



# SFERA II

Solar Facilities for the European Research Area

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## SFERA II Project

### Solar Facilities for the European Research Area

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<i>Author(s)</i>	ENEA: S. Sau, A. Tizzoni, N. Corsaro, E. Veca, CIEMAT: M. Navas, A. Martinez-Tarifa
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Date	Name	Signature
16/02/2015	Salvatore Sau (ENEA)	.....

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## INTRODUCTION

The present report is concerned with the description of possible standardized analytical methods to be applied for the characterizations of HTF (heat thermal fluids) and HSM (heat storage materials, both based on specific and latent heat: PCM, phase change materials). Evidently, given the wide variety of fluids that are or can be proposed as HTF/HSM, a precise protocol has to be specifically determined for each of them. The aim of this document is to provide general rules and practical, laboratory validated, examples, to be used as principles for the several materials characterizations; the reported results clearly demonstrated that most of the described procedures are absolutely feasible to be proposed as standard protocol for a large range of materials.

Procedures for thermal oils are well established and were already addressed in the SFERA I project (see task 12.1, R12.6 “Guidelines for Testing of CSP components”).

The first part is focused on thermo-physical characterizations; the second on material compatibility (corrosion) tests procedures.

The reported techniques are mostly dedicated to nitrate and nitrite mixtures, regarding the other possible materials:

- Halides can be analyzed respect to their specific heat, viscosity, heat conductivity, density and chemical composition in exactly the same way and with the same procedures described for nitrates/nitrites. Concerning their thermal stability, their oxidation under air, with contemporary release of halogens, is the major issue; therefore, also in this case, the degradation onset can be defined as the temperature at which alkaline or heart alkaline oxides are detectable.
- Carbonates present characteristics similar to molten nitrates/nitrites but a quite higher freezing points; for this reason the experimental equipment necessary to investigate these materials in their molten state can be very difficult to get and, in case, pretty expensive. Carbonates (especially the alkaline ones) are expected to present far higher thermal stability limits respect to nitrates.
- Liquid metals are in general chosen with low melting features, they can be analyzed with practically the same methodologies of molten nitrates, provided the compatibility with the equipment materials is ensured. Chemical analysis can be performed by solubilization in water (by reacting them with acids, for example). As said, the main issue concerning these fluids is their compatibility with construction materials.
- Concerning solid fillers as HSM, the same below described techniques can be employed for the specific heat. More than thermal stability, the compatibility with the complementary HSM fluid needs to be investigate; this topic depends specifically on the type of filler under considerations, and won't be addressed in this report. Apparent density and, especially, heat conductivity can be determined with simpler methods than the ones for molten salts, where, for instance, the effects of convective heat must be separated from heat conductivity.
- Gases eventually employed as HTF are species of large use (steam, CO<sub>2</sub>...) and in general quite well characterized.

The first part of this report is organized as follows:

- Initially, the chemical-physical parameter is defined
- Then, an experimental equipment is suggested for its quantification, according to: economic convenience, commercial availability, verified sensibility, accuracy and precision for the required determination

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- A proper sample handling and preparation is proposed, along with an experimental procedure to obtain an useful accuracy and precision
- Finally, and when possible, a practical example, from ENEA experience, is illustrated
- 

The following table summarizes the report content regarding thermo-physical features determinations.

Properties	Interest for HTF	Interest for HSM	Equipment proposed
specific heat	Capacity of solar heat transfer, by sensible heat, to the storage system	Capacity, as sensible heat, of heat storage	Differential scanning calorimeter (DSC)
melting points (phase diagrams)	Determination of the lowest T <sub>liq</sub> (liquidus point)	Determination of the lowest T <sub>liq</sub> (liquidus point)	Differential scanning calorimeter (DSC)
latent heat		Capacity, as latent heat, of heat storage	Differential scanning calorimeter (DSC)
viscosity	Determination of the necessary pumps hydraulic head	In "Archimede " like configurations HTF and HSM are the same fluid, and, in general the HSM is transferred (going through a heat exchanger) from a heat to a cold tank). In thermocline based system, employing natural or forced convection, it is as well a parameter of the utmost importance.	Rheometer
density	Related to heat capacity; capability of heat storage per volume	Related to heat capacity; capability of heat storage per volume	Archimedean method (total immersion of a probe of known weight)
heat conductivity	Necessary parameter to determine the heat exchange surfaces	Necessary parameter to determine the heat exchange surfaces	Homemade or commercial equipment? To be defined
thermal stability	Maximum operative T	Maximum operative T	See the proposed set up
chemical composition	Composition and impurities check	Composition and impurities check	Ion Chromatography (Inductively coupled plasma atomic emission spectroscopy (ICP-AES) or polarography for traces determination). Thermogravimetry or Karl Fisher titration for water content.



## THERMOPHYSICAL CHARACTERIZATION METODOLOGY

### MELTING POINTS, SPECIFIC AND LATENT HEAT

#### THEORY – MELTING POINTS

The melting point of a solid is the temperature at which it changes state from solid to liquid at atmospheric pressure. This transition temperature is called “freezing” point where it indicates the changes from the liquid to the solid phase. If hysteresis phenomena are not present, melting and freezing points are approximately equal for pure substances. Where a mixture with two or more components is presents, phase diagrams are drawn in order to describe the phase boundaries at equilibrium conditions. By working at a fixed pressure, for instance at 1 bar, phase diagram can be determined in function of the mixture composition. In order to simplify the interpretation, it is useful to define two parameters: the liquidus temperature ( $T_{liq}$ ) as the temperature at which the mixture starts solidifying by cooling down, and the solidus temperature as the onset for liquid formation by heating up.

#### THEORY - SPECIFIC HEAT

The heat  $Q$  absorbed by a body when it is heated is proportional to the temperature according to the relation:

$$Q=C (T_2-T_1)$$

where  $C$  is a quantity known as heat capacity. The heat capacity is directly proportional to the mass of the heated body according to the law:

$$C= m c_s$$

so as to obtain

$$Q=m c_s (T_2-T_1)$$

where  $c_s$  is called specific heat.

The *specific heat* is the heat that must be interchanged for mass unit of a given substance, at the  $T$  temperature, in order to make vary its temperature of  $1^\circ \text{K}$ . The temperature is a state function and its variation is not dependent on the particular transformation. Conversely, the heat is not a state function but depends on the type of processing carried out, exactly as their relative ratio: the specific heat.

$$c_s = \frac{dq}{dT}$$

In adiabatic conditions the specific heat is not definable, as the heat exchanged is null. Conversely, in first order phase change, the temperature remains constant while the heat exchanged is non-zero, therefore the specific heat is infinite. So it is possible to define different specific heats depending on the thermodynamic transformation.

The instrument used in this work (DSC) is similar to an open system with only heat exchange, in which do not intervene elements that can produce a change in pressure.



From Eulerian formulation of the first law of thermodynamics:

$$c dc + g dz + dh = dq + dl$$

and taking into account the fact that within the instrument there is no change in kinetic, work and potential energy, it is possible to write:

$$dh = dq$$

from which we obtain the specific heat at constant pressure:

$$c_p = \frac{(dq)_p}{dT}$$

expressing now the differential enthalpy:

$$dh = dh(T, p) = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

for isobaric transformation:

$$c_p = \frac{(dq)_p}{dT} = \left(\frac{\partial h}{\partial T}\right)_p$$

---

## THEORY – LATENT HEAT

A specific latent heat (L) expresses the amount of energy in the form of heat (Q) required to completely effect a phase change of a unit of mass (m), usually 1kg, of a substance :

$$L = \frac{Q}{M}$$

From this definition, the latent heat for a given mass of a substance is calculated by:

$$L = Q \cdot M$$

Q is the amount of energy released or absorbed during the change of phase of the substance (in kJ), m is the mass of the substance (in kg), and L is the specific latent heat for a particular substance (J/g), either L<sub>f</sub> for fusion, or L<sub>v</sub> for vap.

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## INSTRUMENT: DIFFERENTIAL SCANNING CALORIMETRY- DSC

The Differential Scanning Calorimetry, also known by the acronym DSC, is one of the most commonly used techniques for thermal analysis. The basic principle consists in obtaining information on the test material while it is being subjected to cycles of controlled heating and/or cooling. In particular, it goes to monitor the difference in heat flow between the test sample and a reference, which remains inert to temperature changes, while both are bound to the same heat treatment. The differential measurement of the system is extremely important because the resulting signal can be studied independently of all those thermal effects external to the system, allowing receiving outputs about the behavior of the material regardless of the test conditions.

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The instrument is prepared by placing on the housings two identical pans chosen so as to withstand the test temperatures without interacting with the sample under examination. One of the two pans will remain empty because it will serve as a reference for differential measurement. After inserting the thermal program (a temperature ramp), inside the furnace containing the material to be analyzed, it is possible to work under air or in an inert atmosphere with a continuous and uniform flow ( $N_2$  or chromatographic air). The heat transferred from the furnace heats both the sample and the reference in the same way; a control circuit of the temperature compares the mean value between the temperatures detected on the sample and on the reference with the one selected by the temperature programmer. Any temperature variation is due to phenomena that arise in the material to be analyzed: an exothermic reaction will raise the temperature of the sample while an endothermic will do the opposite.

The value of the difference then provides a correction signal of heating units necessary to perform scans of temperature. The sample can be in liquid form, solid, powder, films or granules but still present in small quantities (20-70 mg, depending on the pan used) and should be well distributed in the sample holder. The weight procedure must be carried out with a balance presenting at least an accuracy to the tenth of milligram. In case of hygroscopic substances, it is important to determine the weight of the dry material; the most feasible way is to weigh the sample and the holder (pan plus lid) together and dry them inside the instrument, under water-free gas atmosphere, by heating up at 250 °C (10 °C/min) and keeping that temperature for 30 min; then, the holder plus the sample are rapidly weighed again, repositioned in the calorimeter, and the DSC measurement program (always under dry atmosphere) will be carried out.

