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Solar Facilities for the European Research Area

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INTRODUCTION

The objective of the SFERA II work package 15 is to improve the quality of performances and procedures regarding laboratory studies, and to summarize and make available the presented or investigated data about the main characteristics of each feasible HTF (heat thermal fluid)/HSM (heat storage material) for CSP applications.

The first necessary step for the wp development is to collect and classify, according to shared evaluation criteria, the currently available fluids feasible to be used as HTF and/or HSM.

The following materials are taken into account

1) Alkaline/alkaline earth metals nitrate/nitrite mixtures
2) Thermal oils
3) Solid Media Storage Technology (as HSM)
4) PCM (phase change materials) (as HSM)
5) Gas/steam (as HTF, pressurized liquid water also proposed for buffer storage systems)
6) Liquid metals
7) Nanoparticles materials (nanoparticles additivate to HTF/HSM)
8) Thermochemical heat storage

The following characteristics have been considered for the rating

1) Environmental safety
2) Risk for human health
3) Freezing temperature
4) Upper thermal stability point
5) Thermo-physical properties (density, viscosity, heat capacity, thermal conductivity)
6) Construction materials compatibility
7) Material cost
8) Cost of handling equipment and system
9) Efficiency of the power block associated (for HSM)

The obtained results are reported and discussed.

SURVEY ON THE STATE OF ART REGARDING HTF/HSM FOR SOLAR APPLICATIONS

Alkaline/alkaline heart metals nitrate/nitrite mixtures

Among the several thermal fluids employed and proposed both as HTF and HSM, nitrate/nitrite mixtures along with thermal oils, represents the most widespread ones. In general they present heat capacity values ranging from 1.2 to 1.6 J/K gr, dynamic viscosity in the order of a few cP units at 400-500 °C, and density values below 2 kg/m^3 in the same temperature interval; the thermal conductivity is reported of about 0.5 W/m K for practically all studied mixtures [1]. Given the differences regarding their different operating temperature range (depending on the initial solidification point from now on defined as "liquidus point"), these mixtures are here further divided into subcategories.

Sodium/potassium nitrate (60:40 wt%) mixture "solar salt"

One of the most currently used mixture consists of $NaNO_3$ (sodium nitrate) and KNO_3 (potassium nitrate) in a weight percentage ratio of 60/40 respectively; given its large employment in CSPs, this material is generally known as "solar salt". This composition presents an upper temperature limits around 600°C, relatively low cost, good safety characteristics and low environmental impact [2] . It is interesting to note that the mixture 60/40 does not correspond to the eutectic composition (50/50 %wt) for these two nitrates, it is preferable to use a greater percentage of sodium nitrate in order to reduce the material costs to a better level, not significantly increasing the liquidus temperature value, which is around 238 °C. [3][4] .

Clearly the "solar salt" also presents several drawbacks. A primary disadvantage is a relatively high freezing point, to be compared with about 13°C for organic fluids coupled with the decrease of density in the solid phase. Consequently, particular procedures have to be dedicated to prevent salt solidification in a CSP plant because melting it again can cause important damages due to volume expansion. One solution is to add electrical heating systems all along the pipes filled with solar salt and around storage tanks and it is a quite expensive solution. At temperatures above 500-550 °C only relatively costly stainless steel (SS 321H, SS 347) alloys have so far showed full compatibility with this molten salt in all the possible operating conditions [5].

All considered, the following ratings may be assigned to this mixture, (starting from 1 that stands for "very poor", to 5 that stands for "very good").

Table 1: rating of NaNO$_3$/KNO$_3$ 60:40 wt% as HTF

Environmental safety	5
Risk for human health	5
Freezing temperature	2
Upper thermal stability point	4
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	5
Cost of handling equipment and system	2

A further point in favour of the employment of the solar salt in CSP plants using a Rankine cycle power block, is that the efficiency of this thermodynamic cycle is slightly affected by a decrease of the operative point of the thermal fluids below 270 °C [6], and regarding this aspect, it seems useless the employment of lower freezing mixtures; on the other hand, the use of low melting materials can clearly facilitate CSP plants maintenance operations, involving, for instance, emptying and filling of the lines.

Table 2: rating of NaNO$_3$/KNO$_3$ 60:40 wt% as HSM

Environmental safety	5
Risk for human health	5
Freezing temperature	3
Upper thermal stability point	4
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	5
Cost of handling equipment and system	3
Efficiency of the power block associated	5

Lithium or calcium nitrate containing ternary mixtures

Interesting alternatives to the "solar salt" mixture can be obtained by adding lithium or calcium nitrate. In both cases low melting ternary mixtures can be obtained, with a liquidus point of 120 °C adding lithium [1] ($LiNO_3$/KNO_3/$NaNO_3$ 30/18/52 wt%), and of 133 °C adding calcium [1] ($Ca(NO_3)_2$/KNO_3/$NaNO_3$ 42/16/42 wt%). The main advantages of introducing lithium nitrate is to obtain a very low freezing point without significant difference respect to the "solar salt" concerning the thermal stability; an evident drawback is the high cost of lithium. Also with calcium nitrate a low melting point can be reached, but thermal stability is likely limited below about 450 °C[2], given the instability of calcium nitrate with respect to the formation of its oxide compound (and eventually carbonate), another disadvantages is the high viscosity especially approaching the freezing point; on the other hand, $Ca(NO_3)_2$ is maybe the less costly among the employable nitrates.
Regarding material compatibility, it could be established from the few literature present [1].
The following tables report the proposed rating for the two ternary mixtures, clearly, the use lithium nitrate mixture is most advisable as HTF (given the high lithium cost and the relative small amount of a HTF fluid with respect to a storage medium), instead the ternary mixtures containing calcium are maybe most useful as HSM, because of their low cost and the difficulties associated to their use as HTF, (relatively high viscosity value). Of course, the use of two different materials as HTF and HSM implies the necessity of an intermediate heat exchanger, differently from the situation with the "solar salt", which can actually be (and is) employed in both cases.

Table 3: rating of $LiNO_3$/KNO_3/$NaNO_3$ 30/18/52 wt% as HTF

Environmental safety	4
Risk for human health	4
Freezing temperature	4
Upper thermal stability point	4
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	2
Cost of handling equipment and system	3

Table 4: rating of $LiNO_3$/KNO_3/$NaNO_3$ 30/18/52 wt% as HSM

Environmental safety	4
Risk for human health	4
Freezing temperature	4
Upper thermal stability point	4
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	1
Cost of handling equipment and system	3
Efficiency of the power block associated	5

Table 5: rating of $Ca(NO_3)_2$/KNO_3/$NaNO_3$ 42/16/42 wt% as HTF

Environmental safety	5
Risk for human health	5
Freezing temperature	4
Upper thermal stability point	2
Thermo-physical properties	3
Construction materials compatibility	3
Material cost	5
Cost of handling equipment and system	3

Table 6: rating of $Ca(NO_3)_2$/KNO_3/$NaNO_3$ 42/16/42 wt% as HTF

Environmental safety	5
Risk for human health	5
Freezing temperature	4
Upper thermal stability point	2
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	5
Cost of handling equipment and system	4
Efficiency of the power block associated	3

Lithium and calcium nitrate containing quaternary mixtures

The contemporary addition of lithium and calcium nitrate was also investigated [1]. According to the composition, the freezing point can also be lowered below 100 °C [1]; these mixtures present the disadvantages of lithium (high cost) and calcium (calcium nitrate thermal instability). Though potentially very interesting, they are not considered for rating in this report.

Sodium nitrite containing mixtures

Another way to low the freezing point is the addition of sodium nitrite $NaNO_2$. A mixture presenting a composition of $NaNO_3$/KNO_3/$NaNO_2$ with a ratio (wt%) of 7/53/40 (%w/w) is known as a commercial product named "Hitec©" salt [7]. The liquidus point was lowered to 141°C, and it has found great applications despite those mixtures suffered of a marked decrease in terms of thermal stability which is limited to 450° under air [2,7], and 538 °C under nitrogen [7]. Thermo-physical properties, below the upper temperature limit, are more or less similar to the "solar salt" ones [7]. Compatibility with CSP materials seems reasonably good inside the thermal stability range [7]. The proposed rating is shown below.

