Molten salt energy storage system for DEMO operated in pulsed mode

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Abstract

DEMO (DEMOnstration Power Plant) is intended to be the direct predecessor of commercial Fusion Power Plants. The reference European DEMO is a steady-state device with an output power of 1 GW_e. Recognizing the challenges which need to be met for steady-state operation of DEMO, an examination of the consequences of operation of this device in pulse mode is included as part of the European study.

Molten salt energy storage systems are well known and have been used in applications as simple as heating houses. High power applications related to electric energy production for the grid are known from the solar industry. In existing industrial facilities, the sensible heat of a molten salt is always used, but involving a phase transformation (melting) the associated heat of fusion is added to the heat storage capacity of the system.

The power output of the DEMO device during operation is 1 GW_e, and with a pulse duration of 4-8 hours and a dwell time of only 5-20 minutes, supply to the grid and re-ignition of the plasma would require several hundred megawatts from the storage system to maintain the power output within acceptable limits.

An intense search for available technologies regarding molten salt energy storage has been carried out, and possible salts and systems to meet the requirements will be presented and directions for further research proposed. Metal hydrides could be the best candidates for such a system for several reasons, like very large heat of fusion and, moreover, an option for combining heat of fusion with heat of chemical reaction, thereby increasing the latent heat based thermal storage capacity. This latter offers controlled recovery of heat and even partial direct conversion of heat to electricity by thermally regenerative electrochemical cells.

INTRODUCTION

Power systems for high energy output always have the disadvantage that in case of low power demand the excess energy produced may have to be stored if reducing power is not simple or too costly and compensation by other power input elements of the grid is not possible. For regular fission reactors for example, the kinetics of the chain reaction does not permit us to reduce or increase power output at will. The other problem is the thermal stress caused by high temperature fluctuations which may result in fatigue.

It is forecasted that DEMO may be operated in pulsed mode which requires energy storage for the opposite reason: sudden drop of the very high power output (1 GW or more) may not be compensated smoothly even in a huge grid containing numerous power input sites, so some energy output should be produced even when the plasma is down. For DEMO, it is expected that 5-20 minutes long periods (dwell time) should be overcome. It is expected that the energy storage system should be able to store more than 1 TJ energy (i.e., electric energy equivalent).

Possible ways of energy storage such as thermal energy storage (TES), compressed air energy storage (CAES), kinetic energy storage systems (KESS), fuel cells, superconducting magnetic energy storage (SMES), pumped hydro storage, ultracapacitors, and batteries have been reviewed earlier and reported in an EFDA study TW5-TRP-007 by Lucas and Cortes [1].

Since the prospected system must be dynamic, i.e. energy output should reach high power in minutes time, energy conversion from thermal to any other kind of energy may not be advantageous. Thus thermal energy storage is considered as one of the best candidates from the methods listed above.

Thermal energy may be stored in materials having high heat capacity (specific heat) in the temperature range where the heat is tranferred to the energy conversion system (steam generator, etc.). Stored heat (Q) may then be calculated as:

$$Q = c_V \Delta T m$$

where c_V denotes the specific heat (approximated as temperature independent) measured at constant volume (if closed wessels are used), ΔT is the temperature difference, m is the mass of the storage medium. Applicability of the method is based on the magnitude of c_V. This type of heat is sometimes called sensible heat because any small absorption of heat in the system results in raising temperature which can be sensed.

Thermal storage capacity can be greatly enhanced if not the sensible heat but latent heat is used. This means thermal effects of phase transformations, in most cases solid-liquid phase transformations, i.e., melting. In this case, the stored heat is:

$$Q = \Delta H_f$$

where ΔH_f is the heat (enthalpy) of fusion. This method has the advantage of potentially very high thermal storage capacity at constant temperature which helps avoid fatigue of construction materials.

