solid	0.45 (DSC) 5 (drop)

Table 1: Setaram calorimeters and DSC instruments for Cp determination

Latent heat

Energy can be stored by heating or cooling a liquid or a solid without changing its phase. This 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 dependent on the heat capacity, Cp, of the material and is also dependent on the following relation between T1 and T2:

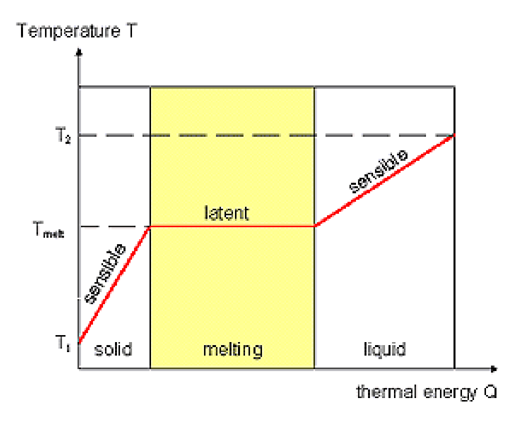


Figure 4: Sensible heat and latent heat diagram

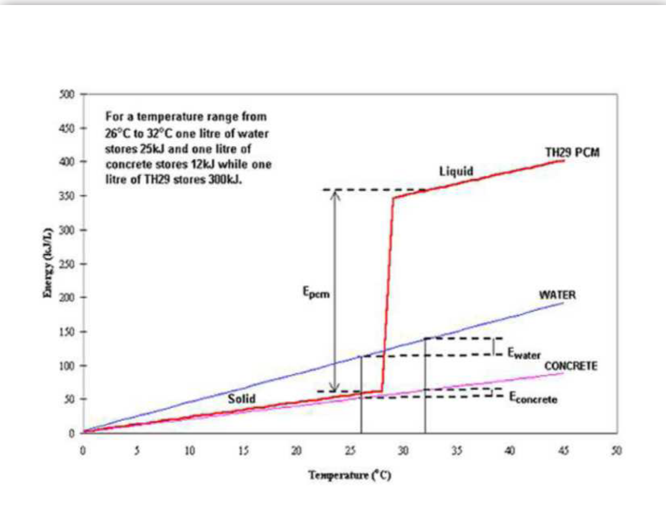


Figure 5: Comparing sensible heat storage and latent heat storage (From Netgreensolar website)

Phase Change Materials (PCM's) with large latent heats are substances that can be used based on different temperature ranges:

- For low temperature ranges (less than 100°C), mostly organic materials such as paraffins, fatty acids and salt hydrates are used.
- For medium temperature ranges (less than 200°C), organic materials such as sugar alcohols (erythritol) are used.
- For higher temperature ranges (above 200°C), inorganic salt materials such as nitrates, hydroxides, chlorides, carbonates, fluorides are used.

Gas hydrates (especially CO2 hydrates) are also used for their large heat of formation and dissociation.

To be suitable for energy storage, a PCM needs to have the following specifications:

- a large phase change enthalpy
- a phase change temperature which is suitable for a certain energy storage system
- a reproducible phase change
- a limited subcooling

All of these parameters are measured using calorimetry. The calorimeters and DSC's described in Table 1 that can measure solid and liquid materials can be used to determine latent heat. However, there are significant differences in terms of sample volume and temperature scanning rate. These two parameters are important when investigating PCM's.

1- Phase Change Material - Sensible & latent heat

EXPERIMENT

The following example involves a plaster containing a PCM. Approximately 50 mg of sample is placed in a closed aluminum crucible (100uL), and is analyzed using the SETLINE DSC, a standard plate-type DSC, between -5°C and 45°C at a heating rate of 3°C/min (Figure 6).