Table 7: rating of NaNO$_2$/KNO$_3$/NaNO$_3$ 40/53/7 wt% as HTF

Environmental safety	3
Risk for human health	3
Freezing temperature	4
Upper thermal stability point	3
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	3
Cost of handling equipment and system	4

Table 8: rating of NaNO$_2$/KNO$_3$/NaNO$_3$ 40/53/7 wt% as HSM

Environmental safety	3
Risk for human health	3
Freezing temperature	4
Upper thermal stability point	3
Thermo-physical properties	4
Construction materials compatibility	3
Material cost	3
Cost of handling equipment and system	4
Efficiency of the power block associated	3

Comparison among nitrate/nitrite containing mixture

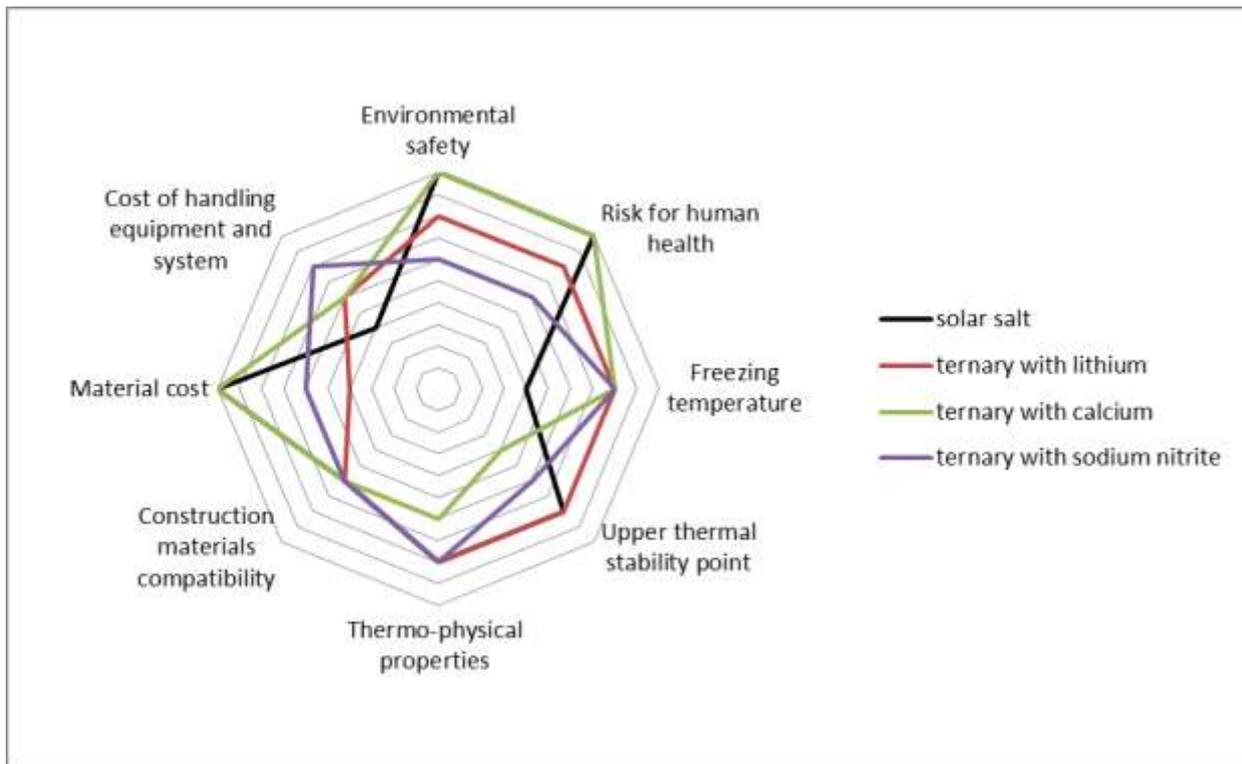The above described ratings are compared in the following radar graphs, see figure 1-2.

Fig. 1: comparison between nitrate/nitrite mixtures as HTF.
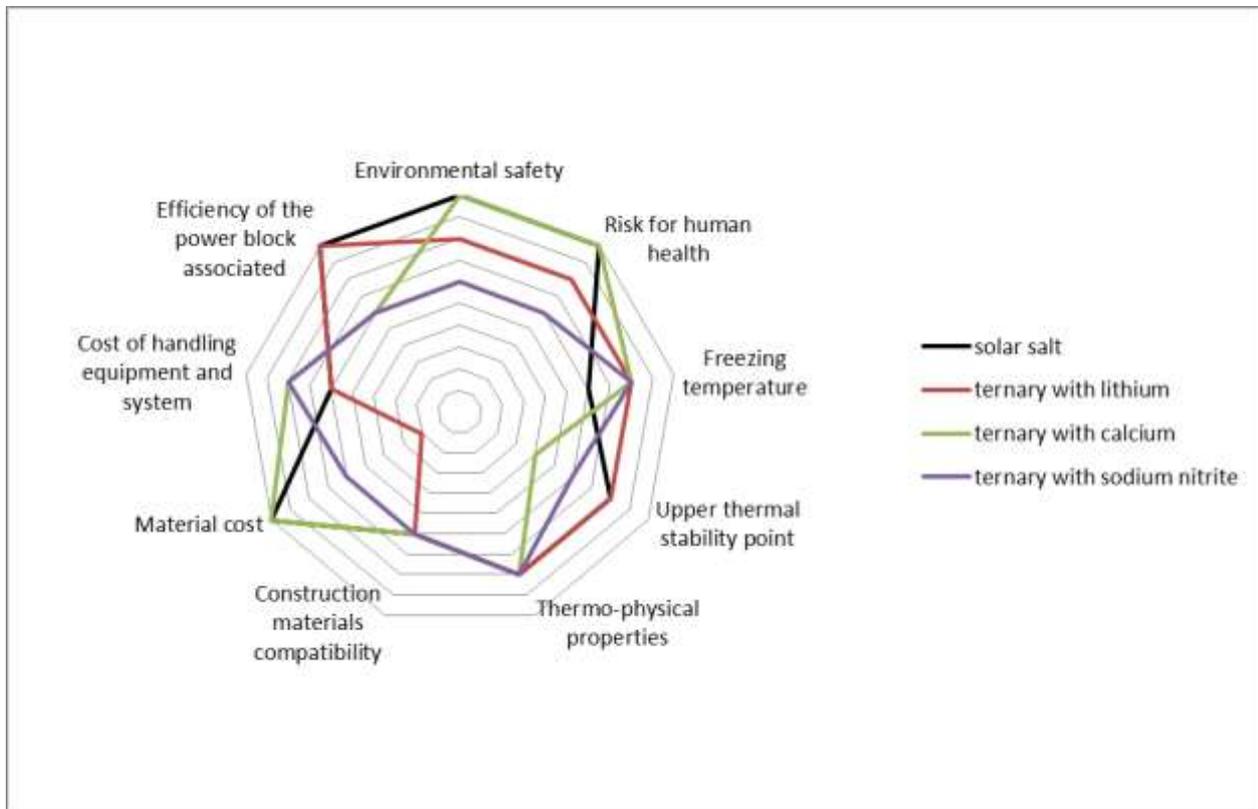
Fig. 2: comparison between nitrate/nitrite mixtures as HSM.

The "solar salt" mixture can still be considered the best choice as HTF and HSM, with the only real disadvantages associated with the plant equipment cost and the difficulties for CSP plants maintenance operations; sodium nitrite and, especially, calcium nitrate containing fluids are anyway quite potentially interesting, and could be very useful to consider their applications for ORC (organic Rankine cycle) power blocks. The ternary mixture containing lithium nitrate could be considered as HTF coupled with an intermediate heat exchanger, with a "solar salt" based heat storage system.

Thermal oils

Two of the most used thermal oils can be considered Therminol VP1 (Gilotherm DO) [8] and Therminol 72 [9]. The former is an azeotropic mixture of 26.5% diphenyl (($C_6H_5)_2$) and 73.5% diphenyloxide (($C_6H_5)_2O$). The melting and boiling points are respectively 12°C and 258°C [8]; the latter is a mixture of diphenyl oxide (around 45w %), terphenyl (around 32 w %), diphenyl (around 16 w %) and phenantrene (around 3 w %). The melting and boiling points are -18°C and 271°C respectively under atmospheric pressure [9]. In both cases, higher operating temperatures (never above 400 °C) can be reached only under inert gases pressure; very few data are available about the decomposition products and kinetics of these materials [10].

The evident benefits of these materials are the very low freezing points (and very low viscosity values also at low temperatures)[8,9]; the low density (with respect to, for instance, nitrate/nitrite mixtures) is compensated with high specific heat values [8,9]. Drawbacks are the low thermal conductivity, the low upper limit for the thermal stability, which can be only partially overcome by employing inert pressurized pipelines, the toxicity and flammability and a relative (with respect to other HTF/HSM) high cost.

In summary, thermal oils, despite their current large employment (in general, as HTF with molten nitrates as HSM), do not look like the most feasible HTF material. On the other hand, they present several evident advantages, such as their low melting point; at reasonable temperature levels (300°C for example using Therminol 66), there are very useful without any freezing and so avoiding systems to maintain all the HTF circuit in temperature during nights or maintenance interventions. Intermediate temperature level around 300°C are compatible with the use of ORC to produce electricity. Thermal oils are very often used also in industry, perhaps a difference can be made between the use of thermal oils at high pressure levels or near atmospheric conditions. Given the former is typically the situation for CSP plants, a very low score is associated with the "risk for human health" field.

Their use as HSM certainly seems inadequate, especially considering their cost and their very reduced temperature operating range, unless an inertized storage tank is employed.

Table 9 and 10 show the rating of thermal oils as HTF and HSM, respectively.

