Universitat de Lleida

Advanced thermal energy storage research in demo plants for commercial systems

Cristina Prieto Ríos

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PhD Thesis

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Author

Cristina Prieto Ríos

Directors of the PhD thesis

Dr. Luisa F. Cabeza (University of Lleida, Spain)

Dr. A. Inés Fernández (University of Barcelona, Spain)

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Programa de doctorat en Enginyeria i Tecnologies de la Informació

Directors of the PhD thesis:

Dra. Luisa F. Cabeza (University of Lleida, Spain)

Dra. A. Inés Fernandez (University of Barcelona, Spain)

La Dra. Luisa F. Cabeza, Catedràtica de l'Escola Politècnica Superior de la Universitat de Lleida i la Dra. A. Inés Fernández, professora Agregada del Departament de Ciència de Materials i Química Física de la Universitat de Barcelona.

CERTIFIQUEN:

Que la memòria "Advanced thermal energy storage research in demo plants for comercial systems" presentada per Cristina Prieto Ríos per optar al grau de Doctor s'ha realitzat sota la seva supervisió.

Lleida, 2 de Septiembre de 2016

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Resumen

La presente tesis se encuadra en el campo del almacenamiento de energía térmica, en concreto en el proceso de diseño y optimización que conlleva el desarrollo de una tecnología de almacenamiento térmico. La energía solar concentrada (CSP en inglés) se ha consolidado como una tecnología renovable gestionable capaz de almacenar parte de la energía solar recibida durante el día y entregarla posteriormente a la red durante la noche. En la actualidad las tecnologías de almacenamiento térmico comerciales se dividen en: (i) almacenamiento directo e indirecto de sales fundidas, y (ii) acumuladores de vapor, siendo el primer sistema el más ampliamente extendido.

A lo largo de esta tesis, se muestra el proceso de análisis, estudio y optimización realizado para permitir desarrollar los sistemas de almacenamiento térmico con sales fundidas desde su etapa inicial de desarrollo hasta su etapa de demostración y su extrapolación a diseños comerciales, permitiendo el desarrollo de tecnologías de almacenamiento que ayuden a reducir costes y a aumentar la eficiencia de las plantas de CSP con un objetivo claro: que la electricidad de origen solar sea competitiva frente a las plantas fósiles en el horizonte 2020.

Para ello se han diseñado, construido, operado y analizado dos plantas prototipos, la primera de ellas sita en la Universidad de Lleida con una capacidad de 1.6 ton y la segunda sita en la plataforma Solúcar de Abengoa, con 450 toneladas. El estudio de sus principales componentes para la optimización del diseño, los análisis exergéticos realizados así como la retroalimentación de los proceso que se lleva a cabo en esta tesis ha permitido que actualmente Abengoa, empresa española líder del sector energético de renovables, tenga en operación la mayor planta de almacenamiento térmico del mundo en operación (Solana, 2013).

Finalmente, y aunque la tesis describa con éxito el proceso de desarrollo de una tecnología de almacenamiento, la optimización de estos sistemas debe continuar. De ahí que se describan en esta tesis algunos de los nuevos conceptos de almacenamiento que deben seguir un proceso de desarrollo similar para alcanzar soluciones para la estabilidad de red: consiste en el desarrollo de una nueva tecnología conjunta del almacenamiento de energía termoquímica y energía térmica de alta capacidad. El reto que se plantea, o mejor dicho, que ya está en curso, deberá servir para aumentar la competitividad de la tecnología termosolar mediante la reducción de costes, en particular, aquellos relativos al almacenamiento térmico, mitigando la incertidumbre respecto a la problemática del suministro energético en las décadas venideras.

Resum

La present tesi s'enquadra en el camp de l'emmagatzematge d'energia tèrmica, en concret en el procés de disseny i optimització que comporta el desenvolupament d'una tecnologia d'emmagatzematge tèrmic. L'energia solar concentrada (CSP en anglès) s'ha consolidat com una tecnologia renovable gestionable capaç d'emmagatzemar part de l'energia solar rebuda durant el dia i entregar-la posteriorment a la xarxa durant la nit. En la actualitat les tecnologies d'emmagatzematge tèrmic comercials es divideixen en: (i) emmagatzematge directe i indirecte de sals foses, i (ii) acumuladors de vapor, essent el primer sistema el més àmpliament estès.

A lo llarg d'aquesta tesi, es mostra el procés d'anàlisi, estudi i optimització realitzat per permetre desenvolupar els sistemes d'emmagatzematge tèrmic amb sals foses des de la seva etapa inicial de desenvolupament fins a la seva etapa de demostració i la seva extrapolació a dissenys comercials, permetent el desenvolupament de tecnologies d'emmagatzematge que ajudin a reduir costos i a augmentar l'eficiència de les plantes de CSP amb un clar objectiu: que la electricitat d'origen solar sigui competitiva front a les plantes fòssils en l'horitzó 2020.

Per això s'han dissenyat, construït, operat i analitzat dues plantes prototipus, la primera d'elles situada a la Universitat de Lleida amb una capacitat de 1.6 ton i la segona situada a la plataforma Solucar d'Abengoa, amb 450 tones. L'estudi dels seus principals components per a l'optimització del disseny, els anàlisis exergètics realitzats així com la retroalimentació dels processos que s'hi dur a terme en aquesta tesi ha permès que actualment Abengoa , empresa espanyola líder del sector energètic de renovables, tingui en operació la major planta d'emmagatzematge tèrmic del món en operació (Solana, 2013).

Finalment, i encara que la tesi descrigui amb èxit el procés de desenvolupament d'una tecnologia d'emmagatzematge, l'optimització d'aquests sistemes ha de continuar. De aquí que es descrigui en aquesta tesi algun dels nous conceptes d'emmagatzematge que ha de seguir un procés de desenvolupament similar per aconseguir solucions per a la estabilitat de xarxa: consisteix en el desenvolupament d'una nova tecnologia conjunta de l'emmagatzematge d'energia termoquímica i energia tèrmica d'alta capacitat. El repte que es planteja, o millor dit, que ja està en curs, haurà de servir per augmentar la competitivitat de la tecnologia termosolar mitjançant la reducció de costos, en particular, aquells relatius a l'emmagatzematge tèrmic, mitigant la incertesa respecte a la problemàtica del subministrament energètic en les dècades properes.

Summary

This thesis is framed in the field of thermal energy storage, particularly in the design and optimization process needed for the development of a thermal storage technology. Concentrated solar power (CSP) has become a manageable renewable technology capable of storing part of the solar energy received during the day and then returns it to the network overnight. At present commercial thermal storage technologies are divided into: (i) direct and indirect molten salt storage, and (ii) steam accumulators, being the first system the most widespread.

Throughout this thesis, a process of analysis, study and optimization has been done in a thermal storage system with molten salt from its initial stage of development to a demonstration stage in order to be able to extrapolate the results to commercial designs, allowing the development of storage technologies more efficiently. This work helps to reduce costs and increase the efficiency in CSP plants with a clear objective: that solar electricity will be competitive with fossil plants in 2020.

For this purpose we have designed, built, and operated two energy storage prototype plants, the first one located at the University of Lleida with a thermal capacity of 66 kWh_{th} and the second located at the Solúcar Platform Abengoa, with 8,5 MWh_{th}. The study of its main components for design optimization, the exergy analysis as well as feedback from the process carried out in this thesis has allowed currently Abengoa, a leading Spanish renewable energy company, keep in operation the greater thermal storage plant in the world in operation (Solana, 2013).

Finally, although the thesis successfully describes the process of development of storage technology, the optimization of these systems must continue. Hence they are described in this thesis some new storage concepts that must follow a similar process of development to achieve solutions for network stability: is the development of a new storage technology based on the thermochemical energy of a reversible reaction which have much more thermal energy density than the current system. The challenge, already underway, will serve to increase the competitiveness of solar thermal technology by reducing costs, in particular those relating to thermal storage, mitigating the uncertainty regarding the problem of supply energy in the coming decades.

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1. Introduction

1.1. Concentrated solar energy in the world

The current model of economic development is based on the intensive use of fossil energy resources, causing negative environmental impacts and socio-economic imbalances which require a new model of sustainable development. Renewable energies are crucial to ensuring the long-term energy supply while in addition to being indigenous and inexhaustible energy sources. Today's society, in the context of reducing dependence on foreign energy, better use of available energy resources and increased environmental awareness is increasingly demanding the use of efficient and cost-competitive renewable as basic principle for sustainable development from an economic, social and environment's point of view. Furthermore, the global energy policies should allow, by seeking energy efficiency in the electricity generation and use of renewable energy sources, to reduce greenhouse gases according to the commitments made by signing the Kyoto protocol.

If we see the world electricity demand by region in Figure 1 is forecast to be double in the next 30 years, being almost double in 15 years in China.