During the experiments a system of thermocouples collects the temperature data and sends them to a specific software, generating output the DSC diagram. The differential heat flow is directly proportional to the temperature difference between the output signals from the thermocouples. The DSC diagrams are graphs in which the differential speed of heating (in mW) is shown as a function of temperature or time of reaction. After the choice of an adequate base line, the area under the curve is the total heat developed during the process.

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## MELTING POINTS AND LATENT HEAT MEASUREMENT: DESCRIPTION OF THE METHOD

Before starting the measurements, a calibration of DSC has to be performed by placing samples of indium, zinc and tin (whose onsets, that is, initial solidification and liquefaction, and latent heats are known from literature) in the pans.

After the instrument has been calibrated, or calibration has been verified, 20-30 gr of the sample are placed inside a 100 $\mu$ l aluminum crucible (pan) and the lid is sealed. In case of mixtures presenting a very low enthalpy of phase change (such as, for instance, ternaries/quaternaries containing calcium nitrate) at least 100 mg must be used. As reference, an empty crucible (100 $\mu$ l of aluminum with lid) is used. The measurement is directly carried out using a 10 K/min ramp, there is no the necessity for a blank curve.

Onset (liquidus and solidus) phase change temperatures are determined using the instrument software (see example below) or by determining a criteria to detect the phase change onset.

Latent heat is calculated by integrating the endothermic (liquefaction) or esothermic (solidification) peaks. The effect of specific heat change between the two phases is well compensated by integrating from the baseline just before the peak to the baseline just after the transition.

Provided DSC is properly calibrated, the method leads to little measurement errors that can be estimated, by statistical analysis, below 3% for a single measurement.





## SPECIFIC HEAT MEASUREMENT: DESCRIPTION OF THE METHOD

It is possible to measure heat capacity values of molten salts with the use of a known heat capacity substance as reference. We used the sapphire ( $C_{p_z} \approx 1 \div 1.1 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ ) [1], as in the following:

$$W_z = C_{p_z} \cdot m_z \cdot \beta \cdot \Delta T$$

$$W_{\text{salt}} = C_{p_{\text{salt}}} \cdot m_{\text{salt}} \cdot \beta \cdot \Delta T$$

where  $W$  is the absorbed power,  $C_p$  is the heat capacity,  $\beta$  is the temperature ramp with the corresponding  $\Delta T$ ,  $m$  is the weight. From the ratio between the two equations we obtain:

$$\frac{W_z}{W_{\text{salt}}} = \frac{C_{p_z} \cdot m_z}{m_{\text{salt}} \cdot C_{p_{\text{salt}}}}$$

and the specific heat of the salt:

$$C_{p_{\text{salt}}} = \frac{C_{p_z} \cdot m_z \cdot W_{\text{salt}}}{m_{\text{salt}} \cdot W_z}$$

A modulated temperature ramp is used, an example is shown in Figure 1:

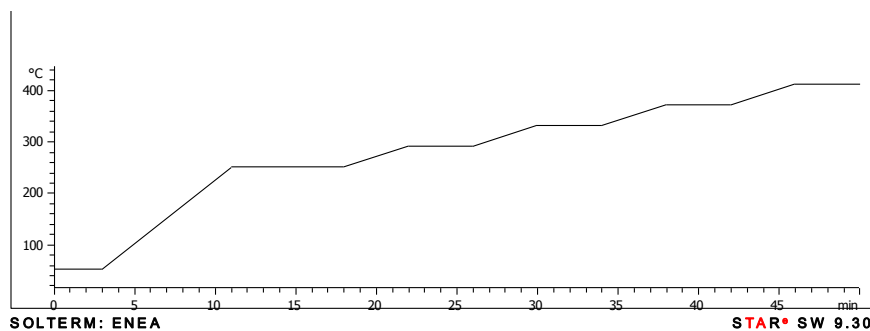


Figure 1 Temperature ramp example

After calibrating the instrument, two pans were placed on the two DSC zones. In order to better evaluate the baseline, a modulation like method is preferably to be used, in this way a series of isothermal (typically 4-5 minutes) and temperature ramp (typically 10 K/min for 4 -5 minutes) steps are alternatively set, the absorbed heat can be measured by the height or the area of the obtained rectangular like peaks. The weight of the sample must be around 35-40 mg, and of sapphire 40-50 mgr. Crucibles (pans) are of aluminum and with 100 $\mu$ l of capacity.

This is the standard DSC method for this instrument and it is divided in three distinct phases.

The pan used as a reference has been left empty during the whole measurement range and does not have the lid, in order to increase the temperature difference between two pans, and, consequently, improve the reproducibility of the blank curve, while the other one was filled in each step.



- **Blank:** controlled heating is carried out on both empty pans as calibration;
- **Sapphire:** controlled heating is carried out on both pans; the reference pan remains empty while in the other one are inserted 2 known weight sapphire disks (about 40 mg), necessary for the comparison with the salt.
- **Sample:** controlled heating is carried out on both pans; the reference pan still remains empty while in the other one is inserted a known amount (approximately 40 mg, measured it on a precision balance) of the mixture of salt and then sealed.

This method is simple to operate, and it will take around 3 hours per sample. By performing a statistical analysis, precision can be estimated by measuring data dispersion over 5 samplings and measurements, and repeat this method 5 times with different mixtures, nitrites and nitrates. Using a Gaussian error distribution, a mean value with estimated error of 10% can be obtained in a confidence range of 90%. Hence, this is the can be considered as a conservative averaging error if five different samplings and analysis of a mixture are performed. Increasing the sampling figure, the precision of the average value will decrease inversely to the square root of the sampling number, but, evidently, measurement time will increase.

## EXAMPLE OF MELTING POINTS (PHASE DIAGRAM), LATENT HEAT AND SPECIFIC HEAT MEASUREMENT

For the determination of the specific heat of the mixtures of salts, it was used "Mettler Toledo DSC". Of course, any other brand can be employed provided the allowed temperature range is feasible

The instrument, present at the ENEA laboratories, is equipped with a silver oven capable of reaching up to 700 ° C, in the bottom of which it is placed a ceramic coating sensor, which protects from contamination, connected with a system of 56 gold thermocouples so as to have a very precise measurement and compensate any possible temperature gradient. This ensures flat baselines and reproducible results with a theoretical error less than 0,04 μW. The ceramic coating has the housings for two pans (Aluminum 100 ul) covered by perforated lids (to allow the release of any gases).

The tests were carried out in air atmosphere and free cooling. The instrument interacts with a computer using "Star Evaluation" software.

Figure 2 shows the onset temperatures and measured latent heat for, respectively, NaNO<sub>3</sub>, KNO<sub>3</sub> (130 °C is a solid KNO<sub>3</sub> phase transition) their eutectic mixture (50/50 mol/mol), and the "solar salt" (60/40 wt/wt). The onset temperatures are determined by the intersection of two straight lines, one corresponding to the baseline before the peak, and another one tangent to the peak inflection point. As expected, the solidus and liquidus temperatures are the same for the eutectic mixture. Fig. 3 shows the obtained NaNO<sub>3</sub>/KNO<sub>3</sub> phase diagram.

Figure 4 reports a comparison for sample and sapphire heat flows using a modulated ramp (see Fig. 1), Fig. 5 shows the obtained values respect to temperature and the error bars.

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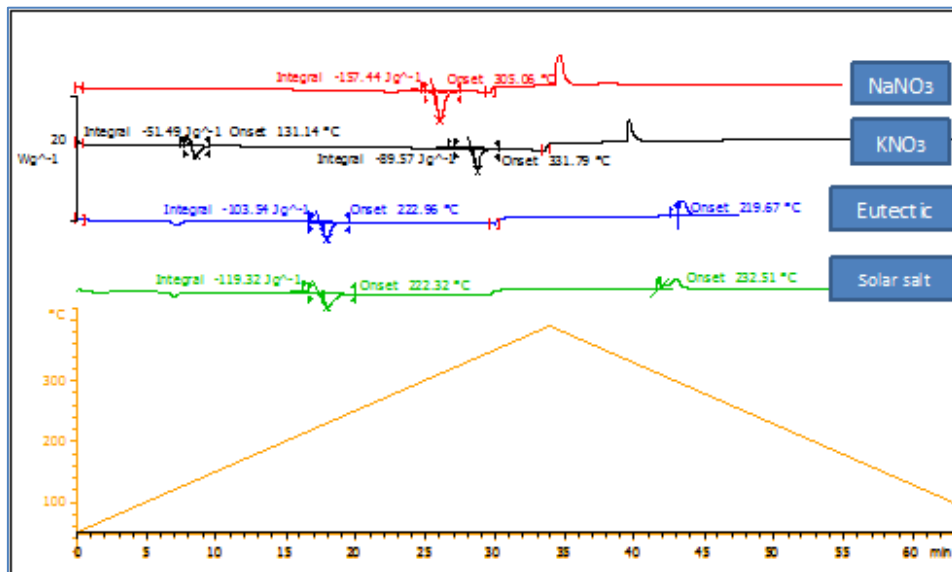


Figure 2 The onset temperatures and latent heats NaNO<sub>3</sub>, KNO<sub>3</sub> their eutectic mixture (50/50 mol/mol), and the “solar salt” (60/40 wt/wt) and the employed temperature ramp (10 K/min)

