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Fast Track School #1

Molten Salt technologies and energy system applications

CASACCIA, ROME, 09.-10.05.2023

SALT MIXTURES FOR MS APPLICATIONS

OUTLINE

NOVEL MIXTURES

MS THERMOPHYSICAL PROPERTIES

MS SAFETY AND RISKS

SALT MIXTURES FOR MS APPLICATIONS

MS COSTS

MS CORROSION

NOVEL MIXTURES

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Outline

CSP-TES Technology

Heat Tranfert Fluids (HTF)

Heat Storage Materials (HSM)

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 .

OUTLINE

Advantages of molten salts (nitrates/nitrites) :

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

Solar salt

The binary mixture of $NaNO_3$-KNO_3, indicated as “**solar salt**” is currently the most employed molten nitrate, used as reference material. (280-565°C)

Solar salt drawback: high melting point, operative issues (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)

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

OUTLINE

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).

Contents

OUTLINE

MS molten salts mixtures:

- ✔Selection criteria
- ✔Experimental characterization of their thermal, chemical and physical properties
- ✔Results and comparison between the most commercial MS mixtures

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Novel mixtures

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Novel mixtures: selection criteria

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

NOVEL MIXTURES - KEY FACTORS

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: considerations

NOVEL MIXTURES

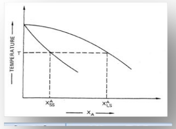
- **Molten salts (MS),** which in general consist of NO_3^-/NO_2^- mixtures are mostly considered, but only salts deriving from Na/K/Li/Ca are taken into account, because other salts are rare and more expensive.

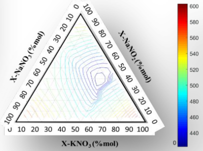
- **Carbonates, chlorides** o other salts are little soluble in molten nitrates, so their addition results not interesting.

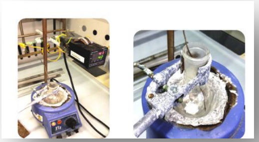
- **$NaNO_2$** cannot be coupled with **$Ca(NO_3)_2$** because of metathetical reaction ($Ca(NO_2)_2$ which leads to $Ca(NO_3)_2$).

- Mixtures must be **stable in air** to avoid inert storage systems.

Selection steps: 1) Working temperatures

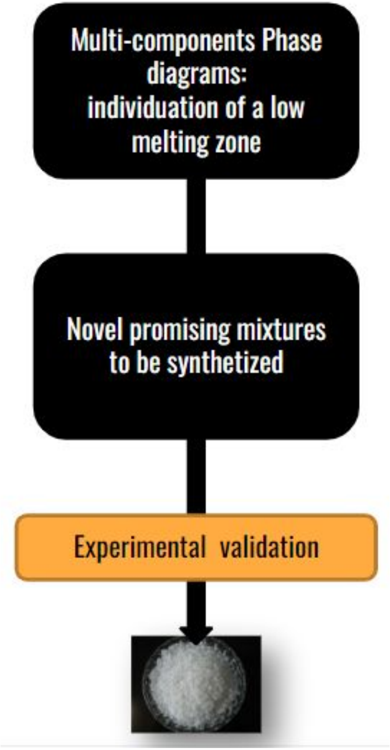






NOVEL MIXTURES

- It is necessary to narrow the candidates **by simulating multicomponent systems** with thermodynamic models;
- **Models** can be used to predict properties of different compounds, without the need to perform long and expensive experimental campaigns.
- The results are generally **low melting composition zones** from which it is possible to synthetize promising mixtures;
- Then, the selected materials **are characterized** against their thermophysical and stability properties.