Table 9: rating of thermal oils as HTF

Environmental safety	2
Risk for human health	1
Freezing temperature	5
Upper thermal stability point	2
Thermo-physical properties	4
Construction materials compatibility	4
Material cost	2
Cost of handling equipment and system	3

Table10: rating of thermal oils as HSM

Environmental safety	2
Risk for human health	1
Freezing temperature	5
Upper thermal stability point	2
Thermo-physical properties	4
Construction materials compatibility	4
Material cost	2
Cost of handling equipment and system	3
Efficiency of the power block associated	2

Comparison between thermal oils and some nitrate/nitrite containing mixtures

The following figures 3 and 4 report a comparison of thermal oils, the "solar salt" mixture ($NaNO_3$/KNO_3 60:40 wt%), the mixture containing calcium nitrate ($Ca(NO_3)_2$/KNO_3/$NaNO_3$ 42/16/42 wt%) and the one containing sodium nitrite ($NaNO_2$/KNO_3/$NaNO_3$ 40/53/7 wt%) considering their use as HTF and HSM, respectively.
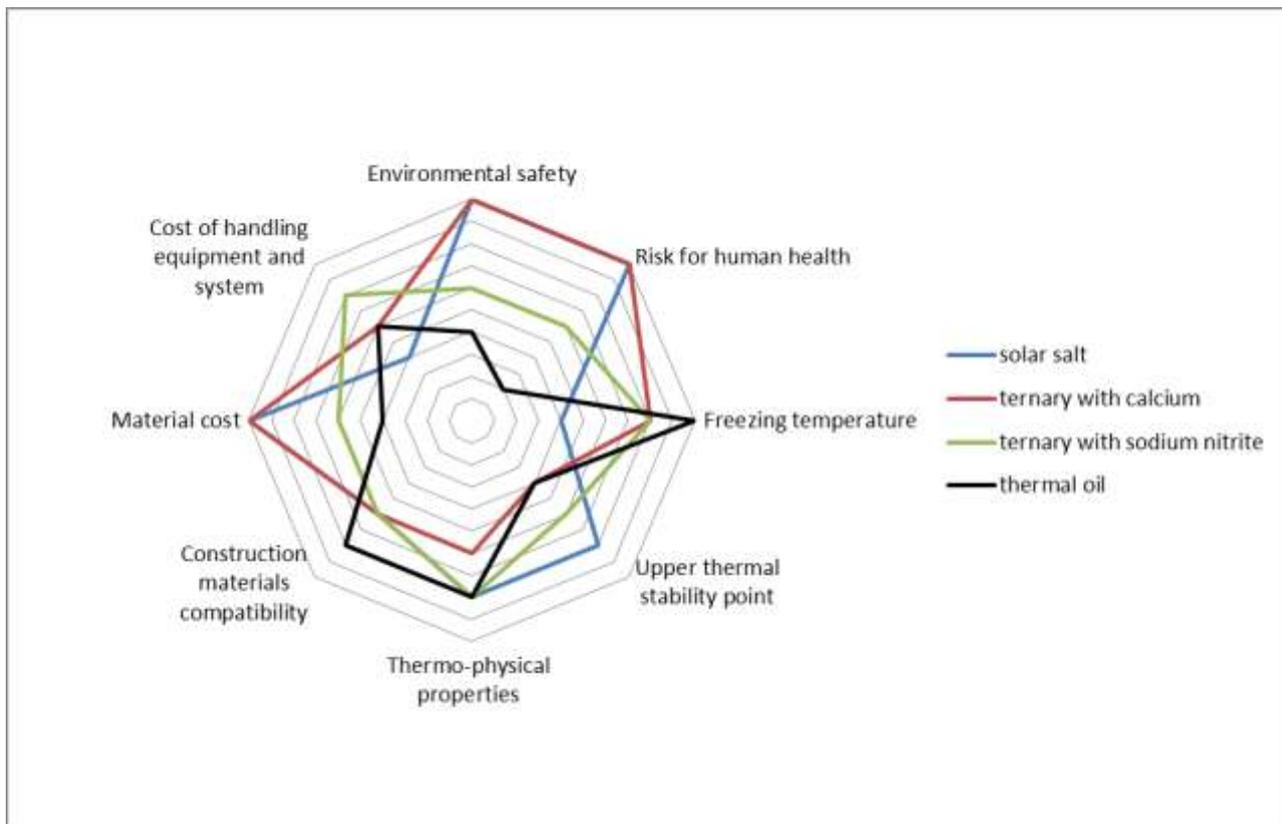

Fig. 3: comparison between thermal oils and some nitrate/nitrite mixtures as HTF.
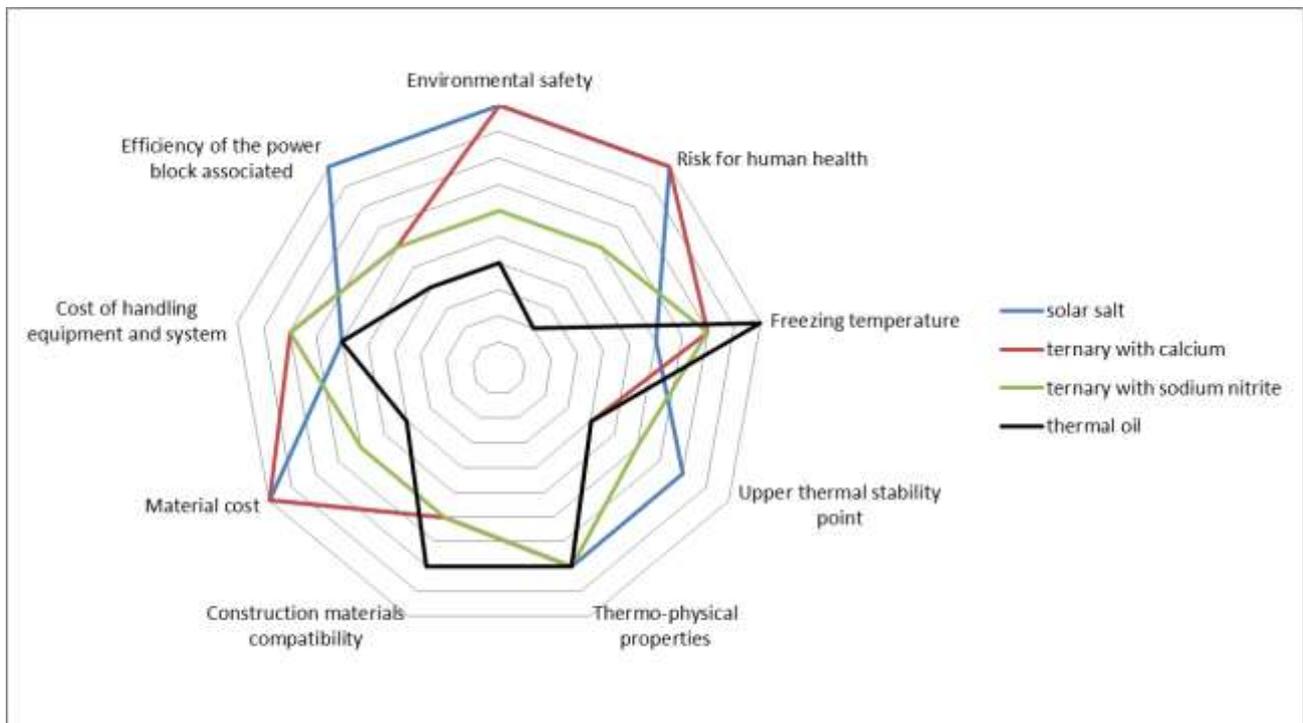
Fig. 4: comparison between thermal oils and some nitrate/nitrite mixtures as HSM.

It is interesting to note that, also as HTF, low melting nitrates/nitrites ternaries can be considered quite competitive with respect to thermal oils.

Solid fillers as HSM

Solid fillers (for instance: sand-rock minerals, reinforced concrete, cast steel, silica fire bricks; as pellets or structured compounds) have been proposed to be used as sensible storage medium, the main advantage of these materials (besides their good thermal conductivity) is their relative high density, which allows a greater sensible heat storage per volume with respect to liquid HSM; also their price per weight (and then per volume) could be quite low, so theoretically leading to a reduction in the cost of a sensible heat storage system, with respect to the case where molten nitrates are employed [11].

A clear disadvantages is the cooling of the filler material during thermal discharge, which would not allow to work at constant temperature; in order to overcome this drawback, systems presenting thermocline stratification coupled with molten nitrates have been proposed; [12] [13], [14] at this aim, concrete, solid oxides or silicon carbide have been investigated as solid HSM; the employing of a complementary HSM in fluid state and in contact with solid fillers is also evidently necessary in order to ensure a proper heat transfer during charging and discharging cycles. The major challenges for this kind of configuration are: to find a good compromise between high temperatures compatibility with molten nitrates and low price of the solid material, and to create and maintain a good thermocline stratification.

In thermocline tanks with solid filling, fluid is not only another HSM but also Heat Transfer Fluid. With a thermocline it is of course possible to ensure a stabilized level of temperature during discharge. The interest is clearly to limit the volume of oil (at low temperature) or

solar salt (at higher temperature). This limitation is interesting for two aspects : cost (rocks are less expensive then salts) and also safety (rocks have no interaction).

The following table reports the rating of solid fillers as HSM.

