SFERA-III

Solar Facilities for the European Research Area

1st Summer School “Thermal energy storage systems, solar fields and new cycles for future CSP plants”
WP1 Capacity building and training activities
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Solar Facilities for the European Research Area

“Novel molten salts for TES applications in CSP plants”

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NETWORKING

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Contents:

- ❖Thermal Energy Storage in general
- ❖Novel molten salts mixtures: selection criteria
  - ❖Working temperatures
  - ❖Thermophysical characterization
  - ❖Environmental safety and risk for human health
  - ❖Material cost
  - ❖Construction materials compatibility and corrosion resistance of alloys
- ❖Results & future perspectives

Overview

Concentrated Solar Power (CSP) is one of the most promising technologies:

- for **carbon free energy production**
- to **store** large amounts of heat that can be reused in many useful ways.

A proper storage systems is a crucial point for the economic dispatchability of CSP technology.

Molten salts are increasingly becoming the most used heat transport fluids (HTF) and heat storage materials (HSM) in these types of installations.

A binary mixture of $NaNO_3$-KNO_3, indicated as "solar salt" is currently the most employed molten nitrate, used as reference material.

High $T_{solidification}$ →an external heating system is necessary during the startup such as the tracing of pipelines, and the electrical heaters are expected to provide for the minimum storage temperature tank.

Outline-Topics

CSP Technology

Heat Tranfert Fluids (HTF)

Heat Storage Materials (HSM)

Useful to investigate other mixtures with low melting points, which can be employed both as HTF or HSM.

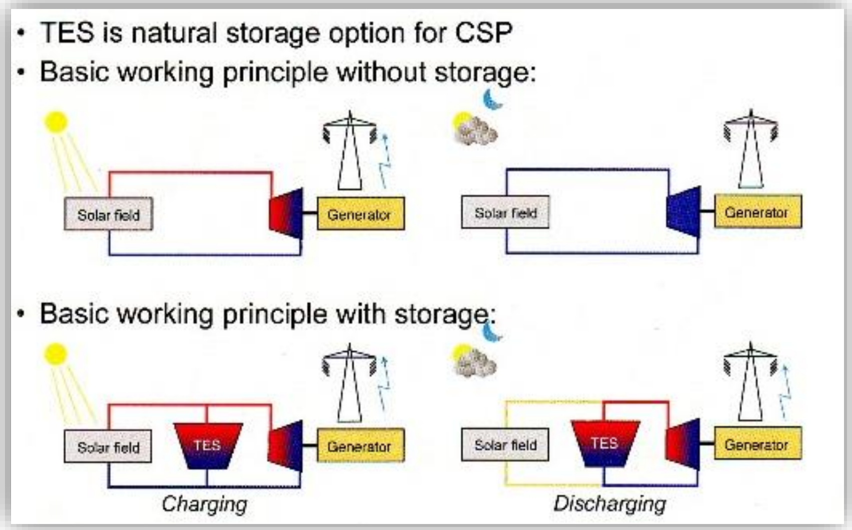
- **Predictive modelling methods for the design of new inorganic low melting fluids.**
- **Exact characterization of their thermal, chemical and physical properties**

Topic of this lesson: define a proper selection criteria and summarize the state of the art about the main molten salt HTFs HSMs for real life CSP applications at **medium temperatures (100-600 °C).**

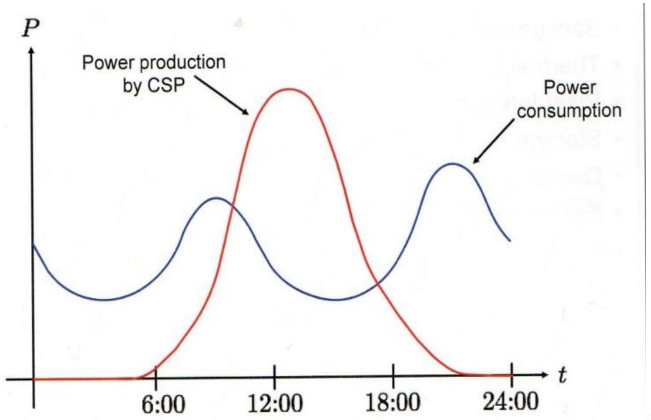
Thermal Energy Storage (TES)

All kinds of **TES** can be classified in four categories:

- **Active/Passive systems**
- **Direct/Indirect systems**

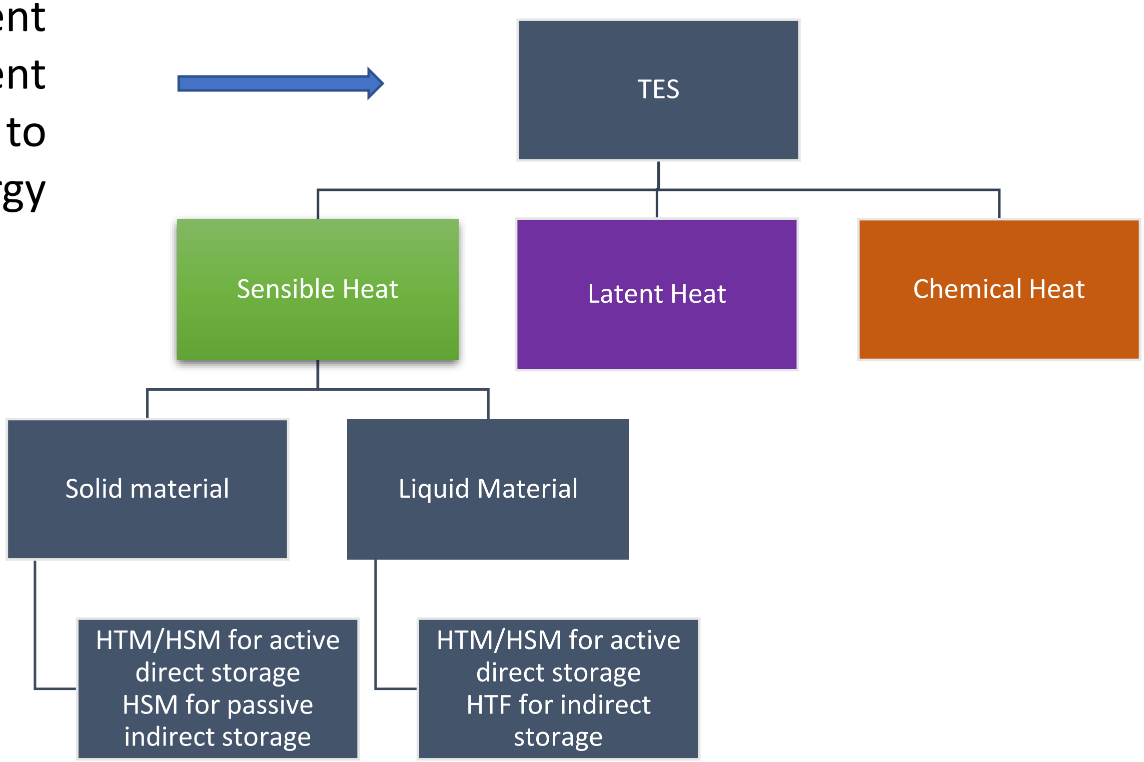


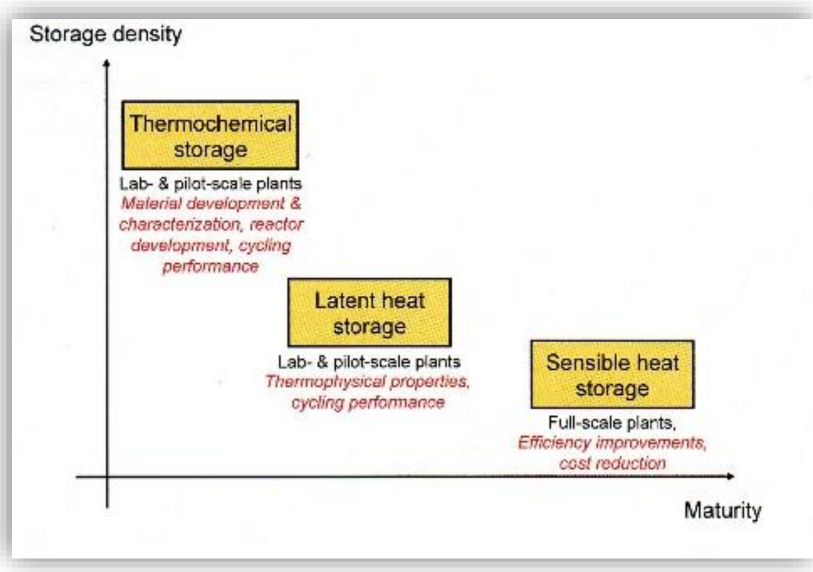
- ✓ In an **active** system the HSM directly transfers the thermal heat to a working fluid in a power block.
- ✓ In a **passive** system another fluid it is employed for transferring the thermal energy from the HSM to the power block.
- ✓ In **direct** storage systems, the HTF and HSM are the same, while, in an **indirect** configuration, the two fluids are different, and the heat is transferred between them by an intermediate heat exchanger (HX).



Storage Modes and Materials

According to the different types of heats, different materials can be used to obtain thermal energy storages.





The choice of feasible thermal fluids (TES) is a crucial point for the dispatchability and economic effectiveness of CSP technology!

Sensible heat storage

Liquid materials

✓Diathermic oils as HTF, that are composed by a mixture of organic compounds, mostly diphenyl and diphenyl oxides.

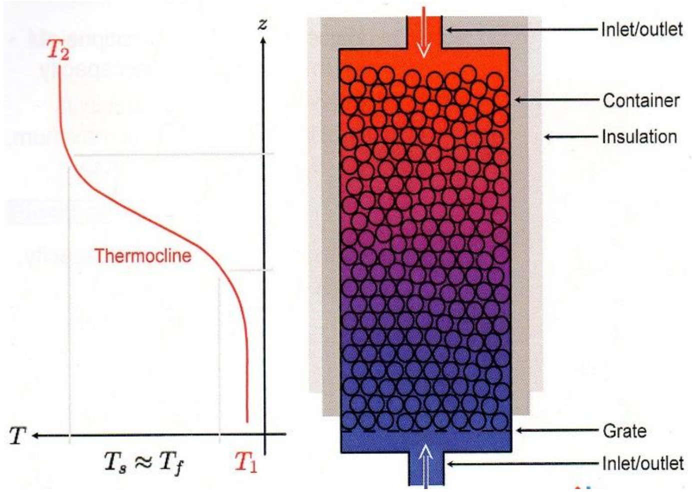
✓Nitrate alkaline mixtures are generally used as HTMs.