RESULTS AND CONCLUSION

The material shows good melting/crystallization reversibility in term of both temperature and enthalpy (25.1 J.g-1) which means this sample is a good TES substance.
The plate type DSC detector has, however, some major drawbacks for the investigation of PCM's:
-Because the calorimetric detection (heat flow) only occurs through the bottom of the crucible, the amount of sample analyzed is small.When studying non homogeneousmaterial, the accuracy will be very poor.
-In order to get a reasonable calorimetric signal, using a small amount of sample, the scanning rate needs to be more than 1°C/min. Such high scanning rates are far from the actual temperature variations during the real use thermal energy storage and also far from thermodynamically stable conditions.

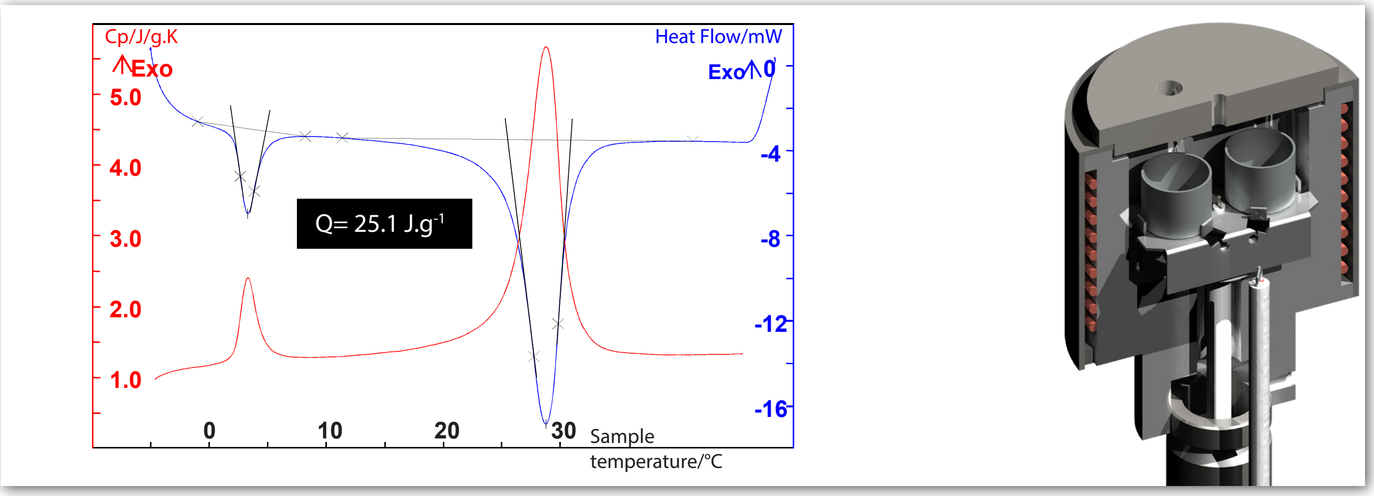
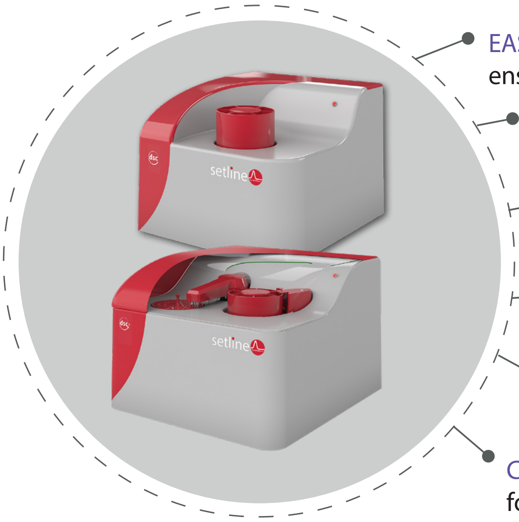


Figure 6: Melting and crystallization of a plaster containing a PCM and cross-section of the SETLINE DSC detector

INSTRUMENT

SETLINE DSC & DSC+

-170°C to 700°C



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CALISTO 2.0 EXCLUSIVE SOFTWARE
for intuitive and easy data handling