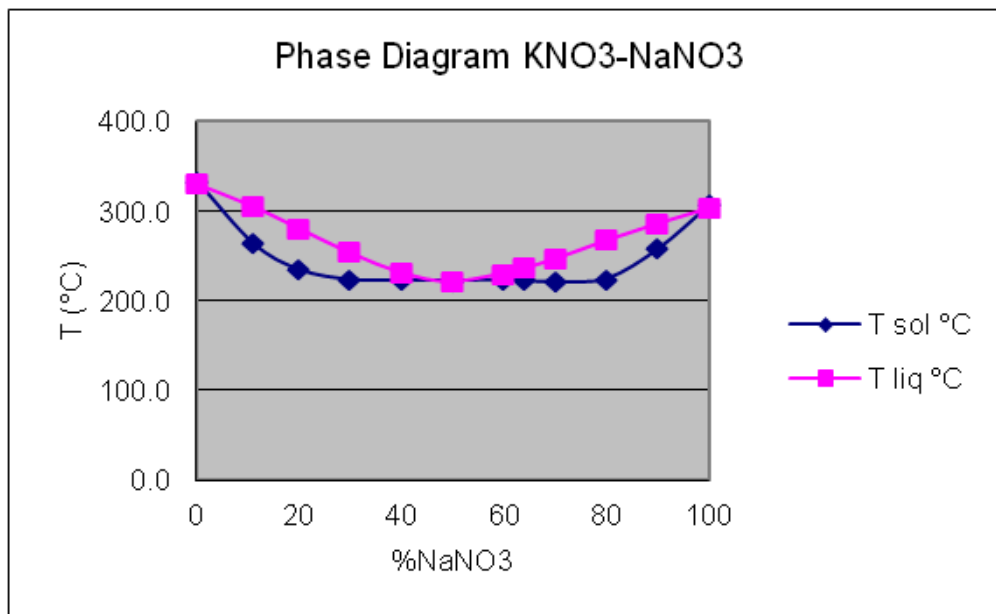


Figure 3 KNO<sub>3</sub>/NaNO<sub>3</sub> phase diagram (P 1 bar)

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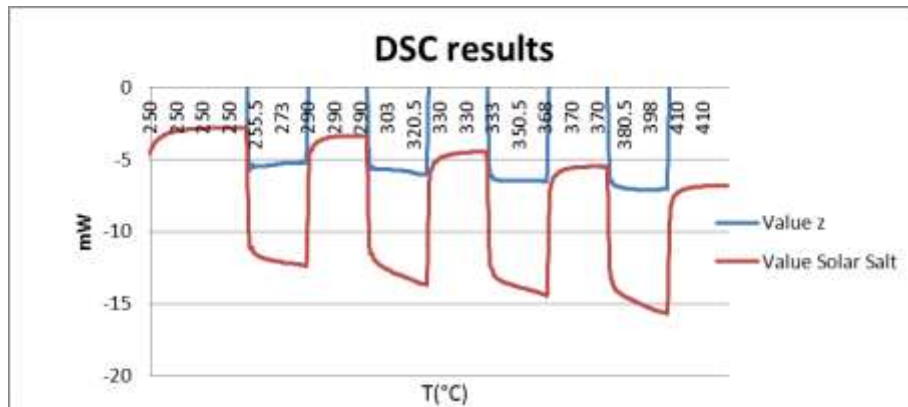


Figure 4 DSC Results and the Cp obtained, on the abscissa are the temperatures in °C

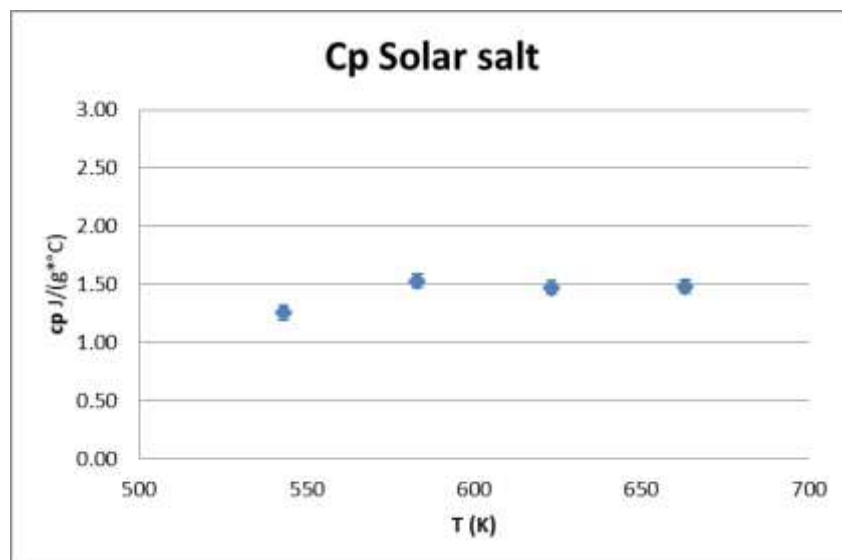


Figure 5 Cp Solar Salt



## VISCOSITY

### THEORY: VISCOSITY

Viscosity is commonly defined as the difficulty that a mass of a fluid (a liquid or a gas) has to change in shape.

This phenomenon depends on the cohesion forces existing between the molecules of the fluid, which exert a braking action to the free sliding between the substance layers.

To correctly interpret the phenomenon it is to be considered the movement of a mass, for example a liquid, inside a cylindrical conduit, each of the concentric layers of a lamellar substance slides on the adjacent one with a speed that is maximum for the central part, while gradually decreases for those more external, until the speed is equal to zero for the lamellar layer adhering to the wall of the duct.

Viscosity is a physical parameter that describes a real fluid; in a fluid there are viscous forces that are expressed as resistance to changes in shape of the fluid mass.

Between the fluid and the total area of a solid body immersed in it, two phenomena occur:

- speed of the fluid in contact with the surfaces of the immersed body becomes zero,
- presence of shear forces parallel to the direction of the velocity.

There are also two consequences:

- in these fluids it is possible the sliding of a fluid layer respect to another;
- dragging forces are exerted on the surfaces of submerged bodies, in contact with their walls, or on the walls of the container that encloses the moving fluid.

The friction force can be seen as the amount of energy required to move a body that slides against another. Instead the viscosity is the friction force exerted by two foils of fluid to be placed in motion one against the other.

Consider a model in which a fluid is delimited between two parallel planes and:

-F is the force applied tangentially to the linear surface of the fluid;

-A is the area of the foil surface of the fluid;

-u is the speed of the fluid;

-h is the distance from the foil adhering to the bottom of the container.

The fluid, being viscous, has a zero velocity in contact with the planes.

Being force and surface parallel, their relationship represents a shear stress:

$$\tau_{xy} = \frac{\vec{F}}{\vec{A}}$$

The shear stress is proportional to the velocity  $\vec{u}$  and inversely proportional to the distance of the two plans. This dependence is called Newton's law for viscous fluids:



$$\tau_{xy} = \mu \frac{du_x}{dy}$$

in which the coefficient of proportionality  $\mu$  takes the name of dynamic viscosity for a fluid ( $Pa \cdot s$ ). We assume that in this model that the gradient of velocity (shear rate) is uniform between the two planes and can be written as the ratio of the speed  $u_x$  and the distance  $y$ :

$$shear - rate = \gamma = \frac{du_x}{dy} = \frac{u_x}{y}$$

$$\gamma = \frac{\frac{cm}{s}}{cm} = s^{-1}$$

The total force  $F$ , acting on the upper plane, exerts its effects on a unit of surface area  $A$  of the same plate, then the ratio  $F/A$  represents the shear stress  $\tau$ :

$$shear - stress = \tau = \frac{dF}{dA} = \frac{F}{A}$$

$$\tau = g \frac{\frac{cm}{s^2}}{cm^2} = \frac{dyn}{cm^2}$$

Then the viscosity is defined as:

$$\mu = \frac{shear\ stress}{shear\ rate} = \frac{\tau}{\gamma}$$

$$\mu = \frac{\frac{dyn}{cm^2}}{\frac{1}{s}} = \frac{dyn \cdot s}{cm^2} = \text{Poise}$$

If the viscosity is measured at different shear rates and the results obtained are equivalent, the material can be considered Newtonian in the field of shear rate in which the measurements were made.

## INSTRUMENT: RHEOMETER

The principle of operation of a parallel-plate type rotational rheometers, can be described by the following relations:

$$C = \int_s r t d s$$

where  $C$  is the torque applied to the rotor surface on the sample and  $d$  the gap. Transforming the integral in spherical coordinates and taking into account that if the fluid is Newtonian the viscosity is not a function of shear rate:

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$$C = \int_0^R \int_0^{2\pi} r \left( \mu \frac{\omega r}{d} \right) r dr d\theta = \int_0^R \int_0^{2\pi} r^3 \mu \frac{\omega}{d} r dr d\theta = \mu \frac{\omega R^4}{d} 2\pi$$

obtaining the viscosity:

$$\mu = \frac{2dC}{\omega R^4 \pi}$$

## DESCRIPTION OF THE METHOD

Before proceeding to the measurement of the viscosity, some daily operations of calibration of the instrument must be performed, such as calibrate rheometer inertia, rotational mapping and set the zero gap. The exact calibration (verification of calibration) steps depend on the particular instrument employed.

Temperature, shear rate, shear stress, pressure, time and the history of the sample can influence measurements. To define how the viscosity changes as a function of these parameters, it is necessary that the others are kept strictly constant. Only with some restrictions Newton's law of viscometry is valid, such as, it is necessary to have laminar and stationary flow, absence of slippage, homogeneity to the sample, and avoid degradation of the sample.