Solid materials

✓An intermediate HTF is necessary in order to ensure the contact with the HX.

✓It must mantain a thermocline stratification.

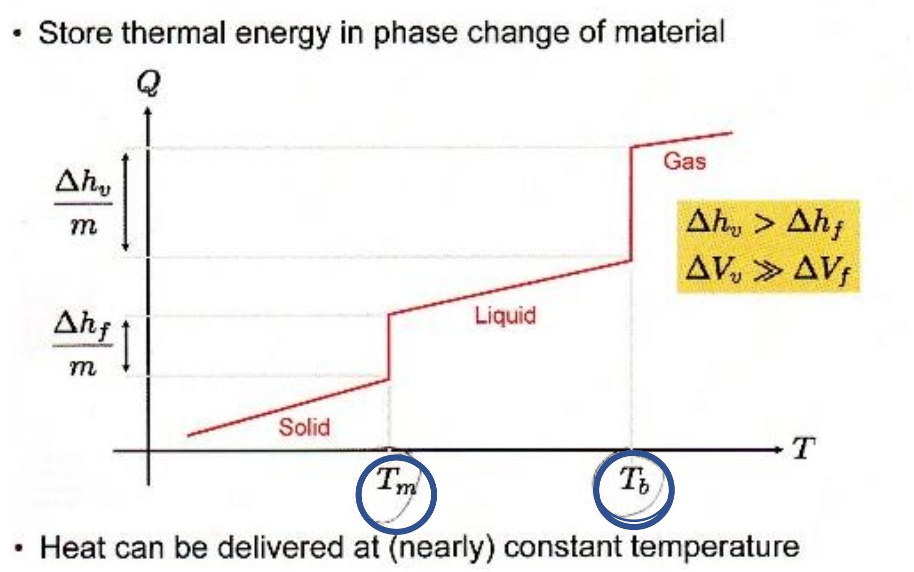
✓ Can be less costly (per weigh and volume) than molten nitrates.

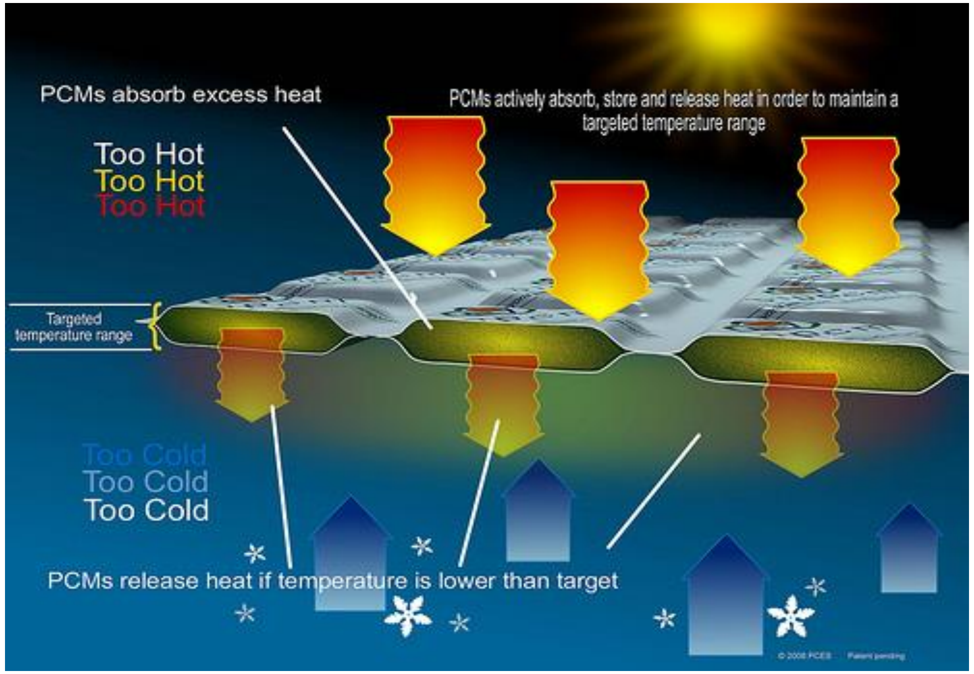


Latent heat storage

Phase change materials (PCMs)

- ✓ energy storage density is high per volume
- ✓ possibility to discharge it at constant temperature
- ✓ problems of designing a proper heat exchanger, given the change in volume during phase transition.





Chemical heat storage

Possibility to accumulate the solar heat in the energy of a single reversible reaction

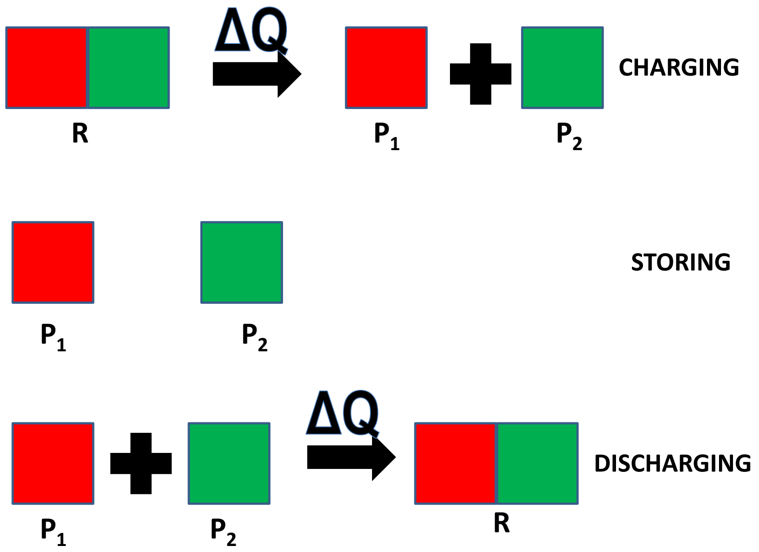
The most common systems use a solid-gas reaction:

R (sol) + Heat = P1 (sol)+ P2 (gas)

✓ By this method can be possible to carry out seasonal heat storage.

Reaction type	Example of Reaction	$T_{charging}$(°C)	$T_{discharging}$(°C)	ΔH_{reaz} (Kj/mol reagent)	Energy density (Gj/m^3)
Hydroxides	$Ca(OH)_2 = CaO + H_2O$	550	450	104.4	1.6
Carbonates	$CaCO_3 = CaO + CO_2$	850-950	550-700	178	2.5
	$MgCO_3 = MgO + CO_2$	510-750	na	125	2.0
	$CaCO_3/CaO/Ca_{12}Al_{14}O_{33}$	850-950	750	178	not available
Oxides	$2BaO_2 = 2\ BaO + O_2$	650-850	450-580	77	1.2
	$2Co_3O_4 = 6CoO + O_2$	915-920	835-850	354.6	1.1
	$6Mn_2O_3 = 4Mn3O_4 + O_2$	920-1000	500-650	202.8	1.2

The whole process can be divided into three parts:



Q= m ΔHreact

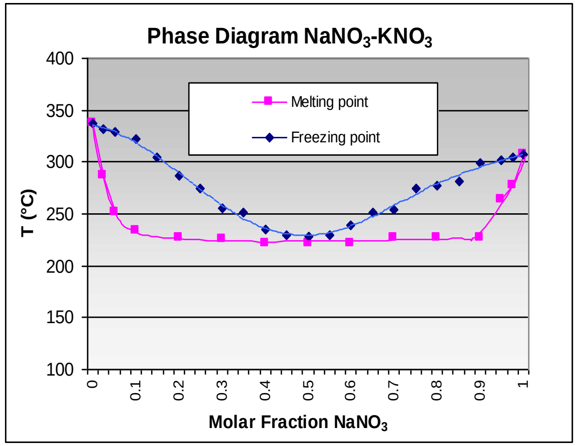
MS as HSM- State of art

- **Molten salts mixtures** are known to exhibit satisfactory thermal and physical features, both for heat exchange and storage, in the temperature range concerned, together with low corrosion properties and a relatively low cost .

Advantages of molten salts (nitrates/nitrites) :

- *safe*
- *non-toxic*
- *available at low cost*
- *stable at relatively high temperatures*

"Solar Salt" ($NaNO_3$-KNO_3 60-40 % w/w corresponding to 64/36 mol/mol) is currently the most employed material both as HTF and HSM.



T liq(°C)	238
Cp(J/ K g)	1.6 (238-600 °C)
Viscosity (cP)	4.5-1.6(238-600 °C)
Density (gr/ml)	1.95 – 1.70 (238-600 °C)
Thermal conductivity(W / K m)	0.50 – 0.55 (320-550 °C)

Diathermic oils vs MS

Advantages

DIATHERMIC OIL

- ✓ low freezing point (-18÷12 °C), which avoids the HTF solidification in the plant receiver tube and pipelines;
- ✓ No necessity for a heating system to maintain the plant lines at a temperature higher than the one in the external ambient.

SOLAR SALT

- ✓quite inexpensive
- ✓not flammable
- ✓high thermal stability point (≈ 600 °C)
- ✓low viscosity
- ✓high heat capacity
- ✓Rankine electric power generating block is slightly affected by a decrease of the lower operative point of the thermal fluids below 270 °C , the "solar salt" formulation can be considered the only realistic choice.

Disadvantages

DIATHERMIC OIL

- ❑ expensive, toxic for humans and environment;
- ❑ relatively low thermal stability, they can be employed up to about 250 °C at atmospheric pressure, and under pressure from nitrogen or inert gases up to around 440 °C.
- ❑ Above this temperature they undergo an irreversible degradation and are also very flammable materials.

SOLAR SALT

- ❑ Compatibility with materials up to 600°C (but expensive 347H-321H stainless steels are to be used at least above about 500°C)
- ❑ relatively high freezing point (238 °C)

Considerable attention must be paid to avoid salt freezing in the CSP plant, which can seriously affect the power plant's operating conditions, by plugging valves and pipes, and reducing heat transfer surface.