2- Phase Change Materials - Real life heating and cooling

EXPERIMENT

The solution is to use larger amounts of sample and very low scanning rates by using Setaram's calorimeters, including the MICROCALVET. These calorimeters have detectors that completely surround the sample. The CALVET and MICROCALVET detectors are shown in Figure 7. These detectors are designed to hold sample volumes of 1 cm3. Because of the high calorimetric sensitivity and stability, scanning rates as low as 0.001°C/mn or 0.6°C/hour can be used! The following example is the analysis of a homogeneous blend of polyolefins encapsulated in polymer beads using the MICROCALVET. The sample mass is 390 mg which corresponds to about 10 beads. The sample is heated from -20°C to 50°C then cooled from 50°C to -20°C at 1°C/min and then the sample is run again using a rate of 0.04 °C/min in order to measure the influence of the scanning rate on the hysteresis (Figure 8).

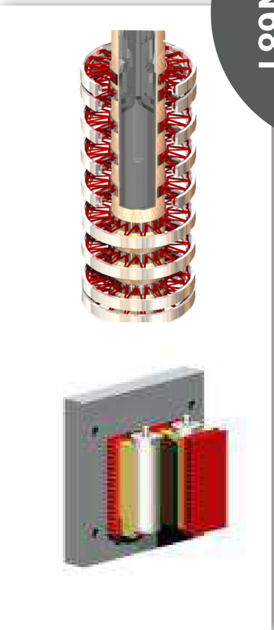


Figure 7: Cross-section of the CALVET (top) and MICROCALVET (bottom) detectors.

RESULTS AND CONCLUSION

By lowering the scanning rate, the hysteresis is considerably reduced and the peak of melting and the peak of crystallization are much sharper.

The enthalpy variation of the PCM sample seen in Figure 9 clearly shows the influence of the scanning rate on defining the correct temperature range for an appropriate thermal energy storage.

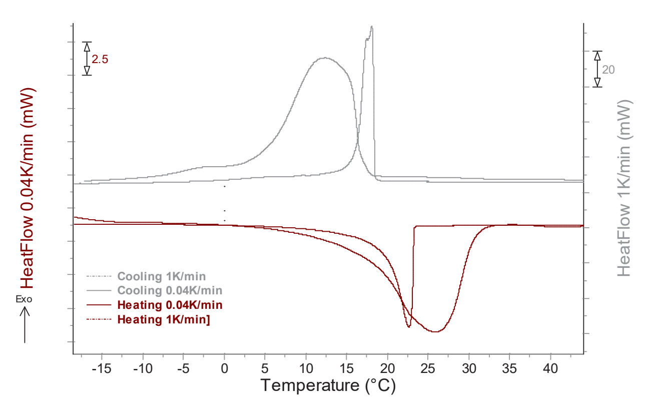


Figure 8: Experimental DSC melting and crystallization profiles of the PCM sample at 0.04°C.min-1 and 1°C.min-1

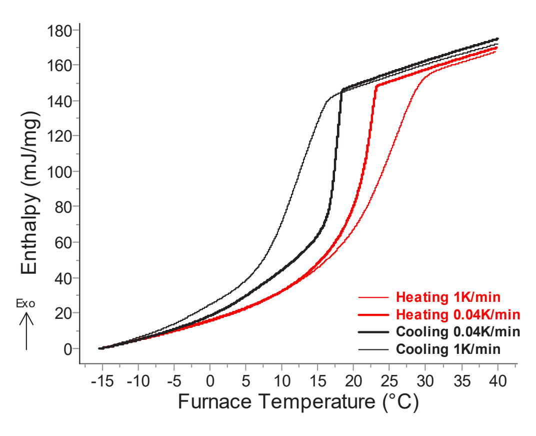
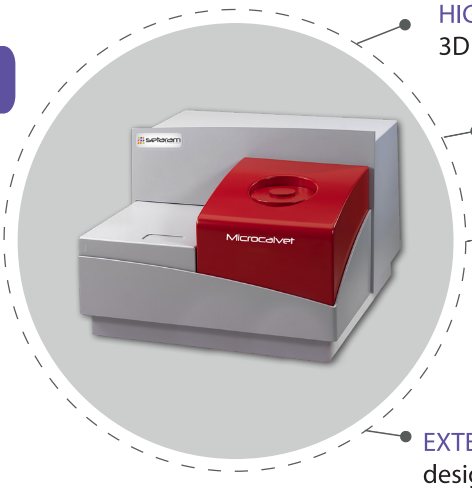


