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Chapter 1

General Introduction

In thermal energy storage (TES) units, the energy can be stored by mean of various kind of physical phenomena involving thermal effects : sensible heat, latent heat, adsorption, absorption, themochemical reactions. In the practical field of Concentrated Solar Power (CSP), current industrial TES units are based upon sensible heat using liquid phase materials (such as molten salts) or solid phase materials at high temperatures (such as refractory ceramics). Major efforts are made to develop liquid-solid latent heat TES highlighted by today by recent pilot scale experiments. The aim of the present report is to gather the various aspects related to the properties of TES materials. According to the above considerations, the work has been focused on sensible and latent heat TES materials only. Conventional currently considered properties such as density or thermal capacity are taken into consideration but not only at room temperature but considering the whole temperature range under operation. Other properties, which are usually not considered despite their real importance, such as thermomechanical behavior or the fatigue of the material under thermal cycling are also included and have been especially studied. A particular attention has been also given to porous materials with a specific devoted chapter.

Chapter 2

Handbook for standardised material characterization

2.1 Introduction

In the following tables are gathered the properties currently considered for sensible heat storage materials and latent heat storage materials respectively. The various encountered parameter name, symbols and units are specified and when available, the range of usual values is indicated. Another part of this document is devoted to corresponding methods and equipments currently used for characterization.

2.2 Sensible and latent heat storage materials

Thermal energy storage is characterized by the amount of the stored heat. In a sensible heat storage, this stored heat is related to the heat capacity C_p at constant pressure and the temperature variation :

$$Q = \int_{T_i}^{T_f} m.C_p \mathrm{d}T \text{ or } Q = \int_{T_i}^{T_f} V.C_p \mathrm{d}T \text{ or } Q = \int_{T_i}^{T_f} n.C_p \mathrm{d}T \tag{2.1}$$

The heat capacity of a material is an extensive property and is consequently currently defined per unit of mass (J.kg^{-1}.K^{-1}), per volume (J.m^{-3}.K^{-1}) or per mol (J.mol^{-1}.K^{-1}).

In a latent heat storage, the key parameter is the latent heat due to phase change. The latent heat, particularly heat of fusion, is the amount of heat stored during the melting process and discharged during the solidification process of a phase change material (PCM). It is currently written L or ΔH_m.

Some reviews or books describe materials and their properties [1-8]

2.3 Heat capacity and heat of fusion

The methods available for determining the heat of fusion, heat capacity and melting point can be classified into three groups, conventional calorimetry methods, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods.

Parameter	symbols	units	range	function of
Thermal properties				
density	ρ	kg m^{-3}	700 - 3200	T
Effusivity	E		200 - 5000	
Sensible heat, Specific Heat Mass specific heat	Cp	kJ kg^{-1} K^{-1}	0.4 – 4.2	T
Volumic specific heat	ρ Cp	MJ m^{-3} K^{-1}	1 – 4.2	T
Thermal conductivity	λ , k	W m^{-1} K^{-1}	0.2 - 400	T
Thermal diffusivity	α	m^2 s^{-1}	10^{-8} - 10^{-5}	T
Mechanical properties				
Thermal expansion coefficient	β	K^{-1}		T
Young modulus	E	MPa		
Practical properties				
Aging, fatigue under thermal stress	-	-		T, t
Inflammability	-	-		T, P
Compatibility with HTF	-	-		T
Corrosion effect/resistance	-	-		T
(stability)	-	-		
Economical properties				
Availability	-			
Price	-	euros ton^{-1} euros / kWh		
Sustainability				
Concurrence with other applications				
Ecotoxicity				
Embedded CO_2 and other GEG		g GHG ton^{-1}		
Embedded energy		kJ ton^{-1}		

Table 2.1: Parameters for sensible heat storage materials

AC and DSC calorimetry are the more common methods adapted to measure heat capacity of solid materials. Flow calorimetry has become an essential method for the measurement of heat effects for determination of heat enthalpy of fluids. These methods can be coupled with TGA devices to complete the analysis if mass changes occur.