Selection steps: 1) Working temperatures

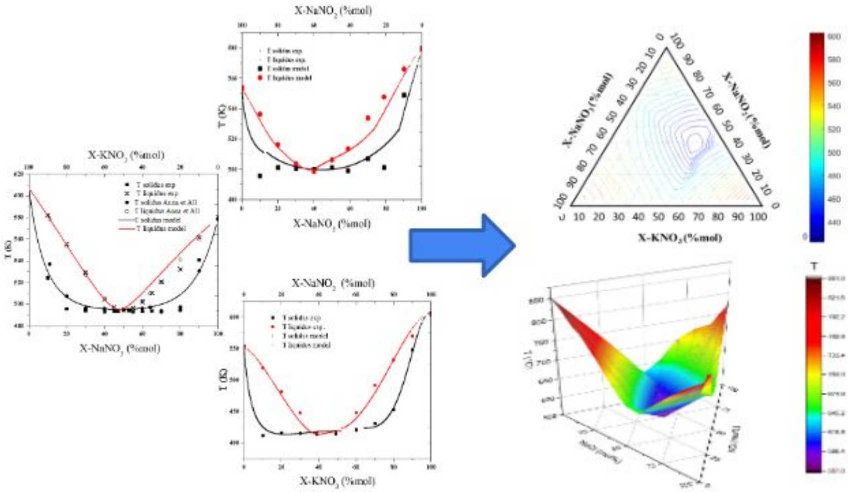
The advantage consists in the possibility of predicting the behaviour of MULTICOMPONENT system,

with only few experimental data of binary systems required.

NOVEL MIXTURES: MODELLING

Lower working temperature

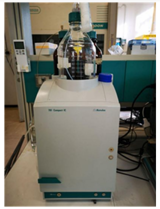
Local composition models: example of the procedure using Wilson theory



Delise T., Tizzoni A.C., Votyakov E.V., Turchetti L., Corsaro N., Sau S., Licoccia S.AUTHOR FULL NAMES:
Modeling the Total Ternary Phase Diagram of NaNO3–KNO3–NaNO2 Using the Binary Subsystems Data(2020)
International Journal of Thermophysics, 41 (1),
art. no. 1, Cited 18 times.DOI: 10.1007/s10765-019-2577-2

Selection steps: 1) Working temperatures

The formation **of oxides** is the factor that determines the upper temperature limit at which is possible to use a nitrate/nitrite salt.



NOVEL MIXTURES: STABILITY

Upper working temperature

Firstly, nitrites and oxygen are produced:

1 step. $MNO_3 \rightleftarrows MNO_2 + \frac{1}{2} O_2$ where M= Na, K, Li

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

2 step. $2MNO_3 \rightarrow M_2O + N_2 + \frac{5}{2} O_2$

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

Presence of oxides: **acid-base titration.**

Presence of nitrites: **Ion chromatography.**

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MS thermophysical properties

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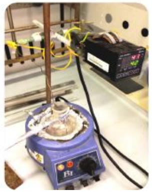
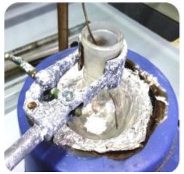
Selection steps: 2) Thermophysical properties

Ion chromatography (IC) is an analytical technique for the determination of major constituents in the ionic form in aqueous samples.

MP-AES (Microwave Plasma Atomic Emission Spectroscopy)allows to measure the presence of **metals**, even in small percentages.

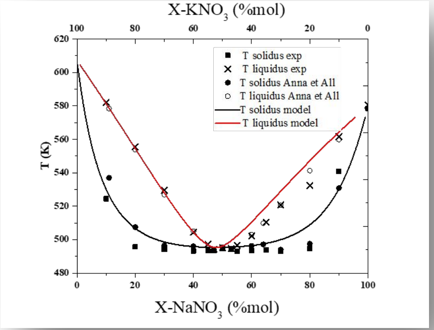



MS
THERMOPHYSICAL
PROPERTIES

PURITY

MAX PERCENTAGE OF IMPURITIES	
Chloride	0,20%
Carbonates	0,03%
Sulfates	0,05%
Alkalinity hydroxyls	0,15%
Perchlorates	0,04%
Magnesium	0,04%
Calcium	0,04%
Insoluble	0,04%
	0,06%
It is not accepted the use of anticaking agents.	

Selection steps: 2) Thermophysical properties



MS THERMOPHYSICAL PROPERTIES

Phase diagrams

TGA/DSC

Applying a controlled temperature ramp, 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.