Table 11: rating of solid fillers as HSM

Environmental safety	5
Risk for human health	5
Freezing temperature *	5
Upper thermal stability point**	5
Thermo-physical properties	4
Construction materials compatibility***	3
Material cost****	4
Cost of handling equipment and system*****	3
Efficiency of the power block associated ******	4
*actually not applicable, the high rating is due to the characteristic of being able to be employed for sensible heat exchange at every temperature, of course, another fluid (molten salts or gases) must be employed to transport the thermal energy from and to a power unity **if stable in contact with molten salts or other complementary HSM ***considering they as coupled with molten nitrates ****including the necessary presence of a complementary fluidized HSM (like molten nitrates) *****the coupling with a heat transport fluid is practically always necessary ******provided another thermal fluid is used to ensure a proper heat transfer and a thermocline is maintained	

Comparison between thermal solid fillers and some nitrate/nitrite containing mixtures as HSM

Figure 5 shows a comparison between solid fillers, considering their most promising (however, not unrealistic) characteristics, the "solar salt" mixture ($NaNO_3/KNO_3$ 60:40 wt%), the mixture containing calcium nitrate ($Ca(NO_3)_2/KNO_3/NaNO_3$ 42/16/42 wt%) and the one containing sodium nitrite ($NaNO_2/KNO_3/NaNO_3$ 40/53/7 wt%) considering their use as HSM.
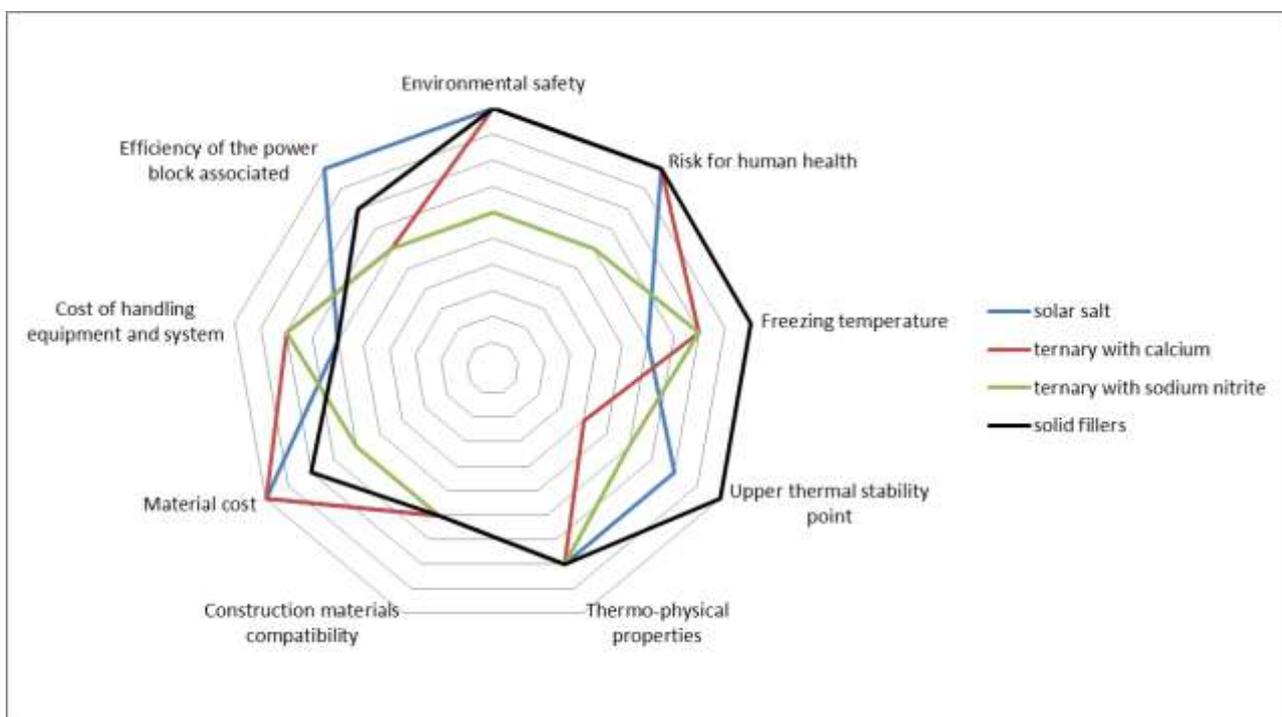
Fig. 5: comparison between solid fillers (considered as coupled with another HSM fluid, typically molten nitrates) and some nitrate/nitrite mixtures as HSM.

In summary, it can be said that solid fillers potentially represents a very promising research field for significantly decreasing the cost of solar powered heat storage systems, especially taking into account the possibility to replace most of the nitrate mixtures present in a storage tank with a cheaper solid material.

Phase change materials (PCM) as HSM

An interesting option for solar heat storage is represented by phase change materials (PCM), where the latent heat of these substances is employed for charging and discharging steps. The main advantages of these HSMs is the higher stored energy density with respect to sensible heat based system. [15]. Inorganic PCMs can store up to 230 KJ/kg, to be confronted with 15-60 KJ/kg (according to the specific heat) for typical sensible heat based storage systems. This feature can lead to a great reduction in the necessary storage material amount, and as a consequence, in storage costs, also they would allow the employment of a single tank for the storage operations; besides, heat charge and discharge can be made at about the same temperature, and this is favourable for the energy efficiency of the process; in case a larger temperature interval is necessary, it is also possible to use a cascaded system of PCMs[16].

The use of PCM for heat storage is particularly interesting for Direct Steam Generation CSP plants because it is adapted to water phase change storage[17]. Both phenomena occurs at constant temperature and heat transfer is possible with a constant temperature gradient along the storage system which is an efficient way to use an heat exchanger.

A major disadvantages is that the phase change involve a solid/liquid (or vice versa) transition, and this implies a significant change in the storage material volume during charging/discharging, consequently, particular design must be taken into account for a proper heat exchanger [18], however direct contact methods have also been proposed [19]. To overcome this problem several solution have been recently proposed [12], such as for instance, the use of encapsulated PCM [12]. Furthermore, PCMs present, in general low values respect to thermal conductivity in their solid state [20], a proposed method to overcome this feature is to employ composite latent heat storage materials (CLHSM) [21], where a compound with good thermal conductivity is added to the PCM, as for instance graphite, can be used [22]. This addition leads to an increase of thermal conductivity from 0.2-0.8 W/m K to 5-10 W/m K depending on the quantity of added graphite [22]. Of course, there must be chemical compatibility between the additive and the employed PCM.
Considering the medium/high temperatures (from 300 ° up to 600°C) in the SFERA II project, several inorganic mixtures have been proposed as PCM: among the most interesting, alkaline nitrates (sodium nitrate, for instance) can be employed at around 300 °C [23], and for higher temperatures a wide range of temperatures can be covered by using fluoride and chloride based mixtures [24]. Moreover, also the application of carbonate mixtures are of interest. [24][25]. If nitrates and carbonates are employed in an interval of 400-600 °C, their material compatibility can be more or less regarded as similar to the one of molten nitrates used as sensible heat storage materials, and this assumption will be made for further considerations.
The table below summarizes a realistic rating for the PCM as HSM.

Table 12: rating of PCM as HSM

Environmental safety	5
Risk for human health	5
Freezing temperature *	4
Upper thermal stability point	5
Thermo-physical properties	3
Construction materials compatibility	3
Material cost	5
Cost of handling equipment and system	2
Efficiency of the power block associated	4

*actually not applicable, the rating reflects the advantages of not using a sensible heat ΔT

Comparison between PCMs and some nitrate/nitrite containing mixtures as HSM

Figures 6 and 7 show a comparison between PCMs (nitrates or carbonates mixtures), the "solar salt" mixture ($NaNO_3/KNO_3$ 60:40 wt%), the mixture containing calcium nitrate ($Ca(NO_3)_2/KNO_3/NaNO_3$ 42/16/42 wt%) and the one containing sodium nitrite ($NaNO_2/KNO_3/NaNO_3$ 40/53/7 wt%) considering their use as HSM.
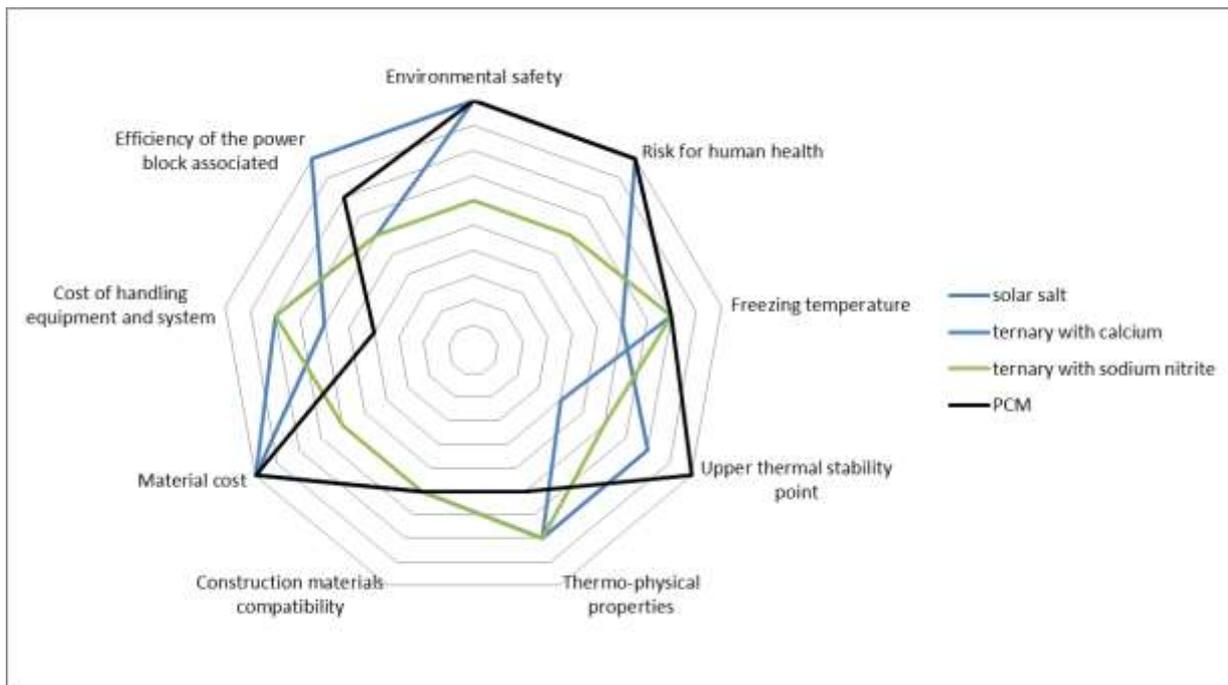

