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Novel Metallic Alloys as Phase Change Materials for Heat Storage in Direct Steam Generation Applications

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Abstract. Concentrating Solar Power (CSP) is one of the key electricity production renewable energy technologies with a clear distinguishing advantage: the possibility to store the heat generated during the sunny periods, turning it into a dispatchable technology. Current CSP Plants use an intermediate Heat Transfer Fluid (HTF), thermal oil or inorganic salt, to transfer heat from the Solar Field (SF) either to the heat exchanger (HX) unit to produce high pressure steam that can be leaded to a turbine for electricity production, or to the Thermal Energy Storage (TES) system. In recent years, a novel CSP technology is attracting great interest: Direct Steam Generation (DSG). The direct use of water/steam as HTF would lead to lower investment costs for CSP Plants by the suppression of the HX unit. Moreover, water is more environmentally friendly than thermal oils or salts, not flammable and compatible with container materials (pipes, tanks). However, this technology also has some important challenges, being one of the major the need for optimized TES systems. In DSG, from the exergy point of view, optimized TES systems based on two sensible heat TES systems (for preheating of water and superheating vapour) and a latent heat TES system for the evaporation of water (around the 70% of energy) is the preferred solution. This concept has been extensively tested [1, 2, 3] using mainly $NaNO_3$ as latent heat storage medium. Its interesting melting temperature (T_m) of 306ºC, considering a driving temperature difference of 10ºC, means TES charging steam conditions of 107 bar at 316ºC and discharging conditions of 81bar at 296ºC. The average value for the heat of fusion (ΔH_f) of $NaNO_3$ from literature data is 178 J/g [4]. The main disadvantage of inorganic salts is their very low thermal conductivity (0.5 W/m.K) requiring sophisticated heat exchanging designs. The use of high thermal conductivity eutectic metal alloys has been recently proposed [5, 6, 7] as a feasible alternative. T_ms of these proposed eutectic alloys are too high for currently available DSG solar fields, for instance the Mg_{49}-Zn_{51} alloy melts at 342ºC requiring saturated steam pressures above 160 bar to charge the TES unit. Being aware of this, novel eutectic metallic alloys have been designed reducing the T_ms to the range between 285ºC and 330ºC (79bar and 145bar of charging steam pressure respectively) with ΔH_fs between 150 and 170 J/g, and thus achieving metallic Phase Change Materials (PCM) suitable for the available DSG technologies.

INTRODUCTION

In recent years, different CSP technologies have been developed to change solar energy into electricity that can be supplied to the grid. In general, most of CSP Plants are composed of three systems: (1) the SF where solar beams are concentrated in a solar receiver and heat transferred to a HTF, (2) the TES system where heat from the HTF is stored in a TES material (3) the Power Block system where heat from the HTF is used for the production of high pressure steam through a HX, and later this steam is leaded to a turbine for the production of electricity. One of the key factors that makes CSP technologies competitive with respect to others renewable sources of energy is the use of a TES system (2) in order to supply energy during night or cloudy periods.

An intense research effort is being dedicated to the design of novel materials with good properties to be used either as TESM or HTF. Nowadays, thermal oil is the most commonly used HTF in CSP Plants, though thermal oil

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is degraded at 400ºC, limiting the possibility of achieving high steam pressures in the Power Block system. Moreover, thermal oil has a high flammability and high environmental impact. Inorganic salts have been proposed and used as an alternative to thermal oil as HTF. Degradation of inorganic salts occurs at higher temperatures than thermal oil, so higher steam pressures can be achieved, and these salts can be used both as HTF and TESM. However, the use of molten salts as HTF has severe drawbacks: even though they are not flammable, they can react explosively with water. In addition, adequate tracing of pipes and valves is required to prevent clogging and periodic maintenance of thermal expansion joints to avoid leaks.