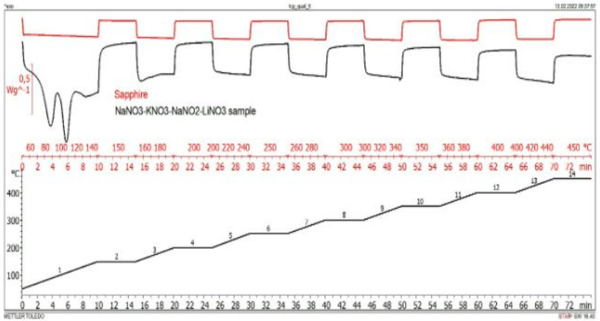
Selection steps: 2) Thermophysical properties

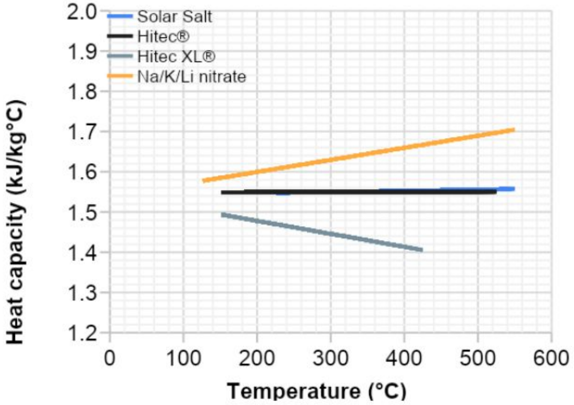
It is possible to estimate **heat capacity** values of molten salts with the use of a known heat capacity substance as reference (high purity sapphire).

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

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

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





MS THERMOPHYSICAL PROPERTIES

Specific heat

Selection steps: 2) Thermophysical properties

If the relationship between shear stress and shear rate is

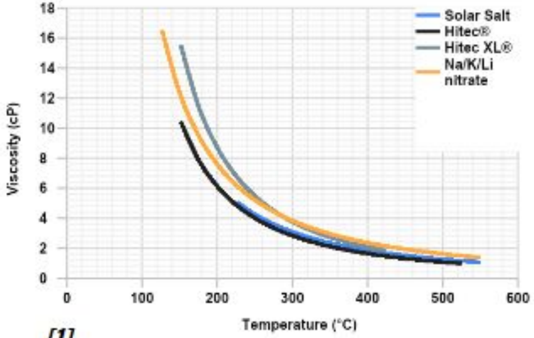
a straight line passing through the axis origin, the fluid is defined Newtonian and the slope is the Viscosity

MS THERMOPHYSICAL PROPERTIES

Viscosity

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

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



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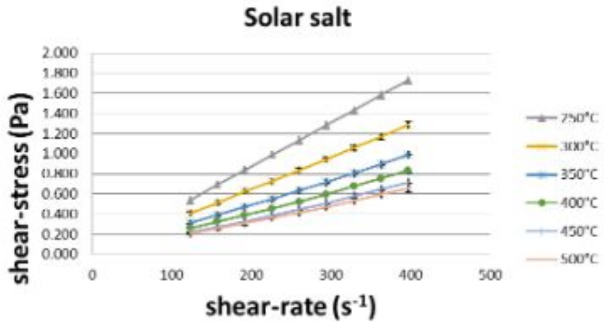


Selection steps: 2) Thermophysical properties

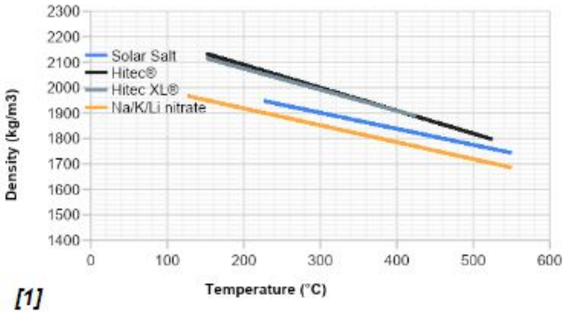
The equipment consists of a thermoregulated **stainless steel container** where the salt mixture is placed and heated; the system is kept under air at atmospheric pressure.

The temperature is regulated by an external PID controller.

The salt is then vigorously stirred, and a steel cylinder connected to the dynamometer is immersed; the weight loss due to the Buoyancy effect was noted.