Thermal storage capacity is only one parameter that is considered for the feasibility of a system proposed for this goal. Satisfactory power input and, more importantly, output requires that the heat transfer capacity, i.e., heat conductivity of the complete system should be high. This involves heat conductivity of the storage material itself and the heat conductivity of the wall of the container used to hold the storage medium. Unfortunately, durable and corrosion resistant materials as stainless steel are not always good heat conductors. Since the heat transfer in high power applications can be provided by using large surface area, the role of the container wall is particularly important.

The storage medium may not be harmful, chemically safe and possibly not too expensive. The range of temperature where energy is taken off the fusion reactor determines the group of compounds which may be used. Figure 1. shows a sketch of a system involving heat extraction from a power system at two different temperatures [1]. For DEMO, these temperatrures are those of the blanket (~444°C) and of the divertor (~642°C). These temperatures point to inorganic salts many of which melting in this range.

Molten salt energy storage systems may thus be realized with salts of alkali and alkaline earth metals formed with inorganic acids as hydrochloric acid, carbonic acid, nitric acid and nitrous acid. Oxides and hydroxides can also be used in some cases. High temperature stability is a crucial factor and this reduces the number of potential applicant salts. This is the primary reason why mostly alkali and alkaline earth salts can be considered. At high temperature, sulfates and nitrates often give off highly corrosive SO_2, SO_3, as well as NO, NO_2, respectively. Carbonates give off CO_2. Chlorides can be stable but chloride ions accelerate corrosion of iron containing construction materials very much. KOH and NaOH are a dangerous materials even at room temperature.