Both explained HTFs, thermal oil and inorganic salts, require an additional HX to produce steam from water. The arising question is if steam can be directly generated in the solar field. This would eliminate the drawbacks exposed in the previous paragraph and would lead to lower investment costs by the suppression of the HX. Some authors are researching on DSG in experimental Parabolic Trough [8] and Fresnel [9] collectors. The proposed system for TES in DSG Plants consists of a PCM unit accompanied by two sensible heat unit for superheated steam and preheating of water (i.e. concrete) [10]. The reason why PCM-based TES is appropriate for this application is that the phase transition from liquid to solid PCM takes place at constant temperature.

Solid/Liquid PCMs are more convenient as they can be confined to a fixed volume. Inorganic salts as sodium nitrate (melts at 306ºC) ([1], [2], [3]) and metallic alloys as $Mg_{49}Zn_{51}$ (melts at 342ºC) ([5], [6], [7]) have been extensively studied. Suitable PCMs for DSG should have a phase transition temperature about 10ºC below the produced vapour temperature in the SF. Up to now, steam can be generated in Parabolic Through (PT) and Fresnel collectors at a maximum pressure of approx. 110 bar.

Sodium nitrate PCM (306ºC) would require an income vapour temperature of 316ºC, that means a saturated vapour pressure of 107 bar. On discharging, vapour temperature would be 296ºC and vapour pressure 81 bar. Sodium nitrate could be a good option to be used as PCM in DSG

$Mg_{49}Zn_{51}$ PCM (342ºC) would require an income vapour temperature of 352ºC, that means a saturated steam pressure above 160 bar, higher than the maximum allowable pressure in current PT and Fresnel Solar Fields, as stated before. Lower T_m alloys, and preferably in the order of magnitude of sodium nitrate T_m (285ºC – 330ºC), are desirable.

In this work, novel alloys based on Mg and Zn, in combination with other metallic elements as Cu, Ni, Sn have been simulated using a ThermoCalc software package with the SSOL4 thermodynamic database, with the aim of finding alloys with lower T_m than $Mg_{49}Zn_{51}$. The simulation software has been previously validated with known literature data. All the eutectics and peritectics have been evaluated and results discussed from the point of view of termophysical performance as PCM for DSG.

EXPERIMENTAL

The Software

In this work, the design of a novel metallic alloy to be used as PCM for DSG applications that fulfills with the specifications required for this system, that is to say, T_ms in the range between 285ºC and 330ºC in different ternary and quaternary metallic systems, was done using Thermo-Calc software package for the calculation of thermodynamic and phase equilibria in conjunction with the SSOL4 thermodynamic database. This is an important thermochemical solution database for many non-ideal multicomponent solution phases within a chemical framework of 78 elements. Combinations of several critically-assessed systems can calculate and extrapolate higher order multicomponent systems.

Ternary System Representation

When studying ternary systems, the liquidus surface is usually represented by a group of constant temperature contours projected onto a composition plane, i.e. the liquidus projection (Fig. 1a). The liquidus univariant lines indicate the conditions at which two solid phases coexist with the liquid phase. Those lines intersect at eutectic and peritectic points. The univariant lines can also be projected onto a temperature vs. composition plane (Fig. 1b); this diagram allows easy identification of the lowest liquidus temperature on the system, covering the whole composition range of each component. This type of representation can also be used in quaternary and multicomponent systems, as a systematic tool to identify low melting point alloys as well as the solid phases involved at that temperature [7].

This approach has been used in the present work to search the best system that is in the range of the required melting point temperature.