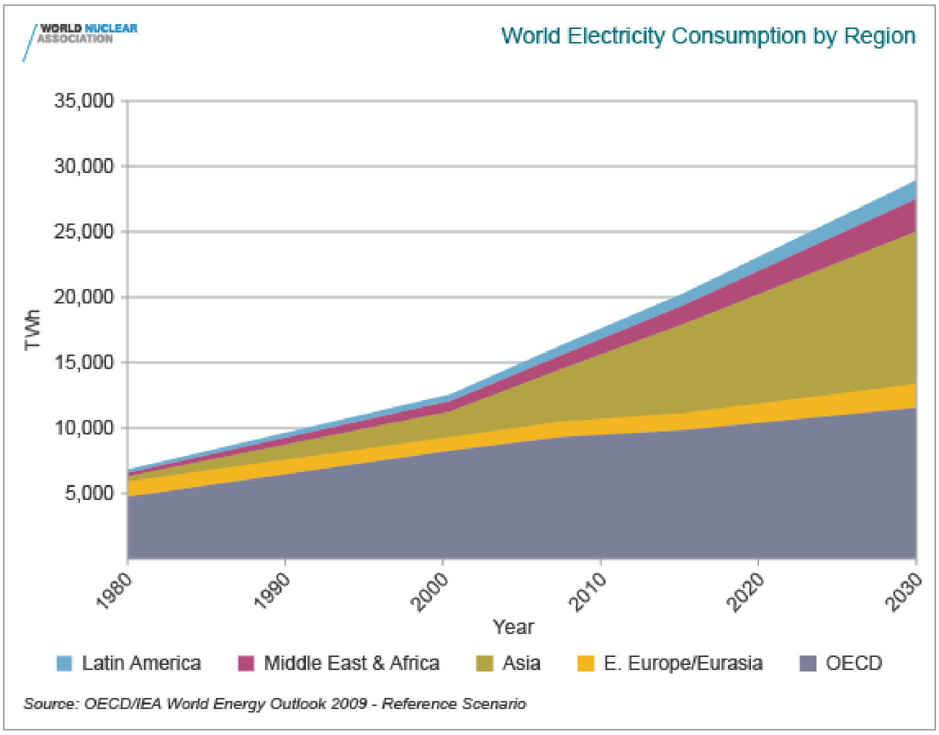


Figure 1. World Electricity Consumption by region

Locations such as Germany, where at least 70% nuclear blackout will occur in the coming years, will need to build 21.3 GW by 2020; India, with a rapid population growth, where the grid will need to add 250 GW by 2020; and California, one of the areas with high direct radiation, where growth is estimated to 23.8 GW by 2020 are some examples of electrical installation needs in the coming years. These geographical areas among others worldwide will require the additional supply of cost-competitive, secure, clean and dispatchable energy. Renewable energies sources such as solar, wind, tidal, etc. are presented as key players in achieving this goal in a sustainable way. Solar energy is considered as one of the cornerstones following the expected installation capacity carried out by the IEA according with the new policies scenario. Figures 2 and 3 show the increasingly prominent role that solar energy will take on the worldwide energy market and more specifically the proliferation of concentrated solar plant (CSP), which will multiply by 35 (70 GW vs. 2 GW) the total installed capacity in the 2011-2035 period.

The installed CSP capacity expectation is shown in Table 1 by geographical area.

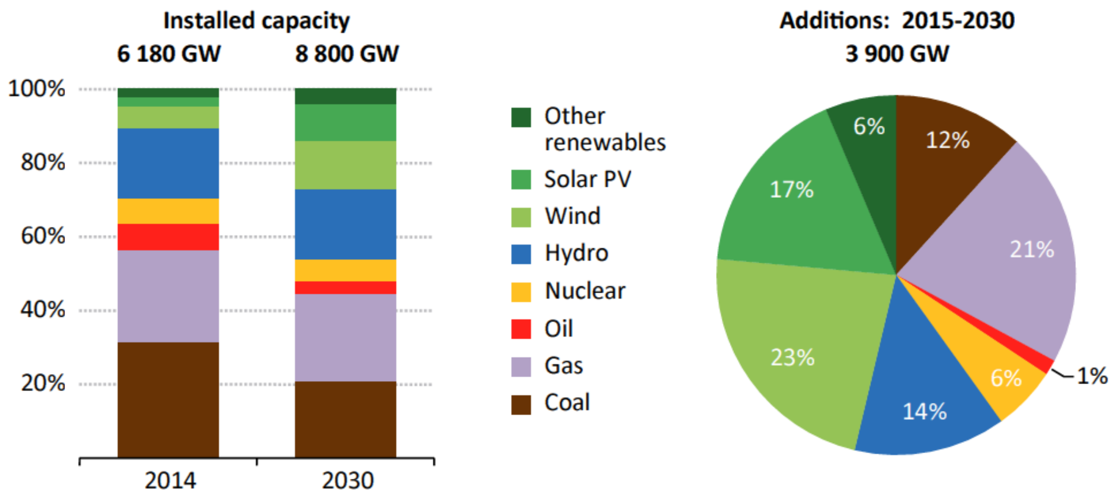


Figure 2. World power generation capacity mix and capacity additions [1]

Table 1. CSP installed capacity expectation for the same period [2]

GW	United States	Other OECD Americas	European Union	Other OECD	China	India	Africa	Middle East	Other developing Asia	Non-OECD Americas	World
2013	1.3	0.01	2.31	0.01	0.02	0.06	0.06	0.10	0.02	0	4.1
2030	87	6	15	4	29	34	32	52	0.3	2	261
2040	174	18	23	12	88	103	106	131	3	7	664
2050	229	28	28	19	118	186	147	204	9	15	982

For 2050 and beyond, a paradigm shift in terms of production, distribution and use of energy should be aligned with an overall energy consumption coming largely from renewable technologies. However, there is a strong mismatch between renewable energy supply and user demand.

Energy storage systems are designed to accumulate energy when production exceeds demand and to make it available at the user's request. They can help match energy supply and demand, exploit the variable production of renewable energy sources (e.g. wind and solar), increase the overall efficiency of the energy system and reduce CO_2 emissions.

Solar thermal electricity or concentrating solar is unique among renewable energy generation sources because it can easily be coupled with thermal energy storage (TES) as well as conventional fuels, making it highly dispatchable [3].

If we analyze more in detail the solar technology, the CSP technology can be classified into parabolic trough, tower, linear Fresnel, and dish, from maturity point of view. According to the way they focus the sunrays and whether the position of the receiver, they can be classified as follows: parabolic trough and linear Fresnel systems where the mirror tracks the sun along one axis (line focus), and tower and dish systems where the mirror tracks the sun along two axes (point focus). The receiver is maintained fixed in linear Fresnel and tower systems, while is mobile in parabolic trough and dish systems.

In parabolic trough technology, the sun´s energy is concentrated by a parabolically curved trough-shaped reflector onto a receiver tube running along the inner side of the collector [4] [5] The energy concentrated in the receiver tube heats a heat transfer fluid (HTF), commonly synthetic oil, that flows through the tube along the trough collector and the heated HTF is then used to generate electricity in a conventional steam generator-turbine. Parabolic trough technology can also be integrated with existing coal-fired plants or combined cycles.

Solar power tower converts sunshine into electricity using many large sun-tracking mirrors, also called heliostats, to focus the sunlight on a receiver located at the top of a tower [4] .The HTF that flows in the receiver, commonly molten salts or water/steam, is heated by theses sunlight and then used in a conventional steam generator and turbine to produce electricity.

On the other hand, linear Fresnel technology [6] uses flat or slightly curved mirrors mounted on trackers on the ground that are configured to reflect sunlight onto a receiver tube fixed in space above the mirrors. A small parabolic mirror is sometimes added atop the receiver to further focus the sunlight.

Parabolic dish systems consist of a parabolic-shaped point focus concentrator in the form of a dish that reflects solar radiation onto a receiver mounted at the focal point [4] .These concentrators are mounted on a structure with a two-axis tracking system to follow the sun. The collected heat is typically utilized directly by a heat engine mounted on the receiver moving with the dish structure. Stirling and Brayton cycle engines are currently favored for power conversion.

For each technology, various options exist for the HTF, TES and power cycle.

Solar thermal energy (STE) plants that are currently operating and being constructed have been reviewed. Details of their solar collector configuration, solar field operating conditions, TES systems and cooling methods have been summarized in Table 2 for the two most mature technologies, trough and tower.

Table 2. Representative features of the trough and tower STE technologies for current and future STE plants ([3] [7] [8])

	Current trough	Current tower
Maturity	High, commercially proven	Medium, recently commercially proven
Key technology providers	Abengoa Solar, Sener Group, TSK-Flagsol, Acciona, ACS-Cobra,	Abengoa Solar, BrightSource Energy, Solar Reserve, eSolar, Torresol
Typical plant capacity [MWe]	100	50-100
Operating temperature of solar field [ºC]	290-390	290-565
Plant peak efficiency [%]	14-20	23-35
Annual average conversion efficiency [%]	13-15	14-18
Collector concentration [suns]	70-80	>1000
Power block cycle	Superheated steam Rankine	Saturated steam Rankine Superheated steam Rankine
Power block fluid conditions	steam @380ºC/100 bar	steam @540ºC/100-160 bar
Power cycle efficiency [%]	37.7	41.6
Heat transfer fluid	Synthetic oil, water/steam (DSG), molten salt (demo), air (demo)	Water/steam (DSG), molten salt, air (demo)
Annual capacity factor [%]	20-25 without TES 40-53 with 6h TES	40-45 with 6-7.5h TES 65-80 with 12-15h TES
Storage system	Indirect 2-tank Molten Salt storage	Direct 2-tank Molten Salt storage, Steam Accumulator
Storage temperature range [ºC]	293-393	290-565 for Molten Salt storage 120-330 for Steam Accumulators
Capital cost [US$/kW] (*)	4700-7300 (without TES, OECD countries) 3100-4050 (without TES, non-OECD countries)	6400-10700 (with TES)
LCOE [US$/kWh]	0.26-0.37 (without TES) 0.22-0.34 (with TES)	0.2-0.29 (with 6-7.5h TES) 0.17-0.24 (with 12-15h TES)
Cooling method	Wet	Wet, dry
Suitable for air cooling	Low to good	Good
Water requirement [m3/MWh]	3 (wet cooling) 0.4-1.7 (hybrid cooling) 0.3 (dry cooling)	1.8-2.8 (wet cooling) 0.3-1 (hybrid cooling) 0.3 (dry cooling)

(*) OECD: Organization of Economic Co-operation and Development

Figure 3 from a) to c) presents the overview of the STE sector with the worldwide capacity depending on countries and type of used technology, for solar thermal plants that are both operational and under construction. The information has been obtained from a project listing hosted by the National Renewable Energy Laboratory (NREL) (http://www.nrel.gov/csp/solarpaces/). As of January 2016, the STE market has a total capacity of 7638 MWe worldwide, among which 4801 MWe are operational and 2837 MWe are under construction. Estimations also consider that there are other 8472 MWe under development, which brings an overview of the growing potential of the STE sector in the development of new future projects to come.