Novel mixtures: selection criteria

The **key factors** to be considered are:

- ✓ heat transport
- ✓ storage efficiency
- ✓ cost effectiveness
- ✓ environmental friendliness

The following characteristics are to be evaluated:

1) **Working temperatures** (freezing temperature, upper thermal stability point, and range of operating temperature)
2) **Thermophysical properties** (density, viscosity, heat capacity, and thermal conductivity)
3) **Environmental safety and risk for human health**
4) **Material cost**
5) **Construction materials compatibility and corrosion** resistance of alloys

Novel mixtures: selection criteria

Considerations

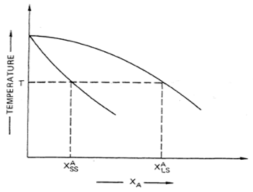
- Molten salts (MS), which in general consist of NO_3^-/NO_2^- mixtures are mostly considered, avoiding rare and costly ones.
- Given temperature ranges, only NO_3^-/NO_2^- containing Na/K/Li/Ca can be taken into account.
- Carbonates, chlorides o other salts are little soluble in molten nitrates, so their addition results not interesting.
- $NaNO_2$ cannot be coupled with $Ca(NO_3)_2$ because of metathetical reaction ($Ca(NO_2)_2$ which leads to $Ca(NO_3)_2$).
- Mixtures must be stable in air to avoid inert storage systems.

1. Working temperatures

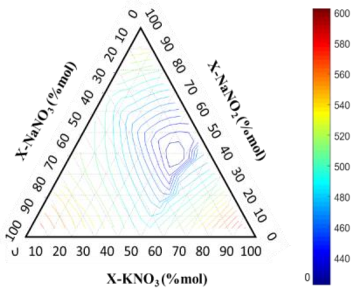
1) Working temperatures
(freezing temperature, upper thermal stability point and range of operating temperature)

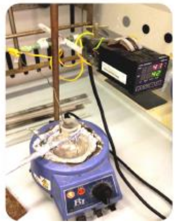
Semi-predictive modelling based on the "Theory of regular solutions" → Multi-components Phase diagrams: individuation of a low melting zone → **Novel promising mixtures to be characterized** → Experimental results validation:

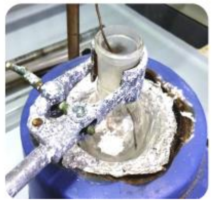
- DSC
- Rheometer
- XRD/Neutron Scattering
- Thermal stability tests



$A_S \rightarrow A_L$	$\Delta H_A - T\Delta S_A$
$A_L \rightarrow A_{LS}$	$\overline{\Delta H}_{mix}^{A_L} - T\overline{\Delta S}_{mix}^{A_L}$
$A_S \rightarrow A_{SS}$	$\overline{\Delta H}_{mix}^{A_S} - T\overline{\Delta S}_{mix}^{A_S}$
$A_{SS}=A_{LS}$	$\Delta G \equiv 0$



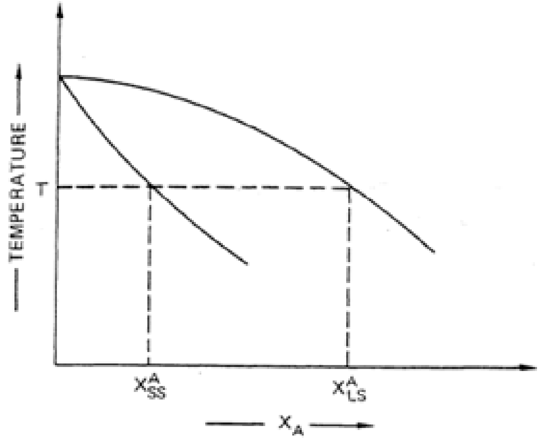




Theory of regular solutions

In order **to simulate the phase diagrams** of the binary mixtures **A and B**

when the **free energy** of one of the components is set equal to zero, the liquid and solid solution of that component are in **thermodynamic equilibrium and the overall free energy of the reaction must be zero**.



$A_S \rightarrow A_L$	$\Delta H_A - T\Delta S_A$
$A_L \rightarrow A_{LS}$	$\overline{\Delta H}^{A_L}_{mix} - T\overline{\Delta S}^{A_L}_{mix}$
$A_S \rightarrow A_{SS}$	$\overline{\Delta H}^{A_S}_{mix} - T\overline{\Delta S}^{A_S}_{mix}$
$A_{SS}=A_{LS}$	$\Delta G \equiv 0$

On an isothermal value of the phase diagram it is possible to calculate ΔH_{mix} and ΔS_{mix} (both for the solid and liquid phase)

Theory of regular solutions

The free energy of the overall reaction for **component A** may be expressed as:

$$\Delta G \equiv 0 = (\Delta H_A - T\Delta S_A) + \left(\overline{\Delta H}_{mix}^{A_L} - T\overline{\Delta S}_{mix}^{A_L}\right) - \left(\overline{\Delta H}_{mix}^{A_S} - T\overline{\Delta S}_{mix}^{A_S}\right)$$

Kirchoff law

$$\Delta H_A = \Delta H^0{}_A - \int_T^{T_{MP}} (C_{PL} - C_{PS})\, dT$$

$$\Delta S_A = \Delta S^0{}_A - \int_T^{T_{MP}} \frac{(C_{PL} - C_{PS})}{T}\, dT$$

Gibbs-Duhem equation

$$\left(\overline{\Delta H}_{mix}^{A_L} = \Delta H_{mix} - X_{BL}\frac{d\Delta H_{mix}}{dX_{BL}}\right)_L \qquad \left(\overline{\Delta S}_{mix}^{A_L} = -R\ ln X_{AL}\right)_L$$

$$\left(\overline{\Delta H}_{mix}^{A_S} = \Delta H_{mix} - X_{BS}\frac{d\Delta H_{mix}}{dX_{BS}}\right)_S \qquad \left(\overline{\Delta S}_{mix}^{A_S} = -R\ ln X_{AS}\right)_S$$

$$\boxed{\begin{aligned} \Delta H_{Lmix} &= X_{AL}\, X_{BL}\,(a_L + b_L X_{AL} + c_L X_{AL}\, X_{BL}), \\ \Delta H_{Smix} &= X_{AS}\, X_{BS}\,(a_S + b_S X_{AS} + c_S X_{AS}\, X_{BS}) \end{aligned}}$$

Assuming that all the non-ideality is from enthalpy and entropy follows an ideal mixing rule

Considerations

Only experimental data that show a good precision and accuracy are the **phase diagrams**.

Starting from experimental AB- BC- AC phase diagrams

↓

Find theoretical $\Delta H_{TOT} = \Delta H_{Lmix} + \Delta H_{Smix}$

optimizing $\Delta G \equiv 0$

↓

Comparison with experimental data for AB-BC-AC

↓

Find theoretical $\Delta H_{mix}^{ABC} = \Delta H_{mix}^{AB} + \Delta H_{mix}^{BC} + \Delta H_{mix}^{AC}$

↓

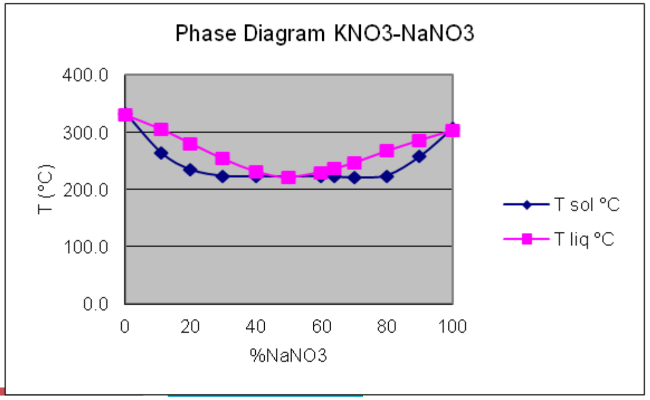
ABC phase diagram

Study and modeling of binary and ternary mixtures

Phase diagrams

DSC

Applying a controlled temperature ramp on a Al pan 100 ul, filled with salt allowing the salt to melt and then to solidify it is possible to detect **“onsets"** of solidification and melting (Tliq and Tsol)



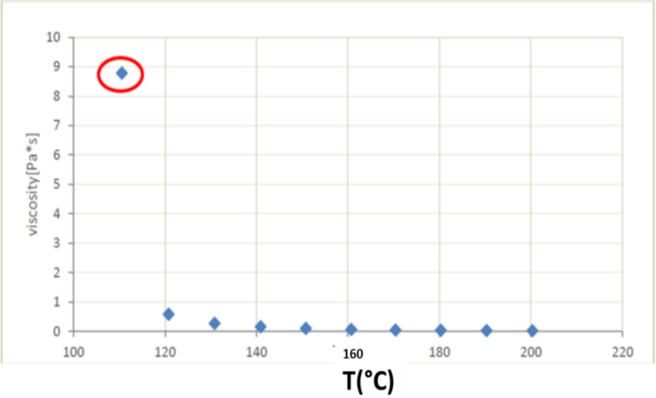
Rheometer

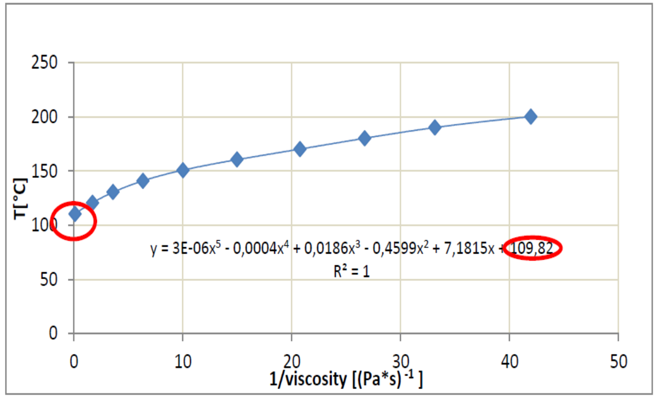
The dynamic viscosity of a Newtonian fluid (such as a molten nitrate) is directly dependent on the materials temperature.

$$\log_{10} \mu = A + BT - T0$$

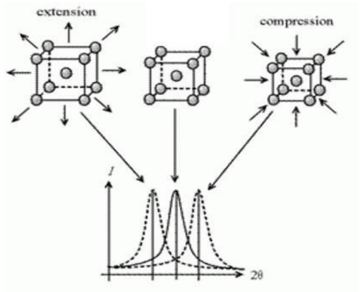
It is not possible to detect phase transition points (liquidus and solidus) of Na/K/Ca//NO_3 mixtures when the calcium nitrate molar percentage exceeds 20%, because of a slow transition rate and low transition enthalpy.