Fig. 6: comparison between PCM (nitrates or carbonates mixtures in a temperature range of 400 – 600 °C) and some nitrate/nitrite mixtures as HSM.

Comparison between PCMs, solid filler materials and the solar salt mixture as HSM

It is very interesting to compare the PCM with the solid fillers discussed in the previous text and with the most used sensible heat storage medium for solar plant, that is the so called "solar salt" binary mixture ($NaNO_3$/KNO_3 60:40 wt%).
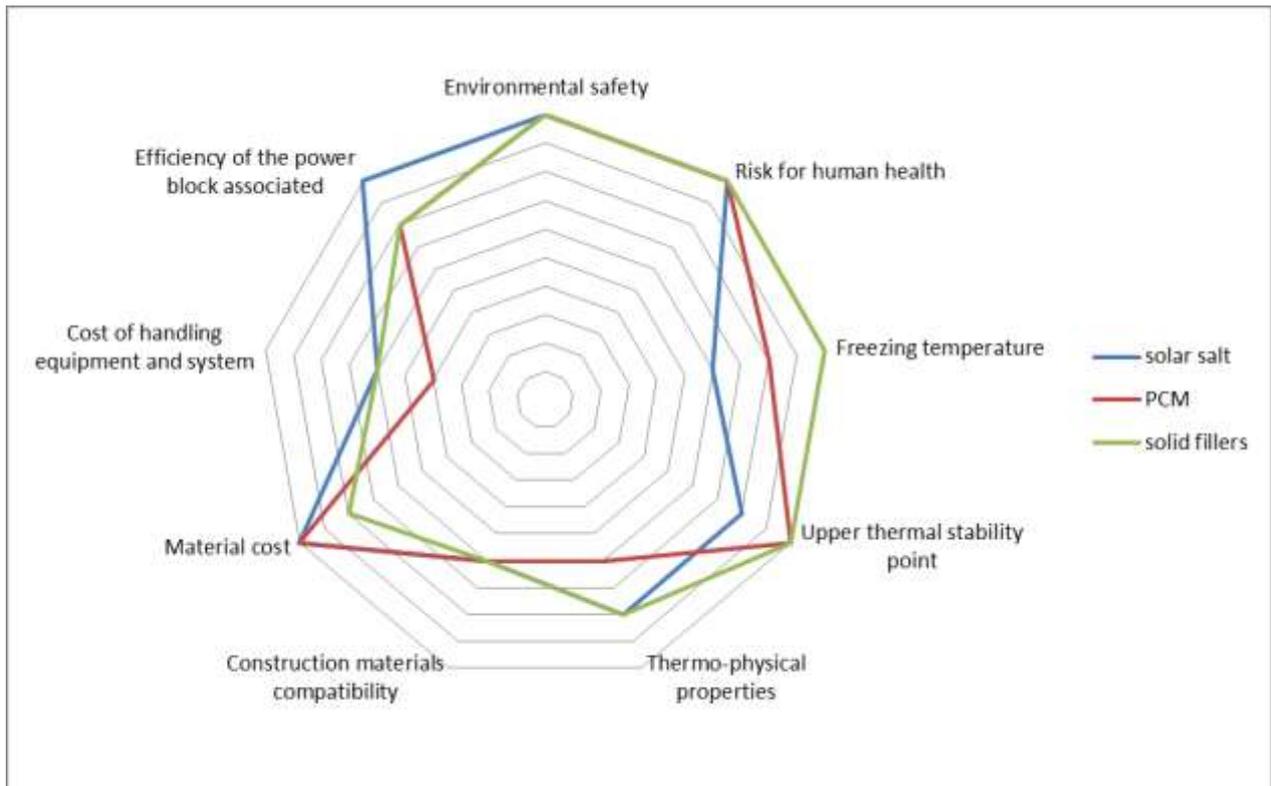

Fig. 7: comparison between PCM (nitrates or carbonates mixtures in a temperature range of 400 – 600 °C), solid fillers (considered as coupled with another HSM fluid, typically molten nitrates), and the "solar salt" mixture, as HSM.

Clearly, both fillers and PCMs can represent a valid alternative to a "solar salt" heat storage. The main disadvantages of PCM materials is represented by their problems about heat exchange features, to be overcome by particular heat exchanger designs and/or by using additives, on the other hand, the main difficulty concerning solid fillers is to avoid their cooling down during the discharge step by establishing and maintaining a thermocline behaviour. This precaution is practically mandatory to couple fillers with a complementary liquid state HSM material.

Gases/steam

Other interesting materials to be used as HTF are gases or steam. In the former case, N_2 and CO_2 have mainly been investigated [26],[27]; the main drawbacks of these thermal fluids is their low capacity to store energy (per volume and per weight). This leads to the necessity to maintain them pressurized, requiring a higher thickness for the walls of the receiver tubes, obtaining, as a consequence, more difficulties for welds and joints. Once pressurized, gases present several evident advantages: good thermal exchange properties, reasonable costs, they are totally environmental friendly and not toxic, and they are stable and monophasic over all the temperature range of employment. Experimentally, CO_2 was tested up to 50 bar and 500 °C [26]; numerical simulation show that in the temperature range 100-600 °C and 80-100 bar of pressures, CO_2 can be competitive as HTF with thermal oils [28].

A interesting, application, is a direct solar heating of the steam of a rankine cycle (direct steam generation "DSG")[29], the management of biphasic systems and sealing at high pressures can be the major problem to be overcome; a DSG numerical model, coupled with a PCM based storage system, has been proposed, where steam operates in charging/discharging condition at 106/80 bars (with corresponding boiling points of 315/295°C)[29]. The use of steam/water based storage systems [12] seems not very advantageous, because of the limitation in the maximum pressure and expected high costs. [29].

The following tables report the proposed ratings for CO_2 and steam as HTF.

Table 13: rating of CO_2 as HTF

Environmental safety	5
Risk for human health	5
Freezing temperature	5
Upper thermal stability point	5
Thermo-physical properties	3
Construction materials compatibility	5
Material cost	4
Cost of handling equipment and system	1

Table 14: rating of water/steam as HTF

Environmental safety	5
Risk for human health	5
Freezing temperature	5
Upper thermal stability point	5
Thermo-physical properties	3
Construction materials compatibility	3
Material cost	3
Cost of handling equipment and system	1

Comparison between CO₂, steam, thermal oils and some nitrate/nitrite containing mixtures as HTF