To measure the viscosity of the solar salt, a parallel plate geometry is used, that is a plate configuration both for the rotating, upper part, and for the fixed, sample holder, the latter with a diameter of 25mm; in order to contain the melt, the sample holder is provided with a rim (see Fig. 6, on the right). The geometry material must be resistant to corrosion, stainless steel is in general a proper material for this purpose. The quantity of sample to be used depends on the melt density, as far as nitrates/nitrites mixtures are concerned, about 2 g is the quantity to be inserted in the holder. The geometry is located inside a thermostatic chamber, before starting the measurements the sample is heated at a temperature above its melting point and not below 250 °C, and kept under those conditions for 30 min, in order to remove all water eventually present. The gap is set equal to 350 μm, shear rate is varied from 100 to 500 s<sup>-1</sup> (15 points) at the several temperatures (it is important not to operate above the mixture stability limit, see thermal stability paragraph).

By using a statistic method similar to the one described for heat capacity, it was established, at each temperature, and using four samplings, a conservative average error of 3%.

## EXAMPLE OF VISCOSITY MEASUREMENT

The viscosity of molten salts at temperatures up to 500 °C was determined using a rheometer AR2000 ex (Fig. 6). The rheometer has a rigid structure that includes a base and a column. In the upper part of the instrument is placed a motor with an armature which constitutes the rotating spindle. To control the angular inclination of the spindle an optical reader is present. During the measurement the sample is positioned in a homogeneous way inside a plate (stator) of stainless steel mounted on a fixed base; another plate (rotor), integrated with the upper part of the rheometer, transfers to the sample the rotational motion of the spindle; everything is enclosed in a small thermostatic furnace.



Figure 6 Rheometric system used and sample positioning for viscosity measurement

Calibration steps:

- 1- make sure to have an air flow of at least 10 l/ min on the instrument;
- 2- testing inertia unladen, then with geometry;
- 3- perform "mapping", which is the real calibration of the instrument to identify its points of reference;
- 4- set "zero gap".

Then the sample was prepared and analyzed as described above.

Figure 7 shows, as an example, the viscosity respect to temperature, of the solar salt mixture ( $\text{NaNO}_3/\text{KNO}_3$  60/40 wt%) and the comparison of the results with the ones from literature [2].



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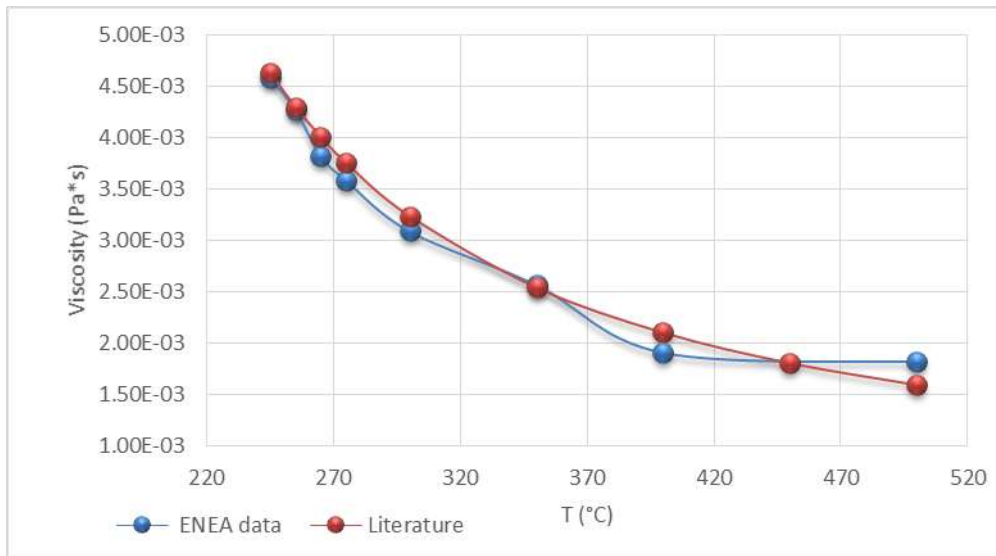


Figure 7 Solar salt (NaNO<sub>3</sub>/KNO<sub>3</sub> 60/40 wt%) viscosity vs. temperature compared with literature data [2]



## DENSITY

Density measurements of mixtures are based on Archimedes' principle. It consists in immersing a solid of known volume, with negligible thermal dilation and connected to a dynamometer into a melt solution where temperature was homogenized. The solid measured weight loss evidently corresponds to the Archimedes buoyancy force. Experimental setup is under assessment and is not currently possible to provide data about the precision of the method. Anyway, it is possible to estimate that the precision is directly correlated with the sensibility of the employed dynamometer. Clearly, the more salt volume is displaced, the more precise is the measured weight difference. The measurement conditions are still to be optimized, however, a stainless steel mass of at least about 1 liter is advised to be used as an immersion object in the molten salt.

## HEAT CONDUCTIVITY

Will be performed heat conductivity (K) measurements of mixtures, using calorimeter in a different way. Alternatively, a commercial equipment based on hot-wired could be used. Considering literature data [3], a great spread among the reported data can be observed; evidently the precision of the measurement method employed was not so far particularly good. It is necessary, in the next future, to establish the best procedure by comparing different instruments and equipment respect to their accuracy and precision.



## THERMAL STABILITY

### THEORY: GENERAL CRITERIA ON THERMAL STABILITY

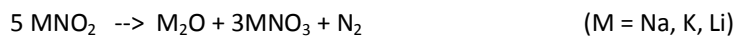
There is not, to date, an agreed criteria to determine the upper temperature of employment for molten salts. Considering molten nitrates, in general, the degradation mechanism consists of two steps, firstly nitrites and oxygen are produced:



This reaction is reversible (that is, it is possible to obtain again the nitrates from nitrites and oxygen (air)).

Furthermore, the presence of nitrites should not worsen significantly the MS corrosion compatibility with the material commonly employed in the CSP plants, nitrites are highly soluble in nitrates and their presence leads to a decrease of the MS mixture freezing point. For these reasons, nitrites formation alone is not considered a cause of molten salts degradation.

In turn, nitrites can lead to a second reaction:



In this case the process is not expected to be easily reversible, so alkaline oxides can accumulate; they can increase the melting point of the mixture, and, in contact with atmosphere, rapidly react producing alkaline hydroxides (very corrosive) and carbonates. These species present a limited solubility in molten nitrates (around 5% in weight percentage for carbonates [4]), so they can precipitate leading to problems with valves and pipelines occlusions.

In summary, oxide formation can be considered as the discriminating point in order to determine the upper stability temperature for MS employment as heat thermal fluids (HTF) or heat storage materials (HSM).

In case nitrites are under investigation, re-oxidation can be (slowly) present at temperature below 400 °C, above that temperature nitrogen formation is the indication for material degradation into oxides [5].

Regarding other salts, oxidation can be a major point for halides heated up under air, especially in presence of heart alkaline cations; therefore, alkaline or alkaline oxides formation can be applied as well as criteria to determine the upper thermal limit onset. Given the few data in the scientific literature it is not possible to address this topic here, anyway the potential interest in using halides mixture as PCM (phase change materials), or as additives for nitrates mixtures, will require in the very next future an accurate experimental analysis on that field.

### INSTRUMENT: EXPERIMENTAL SETTING

At least (about) 1500 grams (in order to make the amount of evolved gases detectable) of salt mixture should be placed inside a heated stainless steel (304 SS or other resistant to corrosion in the experimental conditions) autoclave placed inside a heating system.

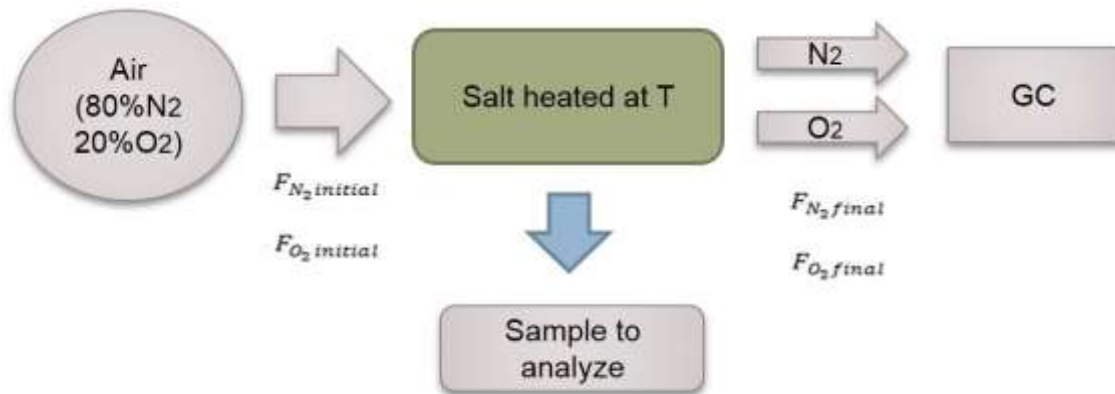


Figure 8 Scheme of the set-up to investigate molten salts thermal stability

Temperatures were measured by at least one thermocouple preferably immersed at about the center of the melt; during each test the temperature value could vary within an interval of  $\pm 5$  °C.

Considering that the nitrite recombination with oxygen leading to back to nitrate can be considered a very slow process, especially at low temperatures, the effect of this reaction during the cooling step can be neglected, and the nitrate molar fraction obtained during the previous test, can be considered as the starting point when the mixtures were heated up again.

A continuous flow of air is necessary in order to carry out experiments under 1 bar of air; supposedly these are the conditions of a “real” molten salt tank (excluding transitory situations), that is reported to be vented to the atmosphere.

The exiting gas flow is the sum of the inlet air and the produced gases inside the reactor. In general an inlet flow of around 5 Nml/min can be enough, in fact, excluding the beginning of the reaction, where, considering nitrates mixtures, tenths Nml/min of oxygen can be produced, only few Nml/min of oxygen are generated during the decomposition (from 1.5Kg of molten salt). From 700 °C upward the air inlet flow should be raised to about 30 Nml/min.