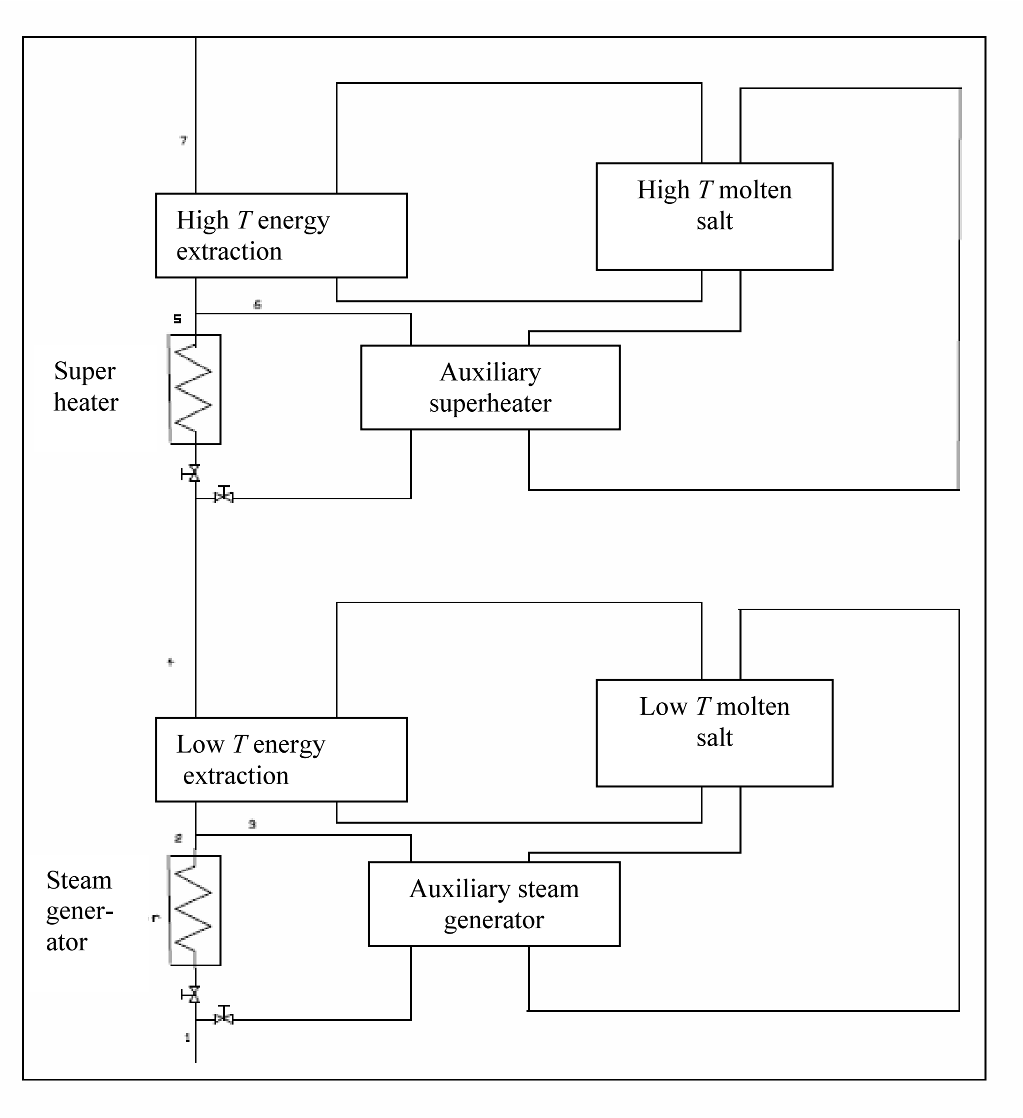

Figure 1. Sketch of a power generation system using thermal storage with power output at two temperatures [1].

EXISTING TECHNOLOGIES FOR MOLTEN SALT ENERGY STORAGE

Even if the latent heat of phase transformations is not used for heat storage, the salts should be used in molten form because the heat transfer is much more effective if not only conduction but material flow (convection) is also present.

Table 1 lists some some salts as Phase Change Materials (PCM) which have been proposed (or actually used) as molten salt heat storage medium. These examples are taken from solar industry applications where heat storage is of primary importance due to unpredictable fluctuations in the power of sunlight.

Table 1. Physico-chemical and technical data for some PCM materials [2].

	Temperature		Average density	Average heat conductivity	Average heat capacity	Volume specific heat storage capacity	Media costs per kg	Media costs per kWh_t
Phase change media	Cold (°C)	Hot (°C)	(kg/m^3)	(W/mK)	(J/kgK)	(kWh_t/m^3)	(US$/kg)	(US$/$kWh_t$)
$NaNO_3$	308		2.257	0.5	200	125	0.20	3.6
KNO_3	333		2.110	0.5	267	156	0.30	4.1
KOH	380		2.044	0.5	150	85	1.00	24.0
Salt-ceramics ($NaCO_3$-$BaCO_3$/MgO)	500-850		2.600	5.0	420	300	2.00	17.0
NaCl	802		2.160	5.0	520	280	0.15	1.2
Na_2CO_3	854		2.533	2.0	276	194	0.20	2.6

Table 2 shows melting temperatures and latent heats (heat of fusion) for similar sytems. As can be seen, the highest temperature is by about 50°C lower than the lower forseeable output temperature of DEMO (blanket site). Thus these materials may be used as PCM for DEMO at the blanket site. It is usually recommended that the melting point (range) of the PCM system should not be much lower than the temperature of the heat source.

Table 2. Physical characteristics of some phase change materials and systems [3].

Phase Change Material (PCM)	**Melting temperature (°C)**	**ΔH (J/g)**
NaCl(42.5%)/KCl(20.5%)/$MgCl_2$	**385-393**	**410**
NaCl(26.8%)/NaOH	**370**	**370**
KOH	**360**	**167**
NaCl/KCl(32.4%)/LiCl(32.8%)	**346**	**281**
KNO_3/KBr(4.7%)/KCl(7.3%)	**342**	**140**
KNO_3	**337**	**116**
KNO_3/KCl(4.5%)	**320**	**150**
NaOH	**318**	**158**
$NaNO_3$	**310**	**174**
KNO_3(10%)/ $NaNO_3$	**290**	**170**
NaCl(5.7%)/ $NaNO_3$(85.5%)/Na_2SO_4	**287**	**176**
NaCl/ $NaNO_3$(5.0%)	**284**	**171**
NaOH/Na_2CO_3 (7.2 %)	**283**	**340**
$NaNO_2$	**282**	**212**
NaCl(5.0%)/ $NaNO_3$	**282**	**212**

The most important feature of these systems is that they are multicomponent systems and therefore their melting occurs in a temperature range (unless the composition is exactly at the eutectic point) where the solid and the liquid phases are present simultaneously. (The melting temperatures indicated are eutectic temperatures.) As mentioned earlier, only a fluid system can provide good heat transfer. Complete solidification of the PCM is not advantegeous.