Figure 9: Enthalpy variations of the PCM sample during heating and cooling at 0.04°C.min-1 and 1°C.min-1

INSTRUMENT

MICROCALVET

-45°C to 120°C



HIGHEST HEAT MEASUREMENT ACCURACY
3D sensor based on Peltier elements with Joule effect calibration.

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for increased flexibility and replication of real life conditions.

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- high pressure (1000bar) and high vacuum
- pressure measurement and control
- mixing experiment

EXTERNAL COUPLING CAPABILITY
designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

3- Hydrates - Latent heat

EXPERIMENT

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 $FeCl_3,6H_2O$ is investigated using the CALVET calorimeter at a low scanning rate (0.1°C/min). 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.

RESULTS AND CONCLUSION

The ferric chloride produces a large melting heat between 30°C and 47°C. The corresponding curve, including the heat capacity of the material and its melting enthalpy, provides the thermal energy storage capacity for such a material.

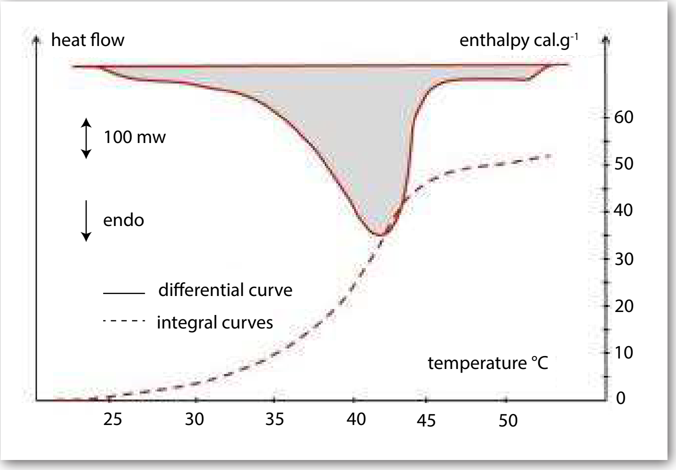

Figure 10: Melting of hydrated ferric chloride (10.29 g) encapsulated in a glass ampoule at 0.1°C/min

INSTRUMENT

CALVET

Ambient to 300°C

HIGHEST HEAT MEASUREMENT ACCURACY
3D sensor based on thermocouples with Joule effect calibration.

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4- Formation and dissociation of CO_2 hydrates (High Pressure microcalorimetry)

EXPERIMENT

High Pressure Calorimetry has proved to be a valuable technique in the investigation of gas hydrate formation and dissociation, especially in the case of CO_2 hydrates. The formation and dissociation of CO_2 hydrates produce enthalpy values that are interesting for thermal energy storage.

The formation of the hydrates requires a CO_2 pressure of around 20 bar and a low temperature.

A High Pressure vessel is used for these types of experiments (Figure 11). The vessel is connected to a high pressure gas panel (FLEXI HP 1000) to monitor the gas pressure and this vessel is placed in the MICROCALVET (Figure 12).

To run the test, water is introduced into the vessel and a pressure of 20 bar CO_2 is applied to the solution.