Spain has a total operational capacity of 2304 MW, making it the world's leading country in CSP. USA follows Spain with a total capacity of 1893 MW. Other countries like South Africa, Chile, India, China and a few Middle East countries have grown their interest to develop solar thermal power plants recently. Among these countries, South Africa and Chile are the most promising ones for future CSP developments due to the great acceptance of STE.

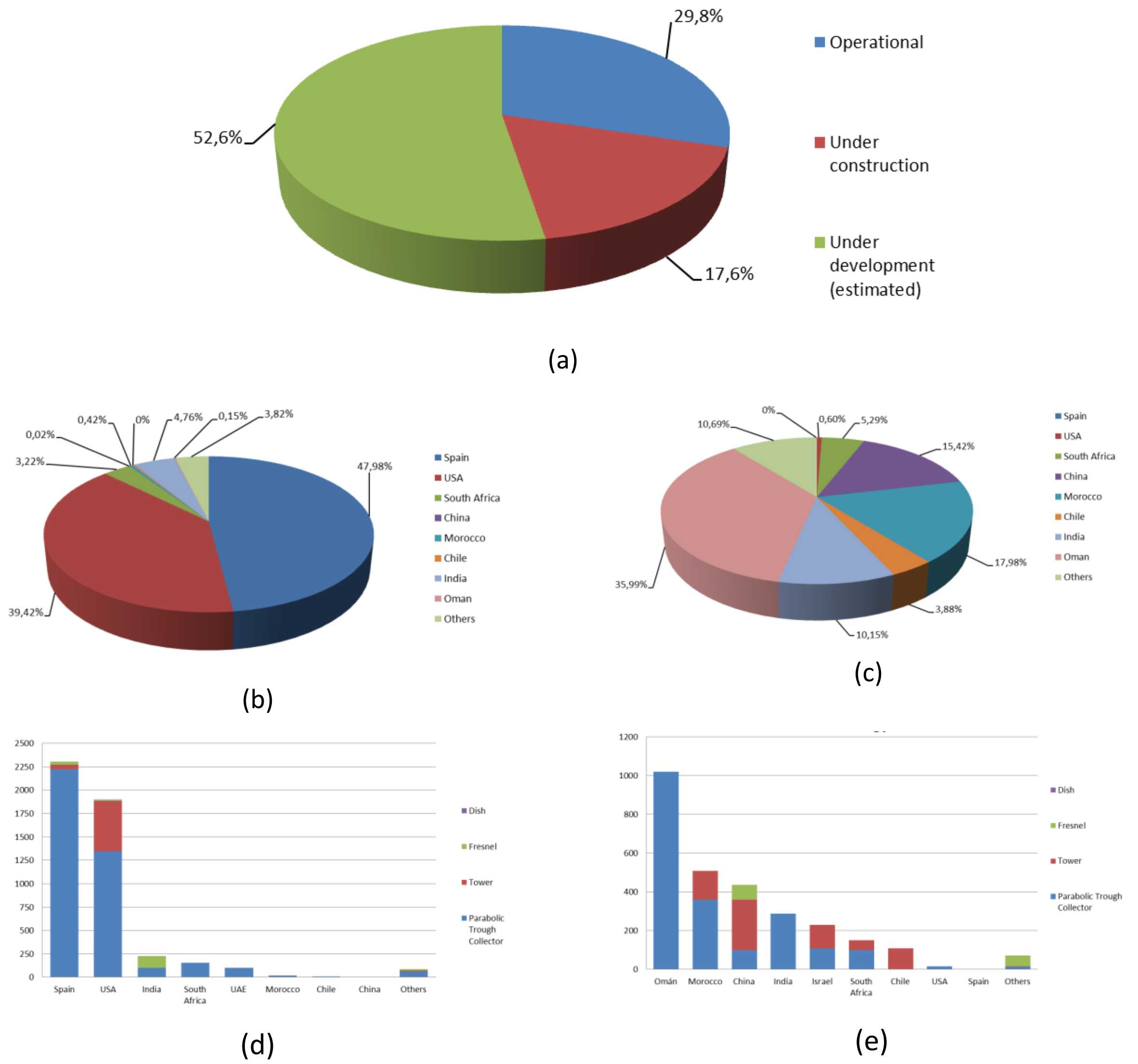


Figure 3. Solar thermal energy worldwide plant capacity (January 2016). (a) Plant capacity; (b) Operational plant capacity; (c) Under construction plants capacity; (d) Capacity in operation by country and technology; (e) Capacity under construction presented by country and technology (Data from NREL).

Parabolic trough systems are currently the most proven STE technology and dominate the global market, being installed in around 81% of the STE plants in operation and around 48% which are under construction. Regarding solar tower systems, there are around 14% of the total STE plants operating worldwide, while this percentage raise up to 28% for the tower plants which are currently under construction. The increase in the number of solar tower projects in the recent years shows that this system has achieved a good level of maturity allowing scaling the technology up to hundreds of MW. Linear Fresnel plants are currently making the transition to commercial applications while parabolic dishes are at the early demonstration stage. Figure 3.d presents the STE worldwide operational capacity by country and used technology. Figure 3.e presents the STE worldwide under construction capacity by country and technology.

Slightly more than one third of the installed CSP capacity is integrated with thermal energy storage. More precisely, a 36% of the total STE installed capacity. With the maturity of molten salt and steam accumulator storage technologies, over 53% of the capacity under construction has energy storage. This percentage increases up to 83% not considering the 1 GW solar plants under construction in Oman. Only considering the tower and trough technology, up to 73% (up to 78% not considering the 1 GW solar plant under construction in Oman) of the under construction capacity uses thermal energy storage. The current thermal storage technology used in STE plant is short-term pressurized steam storage (<1 h) and molten salt for long-term storage. Figure 4 presents the STE capacity with and without storage depending on the used technology.

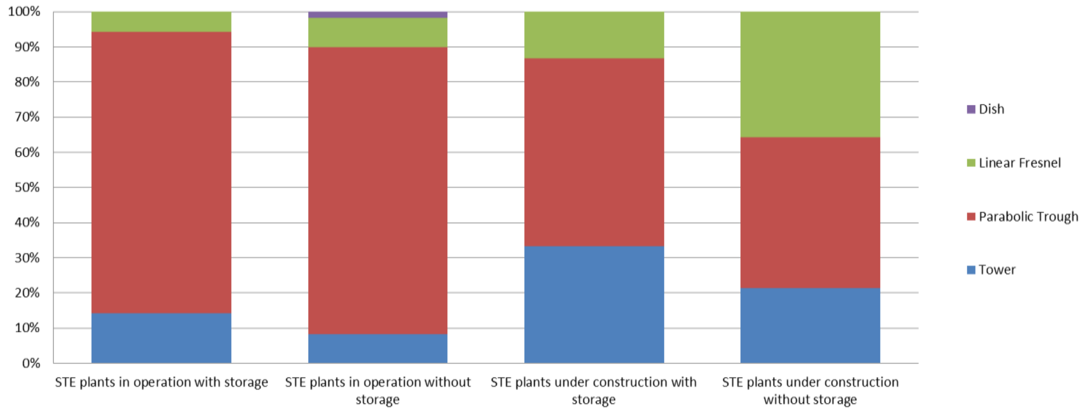


Figure 4. STE worldwide capacity categorized by technology and with/without storage (January 2016) [9]

1.2. State of the art of thermal energy storage technologies

Currently commercially available high temperature TES systems are mainly sensible heat systems [10] to be used in connection with single phase heat transfer fluids such as pressurized water, oil, molten salts or gaseous fluids like air (see Figure 5, commercial plant installed by Abengoa in Arizona (USA)). It should be distinguished between direct storage systems (the HTF is simultaneously the storage material) and indirect storage systems [11], where the thermal energy must be transferred from the HTF to a second material. Within the range 150 to 500/600°C, prevailing storage materials are liquids (pressurized water, synthetic oils and molten salts). Heat storage in molten salts is the dominating technology in solar power applications today. Salt systems used is a binary system – Molten salt mixture - with the temperature range 240-600°C, composed of 60% $NaNO_3$ and 40% KNO_3. The lower limit of the temperature range is defined by the freezing point of the salt, whereas the upper limit is determined by its decomposition temperature. Depending on the temperature range, the investment cost of molten salt storage technology is 15-30 €/kWh in direct storage systems and 30-60 €/kWh in indirect storage systems [12]. In two-tank molten salt storage systems it is achievable energy density ranges from 30 to 70 kWh/m^3.

Figure 5. Molten salt storage of Solana Plant (Abengoa, Arizona, 250 MW)

Solid materials can be utilized in a wider range of storage temperatures. The thermo-mechanical stability of the solid is one of the major issues. Up to 400/500°C, a "shell & tubes" technology using concrete as storage material has been developed by DLR [13] . The investment cost is 30-40 €/kWh and the energy density achievable in combination with solar power generation (oil-based parabolic trough technology) is around 25 kWh/m^3. At temperatures beyond 500/600°C, regenerators operated with hot air or flue gas are commonly used in the steel making industry (Cowper regenerator), coke manufacturing and glass manufacturing. The storage materials are refractory bricks based on oxides (silica, alumina, magnesia and iron oxide), carbonates (e.g. magnesite) and their mixtures. The existing industrial applications are showing high charging/discharging power at relatively low thermal storage capacity. That means that heat exchange aspects are dominating and high specific heat transfer surface is more important than high volume specific storage capacity. Therefore, the specific investments costs are very high (~400 €/kWh) and cannot be directly transferred to applications where the storage aspect is dominating. For low pressure applications, the investment costs for several hour TES regenerators are expected to be in the range of 20-80 €/kWh. Current research is being directed towards new low-cost materials such as rocks (granite, basalt and quartz), high temperature concretes (alumina cement-based, alumina-silicate geopolymers) [14] and recycled industrial ceramics [15].