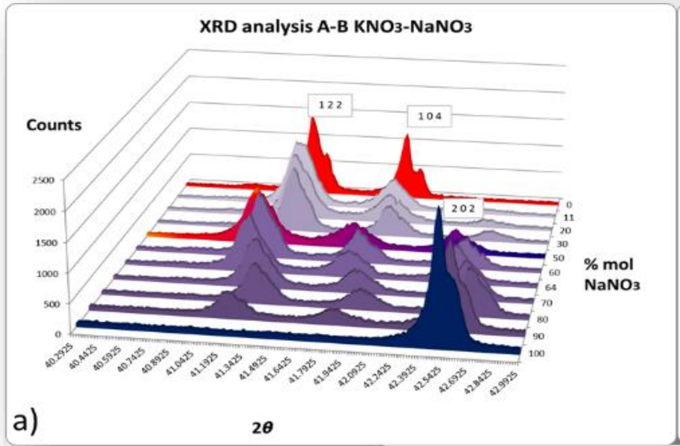
$NaNO_3/KNO_3/Ca(NO_3)_2$ 21-54-25 (% mol)

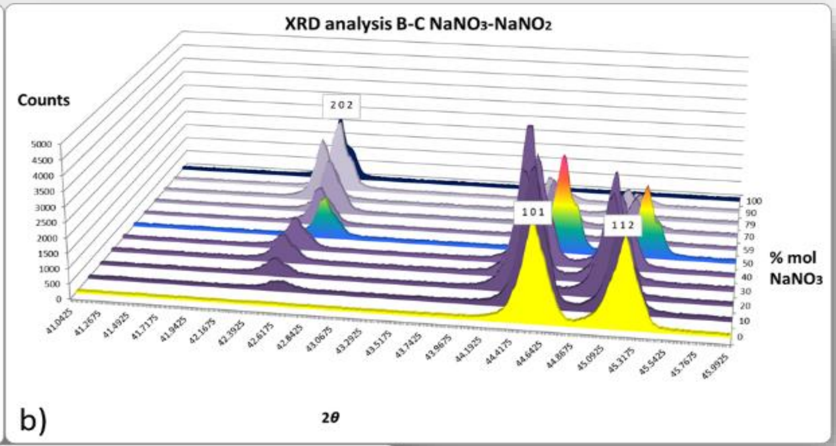


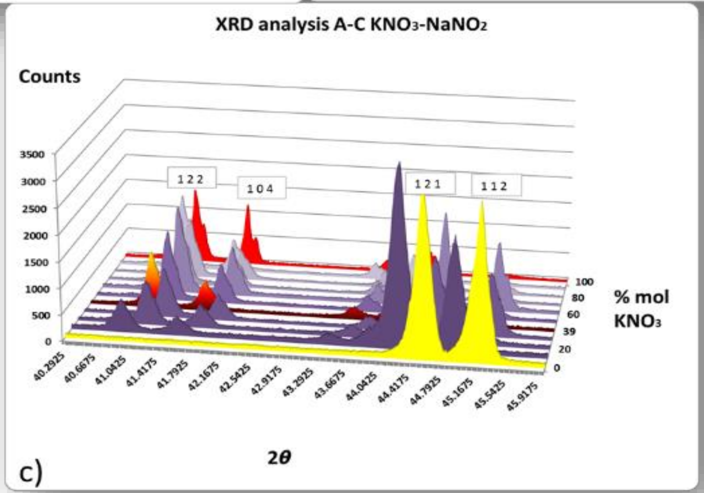


Study and modeling of binary and ternary mixtures
XRD Diffraction









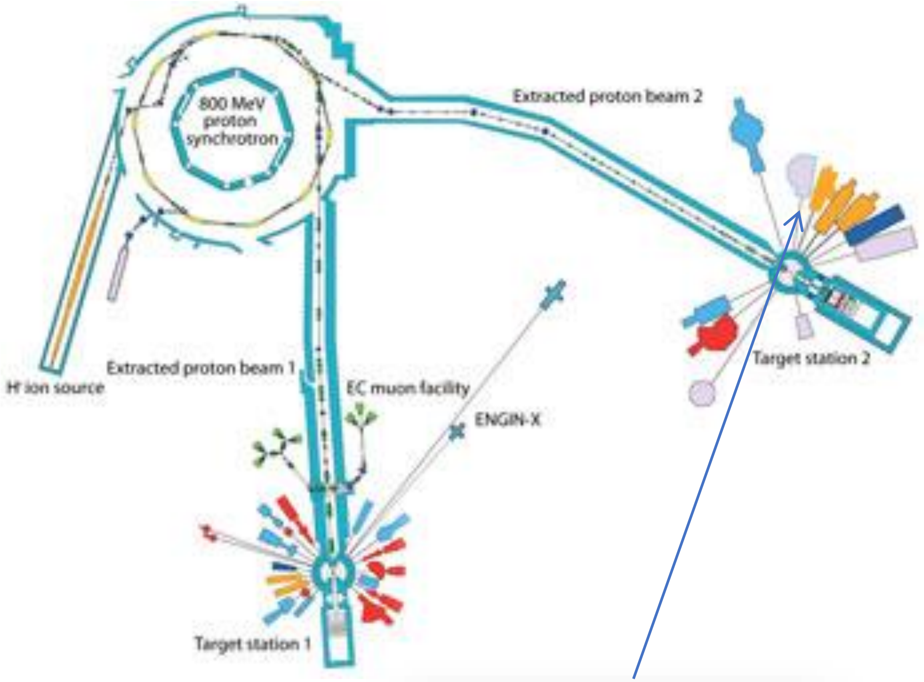
A modification of the distance between the crystallographic planes is related, considering that λ is constant, to a change in the 2θ values.

Not a formation of new phases but, by varying concentrations, **the crystal lattice undergoes a deformation that is maximum in correspondence of the composition of the eutectic point.**

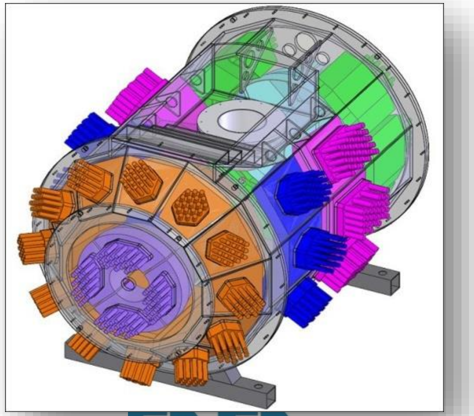
- An exploratory XRD study of the binary mixtures, **AB , BC , AC,** has been carried out, with the aim to improve the understanding of the phase diagrams.
- Given the unavailability of a heating system for the cell of the XRD apparatus used, only **room temperature** data were collected.

Neutron Scattering

- Neutron diffraction experiments determine the atomic structure of a material.
- The technique is similar to X-ray diffraction but the different type of radiation gives complementary information.
- A sample to be examined is placed in a beam of neutrons and the intensity pattern around the sample gives information of the structure of the material



Polaris Instrument- Rutherford Labs (UK)



Study and modeling of binary and ternary mixtures

Neutron Scattering

Delise, T., Tizzoni, A.C., Ferrara, M., Corsaro, N., D'Ottavi, C., Giaconia, A., Turchetti, L., Annesini, M.C., Telling, M., Sau, S., Licoccia, S.
New solid phase of KNO3 salt mixtures studied by neutron scattering and differential scanning calorimetry analysis
(2018) AIP Conference Proceedings, 2033, art. no. 080001, .

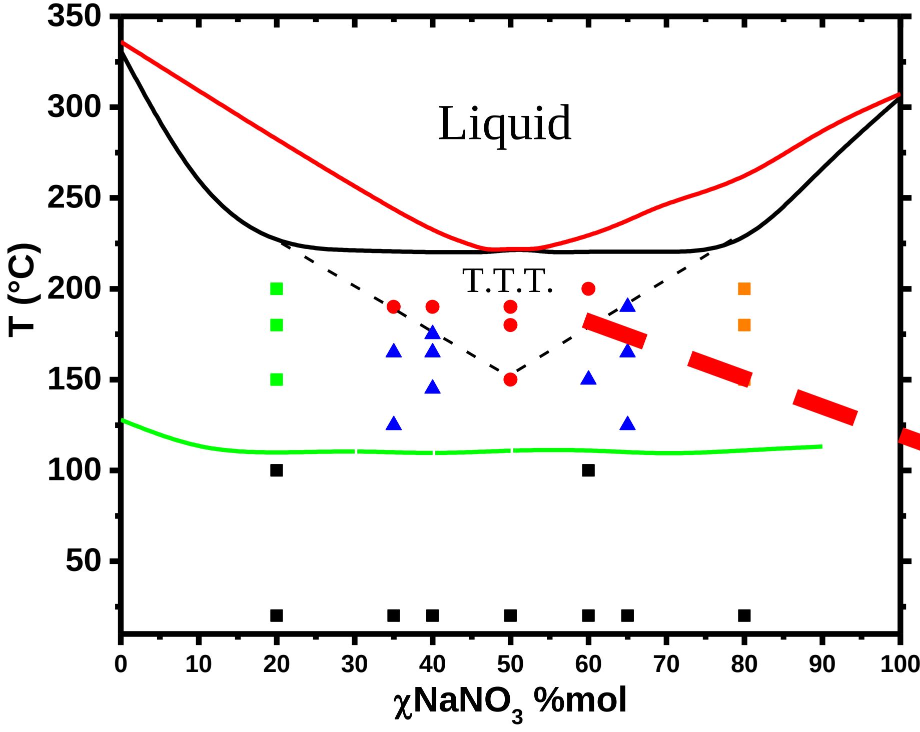
Neutron scattering

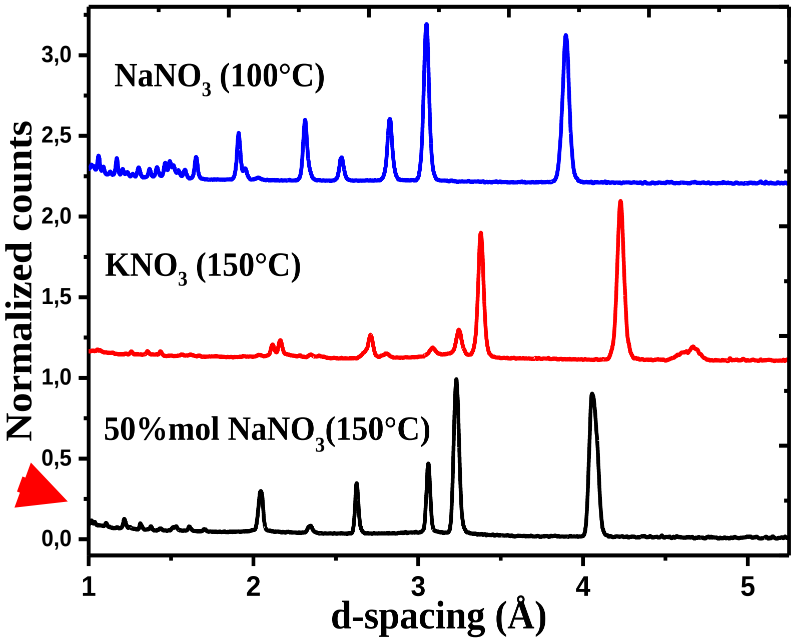
- Orthrombich (KNO_3) + Trigonal ($NaNO_3$)
- T.T.T.
- Trigonal ($NaNO_3$) + Trigonal (KNO_3) + T.T.T.
- Trigonal (KNO_3)
- Trigonal (KNO_3) + Trigonal ($NaNO_3$)