We can consider two sort of experiments : firstly, the measure of the differential temperature a known heat flow is applied to the sample (DTA), and secondly, the measure of heat flow when the surrounding environment is controlled in temperature.

AC calorimetry

AC calorimetry is a suitable method for measuring the heat capacity near a phase transition. The amount of sample required is about 1 mg. A wide range of temperatures (from 1 K to 3600 K) can be screening.

This method consists in measuring the heat capacity in which an oscillatory heat flux is continuously applied, at an angular frequency ω, to a sample. Its heat capacity is determined from the resultant temperature oscillations. The ac temperature T_{ac} follows the relation :

$$T_{ac} = \frac{P_o}{\omega.C_p}[1 + 1/(\omega\tau)^2]^{1/2} \tag{2.2}$$

where P_o is the average power and τ the external relaxation time. Under well established

Parameter	symbols	units	range	function of
Thermal properties				
Density S&L	ρ	kg m^{-3}	700 - 3200	T
Latent heat	L	kJ kg^{-1}	50 - 600	
Effusivity	E		200 - 5000	
Specific latent heat (volume)	L	MJ m^{-3}	200 - 655	
Phase change temperature Melting temperature Transition temperature	T_m	K		
Sensible heat S&L Mass specific heat	Cp	kJ kg^{-1} K^{-1}	0.4 – 4.2	T
Volume specific heat S&L	ρ Cp	MJ m^{-3} K^{-1}	1 – 4.2	T
Sensible heat S&L	Cp	J kg^{-1} K^{-1}	? - 4300	T
during phase change	ΔT	K		
Subcooling		K	0 - 30	Volume, P
Thermal conductivity S&L	λ, k	W m^{-1} K^{-1}	0.1 - 2	T
Thermal diffusivity	α	m^2 s^{-1}	10^{-8} - 10^{-5}	T
Mechanical properties				
Thermal expansion coefficient S&L	β	K^{-1}		T
Viscosity	μ	Pa.s		
Practical properties				
Aging, fatigue under thermal stress				
Compatibility with HTF	-	-		T
Corrosion effect/resistance	-	-		T
hydrophilicity				
inflammability	-	-		
(stability)	-	-		
Economical properties				
Availability	-			
Price	-	euros ton^{-1} euros / kWh		
Sustainability				
Concurrence with other applications				
Ecotoxicity				
Embedded CO_2 and other GEG		g GHG ton^{-1}		
Embedded energy		J ton^{-1}		

Table 2.2: Parameters for latent heat storage materials

conditions (when heat losses are negligeable as $\omega\tau << 1$), the heat capacity is given by :

$$C_p = P_o/[\omega\,|T_{ac}|] \tag{2.3}$$

The Joule heating can be replaced by a light-irradiation. The interest is that is not necessary to attach a heater to the sample. The drawback is that the absolute value of the heat capacity is difficult to obtain with high accuracy, because the amount of ac heat flux absorbed by the sample is difficult to estimate. An ac heat flux was applied to the sample by chopping the light beam from a halogen lamp or solar source with a mechanical chopper. Lasers have also been used as modulated sources.

With AC calorimeters, dynamic thermal effusivity ($\sqrt{k.\rho.C_p}$) measurements can be made on a bulk sample with a flat surface up to high frequencies.

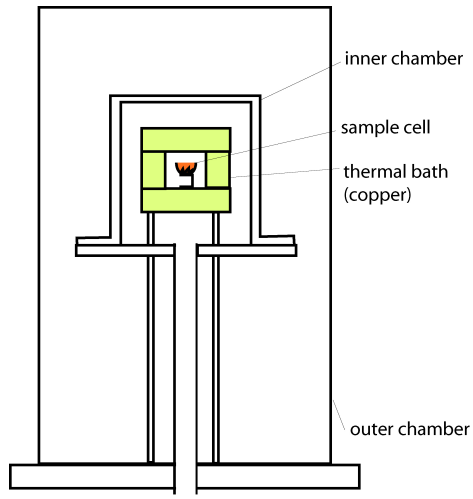

Figure 2.1: Schematic diagram of a Joule heating AC calorimeter

Differential scanning calorimetry

Differential scanning calorimeters (DSC) provide a rapid method for measuring the heat capacity and the latent heat of fusion of a sample when sample vaporization is unimportant [4]. The major advantage of DSC is the ability to obtain fairly accurate heat capacities or the latent heat at a relatively rapid rate.