From the GC analysis concentrations are obtained and we are able to distinguish oxygen from nitrogen. So, by knowing  $O_2$ ,  $N_2$  inlet it is possible to obtain the gas flow of  $O_2$  and  $N_2$  produced. It is better to use flow meters at the exit of the reactor to determine the exiting flows, otherwise it can be possible to calculate the gases flows by volume fractions by using mass balance considerations:

$$F_{N_2\text{produced}} = F_{N_2\text{final}} - F_{N_2\text{initial}} = X_{N_2\text{final}} * F_{TOT\text{ final}} - X_{N_2\text{initial}} * F_{TOT\text{ initial}}$$

$$F_{O_2\text{produced}} = F_{O_2\text{final}} - F_{O_2\text{initial}} = X_{O_2\text{final}} * F_{TOT\text{ final}} - X_{O_2\text{initial}} * F_{TOT\text{ initial}}$$

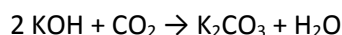
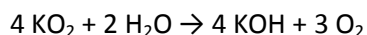
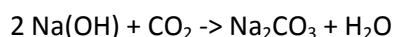
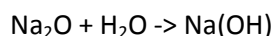
Periodically (daily or every few hours) some grams are sampled, for instance from the bottom of the autoclave by a valve (in Inconel or other equivalent), and analyzed respect to nitrites and oxides contents. Nitrites content is quantified by ion chromatography and alkaline oxides (as hydroxides or, eventually, carbonates) by titration with HCl.



Comparing the presence of nitrites measured by chromatography with those estimated by the produced oxygen flow, it is possible to verify the mass balance in the range of instrumental error.

## DESCRIPTION OF THE METHOD

To determine the upper stability temperature, it is, as said, discriminating the occurrence of alkaline oxides. As reported above, it is possible to detect this onset by two methods: nitrogen evolution by GC or direct melt analysis by acid base titration. Between the two procedures, the later seems the most sensible one, in fact it is clearly not very easy to investigate the increase of nitrogen concentration in the air over a molten salt storage tank. On the other hand, the presence of alkaline oxides (or peroxides and superoxides) can be in principle be detected with great precision by dissolving a proper amount of sampled and frozen molten salt in water where the following reaction are present considering, as an instance, the binary solar salt mixture:



In order to determine the detection limit, that is the alkaline weight percentage value that can be detected with 100% of confidence level, the following method can be employed, using as an example solar salt.

15 grams of solar salt are spiked with the following amount of hydroxides added as NaOH 0.1M solution:

Sample	Solar salt (g)	NaOH 0.1 M added (ml)	Nominal expected value (wt %)
0	15	0	0
1	15	0.152	0.002
2	15	0.304	0.003
3	15	0.608	0.007

In the method we are proposing, about 2.5 grams of each sample are titrated with HCl 0.05N (employing a Mettler Toledo T50, equipped with a glass electrode for the determination of the equivalent points). In order to estimate Type I (that is the probability to reject a true null hypothesis, a "false positive") and Type II errors (that is probability to reject a false null hypothesis, a "false negative"), five specimens were taken from each of the 4 samples.

The instrument detection limit is 0.01 ml of HCl 0.05N. In the following table are reported the results obtained. For the time being, the method accuracy, that is the deviation respect to the nominal value, is not considered.

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	%	%	%	%	%
Sample	Test 1 (2.5g)	Test 2 (2.5g)	Test 3 (2.5g)	Test 4 (2.5g)	Test 5 (2.5g)
0	n.d.	n.d.	n.d.	n.d.	n.d.
1	d	n.d.	n.d.	n.d.	n.d.
2	d	d	d	d	d
3	d	d	d	d	d

\*n.d. stands for not detectable, below the instrument detection limit

\*\* d stands for detectable, above the instrument detection limit

It is interesting to note the absence of false positive samples, evidently due to the purity of the molten mixtures used for CSP applications. Regarding spiked samples, from 0.003% up, it is clear that the presence of alkaline oxides can be detected with practically 100% of probability confidence.

In summary, by a single sampling of just 2.5 grams from whatever quantity of molten salt, it is possible to surely detect the very beginning of occurrence of molten salt degradation. Consequently a periodic (daily, as an instance) check of the melt can be very easily performed.

## EXAMPLE OF THERMAL STABILITY TEST

The experimental set-up in Figs. 9 and 10 was employed to investigate the stability of the solar salt mixture

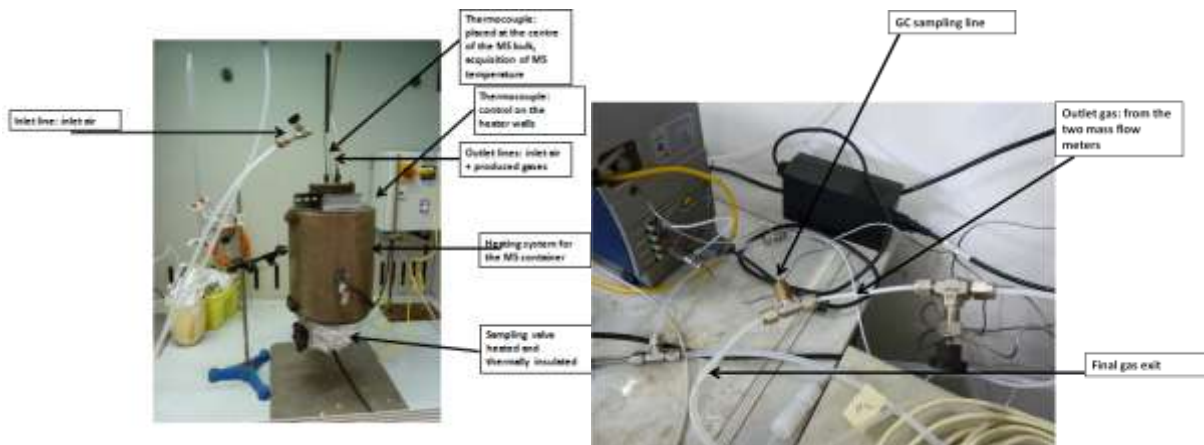


Figure 9 Picture of the experimental rig for thermal stability investigation: on the left the autoclave, on the right the connections with the GC sampling line

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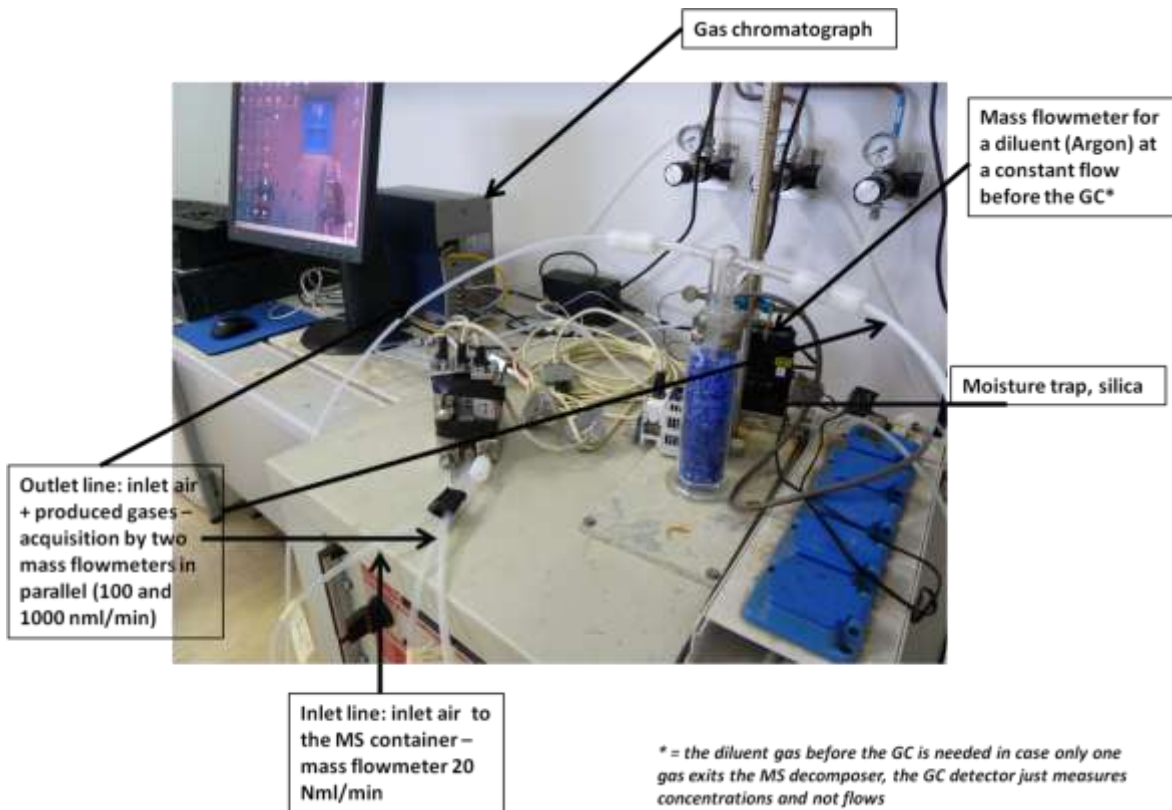


Figure 10 Picture of the experimental rig for thermal stability investigation: mass flowmeter connections

At least 1500 (this way the amount of evolved gases is detectable) grams of salt mixture should be placed inside a heated stainless steel (304 SS or other resistant to corrosion in the experimental conditions) autoclave placed inside a heating system.

The mixture is heated at: 550, 575, 600, 625, 650, 675 and 700 °C.