All of the systems described above are only suited for single phase sensible heat storage and do not lend themselves for a two phase water/steam cycle because of the pinch point problem. State of the art of thermal storage used for steam applications is the steam accumulator technology. Steam accumulators (also called Ruth's storage systems) use sensible heat storage in pressurized saturated liquid water [16]. Steam is produced by lowering the pressure of the saturated liquid during discharge. This TES technology is mainly used in industrial low-pressure applications (2-20 bars). Steam accumulators are preferred as short term storage and are characterized by a short response time and high discharge rate. The first solar commercial plant with this system was installed by Abengoa in 2005 in the plant PS10. The storage system had a capacity of 30 min (Figure 6). For process steam applications until 20 bar operation pressure and capacity from 100 kWh to 1 MWh, the investment cost is approximately in the range of 200-400 €/kWh and the energy density is around 20-30 kWh/m^3.

Figure 6. Steam accumulator in solar plant PS10 (Abengoa, Solúcar platform, Seville)

Latent heat storage technologies for high temperature applications still are under development. Extensive work has been reported in the literature on selection and/or characterization of phase change materials (PCM) for high temperature latent heat storage [17]. Inorganic anhydrous salts have attracted more interest than metals and metal alloys because they are cheaper. The cations are mainly alkali (e.g. Li, Na, K) and alkali earth metals (e.g. Ca, Mg). Anions which are considered include nitrates, nitrites, hydroxides, bromides, carbonates, chlorides, sulphates and fluorides. Many anhydrous salts are miscible and this results in a large variety of potential single salts or eutectic salts. Out-eutectic salts mixtures, which can separate during non-congruent melting/solidification processes, are systematically discarded. Salts with high undercooling or large volume change during melting, as well as highly corrosive salts, are also generally let aside. Most salts have low thermal conductivity (usually less than 0.5-1 W/m·K), which results in poor heat transfer between the HTF and the storage material. Therefore, different techniques for heat transfer enhancement have been investigated: increasing the thermal conductivity of the salt by compositing high conductive materials extending the heat transfer surfaces by fins and capsules, using heat pipes and employing multiple PCMs in cascade. Compared to sensible heat storage, latent heat allows large amounts of energy storage in relatively small volumes. The volumetric energy density achievable ranges from 80 kWh/m^3 to almost 200 KWh/m^3. Besides, thermal energy is stored/delivered at almost constant temperature, thus making latent heat storage attractive only for TES applications using saturated steam as HTF.

A new storage concept for direct steam generation solar power plants working with superheated steam up to 500°C is being developed by Abengoa and is under patent process. It consists in a three-component storage system combining sensible heat and latent heat storage. The heat needed for evaporating the water is stored in latent heat storage, while molten salt heat units store the heat for preheating and superheating. Also DLR has developed an alternative system [18] using concrete to store the sensible heat. A setup of a storage system with a capacity of approx. 1 MWh_{th} has been designed and manufactured and will be tested in a DSG-facility of Endesa in Carboneras (Spain). It must be noticed that using a solid storage medium with embedded heat exchanger for superheating, the temperature of the exiting steam will decrease during the discharge process. Basically, this effect can be compensated by parallel discharge of storage modules with varying mass flow rates but this demands a complex operation strategy. Besides, the poor efficiency of superheated steam as HTF probably leads to oversized heat exchanger in these storage units.

Thermochemical heat storage (TCES) development is still in a fundamental, laboratory stage and far from any proven design and material to be transferred to a commercial scale. However, TCES is being intensively studied because it is a nearly lossless way of storing energy when the chemical reaction partners are stored separately and because it could provide outstanding values of volumetric energy density. Gas-solid reversible reactions are especially suitable for heat storage because of the easy separation of the released gas during the heat absorption. Various kinds of gas-solid reaction systems are under investigation [19]: dehydrogenation of metal hydrides (80-400°C), dehydration of metal hydroxides (250-800°C), decarboxylation of metal carbonates (100-950°C), and thermal desoxygenation of metal oxides (600-1000°C). Although the enthalpy of reaction is usually extremely high (400-1100 kWh/m^3 depending on the temperature), feasible energy density is between 200 and 500 kWh/m^3. The reasons for this are mainly two: firstly, the solid must be in powder or pellets; secondly, the reactants (solid and gas) must be stored in separate tanks in most of the cases (closed systems). In the VII Framework Program of the EU, the project TCS-Power (2011-2015) and RESTRUCTURE (2011-2014) are studying CaO/H_2O reactions and open redox cycles. The heat storage systems based on metal hydroxides, in which water (steam) reacts with a metal oxide (e.g. CaO), are especially interesting for steam power generations applications. However, several problems (e.g. tendency towards agglomeration of the solid, poor heat transport characteristics, low reaction kinetics, possible crystallization after dehydration and sintering at high temperature) have to be solved.

1.3. Advantages and disadvantage of thermal energy storage

The potential for low-cost and efficient thermal storage is one of the claimed attributes of large-scale CSP technologies. Thermal storage allows solar electricity to be dispatched to the times when it is needed most, and allows solar plants to achieve higher annual capacity factors. The list below highlights some of the key advantages that thermal energy storage potentially offers [20]:

- Dispatching of solar power: Thermal energy storage allows the collection of solar energy to be separated from the generation of electric power. This allows solar energy to be collected during the day and used to generate electric power during the part of the day that is most advantageous. Solar energy can be collected during the summer morning and used to generate electricity in the late afternoon or evening when utilities have a greater need for power. Dispatching refers to operating the plant to during specific times typically to help the utility meet their peak load. Power produced during the peak period is usually valued higher than during low demand periods, providing an economic incentive for the addition of thermal energy storage. Thermal storage also allows energy to be shifted from a sunny weekend day to a cloudy weekday when power will have a higher value.
- Firming delivery of solar power: Without thermal energy storage, solar power is an intermittent power resource, dependent on when the sun shines. The ability to store energy and dispatch solar power when it is needed helps make solar power plants a more reliable or firm power resource for the utility. There is a strong correlation between days with high peak loads being sunny days. During 2004, California experienced seven new system peaks. On each of those days the solar resource was at or above the mean long term solar resource. Since the peak load is typically offset by several hours, thermal energy storage allows energy collected in the morning to be shifted to meet the utility peak load later in the day. Firming of delivery is an important aspect of helping solar power plants be deserving of receiving capacity payments.
- Increased Annual Capacity Factor: One of the important features of parabolic trough plants is that the size of the solar field relative to the power plant is a design option. With the addition of thermal energy storage it is possible to oversize the solar field relative to power plant. The solar field can be sized to collector more energy than the power plant can use at any given time. This energy can be stored for later use. A typical parabolic trough plant without thermal energy storage will be able to produce power for the equivalent of 25% (+/- 5%) of the time during the year at full load operation. This is referred to as a 25% annual capacity factor. With the addition of thermal energy storage, the solar field can be sized to allow capacity factors of 75% or higher. As a result, with the addition of thermal energy storage it is possible for solar power plants to operate as a baseload power plant, 24 hours per day.
- Increase power cycle conversion efficiency: Because parabolic trough solar field only track the sun on one axis, during the winter the output from the solar field is decreased due to the high incidence angle between the collector and the sun. As a result, the power plant may operate at partial load, 20 to 30% of design output, and reduced efficiency during the entire day. The addition of thermal storage allows the plant to collect energy and operate the plant at close to design load.
- Reduced power plant starts: Starting up a power plant takes time, energy, puts additional wear and tear on equipment, and is often the time when systems are most susceptible to failure. Solar power plants start up daily and during partially cloudy days, a plant without thermal energy storage is forced to start-up every time sufficient solar energy is available and may be tripped off line every time a large cloud passes over. Multiple plant start-ups in a single day are not unusual. In some cases, a plant will attempt to start-up but will not complete the start-up before the next cloud comes over. The additional of thermal storage allows solar energy to be collected during short sunny periods and stored for later use when sufficient energy has been collected to run the power plant for a sustained period. In addition, for plant that have large amounts of thermal energy storage and oversized solar fields to operate at high capacity factors, the plant can operate for 24 hours per day, significantly reducing the number of start-ups.
- Increased Plant Availability: Thermal storage allows the collection of solar energy to be disconnected from the operation of the power plant. This provides a buffer in case there are any delays in starting up the power plant. In a plant without storage, even minor delays due to intermittent instrumentation, valve problems, or operator inattention can result in significant losses in daily solar electric generation. With the addition of thermal energy storage, small power plant outages can be tolerated without causing any reduction in daily electric generation. During the winter, solar energy

could potentially be collected for one or more days prior to the power plant needing to be operated. This could allow a several day maintenance outage to be scheduled on the power plant if needed.

- Reduce dumping of solar energy: Because there is a strong seasonal variation in solar energy delivery, solar field are typically slightly oversized to allow better utilization of the power plant. This means that the solar field is capable of providing more thermal energy than the power plant can use during some periods of the year. The addition of thermal energy storage may allow this excess energy (often referred to as dumped energy because collectors are defocused) be collected that would otherwise be lost.

On the other hand, the TES have certain disadvantage as:

- Cost: The primary disadvantage of adding thermal energy storage to a solar power plant is cost. However, the cost is still substantial and has a significant influence on plant project economics. The cost of the near-term thermal energy storage technology is on the same order as the cost of the power cycle, meaning that the cost of adding thermal storage to double the plant annual capacity factor is similar to the cost of building a second power plant instead. One of the key goals of the parabolic trough advanced thermal energy storage plan is to develop lower cost thermal energy storage technologies.
- Efficiency Losses: Adding thermal energy storage to a solar power plant results in some loss in efficiency due to thermal losses from the storage system (tanks, piping, heat exchangers and pumps), from reductions in the heat transfer fluid temperature delivered to the power plant steam generators, and the increased parasitic electric loads for pumping and potentially heating of systems. A terminology known as the round trip efficiency is used to determine the effective electric storage efficiency of thermal energy storage systems. This is intended to compare the efficiency of putting thermal energy into storage and then using it to generate electricity, compared to directly converting the thermal energy to electricity. Because this is a rather complex calculation with many interrelated factors, the calculation is done on an annual basis. The thermal losses from high temperature storage tanks are relatively small, on the order of 1% of the energy stored. A reduction in supply temperature can result in reduced power cycle efficiency, especially for indirect systems that require heat exchangers to transfer energy to and from the storage system. Additional pumping parasitic may be required to charge and discharge the storage system.