In a DSC experiment, the reference and sample are heated in a furnace, whose temperature is varied linearly with time (typically in the range of 5 to 10°C/min in the case of latent heat) (fig. 2.2). The difference in temperature between the sample and reference is determined as a function of the furnace temperature. When there is a physical change in the sample, for example, a phase transition, the heat exchanged with the surrounding environment changes, and a temperature difference is observed between the sample and the reference. This difference is usually in the range of some decades, currently 10 to 50°C. Typical results are presented for a commercial PCM (paraffin RT65). The obtained curves are illustrated in Fig. 2.3.

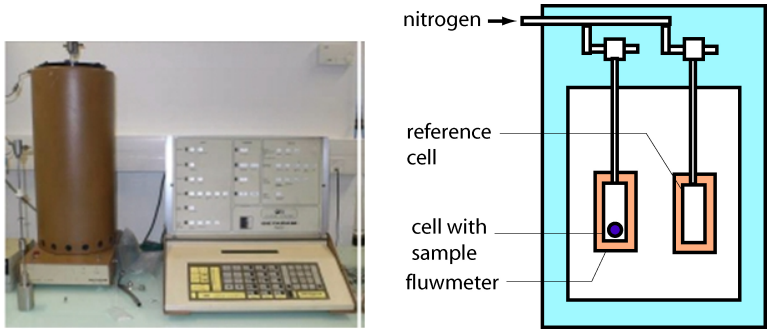

Figure 2.2: Setaram C80 Tian Calvet Calorimeter and scheme of the calorimetric chamber and the two cells.

Power-compensated DSC consists of two independent furnaces placed in the same isothermal surrounding. One furnace contains the sample under study and the other

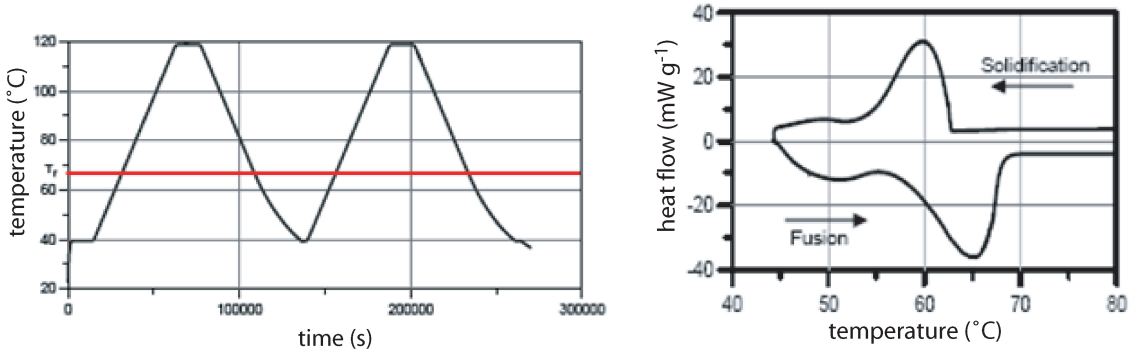

Figure 2.3: Successive heating, stabilisation, cooling cycles with constant heating rate in the range of 5 to 10°C min^{-1} and typical result obtained with the paraffin RT65.

contains a reference sample that has no physical or chemical transformation in the temperature range of interest.