The evolved gases were analyzed by measuring the produced gas with a mass flow meter and O<sub>2</sub> and N<sub>2</sub> volume percentages by gas chromatography. (Varian, GC4900). Each isothermal experiment lasted around 7 days, before equilibrium, that is no more detectable oxygen evolution.

Concerning oxygen evolution, at the beginning the flow increases, due to the fact that the autoclave head space is filling up with oxygen and the melt is reaching its thermal equilibrium; after around 30 - 40 minutes, oxygen production decreases in a regular way, according to kinetics law.

Some approximations were made during this experimental campaign: after any isothermal experiment we take a sample of molten salt to investigate the presence of NO<sub>2</sub><sup>-</sup> (by ion chromatography, "Metrohm 761 Compact IC" with anionic column "Metrosep A Supp 4" and conductimetric determination) and oxides (by automatic acid/base titration, Mettler Toledo T50); the melt was cooled and the mixture was kept solid overnight; the day after, the bulk was heated, as rapidly as possible, up to the designed temperature. Below are shown gas evolutions (N<sub>2</sub> or O<sub>2</sub>) of concerning test of 7 days using solar salt (Figs. 11 and 12). Oxides presence was detected in correspondence with nitrogen evolution.

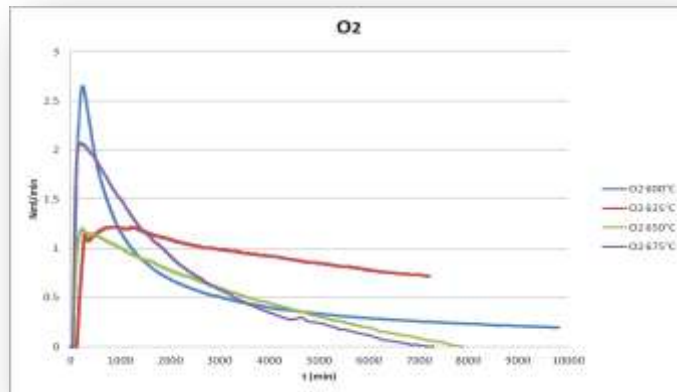


Figure 11 Oxygen evolution respect to reaction time

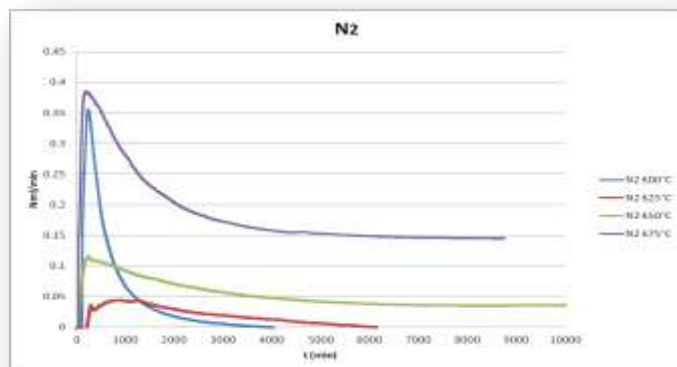


Figure 12 Nitrogen evolution respect to reaction time





## CHEMICAL ANALYSIS

### THEORY: GENERAL CRITERIA

Considering the ionic nature of the inorganic materials generally employed as thermal fluids (excluding liquid metals) ion chromatography is the technique to be used for their chemical analysis. By this method it is possible to determine cations and anions down to ppm (mg/liter) concentrations. Analysis of impurities present at levels below ppb, is generally behind the purpose of HTF and HSM characterization and would require the employment of other equipment, such as spectroscopy or polarography.

Chromatography allows the separation between different chemical substances initially in mixture, or better in solution, restoring individually in time and also isolating them in space. This technique is based on the ability of the individual chemical species contained in a mixture to distribute in a different way between a phase called "stationary" (solid or liquid), that is a chemical substance which can be considered virtually immobile, and an average of different freight, consisting by another chemical substance (fluid) that moves relative to the first and is therefore called the "mobile phase". The substances to be separated, introduced in small quantities within a column containing the two phases, must be able to completely dissolve in the mobile phase and must also have the ability to interact, according to any chemical or physical-chemical principle, with the stationary phase.

As the mobile phase flows, there will be a continuous and repeated passage of the individual substances of the mixture from the mobile phase to the stationary one, and vice versa: more a substance will interact with the stationary phase, more it will pass most of the time bound to this and delay his exit from the column with the mobile phase, which in the meantime continues to flow regularly.

After a long period, there will be a delay in the output of different substances composing the mixture introduced, with the result of a separation in time of the same substances in solution. The output of each individual substance will occupy a certain period of time (minutes for this type of chromatography), within which the concentration of the same substance will rise quickly up to a maximum and then diminish fast, describing a concentration curve similar to a Gaussian respect to the time.

The time taken by each component of the mixture to run through the entire system, from the time of its introduction to the one of its output, rated to the maximum of this Gaussian, takes the name of "retention time" and depends, for a given stationary phase, speed flow and type of eluent, on the nature of the chemical species in question, and then by its molecular structure.

The ion exchange chromatography is based on the principle of attraction between ions of opposite charge. The net charge that these compounds exhibit depends on their pKa (dissociation constant of an acid) and on the pH of the solution. In this type of chromatography separations are carried out in columns packed with an ion exchange resin (eg. For the separation of cations -COO- and for the separation for anions -NR<sub>3</sub><sup>+</sup>).

Conductimetry can be considered a valid post-column detection technique, chemical suppression is in general useful for most anion determinations.



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## DESCRIPTION OF THE METHOD

For each mixture three different samples were taken and diluted, using about the same amount of salt to evaluate, in addition to the composition, also the homogeneity of the compound. The procedure of sample preparation is very delicate; it has to be inserted into the instrument a quantity of the element with a concentration inside the calibration curve extremes.

Among the cations it is necessary to investigate the presence of magnesium and calcium (in case it is not already present in the mixture). Anion impurities include: chlorides, fluorides, phosphates, sulphates, bromides. Nitrites presence is investigated for thermal stability study aims, as above described.

A similar way was used in the analysis of anions, which is useful for assessing the presence of impurities within, for instance, the nitrates of sodium, potassium, calcium and lithium.

Calibration is composed of two parts:

- Three solutions were prepared, each containing 15 ppm of a different standard liquid (cations or anions) so as to identify on the chromatogram the actual retention time of each element;
- At least three standard solutions at three different concentrations are prepared and injected. Then, a calibration curve for each species is plotted and used for quantitative measurements.

Once calibrated the instrument, it is possible to analyze the samples. Before weighing and dissolution (in deionized water) of the samples, it is necessary to know their water content, this analysis can be performed by thermogravimetry (TGA) or Karl Fisher titration. Samples dilution is performed according to the expected nominal values, in case of composition determinations; if the presence of impurities is investigated, the dilution has to be carried out in order to obtain concentrations around 0.1 ppm of the expected impurities, which are typically present in weight percentages well below 1% (see the following table). For instance, for the determination of anionic impurities in the solar salt mixture ( $\text{NaNO}_3/\text{KNO}_3$ , 60/40 wt%) 1 gr of the salt should be dissolved in 50 ml of deionized water and directly injected.

In order to comply with the purity rules for materials to be used as HTF and HSM in CSP plants, the following limits are to be maintained regarding the impurities levels.

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MAX PERCENTAGE OF IMPURITIES	
Nitrite*	0,20%
Cloride	0,03%
Carbonates	0,05%
Sulfates	0,15%
Alcalinity (hydroxides)	0,04%
Perclorates	0,04%
Magnesium	0,04%
Calcium	0,04%
Insoluble	0,06%

\*for not used salts, nitrites are produced during nitrates employment at working temperatures and, in general, their presence do not jeopardize the mixtures thermophysical features (see discussion below about thermal stability)

It is not accepted the use of anticaking agents.

In order to estimate the detection limit, that is a real increase respect to the purity limits, a procedure similar to the one described for alkaline oxides determination, can be followed.



## EXAMPLE OF CHEMICAL ANALYSIS PROCEDURE

To evaluate the actual molecular composition of nitrates/nitrites mixtures and to detect the presence of any impurities has been used an ion chromatograph "Metrohm 761 Compact IC" present in ENEA laboratories and two different columns, a cationic "Metrosep c2 150" and an anionic "Metrosep A Supp 4".



Figure 13 Picture of the ion chromatograph

For the analysis of cations the mobile phase consists of 1.7 mmol/l  $\text{HNO}_3$  and 0.7 mmol/L DPA (Dipicolinic acid: pyridine-2,6-dicarboxylic acid). For anions, the eluent is composed of sodium carbonate (1.7 mmol) and sodium bicarbonate (1.8 mmol).

## COMMENTS, POSSIBLE TROUBLESHOOTINGS

It is important to note that in general a column for ion chromatography is not temperature controlled and elution times will depend on the room temperature during the experiments. For these reasons, and in order to have accurate quantitative results, it is recommendable to build the calibration curve on daily base.

Another source of error can be the inorganic impurities present into the dilution water. Although deionized water is employed, cations and anions could be still present in it. In particular, presence of chlorides can lead to wrong conclusions about the salt purity; in order to overcome this problem, it is necessary to inject the sample a second time doubling its concentration: if the chlorides amount remains the same, that indicates that it stem from the employed water.



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## CORROSION TESTS METODOLOGY

### THEORY: GENERAL CRITERIA

Feasibility of any technology relies on the structural materials behaviour in the operating conditions and on the adequate selection of proper material for each specific use and environmental condition. Scarce reliable data of CSP plant experience are available regarding the behaviour of structural materials and components and in consequence it is still necessary to perform corrosion tests under simulated operating conditions. The information obtained from corrosion tests (type of corrosion, corrosion kinetic law, influence of the pollutants concentration and the characteristics of the own attack process) is relevant for the design, the operation and the maintenance strategy of these type of plants. The main objective of the corrosion testing is to optimize the couple structural material/quality storage material based on corrosion behaviour taking into account the total cost of the system.