The figure 8 shows a comparison between CO_2 and steam, with thermal oils and some nitrate/nitrite containing mixtures.
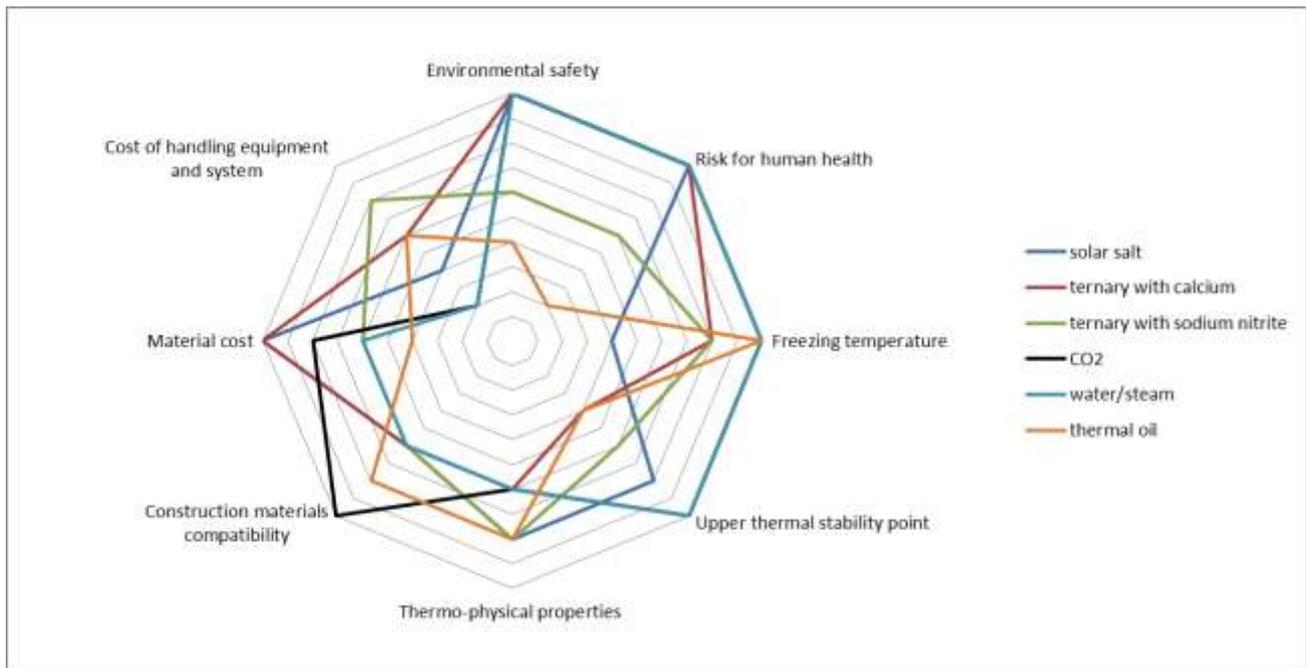

Fig. 8: Comparison between CO₂ (pressurized), steam (water), thermal oils, and some nitrate/nitrite mixtures as HTF .

Clearly, the main disadvantage of the employment of pressurized water and steam is the management of the high pressure operative conditions (together with the relative high temperatures) required for the solar receiving pipelines, especially regarding the receiver tubes.

Liquid metals

Liquid metals (LM), already used as cooling fluids in fast nuclear reactors [30], have also been proposed as HTF and HSM for solar power plant. They can be divided into three main categories [31]: alkali metals (typically sodium or NaK eutectic (22.2/77.8%wt Na–K)), heavy metals (lead, bismuth, or the lead bismuth eutectic (LBE)), low melting metals (indium, tin). The first category presents low melting points (eutectic sodium–potassium is liquid at room temperature), high heat capacity and thermal conductivity and good material compatibility; the evident drawback is their flammability in air and, especially, in contact with water, compared with molten nitrates/nitrites they are about twice as expensive [32], and still they are the less expensive among liquid metals; the second kind present higher boiling points and density, poor heat capacity and thermal conductivity, and relatively high costs. They are enough stable in contact with air, due to the production of a protective oxide layer. They are quite toxic and extremely dangerous for the environment, besides, and present compatibility problems with many alloys and materials, particularly considering their high capacity to dissolve Nickel [31]. So specific construction–materials, such as chromium/aluminium containing alloys, have to be used with them. [33]. Low melting metals, such as tin, are probably the less employed among LM, they present high costs and mostly very severe corrosion problems. All the three types of LM present very high thermal stability (in absence of oxidizing agents, of course).

The following tables report the rating for liquid sodium and lead/bismuth eutectic (LBE) as HTF and HSM, respectively.

Table 15: rating of liquid sodium as HTF

Environmental safety	1
Risk for human health	2
Freezing temperature	4
Upper thermal stability point	5
Thermo-physical properties	3
Construction materials compatibility	3
Material cost	2
Cost of handling equipment and system	1

Table 16: rating of liquid sodium as HSM

Environmental safety	1
Risk for human health	1
Freezing temperature	4
Upper thermal stability point	4
Thermo-physical properties	3
Construction materials compatibility	3
Material cost	2
Cost of handling equipment and system	2
Efficiency of the power block associated	5

Table 17: rating of lead/bismuth eutectic (LBE) as HTF

Environmental safety	1
Risk for human health	1
Freezing temperature	4
Upper thermal stability point	5
Thermo-physical properties	2
Construction materials compatibility	2
Material cost	1
Cost of handling equipment and system	2

Table 18: rating of lead/bismuth eutectic (LBE) as HSM

Environmental safety	1
Risk for human health	1
Freezing temperature	4
Upper thermal stability point	5
Thermo-physical properties	2
Construction materials compatibility	2
Material cost	1
Cost of handling equipment and system	2
Efficiency of the power block associated	5

Comparison between liquid sodium and lead/bismuth eutectic (LBE) with some nitrate/nitrite mixtures, thermal oils and CO₂ as HTF

The figure 9 compares liquid sodium and LBE with already described HTF materials.
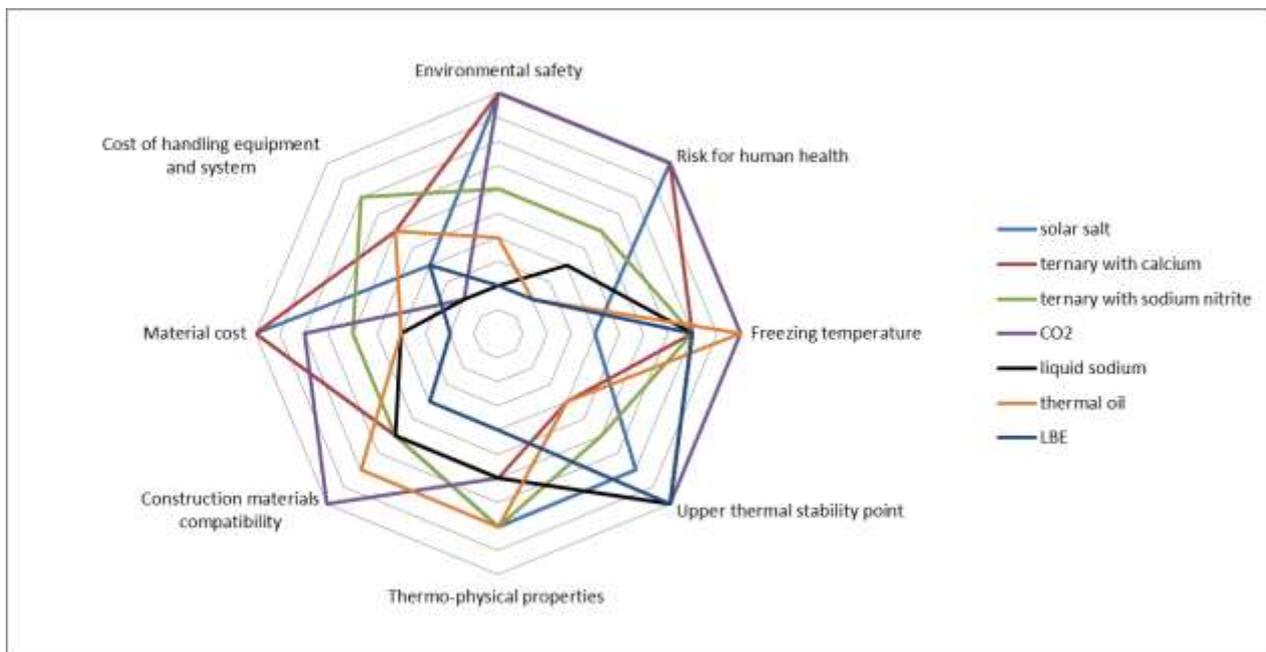

Fig. 9: comparison between two LM: liquid sodium and lead/bismuth eutectic (LBE) with CO₂ (pressurized), thermal oils, and some nitrate/nitrite mixtures, as HTF.

It is quite clear that LM are not in general good options as HTF for solar plants, probably liquid sodium is slightly less worse than LBE.

Comparison between liquid sodium and lead/bismuth eutectic (LBE) with the solar salt, solid fillers and PCM as HSM