The comparison between advantages and disadvantages is a key factor in order to decide the use of TES in STE plants.

1.4. Selection of the optimum thermal storage system in STE commercial plants.

For thermal energy storage systems it can be derived, that there is **more than one storage** technology needed to meet different applications. Consequently, a broad spectrum of storage technologies, materials and methods are needed. The overall target in designing TES systems is the reduction of investment cost and the enhancement of efficiency and reliability. To achieve these objectives, material, design and system integration aspects have to be considered in equal measure.

The assessment of identification and selection of the optimal TES system only is not focus on the storage material, further important components of the power plant also have to be included in this study: the containment, and mainly the heat exchanger and structural parts for charging and discharging, and furthermore devices and sub-components, which are needed for operation and integration such as pumps, valves, control devices, etc.

A key issue in the design of a thermal energy storage system is its thermal capacity. However, selection of the appropriate system depends on a multi-criteria optimization cost-benefit considerations, technical criteria and environmental criteria [21], [22], [10] [3]:

- Cost: the storage material itself, the heat exchanger for charging and discharging the system and the cost of the space and/or enclosure for the TES.

- Technical point of view: high energy density in the storage material (storage capacity); good heat transfer between heat transfer fluid (HTF) and the storage medium (efficiency); mechanical and chemical stability of storage material (must support several charging/discharging cycles); compatibility between HTF, heat exchanger and/or storage medium (safety); complete reversibility of a number of charging/discharging cycles (lifetime); low thermal losses; ease of control.
- Technology: operation strategy; maximum load; nominal temperature and specific enthalpy drop in load; integration into the power plant.
- Power of the cycle and hours number of TES requested.
- Efficiency of the power plant, thus this study should include the assessment of the solar field efficiency and cycle efficiency.
- Investment cost of the solar field and of the storage system and as well as an estimation of O&M cost of the overall plant.
- Assessment of the trend of the HTF cost and of the material storage cost in the market.

Molten salts are the most widespread fluid for thermal storage in CSP commercial applications due to good thermal properties and reasonable cost. Nowadays, molten salts provides a thermal storage solution for most of the technologies available on the market due to this fluid could be used as direct and indirect storage depending of the selected plant philosophy.

Both, trough and tower technologies, use the double tank system as thermal storage configuration. Molten salts are used as indirect storage in parabolic trough facilities which works with oil as heat transfer fluids and as direct storage for tower concepts which molten salts are also used as circulating heat transfer fluid. Other concepts under development like the parabolic trough with molten salts as heat transfer fluid which it could be comparable to the tower with molten salts regarding thermal storage point of view.

In general, molten salts storage system offers the possibility to provide electrical production at constant conditions thanks to maintain the storage material in different tanks when it is charged or discharged. In addition it becomes an interesting solution due it has very high energy density per specific volume and very high thermal inertia due to its characteristic thermal properties of high heat capacity and low thermal conductivity. Due those thermal properties the system can be designed with minimum thermal losses which represent higher global effectiveness.

The double tank of molten salts requires less specific volume for the same energy stored thanks to the higher thermal capacity of the salts, specifically when it is used as direct storage medium where inventory is minimized due to temperature gradients between hot and cold focus are bigger. On the other hand, double tank storage concept involves intermediate equipment's in the system configuration as heat exchangers. In this way, two extra heat exchangers (thermal oil to salts and thermal oil to steam) in the case of indirect storage and one (salts-steam) in the case of direct storage are needed for these configurations.

The most common fluids for double tank storage system are sodium and potassium nitrates mixtures with a composition which optimizes cost and thermal properties. These mixtures, which have prices significantly stable in the market, are well known from decades ago with wide bibliographic information and proven feasibility at pilot scale. Regarding materials compatibility, corrosion phenomena should be taken into account due to impurity content of these mixtures but it can be assured the good performance with the most common materials used in the industry.

Molten salts as storage material have inherent risks due to high freezing point of these fluids. Electric heat tracing systems and tank heaters are installed to minimize freezing risks. These equipment involve high parasitic consumption in terms of maintain the salts hot enough to avoid freezing or plugs even when the system is completely discharged.

The double tank of molten salts represents an optimum system for the parabolic system technology due it matches perfectly the thermal sensible behavior of the thermal oil used currently. Thermal oil operation temperatures are from 300ºC to 400ºC approximately and molten salts are efficient and operable enough at those temperatures.

The power cycle to be used with this system could be with preheater, evaporator, superheater and reheater. Depending on the cycle design common efficiencies reached with this technology are around 37%.

Thanks to the utilization of efficient heat exchangers the hysteresis between charge and discharge could be reduce to a few degrees (around 10 ºC), thus the system is able to generate over 90% of the nominal conditions and, as commented before, it is also able to maintain constant conditions during the whole discharge.

From different experiences with this system several assumptions can be confirmed: the system is able to supply energy at constant conditions; there are no big concerns about corrosion, always related with chloride content on salts; degradation of the salts or other components related with the total impurities in the salts; it is a system with high thermal inertia with the benefit it could represent regarding thermal losses and there are no major toxicity problems than the NO_x control within the tanks (strongly related with the magnesium content on the salts) [23].

On another hand, it has been proven that the system needs of significant time to change from charge to discharge conditions and in relation to that and with the heat exchanger design, it is difficult to produce or to design a system to generate at partial load in order to produce jointly with the regular solar field production.

Finally it has to be mentioned that it is one of the most cost-effective systems for the different technologies apart of the well-known particularities it has thus it becomes the desired thermal storage system for parabolic trough technology with thermal oil as heat transfer fluid.

1.5. A thermal storage demo plant as the previous stage for commercial application TES

We all know of the need for simulation phase as a preliminary stage of new developments [24]. Powerful software let you present the preliminary assessment of a technology without incurring large costs. The innovation is based on having many ideas but that they can be evaluated quickly and at low cost, is the so-called concept of "pretotyping" [25].

However, once past this stage, and after approval in the simulation model, it is a priority developing the technology to a demonstration scale where it is critical the assessment of the failures that can occur in an up-scaling system and are never considered in models.

Using molten salts either as heat transfer fluid or sensible heat storage medium still has certain technological uncertainties and a wide range for optimization in designing components due to the molten salt features: high corrosive potential and high freezing temperature. Since these problems become more important for higher temperatures, it is proposed in this thesis to overcome these uncertainties the implementation of a dynamic molten salt experimental loop:

- *To evaluate* the *corrosion behavior* of materials of hydraulic components in molten-salt circuits (valves, pumps, pipes, etc.).
- *To evaluate* the *heat losses* in molten-salt systems, that means losses in the discharge efficiency.
- *To characterize* the applicability of *hydraulic components*, like valves, whose design may have zones where the auxiliary heating system does not properly supply the necessary heat for avoiding salt solidification.
- *To characterize* the applicability of *measuring devices,* like flow meters, temperature and pressure sensors, since the working conditions in solar thermal power plant are far from the ones assure by manufacturers.

- *For optimization* of *auxiliary heating system*, not only proving the best approach for electrical heating but also evaluating new concepts.
- *For evaluation* of *operation strategies* under *failure due to freezing.*

Prior to its use on a commercial scale, four research projects had demonstrated the feasibility of the molten salt as storage fluid and Abengoa ran two more projects to validate in a relevant scale this viability:

- *CESA-1, Spain*
- *Themis, France*
- *Central receiver test facility (CRTF), USA*
- *Solar two, USA*
- *UdL Pilot plant: Abengoa, University of Lleida, Spain*
- *TES-MS, Abengoa, Spain*

In the CESA-1 plant built in the Plataforma Solar de Almeria (PSA) a eutectic mixture of salts of nitrates and nitrites in the ratio 53% $NaNO_3$, $NaNO_2$ 40% and 7% $NaNO_3$ was evaluated on the concept of double tank, cold heated to 220 °C and 340 °C respectively, with 200m^3 capacity. Inventory sales (260 tonnes) contributed to the installation a maximum storage capacity of 12.7 MWh_{th} obtaining high yields in the process of loading and unloading in the range of 90% [26].

In France, the Themis Central evaluated the same mixture of salts in the CESA-1 project with a temperature range of 250°C to 450°C. The facility had two identical tanks 17 meters long and 5 meters in diameter for a capacity of 310 m^3. The total volume of the installation salts was 537 tonnes with a thermal capacity of 40 MWh_{th}. Efficiencies achieved on the cycles of loading and unloading installation stood at 95% [27].

The CRFT project (Albuquerque, New Mexico) had a storage capacity of 7 MWh_{th} and was built by the government of the United States as a first contact with the design, construction and operation of a solar thermal plant with molten salt as heat transfer fluid. The inventory of the facility was 79 tonnes of a eutectic mixture of nitrates in the ratio 60% $NaNO_3$-40% KNO_3 (solar salt) with an operating range in the range 280°C-560°C. The efficiency measures throughout the project were above 93% [27] [28].

Currently there is a new molten salt test facility installed in PSA, with two 39-ton salt tanks, to continue with the philosophy of learning in demo plants [29].

In Abengoa, and prior to the installation of the first oil parabolic trough commercial plant with storage, the TES technology was validated through two pilot plants at different scales, a demo TES-MS at MW scale (8.5 MWh_{th}) in Abengoa facility and in 2008 a two-tank molten salts pilot plant with same aspect ratio (the ratio between height and diameter of the storage tank) as storage tanks of commercial plants was built at kWh scale (66 kWh) in the University of Lleida (UdL), Lleida, Spain.