In order to select the best type of corrosion studies the most important aspect is the type of corrosion studied. There are two mechanisms of materials corrosion in molten salts: the metal dissolution of the material constituents and the oxidation of the metal to ions. The last one is the main degradation mechanism and it causes the uniform corrosion of materials in molten salts like nitrate mixtures. Nitrate molten salts are ionic liquids that produce the oxidation of the metal elements of the alloy to ions and the corrosion behaviour depends on the formation and stability of protective oxide layers over the material surface which impedes the material oxidation.

Corrosion tests have to simulate as close as possible the operating conditions of the two types of CSP plants (Parabolic Trough and Central Receiver Plants), with different maximum operating temperatures. The evaluation of the uniform corrosion is mainly performed by means of weight measurements of the specimens immersed on the environmental during certain testing times, and these values can be converted to corrosion rates. Allowable corrosion rates are different for each type of material or equipment. In addition, based on corrosion results, extra-thickness can be increased to consider thickness losses by corrosion named as “corrosion allowance” in order to assure the service life of the component. This value, based on corrosion tests results, depends on the engineering design and it is different for each material application of the different equipment or components.

Furthermore, the evolution of the corrosion rates at some different time intervals allows the determination of the kinetic law (Figure 14). Corrosion rates follow a parabolic law when the oxide material is protective or a linear law when the material is continuously dissolved. Usually, the corrodibility of the metal during the test may decrease as a function of time because the material is oxidized up to the formation of protective scale and the parabolic law is obtained. In this case, the service life of the component can be estimated on the basis of the corrosion kinetic law.

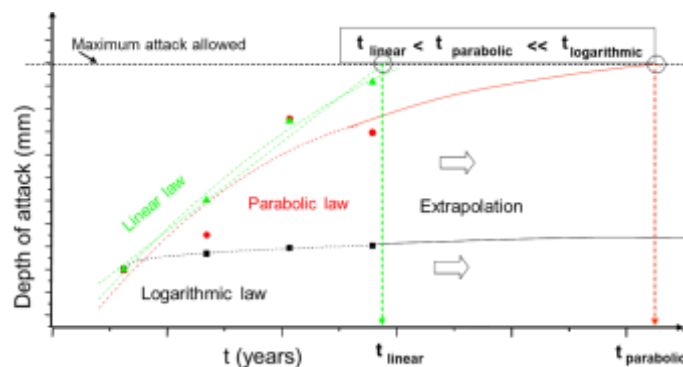


Figure 14 Kinetic laws of uniform material corrosion obtained as function of depth of attack.



## DESCRIPTION OF THE METHOD: CORROSION TESTS IN STATIC CONDITIONS

Different methodologies of corrosion laboratories studies can be selected depending mostly on the type of corrosion or the effect of the different aspects that want to be studied. The most widespread corrosion results of the literature data are related to immersion corrosion tests on isothermal conditions. A static corrosion test is usually used for screening and it is especially interesting for comparing materials, salts or other variables that can influence the corrosion behaviour. This type of tests consists of sealing the liquid environment and heating for long exposure time at constant temperature. Experimental tests are performed in autoclaves which operate at controlled temperature and gas atmosphere. Figure 15 shows the aspect of the autoclaves.



Figure 15 Autoclaves used for tests with molten salts (SMD Ciemat Laboratories)

When the salts are fully melted, the corrosion specimens are immersed on it. At intermediate times, some corrosion specimens are replaced for new ones while others follow until the end of the tests. At the end of the specimen immersion, material corrosion is evaluated by weight measurements to determine both weight gain, due to the incorporation of the oxygen into the oxide layers, and weight loss after the removal of the corrosion products.

Different procedures for removing corrosion products and oxide layers are collected on the ASTM G1 for different type of material or oxide formation [1]. Cleaning procedure may be done chemical, electrolytic or mechanical depending on the properties of oxide layers. As an example, specimens of carbon steels tested in nitrate molten salts are chemically cleaned with a solution of 500ml HCl + 10g Sb<sub>2</sub>O<sub>3</sub> + 25g SnCl<sub>2</sub>. The cleaning procedure should be performed with vigorous stirring during short periods and it should be repeated several times until complete removal of oxides. An ideal procedure should assure that the cleaning removes the whole oxide layer formed without dissolution of the metal elements of the alloys or other alloy degradation like pitting or attack. A good practice is to check it by means of the cleaning of a blank specimen.

Corrosion rates shall be determined as a function of the weight loss divided by the area of specimen and the duration of the tests. Corrosion rates may be expressed as weight or thickness loss per unit of time (considering the alloy density) with different units [2]. The average corrosion rate may be calculated with the following equations:

a)  $V_{\text{corr}} = W / (A t)$                       expressed in mdd (milligrams per square decimeter per day)

Where:                      W= Mass loss (mg)  
                                   A = Area of specimens (dm<sup>2</sup>)  
                                   t = time of exposure (days)



b)  $V_{\text{corr}} = (W K) / (A t D)$  expressed as thickness losses or depth of attack

Where:

- W= Mass loss (g)
- A = Area of specimens (cm<sup>2</sup>)
- t = time of exposure (hours)
- D = Alloy density (g/cm<sup>3</sup>)
- K = constant = 8.76 10<sup>4</sup> expressed in mm/year
- K = constant = 3.45 10<sup>6</sup> expressed in mpy (mils per year)

Figure 16 shows an example of the corrosion rates obtained for carbon steel at different times and different salt qualities. The time evolution of this corrosion rates at different testing times allows determining the kinetic law of the corrosion process (linear or parabolic). The duration of test is a key factor in order to evaluate it with enough accuracy and it depends on the material and molten salt couple.

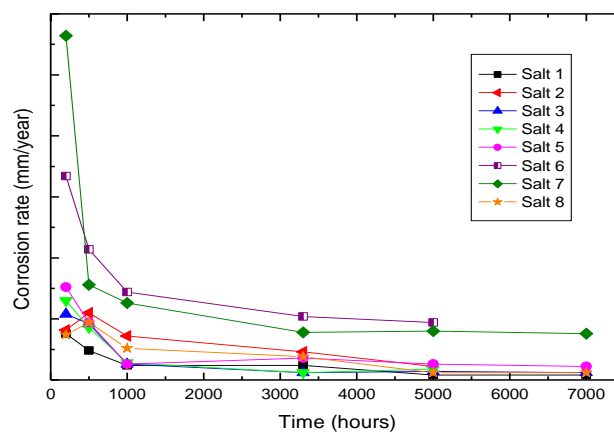


Figure 16 Corrosion rates obtained for carbon steel with different salt qualities

Other samples, tested at same time and with same dimensions, are cross-sectioned and polished for microscopic examination using both optical and scanning electron microscopy (SEM) in order to determine the type of degradation and the protective characteristics of oxide layers (adherence, homogeneity, etc.). Only if no localized attack is detected, (like pitting or intergranular attack), corrosion results based on mass loss are accurate.

When a high material oxidation is obtained, optical measurement of the remained thickness of abovementioned metallographic specimens may be used to quantify the corrosion rate based on the depth of attack and to compare it with corrosion rate determined by mass loss in order to study the corrosion process. Also, thickness measurement of the oxide layer detected may be useful to compare material behaviour on screening tests.

Other post-test examination techniques may provide additional information to study the corrosion process like chemical composition of oxide layers and molten salt. Corrosion scale analyses are performed using SEM equipped with EDX (Energy Dispersive X-ray) in order to obtain the EDX mapping that shows the alloy element distribution and/or the incorporation of salts elements (Figure 17).



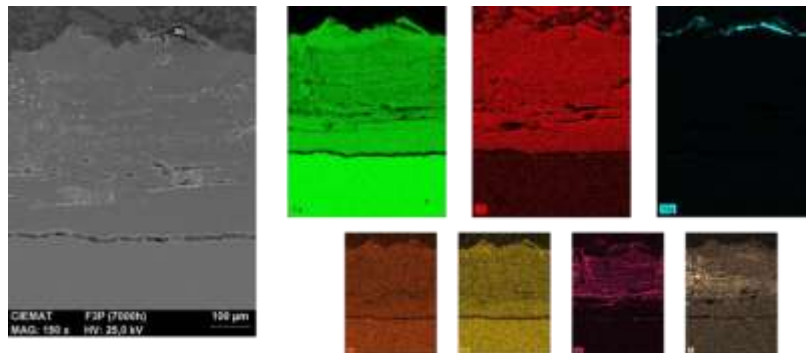


Figure 17 Example of EDX mapping obtained for the oxide layers of carbon steel tested in nitrate molten salts

Depending on the thickness and nature of oxide layers, other surface chemical analyses techniques (Auger Electron Spectroscopy and Electron Spectroscopy for Chemical Analysis) can be carried out at the external surface of the samples to determine the composition of the corrosion scale layers. In some cases depth composition profiling could be obtained by sputtering with an argon ion gun.



Figure 18 Microscopic and surface analysis techniques (SMD CIEMAT laboratories)

Finally, chemical analyses of the molten salts at the beginning of the tests are performed to evaluate the quality/purity of the salt and its effect on material corrosion, taking into account the pollutants concentrations of chloride, perchlorate, nitrite, sulphate, magnesium and so on. Molten salts are also analyzed at intermediate stops to study the chemical composition changes like nitrite formation, due to the thermal decomposition of the salts, or the solubility of metal element of the alloy like chromium. Ion chromatography is used to quantify the concentration of the different anions, while inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used for cations determination.