DSC data

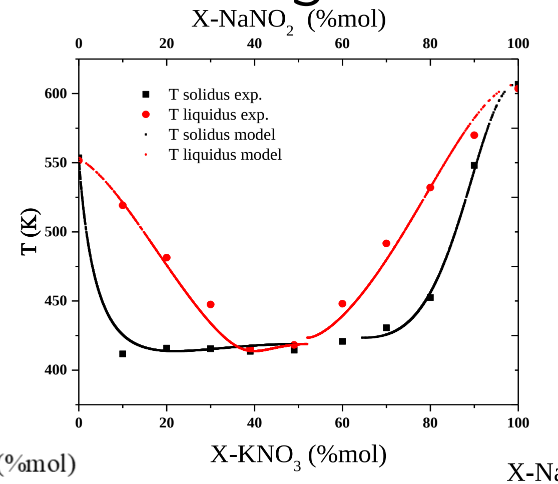
- $T_{solidus}$
- $T_{l\ quidus}$
- $T_{orthorhombic}$
- $T_{T.T.T}$ DSC extrapoled data

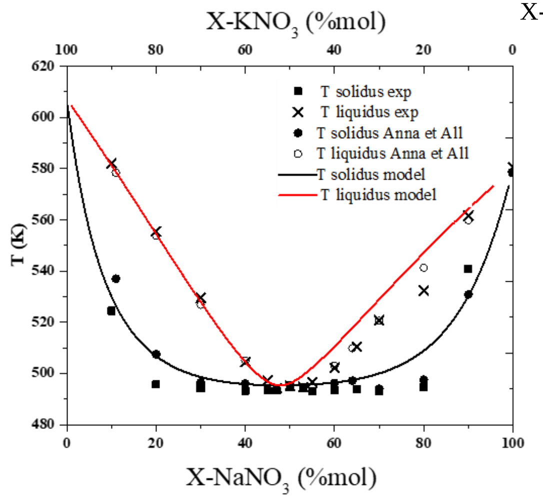
$NaNO_3 – KNO_3$

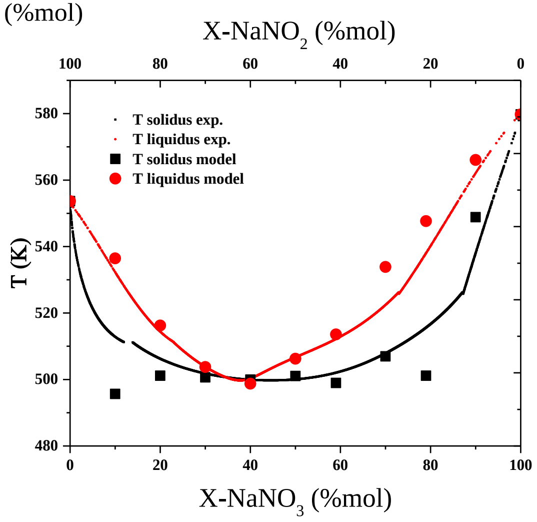


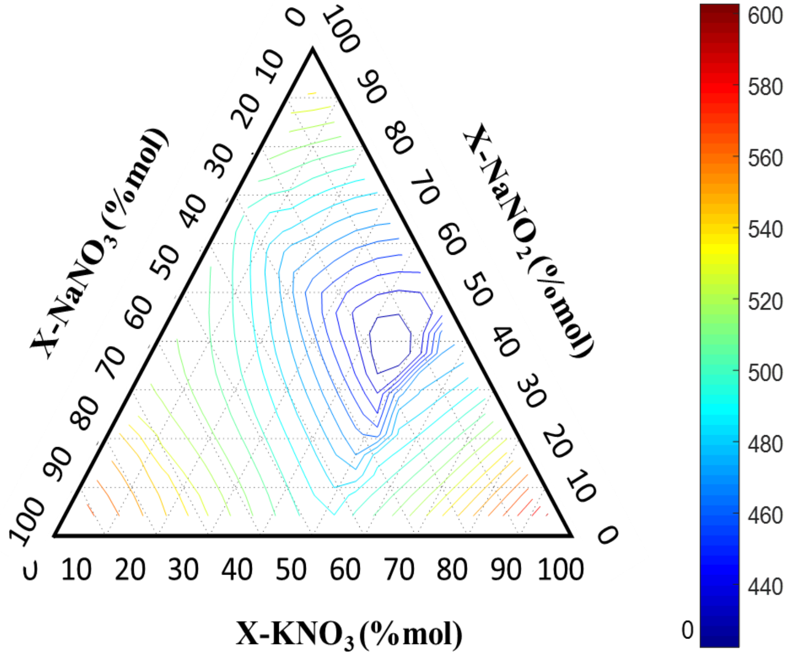


KNO_3-$NaNO_3$-$NaNO_2$:Ternary phase diagrams example









Thermal stability mechanism

The molten nitrates degradation mechanism consists of two steps:

✓ Firstly nitrites and oxygen are produced:

$$MNO_3 \rightleftharpoons MNO_2 + ½\, O_2 \qquad (M = Na, K, Li)$$

This reaction is reversible. In turn, nitrites can lead to a second reaction:

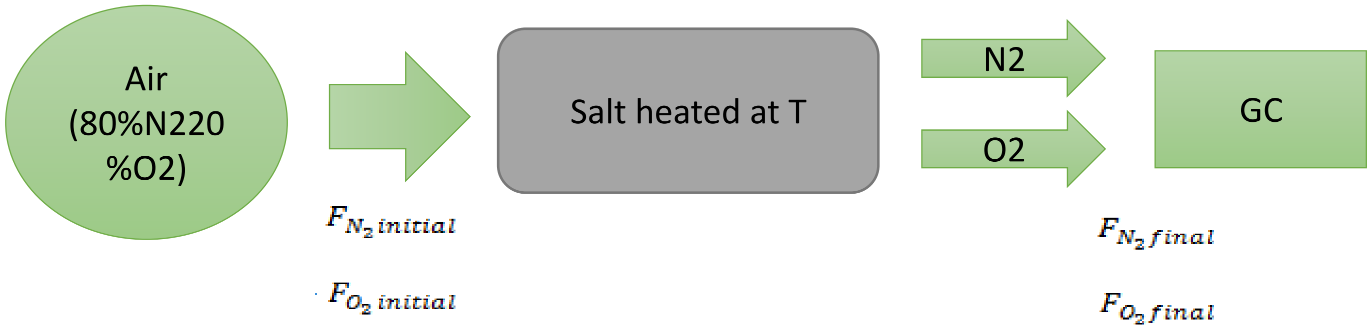
$$5\, MNO_2 \;\text{-->}\; M_2O + 3MNO_3 + N_2 \qquad (M = Na, K, Li)$$

✓ This process is not expected to be easily reversible, so alkaline oxides can:

- accumulate and **increase the melting point** of the mixture
- react **producing alkaline hydroxides (very corrosive) and carbonates**
- **precipitate** leading to problems with valves and pipeline occlusions due to limited solubility

Discriminating point to determine the **upper** stability temperature for MS employment as HTF or HSM.

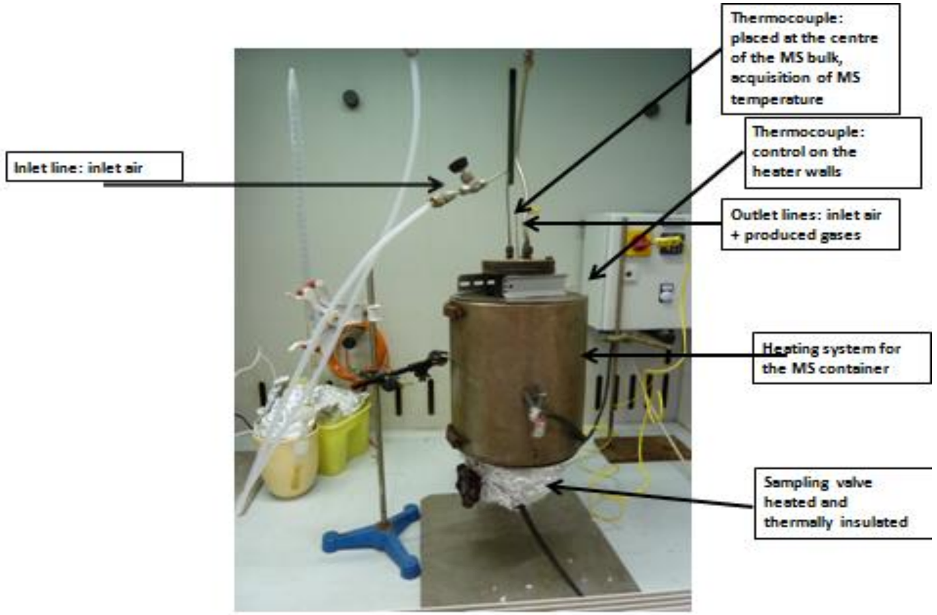
Experimental setup



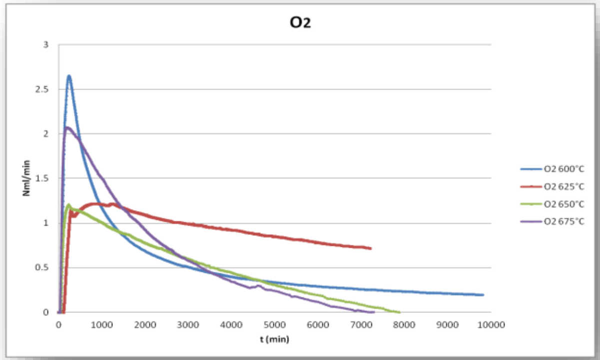
✓Salt mixture is placed inside a stainless steel (304 SS) autoclave.
The mixture is heated at various T.