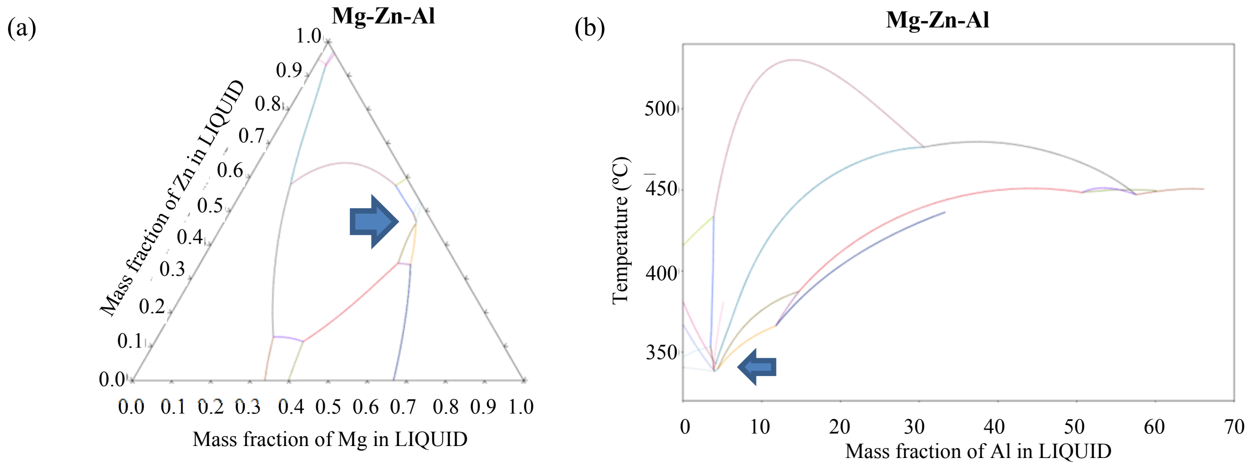

FIGURE 1. (a) liquidus surface projection into the composition axis of Zn and Mg. (b) liquid monovariant line of the Al composition plane. The arrows correspond to the minimum liquidus temperature for 3.97Al-49Mg-47Zn (wt%)

Validation of Software

This methodology was validated by simulation of existing compositions from bibliography. Using this software, the eutectic composition Mg_{49}-Zn_{51} was identified simulating the Mg-Zn system with a T_m of 341.02ºC and a ΔH_f of 170.69 J/g. These results were validated with bibliography data [11] where T_ms between 340ºC and 343ºC and heats of fusion between 138J/g and 210J/g had been published. Together with this, the Mg-Zn-Al system was also studied. In total, 10 invariant reactions were identified in this system. According to the projections of the liquidus monovariant lines into temperature composition lines (as shown in Fig. 1), an eutectic composition of Mg_{49}-$Zn_{47,02}$-$Al_{3,97}$ was identified with a minimum liquidus temperature of 338.08ºC and a ΔH_f of 158.47J/g. Again these values were validated with existing information from bibliography [7], where exactly the same eutectic composition had been characterized with T_ms of 340ºC and ΔH_f of 132±25 J/g. A third eutectic was identified for the system Cu-Mg-Al with the following composition: $Cu_{4.29}Mg_{63.2}Al_{32.5}$. The composition, T_m (425ºC) and ΔH_f (282 J/g) calculated by Thermocalc agreed with existing data from literature [7]. Results from Thermocalc and published experimental data for the three eutectics are presented in Table 1 for comparison.

TABLE 1. Comparison between Thermocalc and existing bibliography data for the systems Mg-Zn, Mg-Zn-Al and Cu-Mg-Al

Composition		**Melting Temperature (T_m,ºC)**		**Heat of Fusion (ΔH_f, J/g)**	
Thermocalc	**Bibliography**	**Thermocalc**	**Bibliography**	**Thermocalc**	**Bibliography**
$Mg_{49}Zn_{51}$	$Mg_{49}Zn_{51}$	341.02	340-343 [11]	170.69	138 [12], 180 [13], 210 [14]
$Mg_{49}Zn_{47,02}Al_{3,97}$	$Mg_{49}Zn_{47,02}Al_{3,97}$	338.08	340 [7]	158.47	132±25 [7]
$Cu_{4.29}Mg_{63.2}Al_{32.5}$	$Cu_{4.29}Mg_{63.2}Al_{32.5}$	425.00	428 [7]	282.00	282.4 [7]

Considering results shown in Table 1, Thermocalc software was validated to identify the eutectic compositions for given ternary systems and to predict their thermophysical properties. Even though the real behaviour of metallic mixtures involves many variables that cannot be simulated by the software (existence of intermetallic phases, reactions with container materials, etc.), the software appeared to be a good starting point for the synthesis and characterization of these metallic alloys.

RESULTS AND DISCUSSION

Once the methodology had been validated, the study was extended to other elements from the periodic table. Table 2 summarizes the T_ms for the metals involved.