A sample of 269.51mg of 10 wt% THF solution in water is cooled down to -20°C to form the gas hydrate. Then the sample is reheated at 1°C/min to dissociate the hydrate. When studying the formation of CO_2 hydrates, one must first cycle the sample (successive heating and cooling) in order to obtain hydrate accumulation.

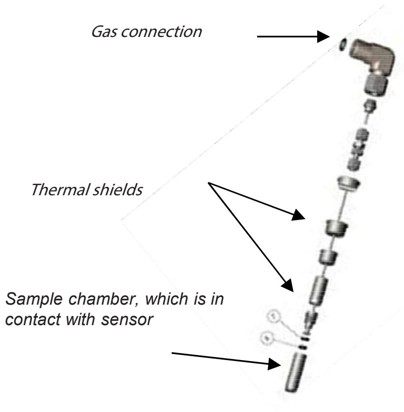


Figure 11: The High Pressure vessel

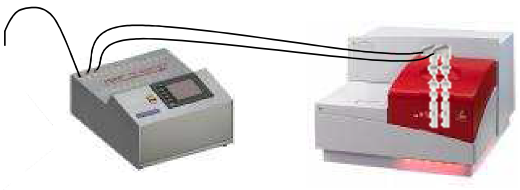


Figure 12: Experimental set up for the investigation of gas hydrates

RESULTS AND CONCLUSION

The figure 13 shows that with successive cycles, there is a decrease in the free water melting peak (0 to 10°C) and we see the appearance of a CO_2/THF co-hydrate melting peak (10°C to 17.5°C) and the CO_2 hydrate melting peak (17.5°C to 20°C).

After 28 cycles (Figure 14), the free water melting peak has disappeared in favor of the co-clathrate and the hydrate dissociation.

The data from cycle number 5 was used to perform a mathematical separation (Marquard routine fitting asymmetric Gaussian peaks) on the three underlying peaks to have a clear separation of the contribution due to free water, the THF/CO_2 co-hydrate and the CO_2 hydrate (Figure 15).

From the peak separation it is possible to evaluate the heat of melting of the CO_2 hydrate which is equal to 12.18 $J.g^{-1}$ of solution, i.e. 13.56 $J.g^{-1}$ of water.

Comparing the literature value of the heat of dissociation of CO_2 hydrate ($\Delta Hdiss$= 500,11 $J.g^{-1}$ H2O) allows us to determine the ratio of hydrate formation, which is 2.7%. after 5 cycles.

The same calculation can be applied to each cycle.

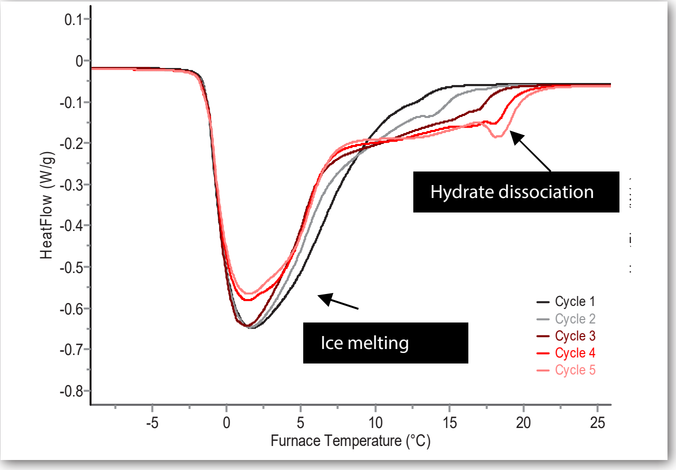


Figure 13: DSC curves recorded during successive cooling/heating cycles (1 to 5)