For proper planning of the test and interpretation of results, the specific influences of the following variables must be considered:

- **Duration of test:** Long tests with intermediate stops are necessary to determine reliable corrosion rates and their time evolution in the case of nitrate molten salts. Corrosion tests must be carried out at least during 2000 hours to define corrosion rates. However, higher testing times like 5000 or 7000 hours are necessary to define a reliable parabolic kinetic law depending on material/molten salt couple studied.
- **Temperature:** The temperature inside the autoclave is measured and recorded. Usually two different baseline operating temperature ranges of CSP technologies are tested: at 390°C for parabolic trough plants and 565°C for component of central receiver systems.
- **Gas atmosphere:** In some cases a continuous gas flow is bubbled into the molten salts and it is controlled and recorded during tests using a volumetric precision flow controller. When the salt is melted the gas flow rate is



fixed to the desired value. Different gas atmosphere must be used depending on the CSP technology plant, for example inert gas is necessary in the case of parabolic trough plant with oil as HTF or in the tests of molten salts with nitrite. The gas atmosphere influences the material corrosion behaviour due to the composition of the oxide layers and its protective characteristics and, also, the chemical evolution of the salt and its aggressiveness.

- **Chemical compositions of molten salts.** The purity/quality of molten salts is a key aspect regarding the formation of a protective oxide layer and materials corrosion like chlorides concentration. In addition, a study on the chemical evolution of the salts and their effects on materials corrosion is also necessary.
- **Number of specimens:** at least two specimens must be tested for each condition
- **Specimen surface preparation:** Corrosion tests may be performed with commercial surface with same type of product of the component studied (tubes or plates) or with a laboratory surface finished by chemical treatment or pickling. The first condition can be used to study both the corrosion rate and the evolution of the defects or finished surface found in service. In both cases, specimens must be cleaned prior to tests with alcohol and/or acetone to prevent any attack or contamination.
- **The shape and size of the specimens** can vary depending on the material and product type. Specimens may be flat, disc, tube ring and so on depending on the material type (plate, bar or tube). In any case it is advisable a large ratio surface-mass and it is necessary accurate measurements of initial and final weight and geometric dimensions (to determine specimens exposed area).
- **Specimen type:** Other aspects like the effect of weld procedure, crevice (metal surface is partially blocked from the corroding liquid with simulate occluded sites) or stress corrosion cracking (SCC) can be also studied with the proper type of specimens. SCC susceptibility can be studied with immersion corrosion of stressed specimens like: C-ring [3], U-bend [4] or Bent Beam Specimens [5].
- **Effect of salt movement** on corrosion behaviour can be studied by means of gas bubbling or stirring the solution. If the specific effects of high velocity need to be studied, special techniques must be employed to transfer the environment through tubular specimens or across to the plane face of the sample. Alternatively, the specimen may be rotated through the environment.
- **Thermal cycling tests:** Actually, thermal cycling tests [6] consist of an intermittent immersion which simulates the effects of the rise and fall of liquid and the wet of the molten nitrates. The primary effect of thermal cycling is to damage protective surface layers via mechanical stresses arising from mismatched thermal expansion coefficients between the surface scale and the alloy.

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## RESULT ANALYSES

As a summary, the experimental procedure includes the post examination of the corrosion specimens with the following measurements and techniques:

1. Gravimetric measurements
  - Weight gain measurements: oxide layer formation
  - Weight loss measurements: material oxidation
2. Visual and optical microscope examinations of specimens surface
3. Post-exposure metallographic examination by optical and Scanning Electronic Microscope (SEM) to determine:
  - Type of material degradation: uniform corrosion, pitting, intergranular attack or stress corrosion cracking
  - Base material: Defects and its evolution with time
  - Oxide layer: Maximum thickness detected and properties



4. Thickness measurement of cross sectioned metallographic specimens by optical techniques to determine depth of attack
5. Chemical characterization of deposits and oxide layers. Depending on the type and thickness of the oxide it is possible to use different techniques like:
  - Energy Dispersive X-Ray (EDX): Mapping with the main element concentration on oxide and base material of metallographic specimens
  - Auger Electron Spectroscopy (AES): Depth profile concentration of the different elements using argon ion sputtering to study the oxide composition from more external layers to base material.
  - Electron Spectroscopy for Chemical Analysis (ESCA/XPS): Determination of the chemical compound of the oxide layers
6. Chemical analysis of the salts
  - Ion chromatography and ICP-AES
  - Chemical composition and time evolution of molten salts
  - Solubility of metal elements (chromium)

## CORROSION TESTS IN DYNAMIC CONDITIONS: GENERAL CRITERIA

In order to complete the information collected from static corrosion tests, it is necessary, in particular where materials to be flowed inside the pipelines are considered to perform experiments under isothermal conditions and flowing molten salts. According to ENEA experience, gathered during past experimental campaigns prevalently carried out at MOSE facility, the following conditions for specimens and thermal fluids are considered appropriate:

Specimen dimensions:

Height: around 50 mm

Width: around 25 mm

Thickness: around 3 mm

At least two molten thermal fluid velocities are to be applied:

0,25 (m/s), 1 (m/s).

At least one temperature as near as possible to the thermal stability limit of the fluid:

Not below 550°C for the solar salt, as an instance. Temperature(s) should be the same of the one(s) used for static corrosion tests.

A contact time:

From 2000 to 8000 hours (at least 2000 h to obtain long term extrapolable results)

## EXPERIMENTAL SETTING

As said, most of ENEA experiments were carried out at MOSE facility, which is a molten salts recirculating system.

In case more economic equipment is necessary, it could be possible to perform the same tests by using a molten salt tank where a rotating system keeps the specimens or the molten salt under stirring.



In that case it is necessary to avoid the occurrence of cavitation phenomena at the interface between molten salts and materials.

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### RESULTS ANALYSIS

A metallographic SEM analysis will be performed in order to detect change in surface and structure composition and presence of corrosion processes: descaling, thickness of the oxidation layer, eventual intergranular attacks, and so on.

It is particularly important to determine the specimen weight gain or loss, both before and after washing the surface.

For the methods to be used, see the previous chapter on static corrosion tests.

To determine the feasibility of a material under the conditions concerned, evidently no intergranular corrosion should be present, a protective layer should be formed and, eventually, the surface thinning should present an acceptable value extrapolated from the expected using period of the material in CSP plant.

Final evaluation would evidently also account for the material cost.

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### COMMENTS ON CORROSION IN STATIC AND DYNAMIC CONDITIONS

Corrosion rates, determined as a function of the weight loss for a specific couple structural material/ storage material, are a valuable data but they must be accurately evaluated. First, corrosion rates based on mass loss are accurate, only if other localized attack is rejected (like pitting or intergranular attack). In addition, for proper interpretation of testing results there are several key factors to take into account like: experimental conditions as close as possible to operating plant conditions; an adequate test duration and a cleaning procedure of specimens that assure the removal of whole oxide layer without dissolution of the metal elements or other alloy degradation.

In general, given the specific employment of pipeline or tank materials into CSP plant, also thermal cycling tests should be performed. Literature data are present for these experiments where temperature was varied, according to realistic applications from about 300°C to 550°C (considering the solar salt). Hence those literature indications are to be followed for eventual tests of that kind.

The effect of impurities (especially chlorides), should also to be taken into account, anyway, the strict specifications required for CSP thermal fluids should prevent any significant effect from this.

As illustrated in the previous chapter, molten salts can be contaminated by corrosion products; as reported in the scientific literature [7], this effect would not affect the fluids thermophysical properties, but the presence of substances such as chromates makes the nitrate mixtures unsuitable to be recycled for agricultural applications. In any case, as also previously discussed, contamination effects can clarify the corrosion mechanism [8].

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## REFERENCES FOR THE CORROSION METHODOLOGY SECTION

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## CONCLUSIONS

Regarding thermo-physical properties, the following conclusion can be drawn:

- The described DSC based methods for phase change onsets, latent enthalpy and specific heat can be applied for practically every HTF/HSM in solid and liquid state. The same pans, temperature ramps and standard/sample amounts are valid for almost all applications. For fluids presenting low latent heat it is necessary to increase the material amount, a particular care should be dedicated to determine the dry weight of hygroscopic species.
- The viscosity method illustrated is valid for all HTF/HSM material in liquid state, in case of not Newtonian fluids also the dependency of the viscosity from the shear rate must be reported
- Oxides formation can be considered the criteria to determine the upper stability limit for nitrate (nitrite mixtures). Two methods can be employed: a direct one where the salt is directly sampled, cooled and chemically analyzed, or nitrogen evolution can be detected. As shown, the former methodology is the most sensible, and we recommend its employment. It is interesting to note that alkaline and/or alkaline oxide formation can be as well used as stability criteria for molten halides.
- An Archimedeian method seems the most feasible one for density determination HTF/HSM in liquid state. The exact characteristics of the procedure (volume of the immersed mass, for instance) in order to obtain the expected accuracy and precision are still to be determined according to the experimental experience.
- Thermal conductivity determination represents a major challenge in the field of HTF/HSM characterization, especially at high temperatures for materials in liquid state. A hot wire method is likely the most promising solution.
- Chemical analysis procedures for anions and cations quantification are already well established. The exact methodology will depend on the species to be determined. In case of weight percentages of 0.01% or more ion chromatography can be used, for trace analysis ICP or polarography are to employed, with recognized procedures for the chemicals to be quantified.

Concerning corrosion tests, the procedures for sample preparation, handling and post characterization are already established and are to be followed. It is necessary to reach a common agreement on parameters like the minimum exposition time, fluids mass flows (for dynamic tests), the eventual necessity for thermal cycles or about HTF/HSM impurity levels. The final choice of a compatible material is also evidently connected to cost considerations.