The configuration of these experimental plants allows testing real CSP storage operation processes at lower scale and with the advantage of having many measurement equipment to fully understand how the processes develops. The idea was to acquire knowledge in design, construction, start-up and operation with two-tank TES configuration and to provide useful information for future designs and construction of experimental and commercial plants in order to avoid future technical problems and to reduce the investment and operation cost of these plants.

The goal of the proof-of-concept project was to develop an efficient high-temperature, lab-scale TES prototype of 66 kWh by utilizing MS indirect system configuration. The laboratory scale prototype TES system were built and tested with the purpose of gathering performance data (e.g., transport properties, system durability, and thermal cycling) regarding a the behaviors of the molten salt. The HTF was thermal oil heated in an electric heater what meant solar transient behaviors cannot be analyzed.

In addition, a large-scale evaluation was needed so a demonstration plant more capacity (8.5) was designed and built facing the technology assessment to a closer commercial scale. These included: the process to preheat the system and to melt the salt in a external furnace, the use of a real solar field to feed the TES heat exchanger, to evaluate the solar transient in order to estimate the performance of the storage system or to reproduce the real atmosphere into the tanks, the real velocity in the pipes and the real delta of temperature in order to reproduce the corrosion phenomena that could appear under commercial conditions. Additionally the heat losses and the performance of key components were other reasons to build the demo plant. The resulting subscale demonstration should be sufficient to interest partners in the use of CSP with storage. The goal of the project was additionally to demonstrate the engineering feasibility. The team carried also out preliminary process components design and experimental validation. The engineering data from demo plant were used for process integration between the CSP plants in commercial facilities and demonstrated the economics and safety of a CSP plant integrated with molten salt indirect storage.

2. Objectives

This thesis aims at generating the knowledge necessary to evolve the indirect energy storage technology based on molten salt from its conceptual and modeling stage to a feasible commercial stage. The procedure carried out in this thesis is in agreement with the methodology defended by Horizon 2020 work programs of Technology Readiness Levels scale (TRLs) [30] that is a systematic metric's methodology that supports assessments of the maturity of a particular technology. The TRLs scale is used as a tool for decision making on RDI investments at EU level [31].

The project started in a conceptual configuration at TRL 2 and evolved to a commercial scale through the lessons learnt in two prototype facilities at different scales. The UdL pilot plant (scale 1/30,000) was built in 2008 with an analytical and experimental critical function to validate the technology at lab scale (TRL 4). At this step in the maturation process of the MS indirect storage, active researches and developments (R&D) were initiated. Those must include both analytical studies to set the technology into an appropriate context and laboratory-based studies to physically validate the analytical predictions were correct. These studies and experiments constituted a “proof-of-concept” validation of the applications/concepts working at phase/temperature/pressure for the molten salt.

The MS-TES plant built in 2008-2009 was a prototype in a more relevant operational environment (TRL 7) it had not been implemented in the past. In this case, the prototype was near the scale of the planned operational system (1/70). The driving purposes for achieving a level of maturity were to assure system engineering and to develop management confidence. Not all technologies in all systems go to this level, losing in this way a lot of information key for the success of a new technology. This thesis presents the evaluation of main components of both facilities and the lessons learnt at different plant scales which have been identified to be useful in order to guarantee the correct start-up and operation of commercial CSP plants. That includes key aspects previously mentioned like:

- Evaluation at different scales of key components, i.e. heat tracing systems, pumps or heat exchangers.
- Identification of key aspects like heat losses, efficiencies or material compatibility.
- The retrofitting of lab/demo models to optimize the design of key components at commercial scale.
- Validation of parameters and codes in the mechanical design of key components.
- Development of a new methodology to measure corrosion rate.
- Need to evolve new storage technologies (like thermochemical technology) through new prototypes

The comparison of results has shown the relevance of the size in the scaling up procedure needed to validate a new technology. The TRL methodology is a cyclic process to be follow in each new development in the area of thermal energy technology. This thesis explains this process in the molten salt storage but it also shows the technological evolution of storage systems toward more efficient systems that need the evaluation at different prototypes to be feasible.

The thermochemical storage concept is the system with greatest potential due to the increased energy density of their materials. Once basic physical principles are observed, at the next level of maturation, practical applications of those characteristics can be identified (TRL 2). For example, this thesis shows different reactions that may be adapted to power cycles under development. At this level, the application is still speculative: there is not experimental proof or detailed analysis to support the conjecture. Prototypes are needed to acquire the knowledge for commercial applications.

3. PhD thesis structure and methodology

The PhD thesis counts with seven papers; five of them have already been published in SCI journals while the other two have been submitted.

The thesis is within the frame of thermal energy storage mainly in the research needed to make feasible the use of the molten salt storage in parabolic trough power plants. It is organized in two big parts, aligned with the work carried out in the two prototypes (Figure 7). These two available TES prototypes have already been presented and explained in detail in the introduction and the main objectives stated in the objective section.

The **paper 1** provides a review of the pilot plant built in Lleida while the **paper 2** shows the study of the thermal behavior of the molten salt tanks at this proof of concept scale. Heat losses were measured and compared both with a simulated 1-D steady state model as well as with previous literature.

The **paper 3** explains the key aspects more related with pre-engineering phase and the operational validation in the demo plant located in Seville. Problems associated with the bigger size or the analysis of new processes not used in the pilot plant are analyzed; such as the pre-heating phase, the melted process, the design and assembly of the tanks, the tracing systems, the optimization of the mechanical construction or the control of the start-up to guarantee the requirement in a commercial size.

The **paper 4** explains the importance of the thermal losses in the evaluation of the demo plant analyzed in a size sufficiently representative for the extrapolation of results at larger scales. A reengineering process was carried out due to the relevant data obtained in the demo plant evaluation.

The **paper 5** explains, in reference with the hypothesis taken in paper 3 in order to design the MS tanks, a new device designed and tested to evaluate the behavior of the yield strength with the temperature that was one of the main suppositions made during the design of the demo plant (explained in paper 3). This paper demonstrates the validation of this hypothesis and guarantees the use of a yield strength value for future designs of MS tanks.

In the **paper 6**, one of the most important issues in molten salt is mentioned, the corrosion in MS. In this study the corrosion measurement techniques are analyzed. To determine the corrosion on a metal plate, the ASTM Standard-G1-03 procedure is usually applied, but in order to minimize the handling of the sample, a new methodology (Dynamic Gravimetric Analysis, DGA) has been developed and used to determine the corrosion produced in carbon steel A516Gr70 samples.

The papers 3, 4, 5 and 6 are an example of the evolution of a technology from TRL 7, system prototype demonstration in operational environment, to TRL 9, actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space).

Finally, the R&D in thermal energy storage has to follow. New concepts have been identified and specific simulations or experiments have to be undertaken. The TRL process must start again by the base. The paper 7 shows a review of the thermochemical reactions, summarizing and comparing the different TCES that are today being investigated as the most promising TES technology under development (TRL 2). TCES has the advantage of nearly no losses during storage and very good volumetric energy density. However, as I mention before, there is not experimental proof or detailed analysis to support the commercial feasibility.

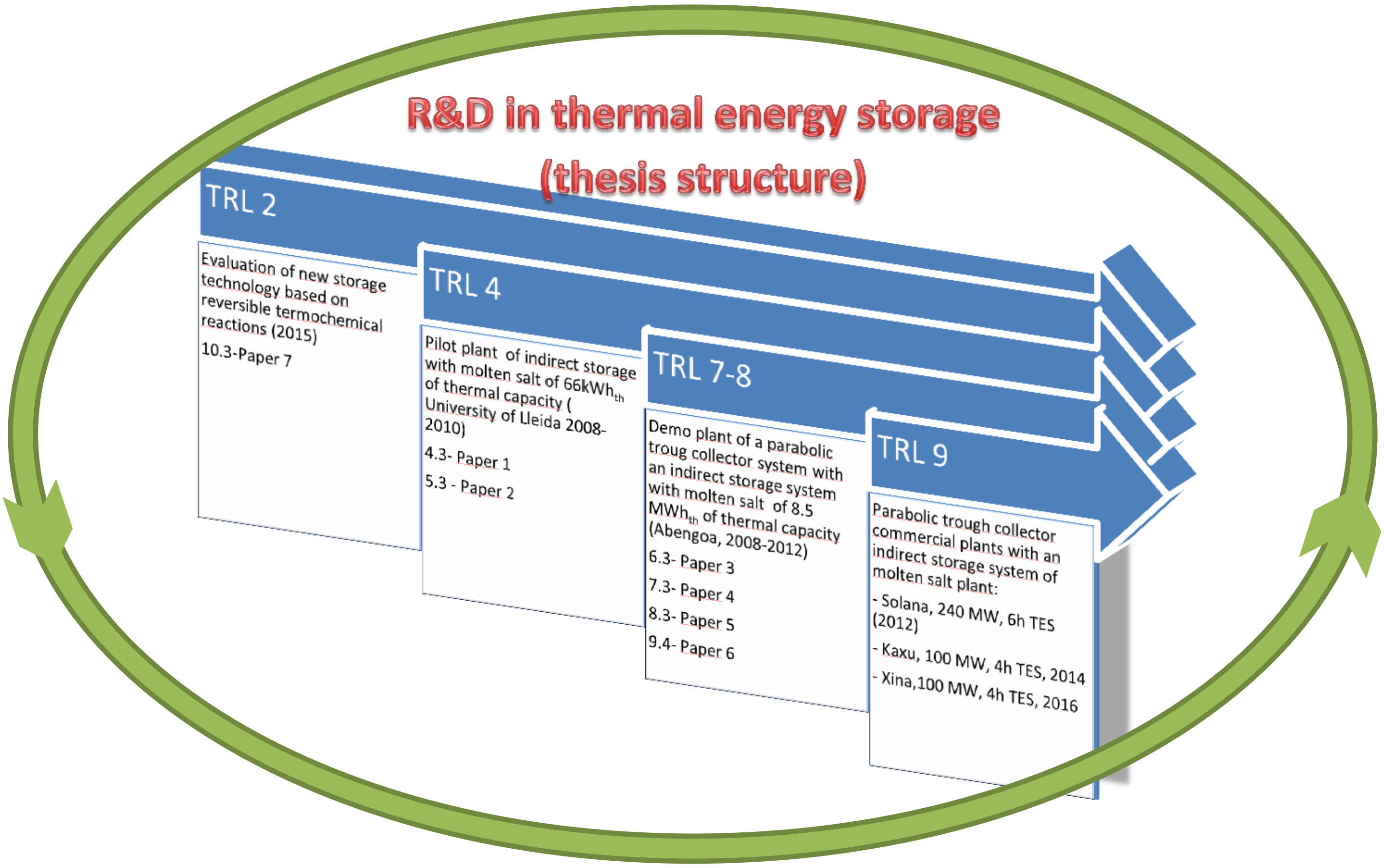


Figure 7. Thesis structure

4. P1: Two-tank molten salts thermal energy storage system for solar power plants at pilot plant scale: lessons learnt and recommendations for its design, start-up and operation