Another method consists of a furnace containing a thermoelectric device to measure heat fluxes and two crucibles, one containing the sample under study and the other the reference material. It is realized by a heat flux DSC apparatus. In this device, the temperature difference between the sample and reference is measured. This difference temperature can be in proportion to the heat exchanged between each crucible and furnace. The heat flux is generally measured by a set of thermopiles.

Note that when a heat flux DSC is integrated with a thermal gravimetric analysis (TGA), the thermal effects can be isolated from those arising from mass changes that occur during a temperature scan.

Temperature modulation has been used in DSC apparatus. The periodic change in the calorimetric signal can complete the interpretation of DSC results.

A high temperature DSC heated with modulated light has been described by Nishikawa and Saruyama [9].

The amount of sample required is from 1 to 30 mg. An accuracy of roughly 1% over a large temperature range the repeatability of the measurements may be better than 0.5%, the accuracy is limited by temperature scale uncertainties, baseline instability, vaporization and equilibration time where diffusion is important.

We can illustrate this part with some results from the characterization of inertized fly ashes (fig. 2.4).

Finally, another way is to utilize the T-history curve [10]. It is more interesting when it is not possible to work on small sample due to inhomogeneities. Figure 2.5 presents the experimental device. If a tube containing a liquid PCM whose temperature is uniform and equal to T_0 ($T_0 > T_m$, T_m is the melting temperature of the PCM) is suddenly exposed to an atmosphere whose temperature is $T_{\infty,a}$ (which can be time dependent), the temperature versus time curve of the PCM, i.e. the T-history curve, is as shown in figure 2.6, where ΔT_m ($T_m - T_s$) is the degree of supercooling.

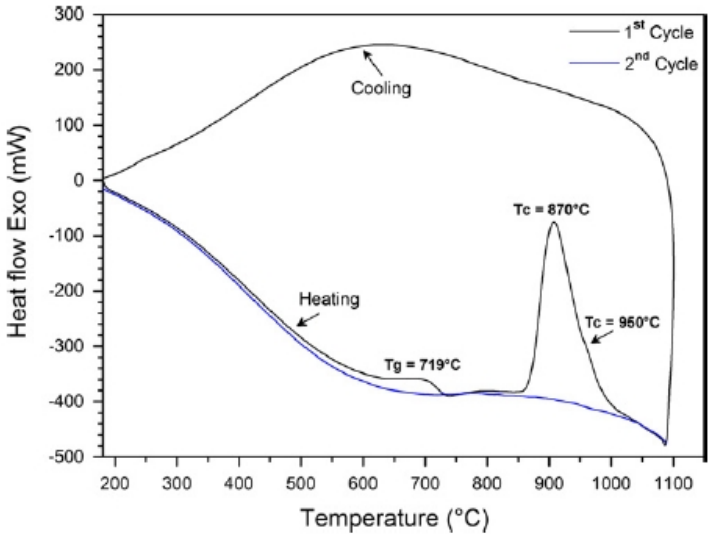

Figure 2.4: DSC curves of Inertized Fly Ashes. In this figure are indicated the glass transition (Tg) and the crystallization (Tc) onset temperatures [11].

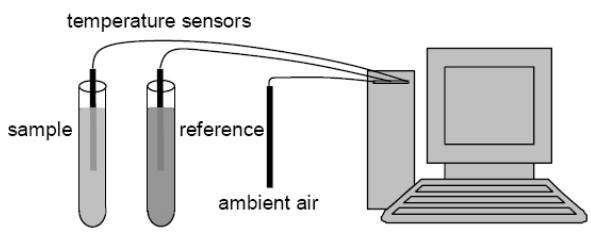

Figure 2.5: Schematic drawing of a T-history device [4]