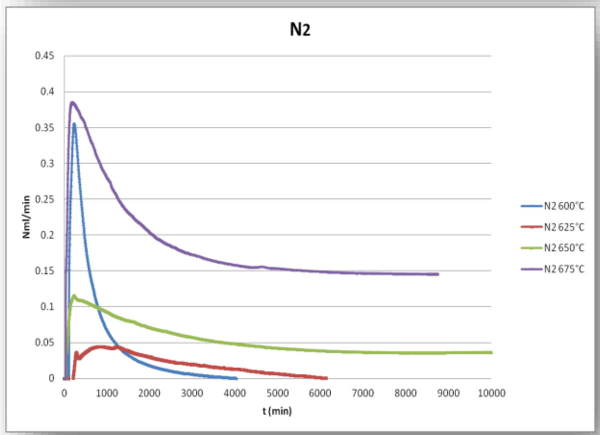
✓A continuous flow of air is necessary in order to carry out experiments under 1 bar of air.

✓Evolved gases are analyzed by using gas chromatography, measuring O_2 and N_2 volume percentages.



7days tests on Solar Salt





During the experimental period (7 days tests for each temperature), the bulk was measured by a thermocouple immersed in the center of the melt.

After each isothermal test few grams of molten salt is sampled to investigate the presence of:

- **NO_2^-** (by Ion Chromatography)
- **Oxides** (by automatic acid/base titration)

7 Day Tests	**600 °C**	**625 °C**	**650 °C**	**675 °C**
wt% NO_2^- (measured)	2.98	3.35	9.00	9.99
wt% NO_2^- (est. from O_2 production)	2.94	6.76	9.14	11.82
wt% OH^-	0.0003	0.0004	0.0010	0.0023
Onset Tsol [°C]	207.90	204.14	180.50	176.67
Onset Tliq [°C]	225.31	226.12	204.32	199.11

Thermal stability upper limit: about 600°C

2) Thermophysical properties

Properties	Interest for HTF	Interest for HSM
phase diagrams	Determination of the lowest Tliq	Determination of the lowest Tliq
specific heat	Capacity of solar heat tranfer to the storage system	Capacity of heat storage
viscosity	Determination of the necessary pumps hydraulic head	It depends on the storage system. In“Archimede “configuration HTF and HSM are the same fluid.
density	Related to heat capacity; capability of heat storage per volume	Related to heat capacity; capability of heat storage per volume
heat conductivity	Necessary parameter to determine the heat exchange surfaces	Necessary parameter to determine the heat exchange surfaces
thermal stability	Maximum operative T	Maximum operative T
XRD diffraction	Integration to investigate solid nitrates structures: predition for phase diagrams	Integration to investigate solid nitrates structures: predition for phase diagrams

DSC

Rheometer

Archimedian based test

C-Therm TCi thermal conductivity analyzer.

2) Thermophysical properties
Specific heat

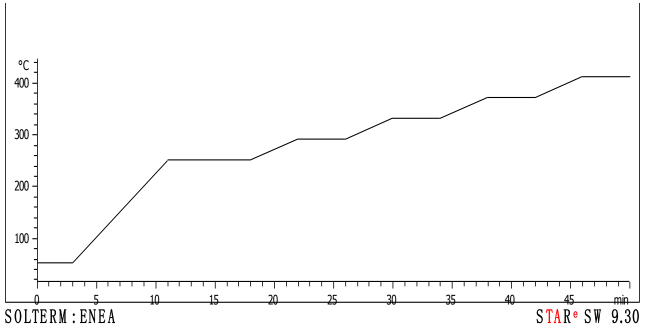
It is possible to estimate **heat capacity** values of molten salts with the use of a known heat capacity substance as reference (high purity sapphire).

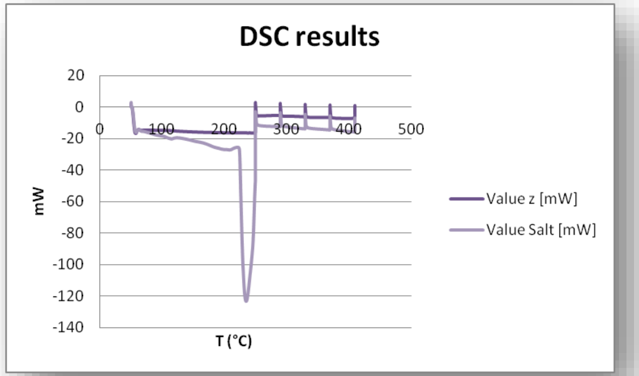
$$W_z = Cp_z \cdot m_z \cdot \beta \cdot \Delta T$$

$$W_{salt} = Cp_{salt} \cdot m_{salt} \cdot \beta \cdot \Delta T$$

$$\Rightarrow \quad Cp_{salt} = \frac{Cp_z \cdot m_z \cdot W_{salt}}{m_{salt} \cdot W_z}$$

Mettler Toledo DSC





2) Thermophysical properties
Viscosity

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

Considering a model in which a fluid is delimited between two parallel planes and 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 μ takes the name of **dynamic viscosity** for a fluid [Pa*s].

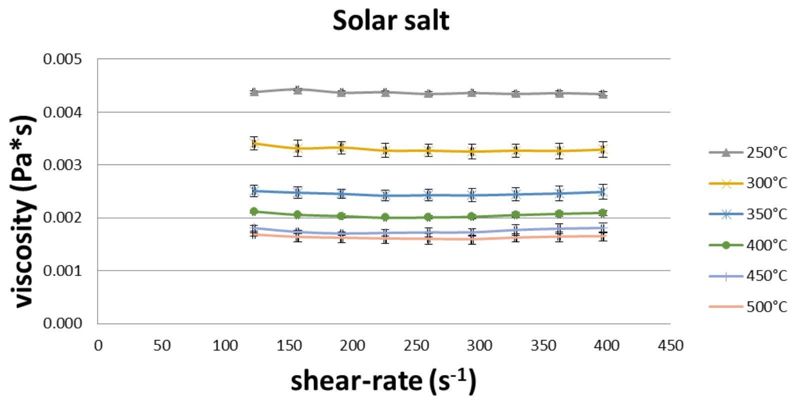
Viscosity

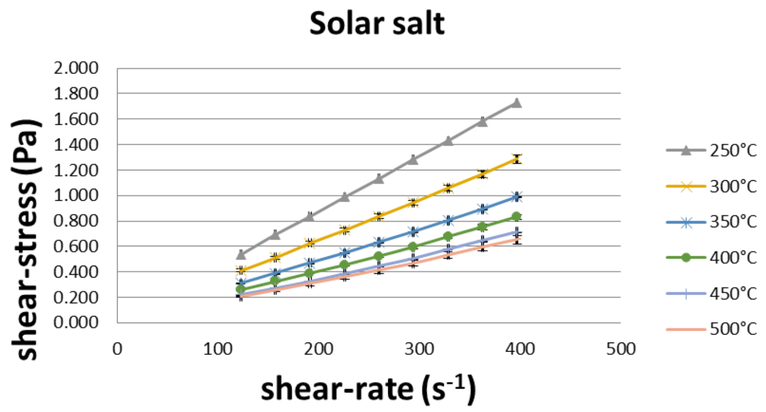
The gradient of velocity **(shear rate)** is uniform between the two planes :

$$\gamma = \frac{du_x}{dy} = \frac{u_x}{dy}$$

Then the **viscosity** is defined as: $$\mu = \frac{shear\ stress}{shear\ rate} = \frac{\tau}{\gamma}$$

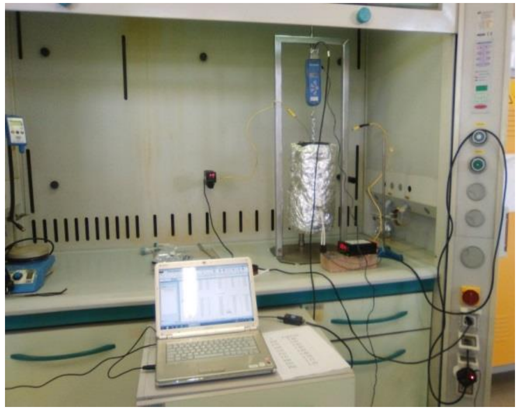
If the relationship between shear stress and shear rate is a straight line passing through the axis origin, the fluid is defined Newtonian and the slope is the Viscosity

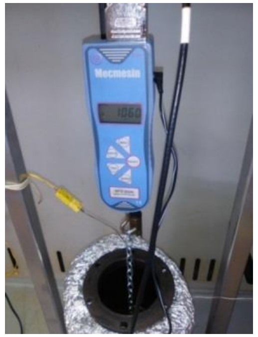




Density - heat conductivity

✓ **Density** measurements of the mixtures are performed with an *Archimedian* based test.





The method is based on the measurement of the buoyance force on a stainless steel cylinder, which is immersed into the ternary melt and is connected with a dynamometer.

✓**Heat conductivity :** instrument based on the "hot wire" method (up to 80°C)

C-Therm TCi thermal conductivity analyzer.