TABLE 2. Melting points for the metals involved

Metal	Mg	Zn	Al	Cu	Sn	Be	C	Cd	Fe	Ir	Li	Ni	Si	Ti	Zr
T_m (ºC)	650	419	660	1085	232	1287	--	321	1538	2466	180	1455	1414	1668	1855

Eutectic mixtures combining three or more of these metals will have lower T_m than the individual components shown in Table 2. Considering that the desired T_m is in the range from 285 to 330ºC, Sn (231.9ºC) and Li (180.5ºC) could be discarded. No other supposition can be done from this initial data, as eutectic alloys may show very much lower T_m than individual components. Therefore, a systematic study was conducted to search all the different eutectic compositions among 21 Ternary systems (Mg-Zn-Al / Mg-Zn-Cu / Mg-Zn-Sn / Mg-Al-Cu / Mg-Al-Sn / Mg-Sn-Cu / Zn-Al-Cu / Zn-Cu-Sn / Zn-Al-Sn / Al-Cu-Sn / Mg-Zn-Be / Mg-Zn-C / Mg-Zn-Cd / Mg-Zn-Fe / Mg-Zn-Ir / Mg-Zn-Li / Mg-Zn-Ni / Mg-Zn-Si / Mg-Zn-Ti / Mg-Zn-Zr / Mg-Sn-Li) and 3 quaternary systems (Mg-Zn-Al-Cu / Mg-Zn-Al-Sn / Mg-Zn-Cu-Sn). Later on, alloys with the desired T_m between 285ºC and ~330ºC were selected among all the eutectics found.

The Table 3 summarizes the eutectic compositions that best fit the goals of this work in terms of liquidus temperature and ΔH_f. Thereby, the most interesting ternaries are: on the one hand, Mg-Zn-Cu with two invariant reactions which correspond to minimum liquidus temperatures, so there are two eutectic compositions that are appropriate. On the other hand, Mg-Zn-Ni alloy is also a good candidate with interesting properties.

The previous work was extended to several quaternaries including Cu or/and Sn to the reference Mg-Zn-Al alloy: Mg-Zn-Al-Cu, Mg-Zn-Al-Sn and Mg-Zn-Cu-Sn .The results showed that the minimum liquidus temperature of the quaternaries corresponds to a lower order system, i.e. a ternary combination of the element describes the minimum eutectic. In this regard, the most promising results of the highest order systems Mg-Zn-Al-Cu and Mg-Zn-Cu-Sn have already been described as depicted in Table 3 and they correspond to the Mg-Zn-Cu ternary system.

In the studied ternary and quaternary systems, all their eutectic compositions and their T_ms were calculated and 3 different most interesting eutectic metallic alloys were designed for latent heat storage in DSG systems with interesting T_ms and good ΔH_f values. Outside the defined T_m range (285ºC to 330ºC), many other eutectic compositions were identified. Three Novel alloys were designed; Mg (40-50%) - Zn (40-50%) - Cu (10-20%) (Ref 2a, T_m 285ºC and 168 ΔH_f J/g), Mg (40-50%) – Zn (40-50%) - Ni (0-10%) (Ref 17, T_m 328ºC and ΔH_f 168 J/g) and Mg_g (20-30%) – Zn (40-50%) – Cu (30-40%) (Ref 2b, T_m 306ºC and ΔH_f 157 J/g). The last one is especially remarkable as its T_m is the same as the $NaNO_3$ inorganic salt, its thermal conductivity is expected to be of two orders of magnitude higher than the salt and its ΔH_f is still high.