4.1. Introduction

Thermal energy storage is an interesting feature which allows CSP plants to produce electricity decoupled from the solar availability as well as to improving the system reliability, by increasing the generation capacity and reducing the costs of generation. The efficiency of this storage system is a critical parameter in the specific cost of energy produced. The study of factors associated with losses of performance is critical throughout the demonstration phase of the technology. Critical parameters have been evaluated in a small pilot plant. This thesis presents the acquired experience since 2008 during the design, start-up and ordinary operation of molten salts two tank TES for CSP applications pilot plant scale built in the University of Lleida in collaboration with Abengoa with a thermal capacity of 66 kWh_{th}. This test facility at lab scale shown in the Figure 8 is used to experimentally investigate different construction materials, instrumentations and concept validation about thermal energy storage at high temperatures between 100ºC and 400ºC. This set-up consist in a heating system, cooling system, heat exchanger, molten salts storage tanks, piping and valves and finally the control and acquisition data system.

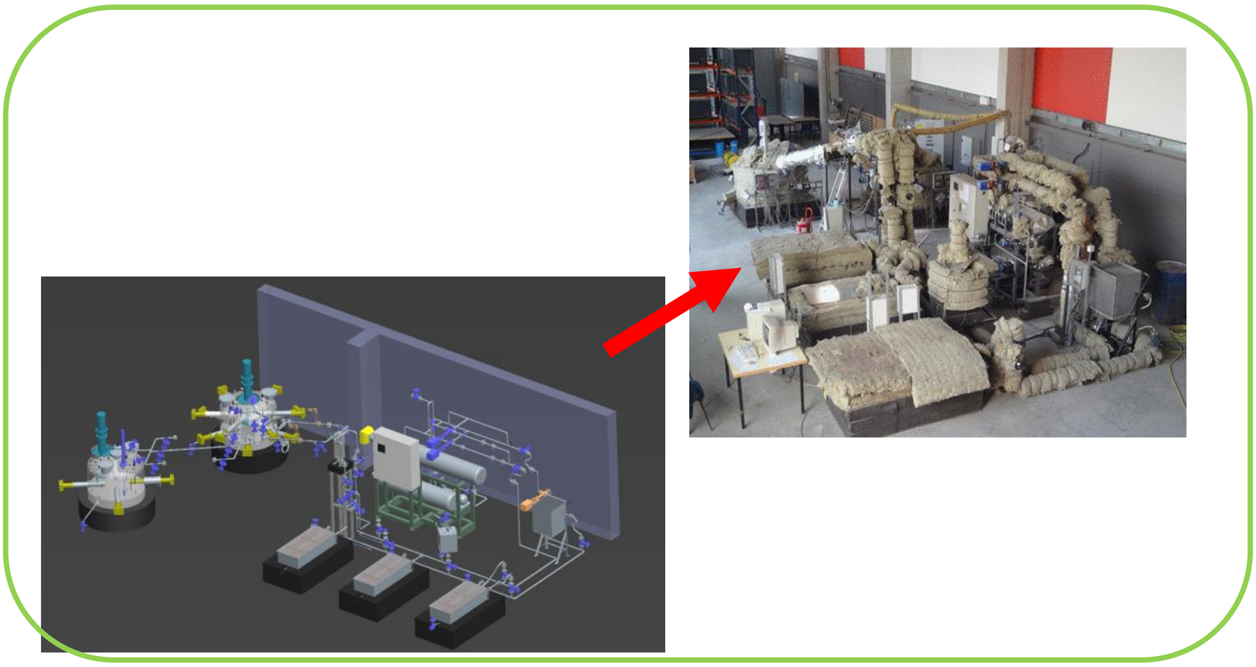


Figure 8. Design and final construction of the pilot plant in the University of Lleida (Abengoa)

The configuration of this experimental plant allows testing real CSP storage operation processes at lab scale and with the advantage of having many measurement equipment to fully understand how the processes develops. This study is divided in three main parts: description and design of the pilot plant, operational modes of the pilot plant and finally the start-up and operation. In the description and design, a detailed description of the pilot plant and its components is showed as well as the justification of the different design aspects. In the following section of this study, the operational modes that can be carried out in this pilot plant have been described. Finally, in the start-up and operation section, the different steps of the start-up process of the plant and the causes of malfunction, limitations and possible recommendations for future designs for demo plants are showed.

The size of this pilot plant agrees with the new tendency of “pretotyping” [25]. Failure is an unavoidable part of the innovation process; but some failures are much harder to take – and survive – than others.

Pretotyping is an approach to developing and launching innovation that helps to determine if we are building the right it before we invest a lot of time, resources and time to build it right.

This plant has allowed the study of the problems when you work with molten salts, limitations encountered and advices of this experimental set-up in order to extrapolate the data to model of plants, to provide solutions to technical problems, mainly aligned with instrumentation and evaluate the behaviors of components and material in dynamic contact with molten salt at working temperature.

4.2. Contribution to the state-of-the-art

The main contribution to the state-of-the art is the acquired experience since 2008 during the design; start-up and ordinary operation of molten salts two tank TES for CSP applications pilot plant scale of 66 kWh_{th} of capacity. Deep evaluations of conventional system such as insulation, mechanical assembly or foundation have been carried out in the following publication:

- Gerard Peiró, Cristina Prieto, Jaume Gasia, Laia Miró, Luisa F. Cabeza. Two-tank molten salts thermal energy storage system for solar power plants at pilot plant scale: lessons learnt and recommendations for its design, start-up and operation. Submitted to Solar Energy.

This thesis shows the acquired knowledge in design, construction, start-up and operation with two-tank TES at lab scale and provides useful information for future designs and construction of experimental plants. This study shows the problems, limitations encountered and advices of this experimental set-up in order to extrapolate the data to real plant, to provide preliminary solutions to technical problems and reduce the cost of demo and commercial plants. However many items have had to be designed and manufactured specifically for this plant because such plants are not standardized.

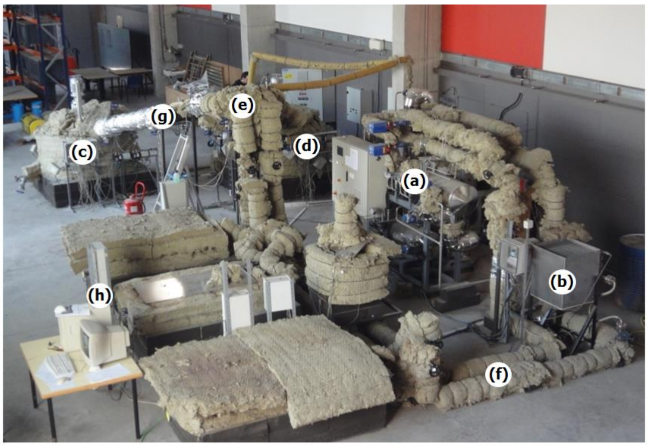


Figure 9. Overview of the high temperature pilot plant facility at the University of Lleida (Spain). (a) Electrical heater; (b) Air-HTF heat exchanger; (c) Molten salts hot tank; (d) Molten salts cold tank; (e) HTF-molten salts heat exchanger; (f) HTF loop; (g) Molten salts loop; and (h) Acquisition and recording system.

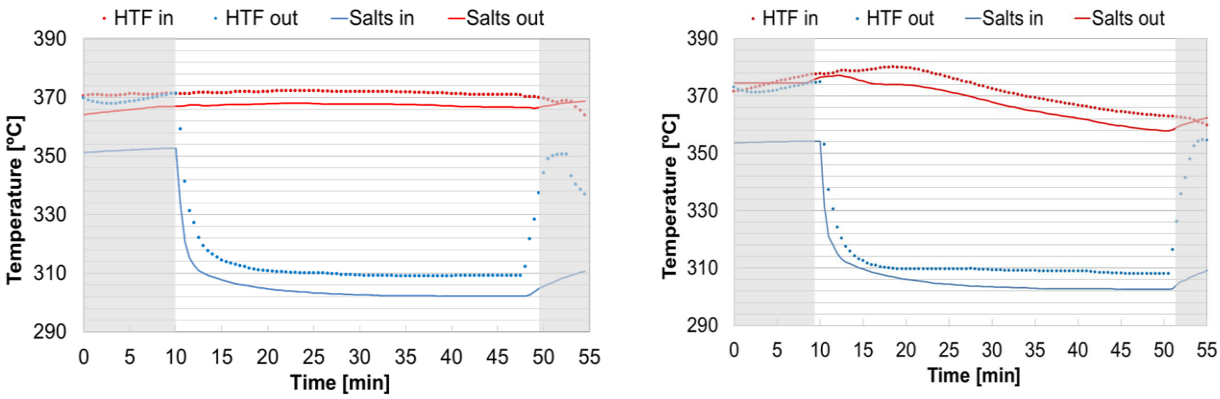
From the start-up it was observed some recommendations for molten salt facilities. The first lesson is the progressive heating to avoid thermal stress during the preheating and melting of the molten salt. This facility had a significant difference with the commercial plant, allowing melting the salts directly in the tanks with immersion heaters and not needing external furnace or preheating system to do it. This implementation gave more flexibility in the operation and evaluation of a pilot plant, allowing long period in stand-by with the salt frozen in the tank while the data or enhancements were evaluated or implemented.