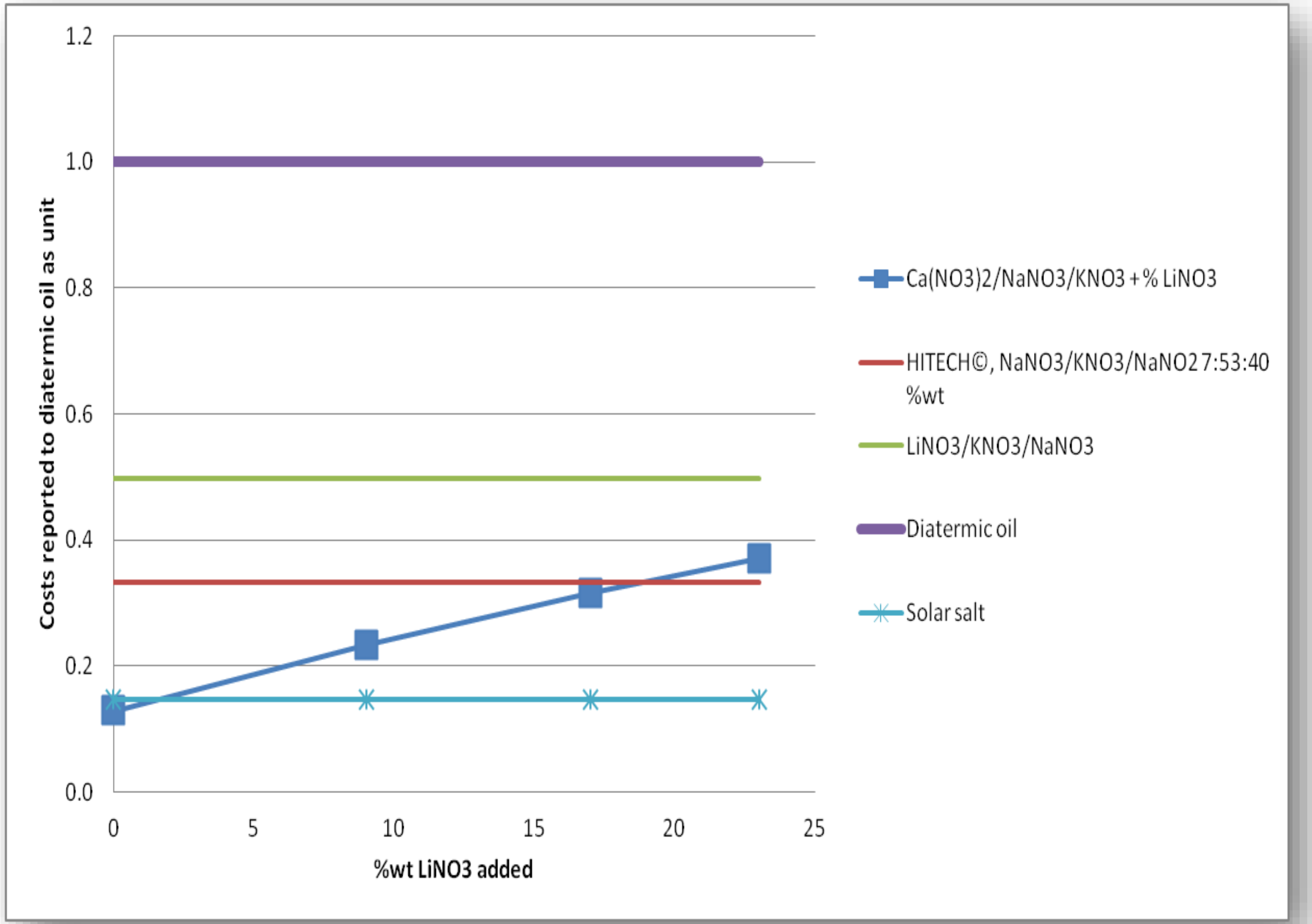
A known current is applied to the sensor's heating element providing a small amount of heat. The heat provided results in a rise in temperature at the interface between the sensor and the sample.

The rate of increase in the sensor voltage is used to determine the thermo-physical properties of the sample material.

3) Environmental safety and risk for human health

	Name	Risk Phrases
Solar salt	M1	H272
Ternary Li/Na/K//NO3	M2	H272- H319
Ternary Ca/Na/K//NO3	M3	H272
Hitech® ($NaNO_3$/KNO_3/$NaNO_2$)	M4	H272-H301-H319-H400
Quaternary Ca/Li/Na/K//NO3	M5	H272- H319
Oil Diathermic (THERMINOL® 66)	M6	Skin Irrit. 2 - H315 Eye Irrit. 2 - H319 Suspected of damaging fertility- H361f Aquatic Acute 1 - H400 Aquatic Chronic 1 - H410

4) Material costs



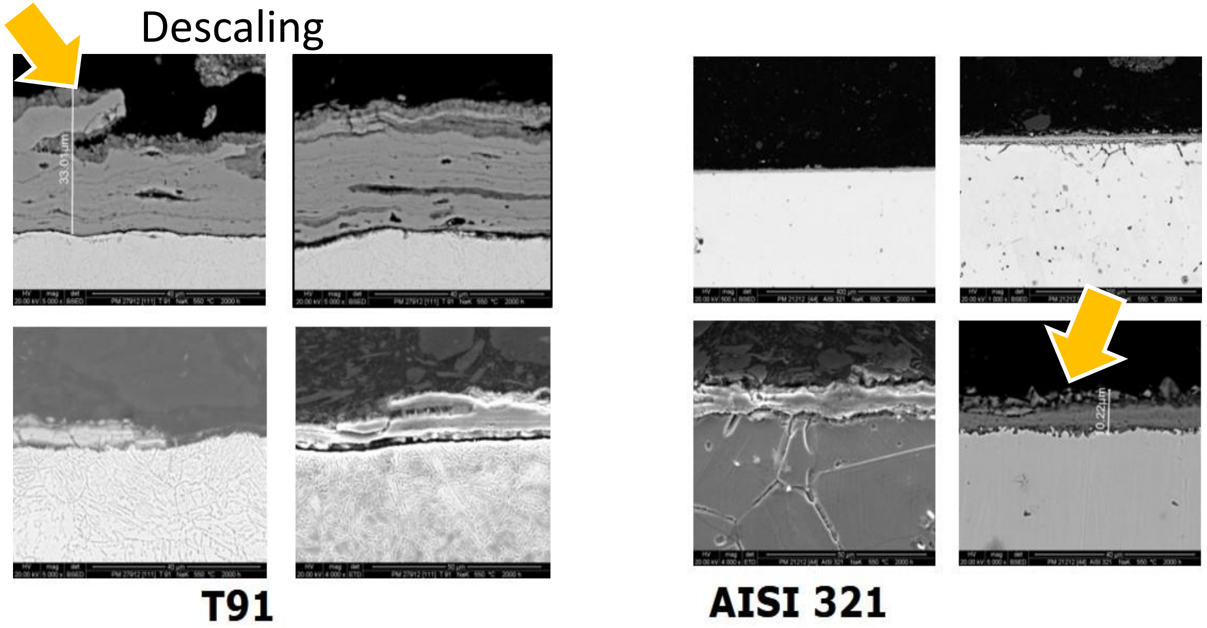
Diatermic oil as unit

- **Ternary with calcium** is the less expensive material can be an alternative especially with respect to thermal oil, which is stable at the same temperature.
- Addition of **lithium nitrate** makes the cost of the mixture more or less comparable to the'"Hitech® salt“
- **Ternary with lithium** has very good thermo-physical features, including thermal stability, but can be considered **too expensive**

5) Construction materials compatibility and corrosion resistance of alloys

There are two mechanisms by which materials corrode in the presence of in molten salts: metal dissolution of the material constituents and oxidation of the metal to ions.

- ✓ The oxidation is the main degradation mechanism which causes uniform corrosion when a material is subject to molten salts like nitrate mixtures.
- ✓ The corrosion behaviour depends on the formation and stability of protective oxide layers over the material surface which impedes the material oxidation.



SEM images for the cross section of a specimen of T91 and AISI 321 after isothermal oxidation test (2000h) at 550°C in a molten salt mixtures.

HTFs and HSMs critical review

❖ **Binary $NaNO_3/KNO_3$ mixtures (M1).**

They present low cost along with good thermophysical properties and are not toxic. Solar salt presents an acceptable freezing point (238 °C) and it is less expensive than the eutectic mixture (freezing point around 222 °C), given the lowest KNO_3 content (the eutectic point is at $Na/K//NO_3$ 46/54 wt%) .

❖ **Ternaries with lithium nitrate (M2).**

The advantages are a low freezing point and a thermal stability comparable with solar salt. The main disadvantage is the high price of lithium nitrate.

❖ **The addition of calcium nitrate to $NaNO_3$ and KNO3 (M3)**

decreases the mixture freezing point to about 110 °C, but also the upper temperature limit to around 450 °C .

❖ **Mixtures containing $NaNO_2$.** By far, the most used one is a commercial product named “Hitec©”, here indicated as **M4,** but they are relatively costly and toxic.

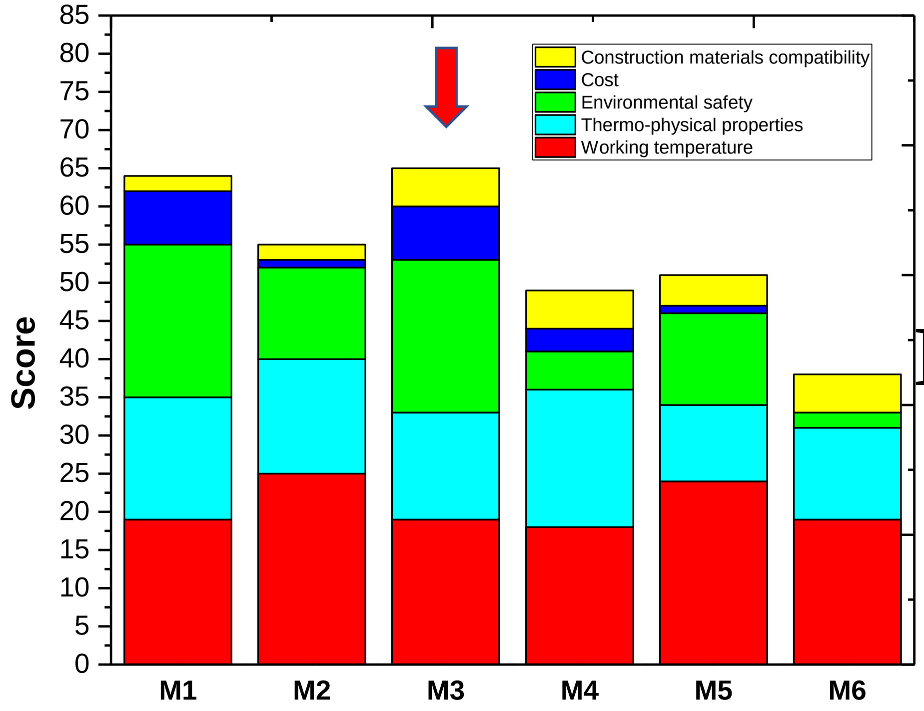
❖ **Quaternary mixtures.**

The choice is limited to $Ca/Li/Na/K//NO_3$ or $Li/Na/K//NO_3/NO_2$ systems. The former seems more significant and investigated and one formulation is taken into account **(M5).** Calcium nitrate and sodium nitrite cannot be mixed together given the formation and rapid reoxidation of calcium nitrite even at low temperatures.