TABLE 3. Simulation results of the systematic search done by ThermoCalc done for 21 ternary systems

Ref.	Alloy	T_m (°C)	ΔH_f (J/g)
1	Mg-Zn-Al	338	158.47
2	Mg-Zn-Cu	285	168
		306	157
3	Mg-Zn-Sn	191.8	61.9
4	Mg-Al-Cu	424.9	-
5	Mg-Al-Sn	202.9	66
6	Mg-Sn-Cu	200.6	65.2
7	Zn-Al-Cu	-	-
8	Zn-Cu-Sn	215	80.2
9	Zn-Al-Sn	214.9	54.9
10	Al-Cu-Sn	-	-
11	Mg-Zn-Be	340.9	-
12	Mg-Zn-C	340.9	152.56
13	Mg-Zn-Cd	340.6	-
14	Mg-Zn-Fe	340.99	-
15	Mg-Zn-Ir	340.96	165
16	Mg-Zn-Li	339.85	170.73
17	Mg-Zn-Ni	328.87	168
18	Mg-Zn-Si	340.99	-
19	Mg-Zn-Ti	340.87	-
20	Mg-Zn-Zr	340.7	242
21	Mg-Sn-Li	134.35	58.34

A techno-economic evaluation of a TES system using the three selected PCMs was done. The base metal prices were extracted from the London Metal Exchange (LME) (Table 5) [15]. The repercussion of the PCM cost on the final price of kWh, considering a 30-year life for the TES system (11,000 cycles at 1 cycle per day) [5], was calculated for the three alloys. Many other variables will affect the final price of kWh as the investment costs, human resources, maintenance, etc. A complete techno-economic analysis of the CSP Plant was not the objective of this work. Though, this cost estimation was useful to compare the feasibility of the three selected alloys. The analysis was also done for $NaNO_3$ and $Mg_{49}Zn_{51}$ as PCM for comparison. Results are shown in Table 4

TABLE 4. Techno-economic evaluation for the selected alloys

Ref.	PCM	T_m (°C)	ΔH_f (J/g)	Price (€/kg)	Cost repercussion of PCM on kWh price (€/kWh)	Cost repercussion Metallic/$NaNO_3$
Ref.	$NaNO_3$	306	175	0.5	0.00094	1
2a	Mg-Zn-Cu	285	168	2.047	0.0040	4.23
2b	Mg-Zn-Cu	306	157	2.567	0.0053	5.68
17	Mg-Zn-Ni	328.87	168	1.914	0.0037	3.97
1	Mg-Zn-Al	338	158.47	1.636	0.0034	3.60
Mg-Zn	$Mg_{49}Zn_{51}$	342	160.2	1.640	0.0033	3.56

TABLE 5. Base metal prices extracted from LME [15]

Metal	Mg	Zn	Al	Cu	Ni
Price (€/kg)	1.819	1.468	1.377	4.607	8.983

Considering only the price and the latent heat for metallic alloys and sodium nitrate, it can be deduced from Table 4 that the prices of the PCMs (€/kg) are 3.8-4.1 times higher for the three selected metallic alloys (Ref. 2a, 2b and 17), and the ΔH_f is lower than the sodium nitrate's one. Therefore, the cost repercussion of metallic alloys in the final price of kWh is 4-5.7 times higher than that of sodium nitrate. However, as it was stated in the beginning of this work, inorganic salts like sodium nitrate, have very low thermal conductivity (0.5 W/m·K) requiring higher contact surface for the heat transfer. Consequently, sophisticated and expensive heat exchanging designs are needed to achieve a good thermal storage performance for inorganic salt PCMs [1]. This will be translated into higher investment costs that will affect considerably to the final cost of the energy (€/kWh). In a previous work, the performance of two PCMs: $Mg_{49}Zn_{51}$ and KNO_3 for DSG was simulated using a simple heat exchanger design composed of a shell and a fixed number of tubes. After a cycle time of 8h, only 78% of KNO_3 was melted. In the case of $Mg_{49}Zn_{51}$, a complete melting of the PCM was achieved in 4h.

Regarding to the metallic alloys with T_m in the desired range 285-330ºC (Ref. 2a, 2b and 17), the presence of expensive metals like Cu or Ni increases the price of the alloy (€/kg). The cost repercussion on the price of kWh is 1.2 to 1.6 higher than $Mg_{49}Zn_{51}$. Nevertheless, lower melting point alloys (285-330ºC) are essential if the maximum steam pressure in DSG is limited to 110 bar for PT collectors.