MS THERMOPHYSICAL PROPERTIES

Density

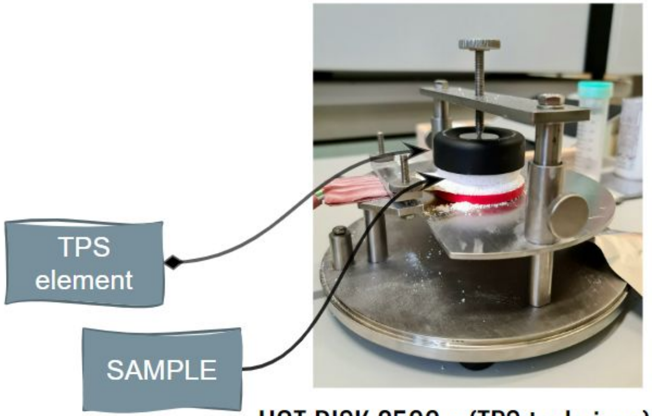


[1]

Selection steps: 2) Thermophysical properties

Heat conductivity: instrument based on the "hot wire" method (only for solid)

Transient Plane Source (TPS) element is used as both heat source and temperature sensor, and the measurement is made by recording the voltage change over the TPS-element while its temperature is slightly heated by an electrical current pulse.



HOT DISK 2500 s (TPS technique)

MS THERMOPHYSICAL PROPERTIES

Heat conductivity

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MS safety and risks

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Selection steps: 3) Environmental safety and risk for human health

	Risk Phrases
Solar salt	May intensify fire - H272
Ternary Li/Na/K//NO3	May intensify fire - H272 Causes serious eye irritation -H319
Ternary Ca/Na/K//NO3	May intensify fire - H272
Hitech® ($NaNO_3$/KNO_3/$NaNO_2$)	May intensify fire - H272 Causes serious eye irritation -H319 Eye Irrit. - H319 Very toxic to aquatic life-H400
Quaternary Ca/Li/Na/K//NO3	May intensify fire - H272 Causes serious eye irritation -H319
Oil Diathermic (THERMINOL® 66)	Skin Irrit. - H315 Eye Irrit. - H319 Suspected of damaging fertility- H361f Aquatic Acute - H400 Aquatic Chronic - H410

MS SAFETY AND RISKS

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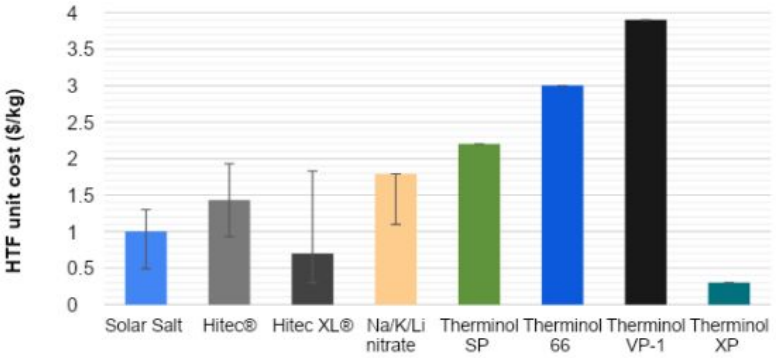
MS costs

Selection steps: 4) Material costs



[1]

MS COSTS

- **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**

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MS corrosion

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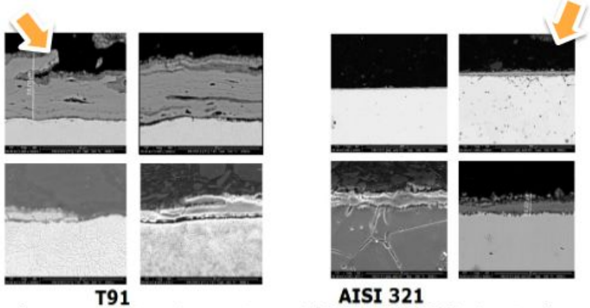
Selection steps: 5) Construction materials compatibility and corrosion resistance of alloys

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.

MS CORROSION

- ✔ **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.

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Novel mixtures

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Critical review

NOVEL MIXTURES

- **Binary $NaNO_3/KNO_3$ mixtures.** They present low cost along with good thermophysical properties and are not toxic.
- **Ternaries with lithium nitrate.** 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 KNO_3** 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©”, 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. Calcium nitrate and sodium nitrite cannot be mixed together given the formation and rapid reoxidation of calcium nitrite even at low temperatures.