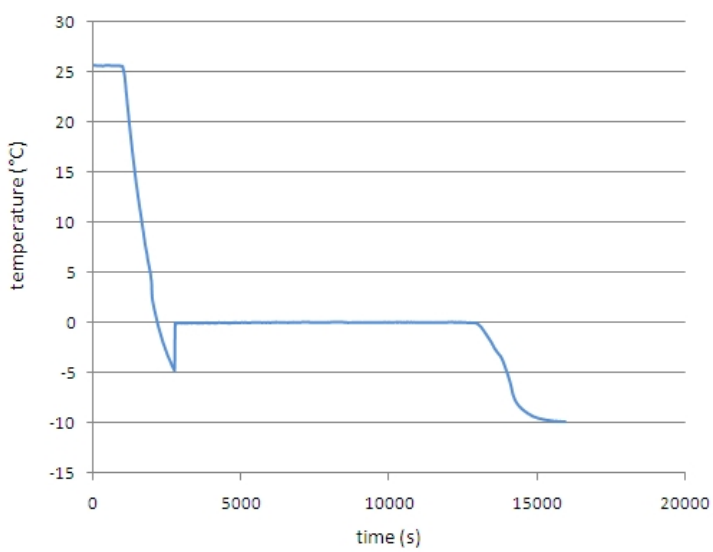

Figure 2.6: Typical temperature-time curve obtained with water

Chapter 3

Selected properties studied in SFERA

3.1 Density of solids

The methods used to measure density for solids are Archimede immersion method, pycnometry and mercury porosimetry. Nevertheless, the most common method is the Archimede immersion method that consists on the loss of weight of a sample when suspended in a fluid of known density (fig. 3.1). This loss is equal to the mass of fluid displaced, from which its volume and hence density can be calculated.

$$\rho_s = \rho_l \frac{m_1}{m_1 - m_2} \tag{3.1}$$

The most common immersion medium is water, but some organic liquids can be used if a problem of compatibility occcurs. The key factors to be respected are the temperature range and the low sensitivity of liquid density to temperature.

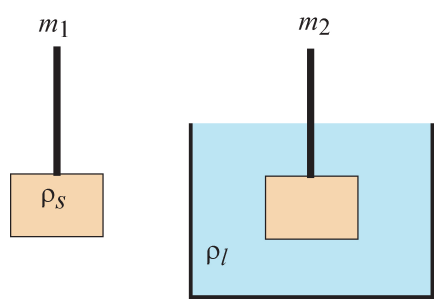

Figure 3.1: Archimede immersion method.

For materials that have open porosity, appropriate conditioning of the material is important before liquid immersion to eliminate or stabilise the residual gas content. Techniques include evacuation and re-pressurisation under the immersion liquid, boiling while immersed in the liquid followed by equilibration, or evacuation followed by high-level pressurisation. From such tests, bulk density and apparent solid density can be determined.

A measurement of true volumes with great accuracy is given by pycnometry. This method is based on the penetration of helium in the sample. Helium gas is able to

penetrate very fine pores down to about 0.2 nm. The value of volume of gas used, corrected for its pressure, serves to determine the apparent solid volume.

In the case of porous materials, the mercury porosimetry technique is interesting to determine the pore size distribution. The pressure applied to mercury to penetrate pores is linked to the pore diameter by Laplace equation [12]. Another techniques to evaluate pore size distribution are shown in the section 3.4.

3.2 Thermal conductivity and thermal diffusivity

Thermal conductivity (k) is the intrinsic property of a material which corresponds to its ability to transfer heat. Heat transfer by conduction involves transfer of energy within a material without any motion of the material as a whole. According to the Fourier's law, the quantity of heat (q) transmitted through a unit thickness (L) in a direction normal to a surface of unit area (A) is proportionnal to the unit temperature gradient (ΔT) under steady state conditions :

$$q = k.A.\frac{\Delta T}{L} \tag{3.2}$$

The thermal diffusivity is determined by the ratio of thermal conductivity and the heat capacity : $a = k/(\rho.C_p)$. It characterizes the dynamic heat transfer.

The thermal conductivity measurement methods are classified as : steady-state and transient methods, absolute and comparative methods, longitudinal and radial heat flow methods [13].