For a possible system for DEMO, materials with higher melting points should be found the melting point of which may be adjusted with additives in order to obtain an optimal eutectic system.

LITHIUM HYDRIDE AS A THERMAL ENERGY STORAGE MEDIUM

Metal hydrides have been proposed for heat storage materials decades ago and LiH is superior amongst them [2,3]. As can be seen in Table 3, the specific heat of fusion of LiH is extremely high: 2900 J/g. LiH can be produced by the highly exothermic reaction of Li and H_2 at about 600°C. LiH is remarkably stable and dissociates into its elements only around 1000°C. The highly exothermic formation made the suggestion logical that not only the extreme high heat of fusion but the heat of formation could be exploited for heat storage. The problem of the combined application is the high solubility of hydrogen in lithium even at high temperature. Easy separation of the two elements has not been solved so far, although thermal decomposition of LiH by the heat of the fusion reactor or other source (heat storage step) and then a controlled regeneration of LiH by the exothermic reaction of Li and H_2 (heat release step) would make it a very effective and flexible temporary heat storage system.

	Li	LiH	K	KH
Melting point, °C	180.5	688	63.7	Decomposition at 200
Boiling point, °C	1330	-	760	-
Specific heat (at 25°C) J/gK	3.31	6.3	0.741	-
Heat of fusion, ΔH, J/g	434	2900	59	-
Heat conductivity J/cm^2/cm/K/s	0.71	-	0.96	-
Density g/cm^3	0.53	0.8	0.86	-
Decomposition temperature, °C	-	1000	-	200

Table 3. Selected thermodynamical parameters of the elements of the LiH-based system proposed for thermal energy storage for DEMO.

A thermal storage system making use only of the melting of LiH was proposed and experimentally checked by Olszewski and Siman-Tow [5] who applied spherical capsules 5 cm in diameter filled with 35 g of LiH containing some 5% stoichiometric excess Li. The wall of the capsules was relatively thin, 0.18 mm stainless steel of type 304L, for good heat transport.

This system with molten Li or a Na-K alloy as primary heat transport fluid could meet the condition of specific energy storage capacity 3 MJ/kg (666 kWh/m^3). This storage capacity is found in the interval. 430-830°C. Note that heating of LiH from room temperature to 1027°C means absorption of an amount of heat 3800 kWh/m^3 (13.7 GJ/m^3). This figure has been measured by Morse and Hückel [4] who investigated the system for application as a heat sink for high thermal load devices. This means that to meet the 1 TJ storage capacity, less than 100

m^3 LiH is required. Taking into account the conversion losses, a 200-300 m^3 LiH charge in the storage system can be considered as a realistic approach.

The melting point of pure LiH is rather high as compared to the output temperature of DEMO. A possible modification of the system can be the application of eutectics with LiCl or other Li-salts.

COMBINING HEAT OF FUSION AND HEAT OF CHEMICAL REACTION FOR THERMAL ENERGY STORAGE

We propose another method which is based on the separation of lithium and hydrogen at moderate temperatures with the help of potassium. This means the exploitation of the heat of decomposition of LiH. As mentined before, thermal decomposition of LiH is hindered by the fact that hydrogen readily remains dissolved in molten lithium and intense pumping is necessary for the separation. However, an alkali metal more electropositive than Li can readily liberate Li from LiH and forms its own hydride. With potassium, the reaction

$K + LiH = Li + KH.$

takes place, but at the temperature this reaction would occur, KH will decompose immediately and gives K metal and H_2 gas:

$2KH = 2K + H_2.$

Note that KH decomposes already at 200°C (see Table 3). Rather luckily, the resultant Li-K alloy hardly exists because Li and K are not miscible only at elevated temperatures. The phase diagram is shown in Fig. 2.