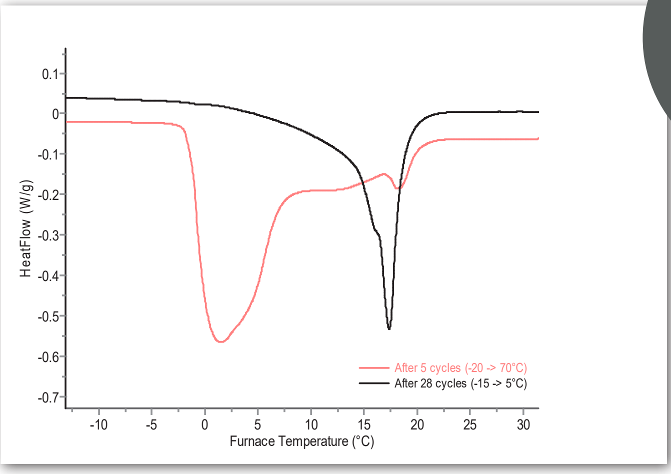


Figure 14: DSC thermograms recorded during successive cooling/heating cycles (5 and 28)

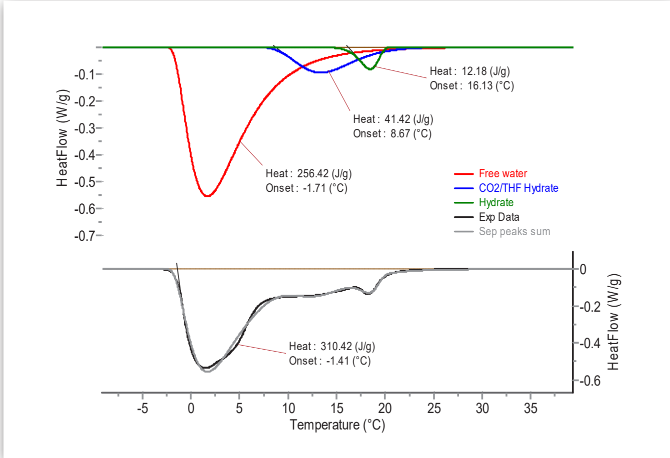
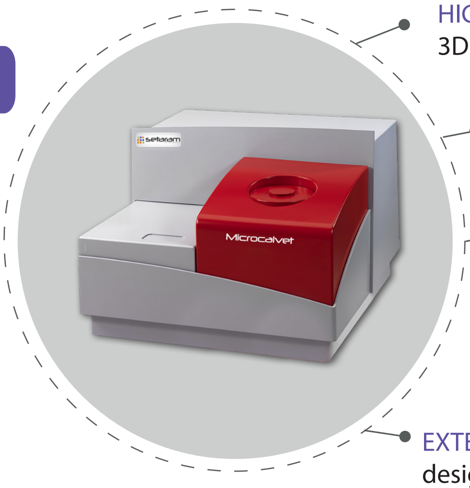


Figure 15: Separation of the thermal contributions of the melting of free water, CO_2/THF co-hydrate, and CO_2 hydrate for the curve of heating cycle 5

INSTRUMENT

MICROCALVET

-45°C to 120°C



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5- Thermochemical heat storage - TG-DSC

INTRODUCTION

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

A (solid)←→B (solid) + C (gas)

This type of reaction, based on the adsorption (exothermic)/desorption (endothermic) process, is achieved using different types of sorbents:

- Silicates, silica gels, silica aerogels, ordered mesoporous silicates (MCM, SBA)
- Zeolites
- Metal aluminophosphates
- Metal Oxide FrameworksMOF's
- Composites : salts + sorbates such as water, methanol, ethanol, ammonia

Calorimetric and thermogravimetric techniques have been used for many years to investigate such adsorption/desorption reactions. Different methods can apply to such experiments:

-The TG-DSC method

-The calorimetricmethod

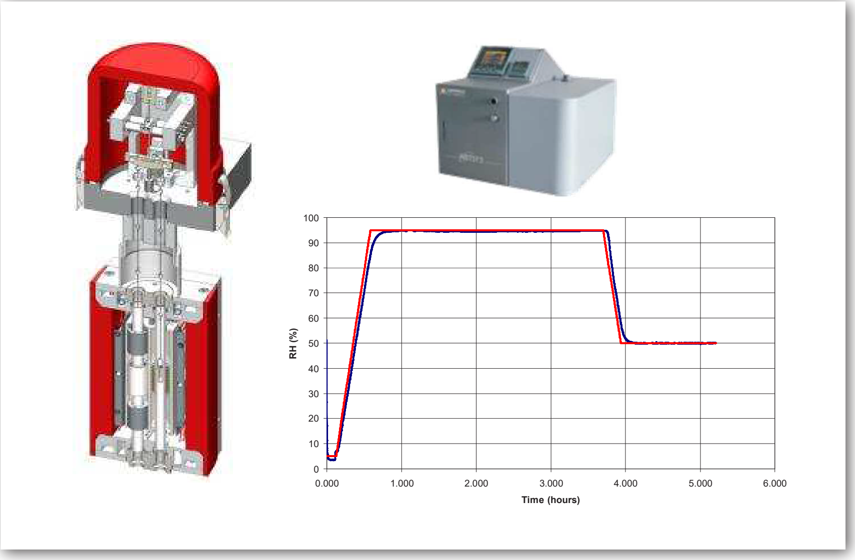

Figure 16: Cross section of CALVET PRO TG-DSC and picture of FLEXI WET relative humidity generator with a RH (relative humidity) profile

EXPERIMENT

The TG-DSC method has the main advantage of being able to measure the adsorption capacity (desorption) in terms of mass and measuring the enthalpy on the same sorbent material.

When the interaction with water is being studied, a relative humidity generator can be connected to the TG-DSC instrument.

The CALVET PRO TG-DSC is especially 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 3D sensor type DSC. Combined with a FLEXI WET 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 used:

- Silica gel is initially activated by heating to 165°C to evacuate any 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%

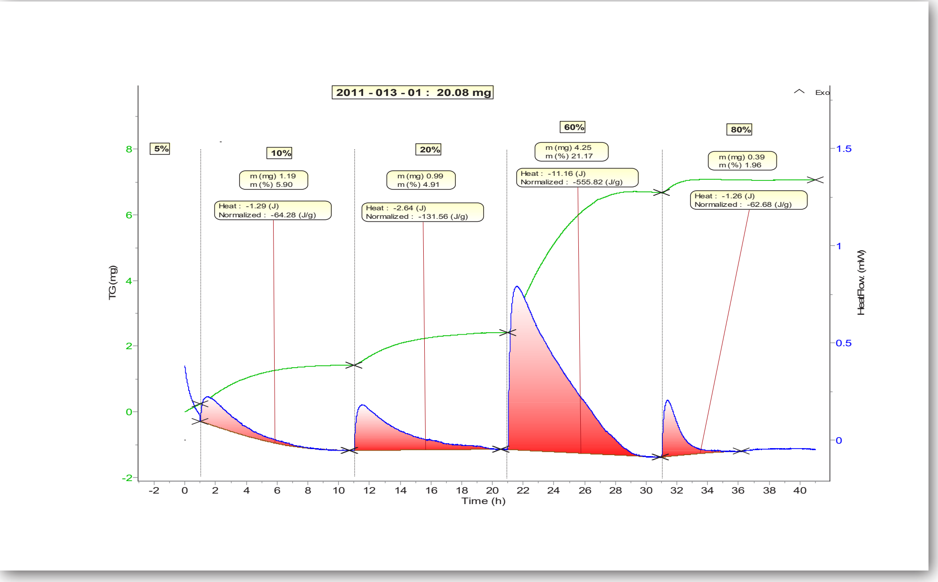

Figure 17: TG-DSC curves for the adsorption of water on silica gel at different RH

RESULTS AND CONCLUSION

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

INSTRUMENT

CALVET PRO TG-DSC

-120 to 830°C

HIGHEST ACCURACY WITH ITS HANG-DOWN SYMMETRICAL BEAM BALANCE

eliminate drift & buoyancy effect, improve gas/sample interaction.