Comparison

**Giaconia, A.; Tizzoni, A.C.; Sau, S.; Corsaro, N.; Mansi, E.; Spadoni, A.; Delise, T. Assessment and Perspectives of Heat Transfer Fluids for CSP Applications.*
Energies 2021, 14, 7486.
https://doi.org/10.3390/en14227486

NOVEL MIXTURES

Solar Salt

Chemical composition (%wt)	$NaNO_3/KNO_3$ (60/40)
Density $\left[\frac{kg}{m^3}\right]$ vs. temperature [°C]	$\rho = 2090 - 0.63 \cdot T$
Dynamic Viscosity [cP] vs. temperature [°C]	$\mu = 71,645 \cdot T^{-1.763}$
Thermal conductivity $[\frac{W}{°C*m}]$ vs. temperature [°C]	$k = 0.3804 + 3.452 \cdot 10^{-4} \cdot T$
Heat capacity $[\frac{kJ}{°C*kg}]$ vs. temperature [°C]	$cp = 1.5404 + 3.0924 \cdot 10^{-5} \cdot T$
Thermal stability (max operation temperature)	600 °C
Liquidus temperature (initial solidification point)	238 °C

Hitec® (Na/K nitrate/nitrite)

Chemical composition (%wt)	$NaNO_3/KNO_3/NaNO_2$ (7/53/40)
Density $\left[\frac{kg}{m^3}\right]$ vs. temperature [°C]	$\rho = -0.9 \cdot T + 2269.4$
Dynamic Viscosity [cP] vs. temperature [°C]	$\mu = 146,452 \cdot T^{-1.903}$
Thermal conductivity $[\frac{W}{°C*m}]$ vs. temperature [°C]	$k = 0.5843 \mp 0.0006 \cdot T$
Heat capacity $[\frac{kJ}{°C*kg}]$ vs. temperature [°C]	$cp = 1.55 - 0.0001 \cdot T$
Thermal stability (max operation temperature)	450 under air; 530 °C under inert gas
Liquidus temperature (initial solidification point)	141 °C

Hitec XL® (Na/K/Ca nitrate)

Chemical composition (%wt)	$NaNO_3/KNO_3/Ca(NO_3)_2$ (15/43/42)	
Density $\left[\frac{kg}{m^3}\right]$ vs. temperature [°C]	$\rho = 2240 - 0.827 \cdot T$	[33]
Dynamic Viscosity [cP] vs. temperature [°C]	$\mu = 509,611 \cdot T^{-2.072}$	(*)
Thermal conductivity $[\frac{W}{°C*m}]$	~0.519 (constant in the operative range)	[31]
Heat capacity $[\frac{kJ}{°C*kg}]$ vs. temperature [°C]	$cp = 1.542 - 0.000322 \cdot T$	(*)
Thermal stability (max operation temperature)	≤425 °C	[34]
Liquidus temperature (initial solidification point)	~125 °C	[35]