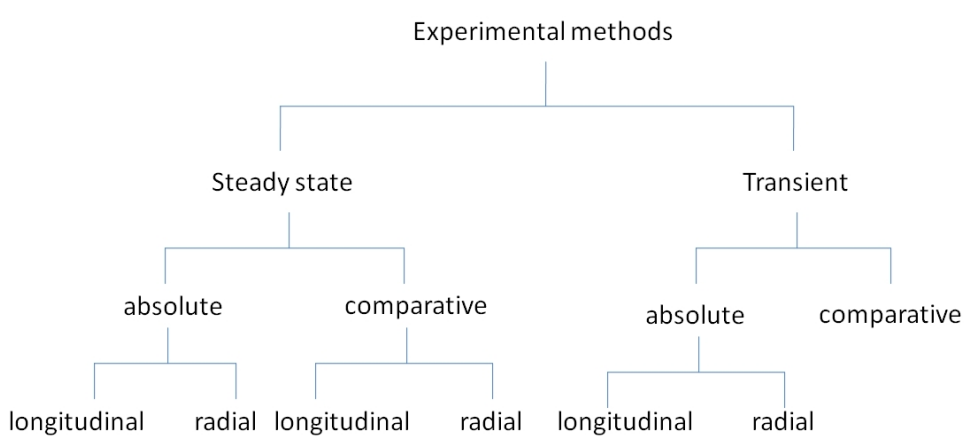

Figure 3.2: Classification of thermal conductivity methods

All the methods are suitable for a limited range of materials, temperatures and properties.

The steady-state methods consist in measuring the heat flow and the gradient of temperature in the material after equilibrium has been obtained. The determination of the thermal conductivity is the direct application of the Fourier's law. In the nonsteady-state methods, the measurement of the rate of temperature change allows the evaluation of the thermal diffusivity.

The comparative methods are based on the knowledge of a material that serves as reference. The heat flow is obtained from the temperature gradient over the reference material with known thermal conductivity. In the absolute methods, the flow is determined directly by measuring the heat by a calorimeter or by the electrical power of the heater applied to specimen.

The classification according to the geometry and the direction of heat flow leads to distinguish the longitudinal and radial heat flow methods.

Generally, the selected geometric form is simply : plate, disk, cylinder. Analytical solutions exist and allow an easier identification of the thermal conductivity. The more practical temperature probes are thermocouples, however IR detectors are interesting in the case of transient methods. To obtain a longitudinal or radial heat flow, a thermal insulation has to be installed. In order to reduced thermal losses due to convection, the tests can be done under vacuum. At high temperatures, the thermal insulation needs mineral materials or ceramics. To enhance this insulation, radiative screens can be used.

Steady-state methods

The sample must be allowed to reach thermal equilibrium before measurements are made. From measurements of the heat flux, temperature difference across the specimen and specimen thickness the thermal conductivity can be determined. To determine the heat flux, the use of electrical heating allows the direct determination of the heat flux. Otherwise, it is possible to measure in a reference material the temperature difference between two isothermal surfaces. The flux that passes through this reference material is imposed to the sample by thermal contact. Another way is to use a heat flux transducer that measures the heat flow through the specimen mounted between two plates.

Longitudinal and radial heat flow methods

- Absolute methods

  In these methods, the range of thermal conductivity imposes the length-to-width ratio to be respected and the adapted geometry. We can note the rod and the plate (or disk) methods (Fig. 3.3). The insulation reduced the thermal losses, but controlled guard heaters can be necessary to ensure longitudinal or radial heat transfer. The rod method is not adapted at high temperatures because heat losses by radiant heat transfer becomes too high.

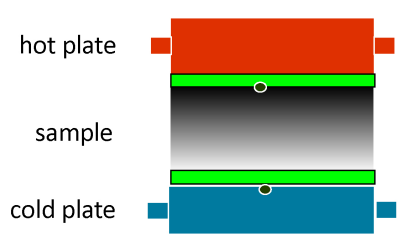

Figure 3.3: Plate method