Fig. 2 (a) shows the T_m (ºC) and ΔH_f for the proposed alloys. The T_m for the metallic alloys referenced 2a, 2b and 17 are within the range 285-330ºC. MgZnAl 1 (338ºC) and MgZn (342ºC) are out of this range. The ΔH_f for all the proposed alloys is higher than 150 J/g. Fig. 2 (b) shows a comparison of the material cost (€/kg) and the repercussion of this material cost on the final price of kWh. MgZnCu 2b has the same T_m as $NaNO_3$ (306ºC), but it is also the most expensive among the proposed alloys.

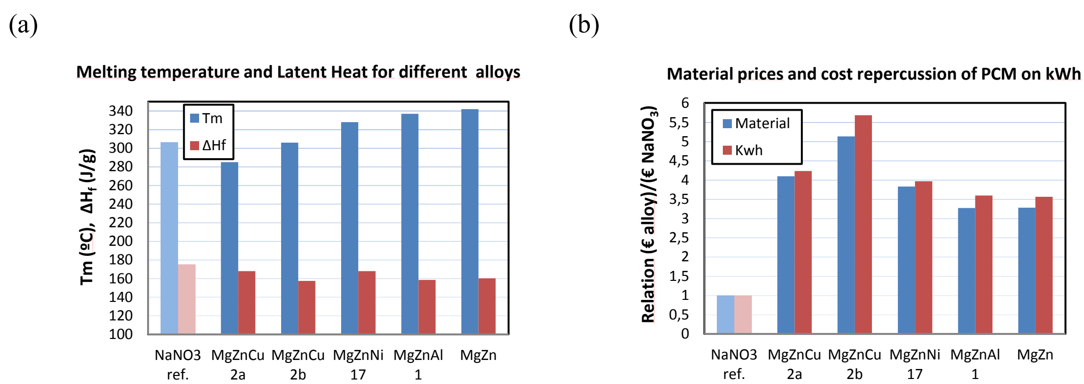

FIGURE 2. (a) Melting temperature and Latent Heat for the studied alloys (b) Material prices and cost repercussion of PCM on kWh. The material cost of NaNO3 and its repercussion on the final price of kWh was taken as reference.

CONCLUSIONS

DSG is an interesting application for modern CSP plants. Water/Steam can be used as HTF instead of inorganic salts or thermal oil. Steam would be directly conducted to the turbine to produce power, avoiding an intermediate heat exchanger. TES based on PCMs would be the most suitable option to be used in this kind of CSP plants, as PCMs stores thermal energy at a nearly constant temperature. Nowadays, DSG experimental plants are able to produce steam at a maximum pressure of 110 bar in the Solar Field (saturated steam temperature 318ºC). With a melting point of 306ºC, $NaNO_3$ is a suitable PCM for this application, considering a gradient of 10ºC between the steam temperature and the PCM melting point. On discharging, a TES system based on $NaNO_3$ would produce steam at 296ºC and 81 bar. The main drawback of $NaNO_3$, and other inorganic salts, to be used as PCM, is their low thermal conductivity (0.5 W/m K), requiring very complicated tanks. Metallic PCMs are considered a good alternative to salt-based PCMs. Their higher conductivity allows lower cycling times and consequently, better performance of the TES facility. $Mg_{49}Zn_{51}$ [5,11] is one of the most researched metal alloys. However, its high T_m 342ºC requires saturated steam pressures of 160 bar, and the technology of DSG cannot supply steam at such a high pressure. Lower melting point metallic PCMs are desirable, preferably in the range between 285 and 330ºC

In this work, three novel alloys combining Mg and Zn, with Cu and Ni have been proposed. Their T_ms are comprised within the desired temperature range (285-330ºC). Their ΔH_fs (150-170 J/g) are high enough to be used as PCMs for DSG, but these values are still lower than ΔH_f of $NaNO_3$ [4]. These three novel alloys were selected among 21 ternary eutectics found by the software Thermocalc in conjunction with de SSOL4 thermodynamic database. The elements Mg, Zn, Ni, Cu, Al, Be, C, Cd, Fe, Ir, Li, Si and Zr were combined. Three quaternaries were also simulated: Mg-Zn-Al-Cu, Mg-Zn-Al-Sn, Mg-Zn-Cu-Sn, though the most promising eutectics in terms of T_m and ΔH_f were the ternary combinations.