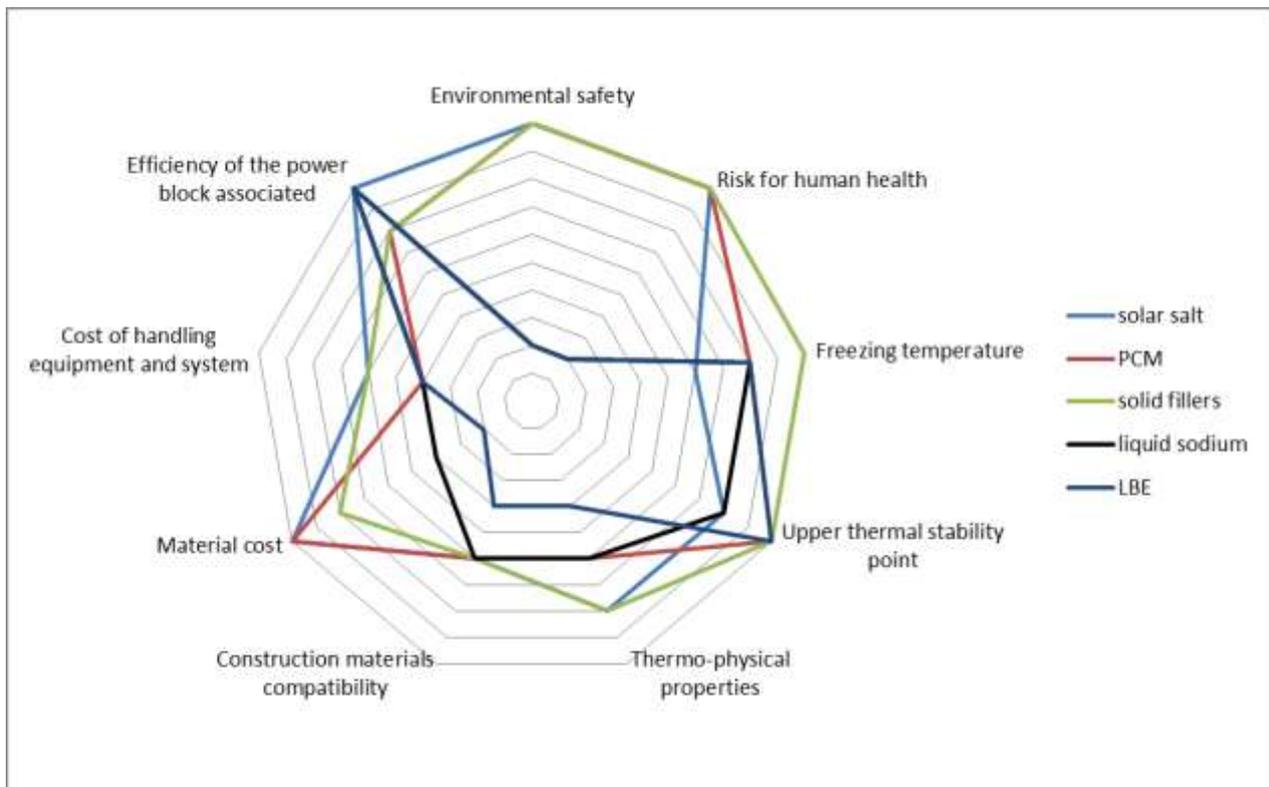The following figure compares liquid sodium and LBE with above discussed HSM materials.

Fig. 10: comparison between two LM: liquid sodium and lead/bismuth eutectic (LBE) with the "solar salt" mixture, solid fillers and PCM, as HSM.

Evidently, also as HSM, LM are not proper alternatives with respect to previously discussed HSM materials.

HTF and HSM additivated with nanoparticles

As discussed above, molten salts (nitrates, carbonates) employed as HTF and/or HSM present poor characteristics with respect to thermal conductivity, and good, even improvable, heat capacity values. One proposed method to improve these features is the addition (in quantities of few weight percentages) of nanoparticles materials [34]. Experimentally was observed: no effect on melting points, an increment both in thermal conductivity [35] and (15-50% more by adding 0.5-1%, in weight percentage, of nanoparticles) in heat capacity values [36], and high stability with respect to sedimentation, due to the very low added percentages [37]. This fact should also prevent pipeline erosion. The used nanoparticle charged materials must be stable in contact with molten salts: with nitrates they should presumably be composed of ceramics (alumina, silica, not soluble in nitrates oxides). The main disadvantages is represented by the high cost of these materials, which can especially be a major concern in case of storage systems, where big HSM quantity are expected to be employed. Besides, thermal recyclability, especially as respect to possible nanoparticles reaggregation, should be more properly investigated.

The tables below report the rating of nanoparticle additivated fluids (typically nitrates/nitrites and carbonates) as HTF and HSM respectively, (based on sensible heat or PCM).

Table 19: rating of nanoparticles additivated materials (typically molten nitrites/nitrates) as HTF

Environmental safety	5
Risk for human health	4
Freezing temperature	3
Upper thermal stability point	4
Thermo-physical properties	5
Construction materials compatibility	3
Material cost	2
Cost of handling equipment and system	2

Table 20: rating of nanoparticles additivated materials (typically molten nitrites/nitrates) as HSM (based on sensible heat storage)

Environmental safety	5
Risk for human health	4
Freezing temperature	3
Upper thermal stability point	4
Thermo-physical properties	5
Construction materials compatibility	3
Material cost	1
Cost of handling equipment and system	3
Efficiency of the power block associated	5

Table 21: rating of nanoparticles additivated materials (typically nitrates/nitrites/carbonates) as HSM/PCM (based on latent heat storage)

Environmental safety	5
Risk for human health	4
Freezing temperature	4
Upper thermal stability point	5
Thermo-physical properties	5
Construction materials compatibility	3
Material cost	2
Cost of handling equipment and system	2
Efficiency of the power block associated	4

Comparison between nanoparticles additivated materials with some nitrate/nitrite mixtures, thermal oils and CO_2 as HTF

A comparison between nanoparticles additivated materials (nitrate/nitrites) and some above described HTF is shown below.
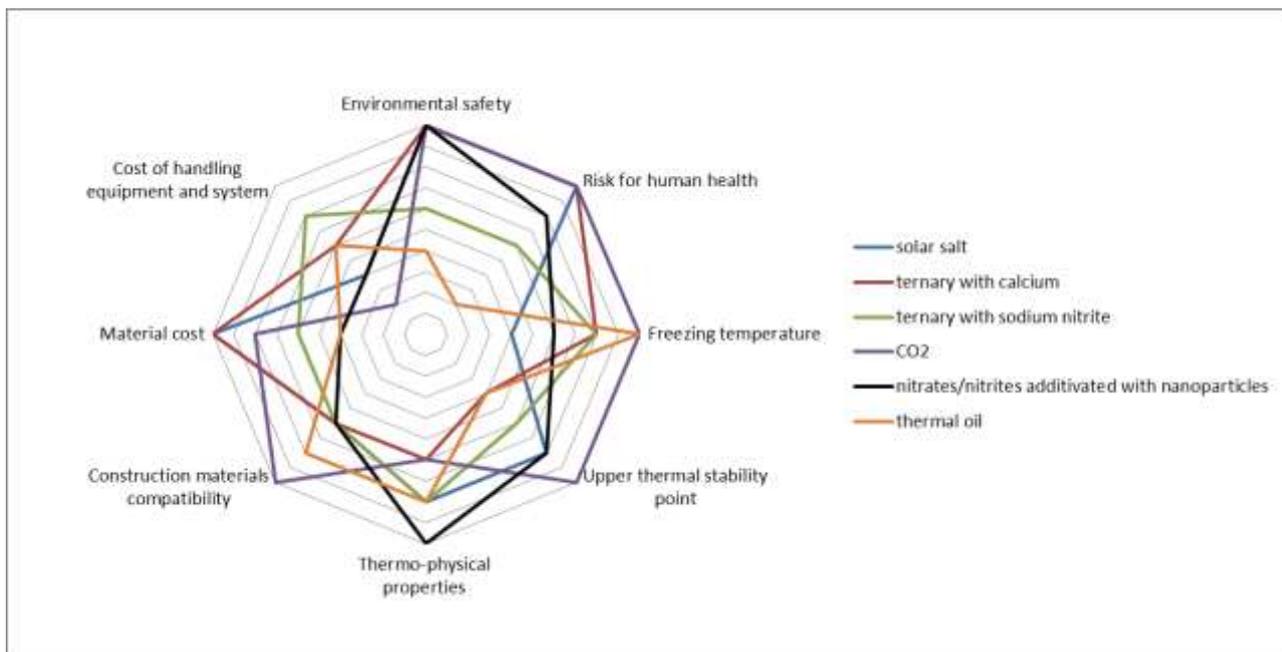

Fig. 11: comparison between nitrate/nitrites additivated with nanoparticles with some nitrate/nitrite mixtures, thermal oils and CO_2, as HTF.

Comparison between nanoparticles additivated materials (both sensible heat based and PCM) with the "solar salt" mixture mixtures, solid fillers and PCM, as HSM