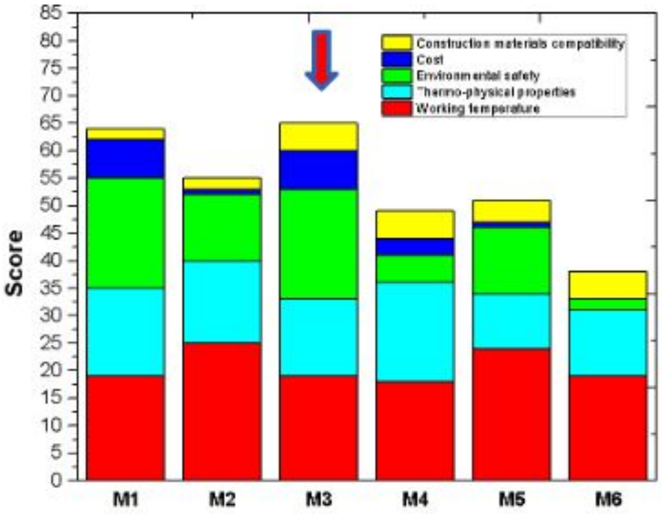
Na/K/Li nitrate

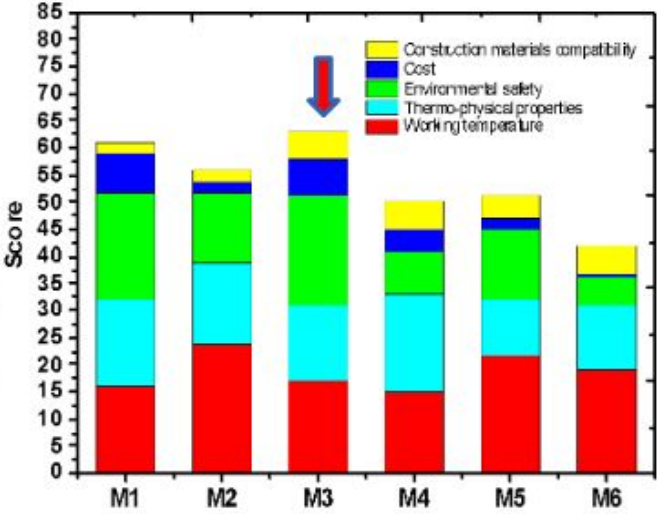
Chemical composition (%wt)	$NaNO_3/KNO_3/LiNO_3$ (18/45/37)	
Density $\left[\frac{kg}{m^3}\right]$ vs. temperature [°C]	$\rho = 2051 - 0.6639 \cdot T$	[31]
Dynamic Viscosity [cP] vs. temperature [°C]	$\mu = 58,725 \cdot T^{-1.69}$	(*)
Thermal conductivity $[\frac{W}{°C*m}]$	$k = 0.0005 \cdot T + 0.4$	[31]
Heat capacity $[\frac{kJ}{°C*kg}]$ vs. temperature [°C]	$cp = 1.5395 + 0.0003 \cdot T$	(*)
Thermal stability (max operation temperature)	600 °C	[17]
Liquidus temperature (initial solidification point)	120 °C	[36]

* data obtained by ENEA in the framework of the "Concentrating Solar Power" project under the "Electric System Research" Programme 2019–2021.

Comparison

Solar salt	M1
Ternary Li/Na/K//NO3	M2
Ternary Ca/Na/K//NO3	M3
Hitech®	M4
Quaternary Ca/Li/Na/K//NO3	M5
Oil Diathermic (THERMINOL® 66)	M6





✓Mixtures with **Calcium nitrate** are very promising both as HSM and HTF.

**Delise, T., Tizzoni, A.C., Ferrara, M., Corsaro, N., D'Ottavi, C., Sau, S., Licoccia, 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.*

The results are going to be published in public domain, online available, reports (in Italian language)

Ongoing activities

The following work has been funded in the framework of the "Concentrating Solar Power" project, research activity lines on solar "process heat for industrial processes", under the "Electric System Research" Programme 2019-2021, with the financial support of Italian Ministry for Economic Development.

NOVEL MIXTURES

- Development and validation of **predictive models** which, starting from the properties of the individual components, allow to establish the thermophysical characteristics of nitrate and nitrite mixtures according to their composition.
- An **experimental campaign** was preliminarily carried out aimed at:
  - filling the gaps present in the scientific literature regarding these data
  - obtaining a minimum number of values, which, would allow an appropriate validation of the predictive systems proposed.

Moreover, an open-source database has been developed, available and easy to consult, to make the results usable quickly and effectively, and allowing the integration the new data obtained with scientific literature.

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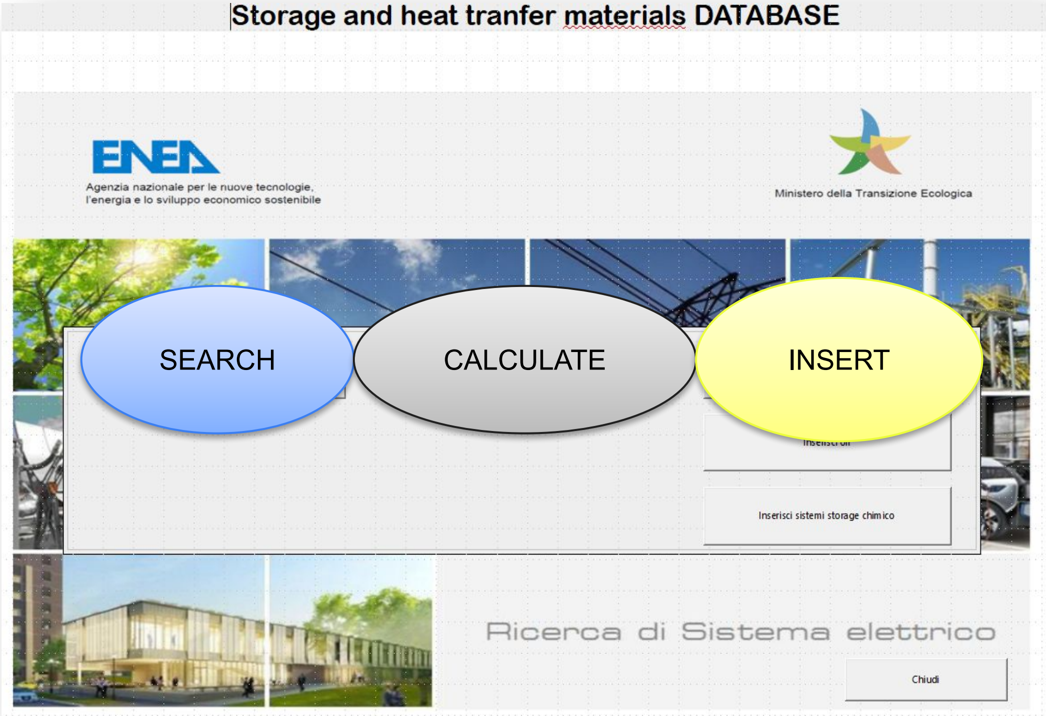