A techno-economic evaluation has been done in order to compare the feasibility of the proposed alloys. Sodium nitrate was taken as a reference. This analysis has shown that the material cost of three proposed metallic alloys is 3.8-4.1 times higher than sodium nitrate's one and, the repercussion of this material cost on the final price of kWh is 4-5.7 times higher than sodium nitrate's one. This is due to the elevated prices of the minor components (Cu, Ni) and also the low price of sodium nitrate (0,5 €/kg). However, the higher conductivity of metallic alloys with respect to sodium nitrate must be highlighted. This improvement on the thermal conductivity would lead to less complicated TES devices as less contact surface is required for heat transfer, and therefore to important savings in the investment costs of the TES system.

The selection of the most suitable metallic alloy for a given DSG facility will depend on the properties of the generated steam (P, T). In this way, Thermocalc software offers the possibility to find the most adequate eutectic to comply with the requirements of a specific DSG plant.

FUTURE WORK

The three novel metal alloys are being synthetized at a laboratory scale and the thermophysical properties will be measured and compared with Thermocalc results. The compatibility between the PCMs and the containing materials is also very important. In this way, some different choices as several kinds of stainless steels, other metals and its alloys will be evaluated as container materials, considering corrosion by the metallic PCMs. The most suitable combination metallic PCM – container material must be selected for a specific TES facility. In this sense, the wall thickness of the container device is the design parameter directly related to the life of the TES system. The best performance on thermal storage at the minimum investment cost must be achieved.

Simulations of the three novel metal alloys will be performed, considering a heat exchanger design composed of shell and a fixed number of tubes. Results will be compared with the performance of sodium nitrate in the same device.

To conclude, a complete techno-economic analysis of the DSG plant (considering investment costs, maintenance, etc.), including the TES system, will be done in order to assure the techno-economic feasibility of these three novel metallic alloys to be used as PCMs in DSG.

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REFERENCES

1. D. Laing *et al*. J. Sol. Energy Eng., **132** (2) (2010)
2. D. Laing, *et al*. Solar Energy, **85** (4):627–633 (2011)
3. D. Laing *et al.* J. Applied Energy, **109**:497–504 (2013)
4. T. Bauer *et al.* "Sodium nitrate for high temperature latent storage" in *11th International Conference on Thermal Energy Storage Eff-Stockholm,2009*
5. P. Blanco-Rodríguez *et al.* Energy **75**:630 (2014)
6. E. Risueño *et al.* "Mg-Zn-Al eutectic alloys as phase change material for latent heat thermal energy storage" in *SolarPaces 2014 International Conference*. Energy Procedia, 69 (2015) pp. 1006-1013

7. T. Gómez-Acebo *et al.* “Systematic search of low melting point alloys in the Al-Cu-Mg-Zn system” in *European Conference on Powder Metallurgy EuroPM2003,* Valencia (Spain)
8. E. Zarza *et al.* Energy, **29** (5-6):635-644 (2004)
9. M. Mokhtar *et al.* Int. J. of Thermal&Environmental Engineering **10** (1): 3-9 (2015)
10. J. Birnbaum *et al.* J. Sol. Energy Eng., **132** (3) (2010)
11. E. Risueño *et al.* “Eutectic $Mg_{49}Zn_{51}$ alloy as Phase Change Material for Direct Steam Generation Application” *Eurotherm Seminar Nº99: Advances in Thermal Energy Storage 2014,* Lleida (Spain).
12. C.E. Birchenall and A.F. Reichman. Metall TransA Phys. Metall. Mater. Sci., **11**(8):1415-20 (1980)
13. D. Farkas and C.E. Birchenall. Metall TransA. Phys. Metall. Mater. Sci., **16**(3):323-8 (1985)
14. C.E. Birchenall “Heat storage in alloy transformations” NASA report cr-159787. University of Delaware (1980)
15. London Metal Exchange www.lme.com (last accessed October, 13th 2015)