Thus the following steps may be followed: 1) LiH is reacted with K at a temperature higher than ~300°C. At this temperature hydrogen can be easily separated and stored. The heat from the fusion reactor is thus stored in the form of chemical energy. 2) The Li-K mixture must be cooled to about 200°C (by generating steam) so that Li and K gets separated. 3) Li metal and H_2 gas can then be reacted when needed and heat produced.

The reaction between LiH and K has been checked by us and was found to be very fast in a preliminary experiment. The hydrogen pressure observed in the system after the reaction was well over the value reported in the literature for the pure Li-H system.

This procedure offers extension into three directions relevant to the improvement of the efficiency of energy production methods. i) The method for hydrogen separation from LiH can be important for the „hydrogen economy" since LiH may be used as hydrogen storage medium. ii) Since the LiH + K reaction occurs at relatively low temperature but the Li + H_2 reaction produces heat at high temperature, the system works as a heat pump. iii) There are reports and patents in the literature on the Li-H electrochemical cell which uses the formation of LiH as the cell reaction. Thus „direct" conversion of heat into electricity by this „thermally regenerative elctrochemical cell" may become feasible and that would increase the efficiency of energy production considerably.

LiH is a dangerous material as reacts with oxygen and moisture rather heavily. On the other hand, fusion reactors are designed to apply molten Li or Li-Pb alloy as blanket material, so the technology that handles safety issues will be readily available. On the other hand, the highly reductive feature of both LiH as well as Li and K prevents any oxidative corrosion of the steel wessels.

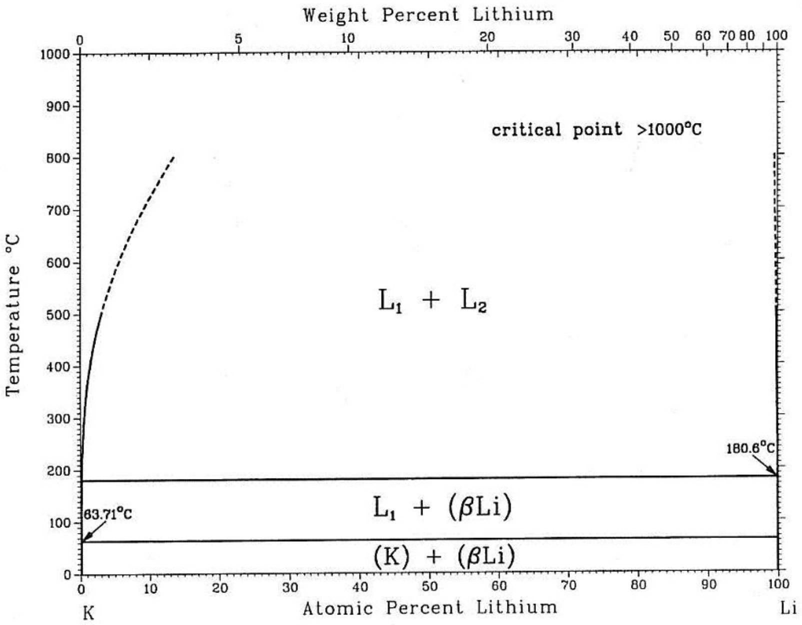

Figure 2. Phase diagram of the Li-K system [6].

For a cost estimate, the current price of Li can be a starting point which is ~90 USD/kg. The world production is about 13-14000 t/year (calculated for metallic lithium) and is increasing, so prices may go down. Calculating with the thermal storage capacity, the specific cost is roughly 17 USD per kWh_t (LiH automatically forms in the system; the price of hydrogen is negligible as compared to that of Li). This is equal to that of the $NaCO_3$-$BaCO_3$/MgO system and performs better than KOH proposed in Table 1. One may add that since LiH is recycled with probably very little loss, this one-time investment will not make the method economically incompetitive.

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