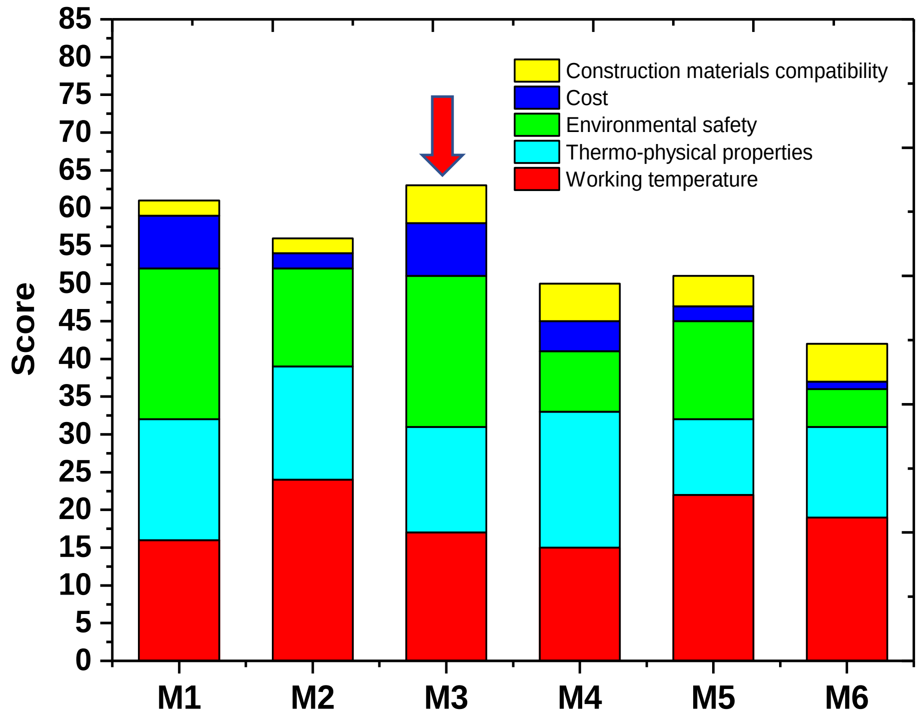
HTFs and HSMs critical review

		Tliquidus (°C)	Tdegradation (°C)	ΔT (°C)
Solar salt	M1	238	550*	312
Ternary Li/Na/K//NO3	M2	100-120	550*	440
Ternary Ca/Na/K//NO3	M3	133	450	317
Hitech®	M4	141	450	309
Quaternary Ca/Li/Na/K//NO3	M5	95	520	425
Oil Diathermic (THERMINOL® 66)	M6	-12	345	357

*Delise, T., Tizzoni, A.C., Ferrara, M., Corsaro, N., D'Ottavi, C., Sau, S., Licoccia, S. **Thermophysical, environmental, and compatibility properties of nitrate and nitrite containing molten salts for medium temperature CSP applications: A critical review (2019)***
Journal of the European Ceramic Society, 39 (1), pp. 92-99.



HTFs



HSMs

Techno-economic analysis

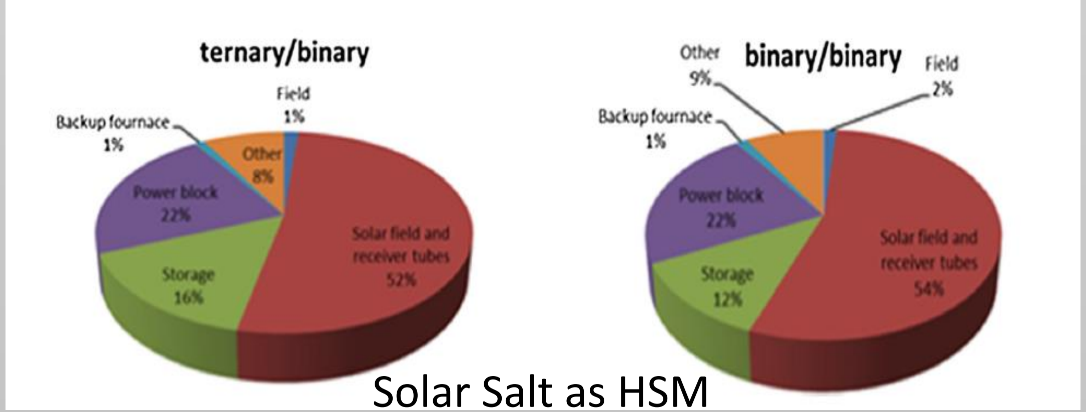
- Very useful to investigate the possible advantages of using a low melting nitrate mixture in place of the solar salt.
- The economic performance of a solar power plant is estimated by breaking down the equipment investment costs in detail, and by using common financial indicators.
- Each investment cost category is calculated based on a reference specific cost per size unit, modified by a scaling effect, a production volume effect and the price index from the reference year until now.

The total investment costs of a solar power plant with a storage system can be classified into major cost components:

✓*size of the plant ground field*
✓*size of the solar field*
✓*heat storage materials and the tanks*
✓*power block: heat generator, turbine, alternator, pre-heater, super-heater, degasser, and condenser*
✓*integration back up heater*
✓*civil work and infrastrutture.*

Lithium ternary mixture as HTF

Solar Salt as HTF



Solar Salt as HSM

*Sau, S., Corsaro, N., Crescenzi, T., D'Ottavi, C., Liberatore, R., Licoccia, S., Russo, V., Tarquini, P., Tizzoni, A.C. **"Techno-economic comparison between CSP plants presenting two different heat transfer fluids"** (2016) Applied Energy, 168, pp. 96-109. Cited 23 times.*

Techno-economic analysis

	Binary mixture as HTF	Ternary mixture as HTF	Measurement unit
Ground field specific cost	2.5	2.5	€/m^2
Ground field cost	3 449	3 521	k€
Foundations specific cost	10	10	k€/collector
Solar field foundations cost	7 600	7 760	k€
Solar field specific cost	275	261	€/m^2
Specific binary mixture cost	0.8		€/kg
Specific ternary mixture cost		1.6	€/kg
HTF in the receiver tube cost	2 940	5 497	k€
Total solar field cost	126912	126029	k€
HSM (binary mixture) total cost	6 736	6 808	k€
Specific cost per storage tank	510	510	€/m^3
Specific cost for melter + pumps + power system + foundations cost	1 700	1 700	€/m^3
Storage tanks cost	5 481	5 540	k€
Melter pump's power system foundations cost	15226	15390	k€
Storage cost per MS (binary mixture) volume	2 210	2 210	€/m^3
Intermediate HX cost	0.0	8940	€/kW h
Total cost for heat storage	27 443	36 679	k€
Total cost for heat storage without an intermediate HX	27 443	27 739	k€
Total cost solar field and storage	157 803	166 229	k€
Cost Power block	850	850	€/kW$_{el}$
Control construction, engineering and contingencies	204.0	204.0	€/kW$_{el}$
Power block			
Electric energy production cost	52 700	52 700	k€
Backup heater	3000	2500	k€
Other	20 000	20 000	k€
Investment cost	233 503	241 429	k€
Specific cost backup fuel (CH_4)	0.25	0.25	€/m^3
Fuel cost	1 673	1 101	k€/y
Specific O&M cost	2	2	% inv
O&M cost	4 670	4 829	k€/y
Annuality factor	9.11	9.11	
Depreciation rate (15 years, 7% actual discount rate)	25 660	26 531	k€/y
Annual cost	32 003	32 460	k€/y
Electric energy production	144 607	[illegible] 558	MW h$_{el}$/y
Electric energy cost	221	216	€/MW h$_{el}$

Levelized Electric Energy Cost (LCOE) is defined as the total cost of a system over its lifetime divided by the expected energy output over its useful lifetime.

$$LCOE = \frac{crf \cdot C_{invest} + C_{O\&M}}{E_{net}}$$

$E_{net} = annual\ electricty\ output;$

$C_{O\&M} = annual\ operating\ and\ maintenance\ costs;$

$C_{invest} = total\ investiment\ cost\ of\ the\ plant;$

$k_d = real\ debt\ interest\ rate = 8\%;$

$n = life\ time = 25 years;$

$$crf = capital\ recovery\ factor = \frac{k_d * (1 + k_d)^n}{(1 + k_d)^n - 1}$$

*Sau, S., Corsaro, N., Crescenzi, T., D'Ottavi, C., Liberatore, R., Licoccia, S., Russo, V., Tarquini, P., Tizzoni, A.C. ***"Techno-economic comparison between CSP plants presenting two different heat transfer fluids"*** (2016) Applied Energy, 168, pp. 96-109. Cited 23 times.*

Conclusions

- ✓ Mixtures with **Calcium nitrate** are very promising both as HSM and HTF.
- ✓ The **predictive simulation tools** have to be improved. However, it is difficult to find out parameters for other models and, for instance, some methods only consider non-ideality for the liquid state (e.g. NRTL), while it is experimentally verified that also nitrate solid mixtures present a non null enthalpy of excess. In these cases, an empirical expression can be proposed to describe the solid phase at the equilibrium.
- ✓ Regarding **corrosion data**, there is a lack especially from 400°C to 500°C and it is very important to optimize the price of the CSP construction materials.
- ✓ ENEA developed criteria for **techno-economic analysis** that are relatively rapid and easy to apply.
- ✓ Clearly, a very promising scenario is represented by the possibility **to couple sensible heat storage materials with other types of accumulation systems**, typically PCMs .

ENEA Transnational access

- A couple of words about the presence of the ENEA TFC-LAB in the SFERA III transnational access activities.

- An experimental set-up to investigate the chemical stability was assessed during the last SFERA II project and is present at the DTE/STSN/SCIS ENEA thermo-physical characterization laboratory. The equipment allows the determination of the produced gases and the liquid chemical composition, and permits to work in isothermal conditions and to control the reaction atmosphere.

- Moreover, the TFC labs include instrumentations specifically dedicated to the characterization of thermal fluids.



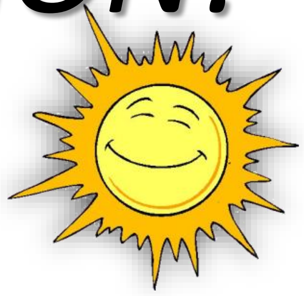







Looking forward to proposals!

THANK YOU FOR YOU ATTENTION!



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