A comparison between nanoparticles additivated materials (considering both additions to sensible heat based storage fluids and PCM) and some above described HSM is reported in the following radar chart.
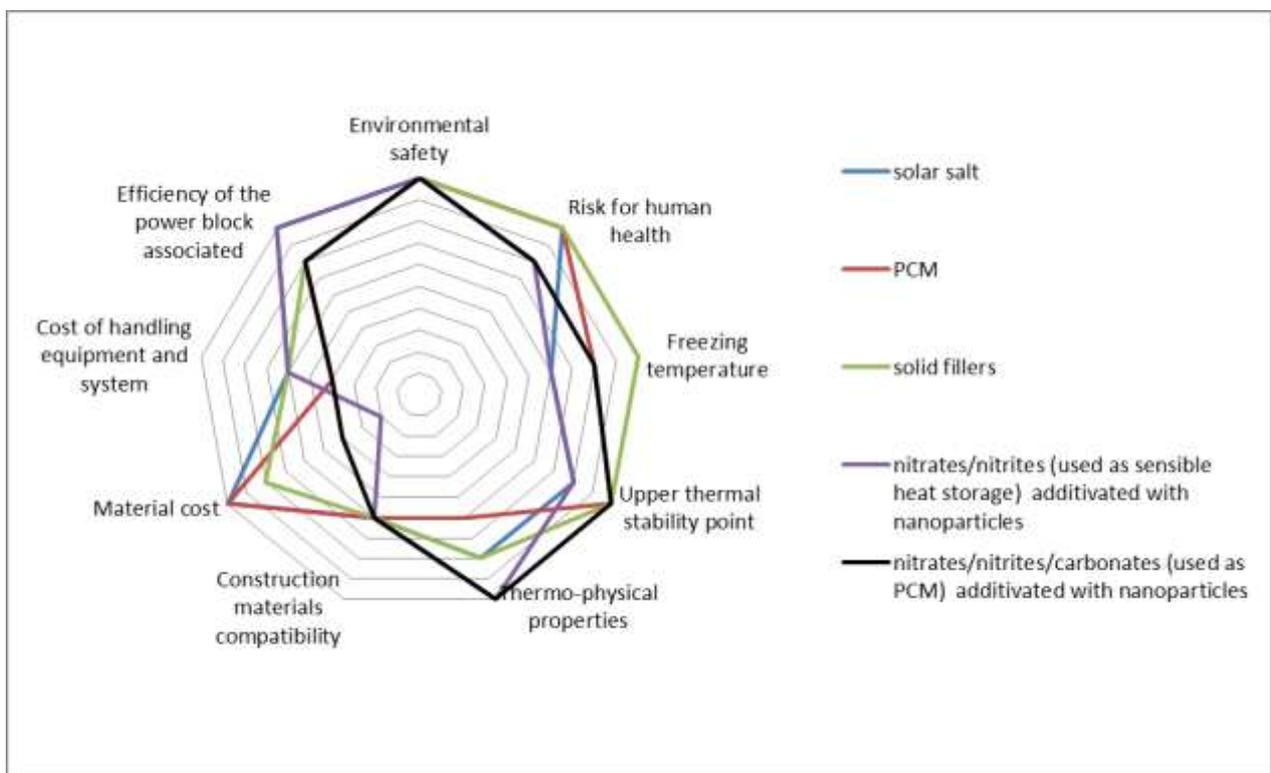

Fig. 12: comparison between nanoparticles additivated materials (considering both additions to sensible heat based storage fluids and PCM) with the "solar salt" mixture, solar filler and PCM, as HSM

In both cases (HTF or HSM) is to be discussed if the improvements in nanoparticle additivated materials in terms of chemical physical features can compensate their high costs; presumably, their most convenient use is the addition to PCM, given the lower quantity required for those materials as latent heat storage HSM.

Thermochemical heat storage

The employment of simple, reversible, chemical reactions to stock solar heat looks like a very promising alternative method for energy storage. The advantages are: the possibility to obtain (if the chemical intermediate state is stable) monthly or even seasonal thermal storage, differently from sensible or latent heat based systems, where the accumulated heat should typically be discharged during the day after the charging; the possibility to employ quite cheap materials (oxides, carbonates), given the relative high reaction enthalpies, is good to store big energy amounts per weight and volume unity [12][38]. As a drawback, it is to be considered that the techniques for coupling the charge/discharge phase with the employed fluid as HTF and the power block respectively are still to be studied in detail, and maybe could present some technical difficulty.

For the medium/high temperatures mainly considered in the SFERA II project (from 300/400 °C up to 600°C), the most interesting thermochemical storage processes could be considered the use of the calcium oxide/hydroxide, which presents a dehydration enthalpy of about 100 kJ/mol at 521 °C, and the calcium oxide/carbonate system, which presents 167 kJ/mol for the carbonation at 896 °C [39].

The following table summarizes a proposed rating for thermochemical storage.

Table 22: rating for thermochemical heat storage

Environmental safety	5
Risk for human health	5
Freezing temperature*	5
Upper thermal stability point	5
Thermo-physical properties	5
Construction materials compatibility	4
Material cost	4
Cost of handling equipment and system**	2
Efficiency of the power block associated**	2
*not applicabile, high rating because this problem is not present, differently from sensible heat storage ** to be properly investigated yet	

Comparison between thermochemical storage with the "solar salt" mixture mixtures, solid fillers and PCM, as HSM

The potential competitiveness of thermochemical storage, provided that the technical issues related to heat transfer during charging/discharging are overcome, see the following figure.
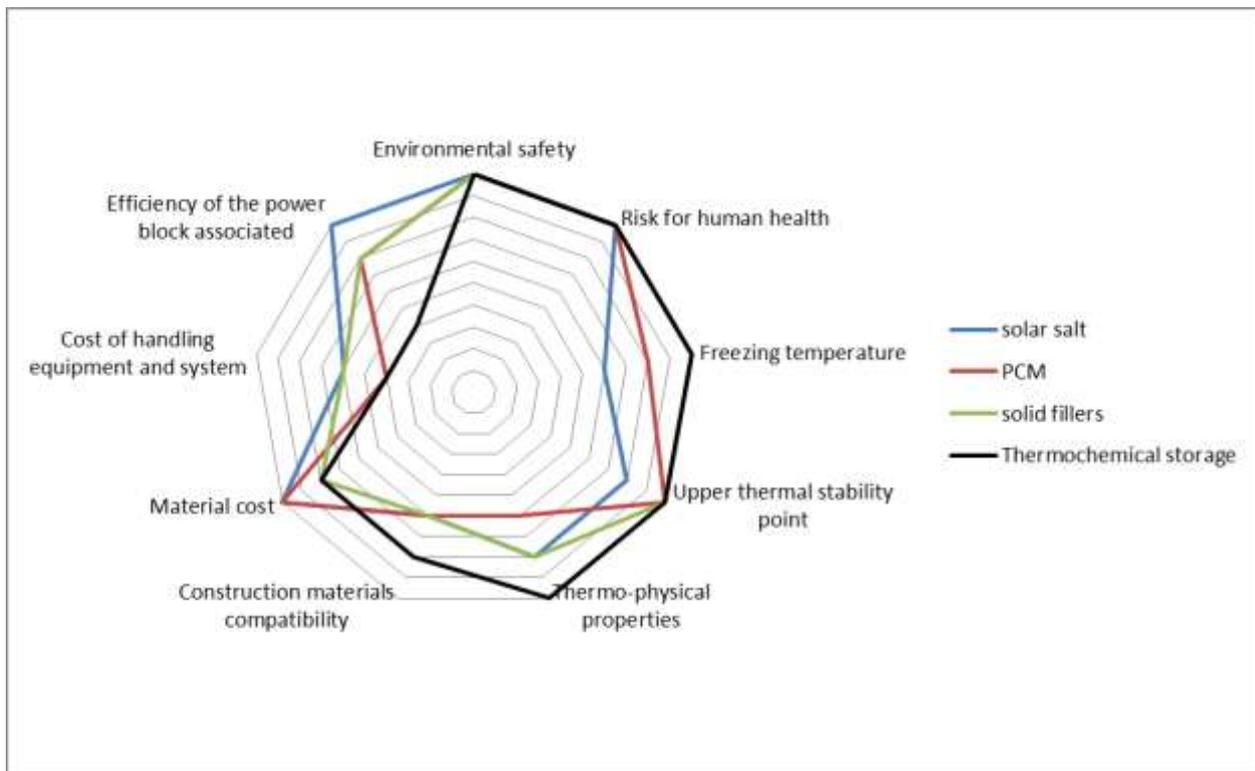

Fig. 13: comparison between thermochemical storage with the "solar salt" mixture, solar filler and PCM, as HSM.

CONCLUSIONS

Regarding HTFs, despite their large use, thermal oils do not seem to be the best option, given their cost, toxicity, flammability and considering their relatively narrow temperature operating range, which leads to the necessity to increase the size (and cost) of the storage system. On the other hand, at reasonable temperature levels (300°C for example using Therminol), they are very useful given the low freezing point, so avoiding systems to maintain all the HTF circuit in temperature during nights or maintenance interventions. Besides, intermediate temperature level around 300°C are compatible with the use of ORC to produce electricity. The ternary mixture containing calcium nitrate can be considered as a quite valid alternative for those low enthalpy applications, given its very low cost and toxicity, and a melting temperature that, though higher than the ones presented by thermal oils, can be as well feasible to decrease overnight heating operations and facilitate maintenance procedures.

The employment of the "solar salt" mixture present, on the other hand, several clear advantages: low cost, no toxicity and good environmental compatibility, and, furthermore, the possibility to avoid the use of an intermediate heat exchanger in case the same material is used as HSM.

Pressurized gases can also be good alternatives, to be further evaluated are direct steam heating systems.

Probably more complex, and quite open to further developments is the situation related to HSMs. A sensible heat based system, typically made using the "solar salt", presents the disadvantages of a relative high cost. Three alternative routes can be potentially be very promising in the near future: use of solid fillers, PCMs and chemical storage. The first option has to be investigated concerning the compatibility with the transfer thermal fluid and must maintain a thermocline during the discharge phase; PCMs present a practical problem concerning the difficulties in the heat exchange phase, the confinement of these material into a proper vessel should be further investigated. Given the wide number of chemical reactions potentially feasible as storage systems, single configurations have to be separately studied in order to evaluate advantages and disadvantages for each of these techniques. In any case, the production of chemical intermediates seems to be the only way to perform seasonal storage; leading to an increase of the CSP manageability and of cost effectiveness.

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