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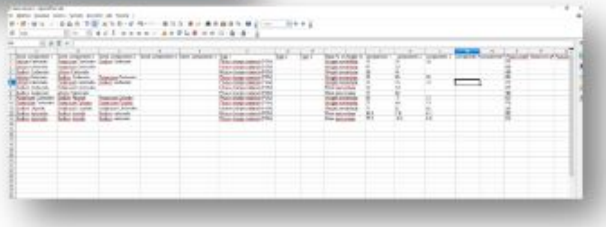

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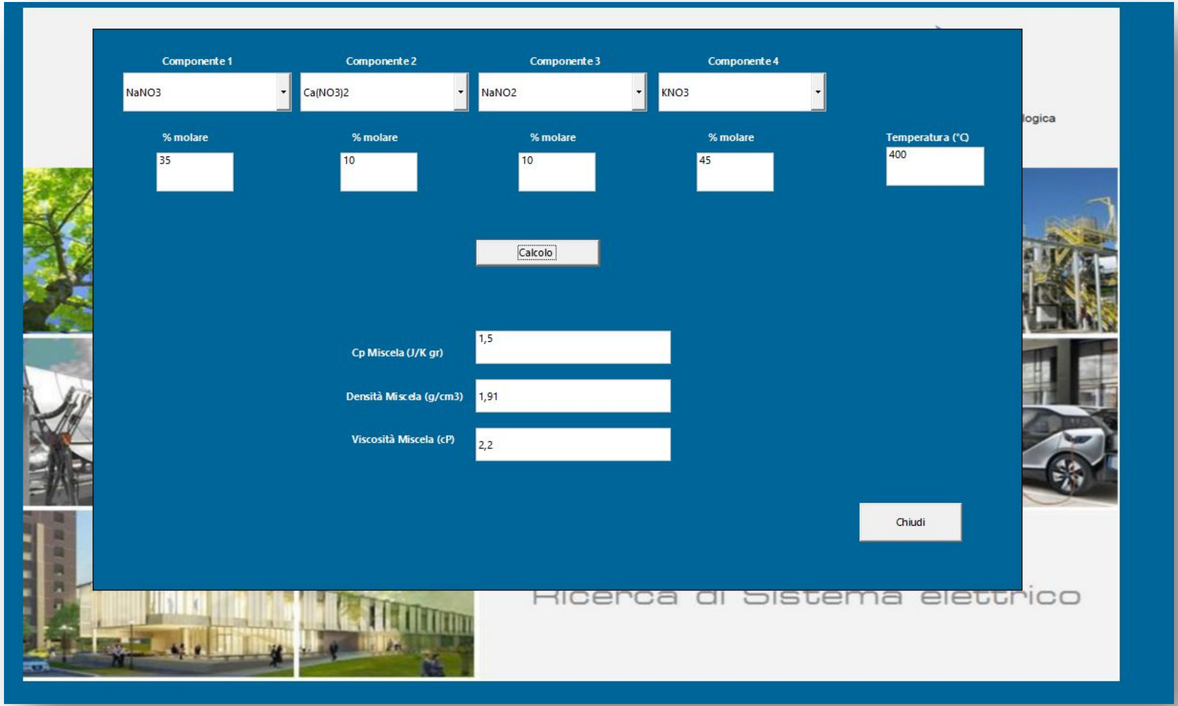

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