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6- Thermochemical Heat Storage - calorimetry - zeolite

EXPERIMENT

Calorimetry is another method for investigating the adsorption/desorption process. With the CALVET calorimeter (see cross section of the detector in figure 7), a gas flow vessel is available where a vapor can be introduced onto a dry sample at a given temperature. An example is shown with the adsorption of water vapor on a zeolite at 24°C under different water vapor pressures (Figure 18).

The zeolite is initially activated for 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 vapor generator. This generator is designed to work under reduced vapor pressure. For the test, two vapor pressures are investigated: 4.58 mmHg and 9.20 mmHg.

RESULTS AND CONCLUSION

The data that is obtained is heat storage capacity versus vapor pressure. Depending on which zeolite is used, however, these values can change drastically.

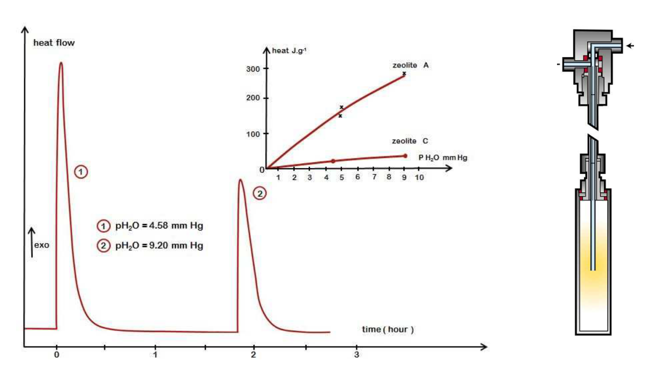

Figure 18: Water adsorption on a zeolite at different water vapor pressures at 24°C and a diagram of the gas flow calorimetric vessel used in these studies

INSTRUMENT

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7- Thermochemical Heat Storage - calorimetry - salts

EXPERIMENT

The same type of gas flow calorimetric vessel is also very useful to be able to measure 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 provides a high heat storage capacity. For the desorption process, a limited temperature up to only 130°C is needed.

RESULTS AND CONCLUSION

Figure 19 shows an example where the gas flow vessel of the CALVET calorimeter is used for measuring 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

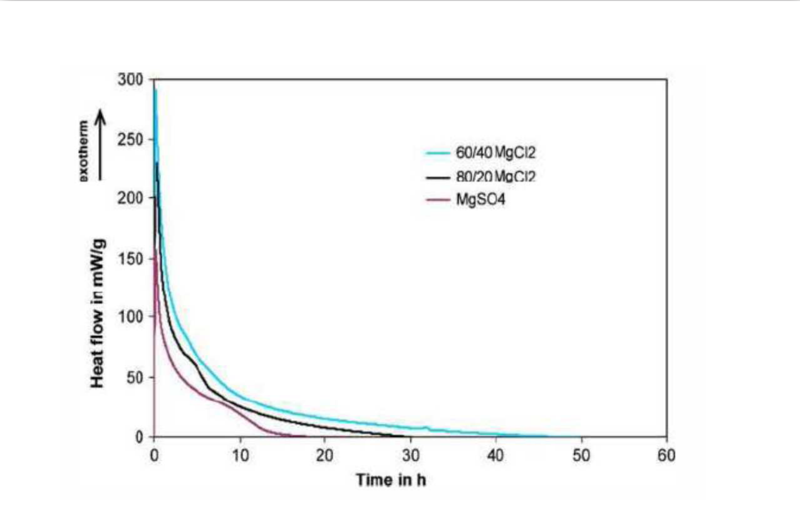

Figure 19: Hydration of attapulgite granulate impregnated with different salt mixtures at 30°C and 85%RH (from K. Posern and C. Kaps, Thermochimica Acta,502 (2010) 73-76)

INSTRUMENT

CALVET

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