The piping of the pilot plant facility was very flexible to allow different tests and it was divided into two different loops: the HTF loop and the molten salts loop (Figure 9b). The HTF loop consisted of a stainless steel 316 L piping with a diameter of 1” designed, with the implementation on by-passes, in order to achieve different flow arrangements (parallel and counter flow) in the heat exchange system. On the other hand, the molten salts loop consisted of a stainless steel 316 L piping, in order to withstand high temperature and corrosive environments, which was divided in four different circuits in order to introduce a greater versatility to the pilot plant facility. The first circuit allowed the connection in parallel to the current heat exchange system of a new one in order to extend possible studies. The second circuit was designed as a by-pass for the cold tank in order to study the reaction of different equipment such as simple valves, gaskets, etc. under the working operation with molten salts. The third circuit consisted of three parallel pipes, connected to the hot tank in order to test the influence of the piping and the behavior of different electrical components. Finally, the fourth circuit consisted of a by-pass on the cold tank which went through the heat exchanger and allowed the molten salts leaving the heat exchanger to enter to the cold tank again and increased their temperature in order to avoid undesired temperatures.

Two different HTF have been tested in the pilot plant facility: the synthetic oil Therminol VP-1 [32] and the silicone fluid Syltherm 800 [33]. Peiró et al. [34] have experimentally demonstrated the importance of selecting a proper HTF for improve the thermal performance of CSP plants and increase the total power that the HTF can provide and absorbed.

The heat exchanger was a plate heat exchanger, which allowed the heat exchange between the molten salts and the HTF. It was the first time that this type of heat exchangers worked with molten salts and it had been chosen because of its high thermal efficiency, compactness and flexibility against changes in load operation.

During the operation the heat exchanger was deeply analyzed, Figure 10a shows a good behavior of a charging process in HTF–salts heat exchanger and Figure 10b shows the behavior of the same process as Figure 10a but with malfunction in HTF-loop which becomes visible in a constant decrease of the HTF inlet temperature due to a presence of the air in pipes or an electrical problem in the heater.



(a) (b)

Figure 10: (a) Good behavior of the charging process in the HTF-Salts heat exchanger; and (b) Bad behavior in the HTF loop

Other systems were tested as instrumentation, valves, and electrical heat tracing and insulation behavior. Some of the recommendations included in this paper were:

- Leaks and salts solidification are main problems in HTF-salts circuit.
- Good installation of electrical heat tracing and insulation is a key factor for proper operation of these plants.
- Protection of signal wire against disturbances and high temperatures.
- Radar level meter is extremely sensible to disturbances.
- To avoid the presence of salts inside the mechanical level meter.
- Bellow-type Pressure sensors for salts are not good. Need to be improved.
- The plate orifice flow meter can be a good an accurate solution with a good pressure sensors.

4.3. Journal paper

Elsevier Editorial System(tm) for Solar Energy
Manuscript Draft

Manuscript Number:

Title: Two-tank molten salts thermal energy storage system for solar power plants at pilot plant scale: lessons learnt and recommendations for its design, start-up and operation

Article Type: Research paper

Section/Category: Concentrating Solar Power & high temperature processes

Keywords: thermal energy storage (TES); concentrated solar power (CSP); lessons learnt; pilot plant

Corresponding Author: Prof. Luisa F. Cabeza, PhD

Corresponding Author's Institution: Universitat de Lleida

First Author: Gerard Peiró, Engineer

Order of Authors: Gerard Peiró, Engineer; Cristina Prieto, Engineer; Jaume Gasia, Engineer; Aleix Jové, Engineer; Laia Miró, Engineer; Luisa F. Cabeza, PhD

Abstract: Renewable energies are main players to ensure the long-term energy supply, being solar power plants with thermal energy storage (TES) one of the available renewable technologies with more potential. Still today there are several aspects in design and operation of TES plants that need to be improved, as for example, the functioning of some specific instrumentation, the compatibility of materials under real operation conditions and test different components. TES technology was validated by Abengoa through two pilot plants at different scales, kWh and MWh scales. This paper presents the acquired experience since 2008 during the design, start-up and ordinary operation of a kWh scale pilot facility built at the University of Lleida with Abengoa. This test facility is used to experimentally investigate different materials, components and operational strategies about thermal energy storage at high temperatures between 100 °C and 400 °C. In this study, authors show the problems and limitations encountered, and give advices of this experimental set-up in order to extrapolate the data to real plant, to provide solutions to technical problems and reduce the cost of commercial plants.

The pages from 20 to 52 contain the submitted article:

- Gerard Peiró, Cristina Prieto, Jaume Gasia, Laia Miró, Luisa F. Cabeza. Two-tank molten salts thermal energy storage system for solar power plants at pilot plant scale: lessons learnt and recommendations for its design, start-up and operation. Submitted to Solar Energy.

5. P2: Temperature distribution and heat losses in molten salts tanks for CSP (UdL)

5.1. Introduction

If energy is stored as thermal energy, the thermal heat losses during the length of time for which the energy is to be stored is a key parameter to meet the energy requirement. In that sense, the thermal behavior of the storage plant is one the most important component to be analyzed. Any loss of temperature in the inventory tanks will mean a significant impact on the specific sensible heat storage capacity.

To be able to achieve a deep understanding of the two-tanks solar storage systems with molten salts, an experimental evaluation of the temperature distribution inside the molten salt tanks and their heat losses are been studied in the pilot plant built at the University of Lleida (Spain).

In this paper, both the molten salts temperature distribution and the heat losses of the storage tanks are widely evaluated and discussed to evaluate the thermal performance of a two-tank molten salts system.

5.2. Contribution to the state-of-the-art

The main contribution to the state of the art is to show an experimental methodology to obtain the conduction heat losses of the external surface wall of the tank and the conduction losses at the bottom of the tank. These parameters will have an impact in the efficiency of the system. This is presented in the following paper:

- Cristina Prieto, Laia Miró, Gerard Peiró, Eduard Oró, Antoni Gil, Luisa F. Cabeza. "Temperature distribution and heat losses in molten salts tanks for CSP plants". Solar Energy 135 (2016) 518–526.

A full monitoring system based on thermocouple at different level had been installed to evaluate the temperature distribution and the heat losses in a tank with molten salt. It was relevant the location of the thermocouple to study correctly a thermal distribution. Two methods could be employed to acquire the data necessary to determine heat losses: the isothermal method and the cool-down method. The isothermal method involved measuring the power consumption of the heat trace and immersion heaters over a long, steady-state period (several days) as the vessels and components were maintained at a constant temperature (used by Prieto et all in the paper "Molten salt facilities, lessons learnt at pilot plant scale to guarantee commercial plants; Heat losses evaluation and correction", Renewable Energy 94 (2016) 175-185). In the cool-down method, methodology used in this test, rate of change of the mean tank temperature was measured to estimate the thermal losses. This test required all the heat tracing and immersion heaters to be turned off so the decay of the tank temperature could be tracked over several days.

A similar study was done by Sandia in Solar Two [35] where they do not detect significant losses in the study. The new study carried out now provides interesting data to take into consideration the state of the art. It has detected a decrease of temperature in sensors that were closer to the walls. This drop in temperature is associated with a number of parameters among which the insulating material used and its correct assembly, the filling of the tank or tanks own orientation. A temperature reduction in the upper surface of salt in contact with the atmosphere of the tank is also detected (Figure 11).

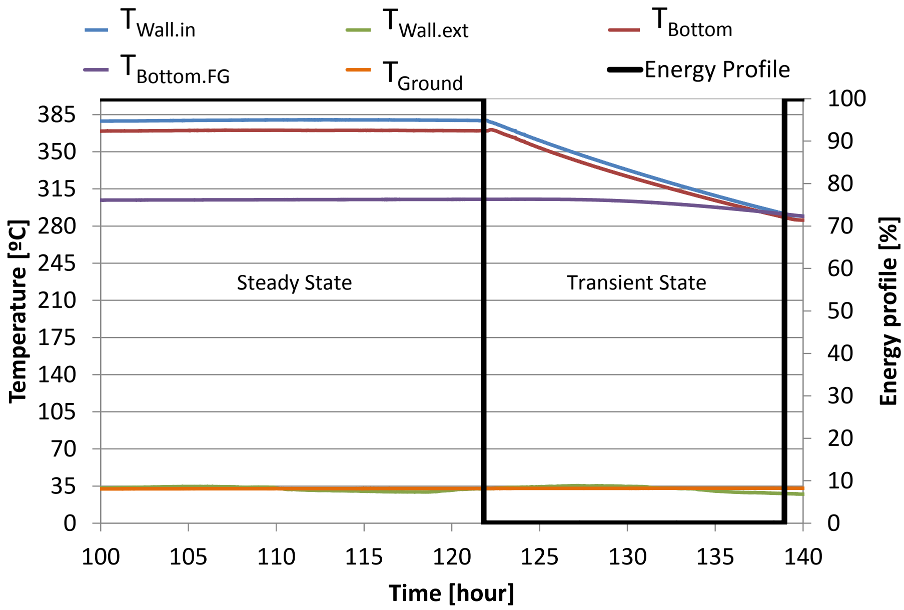


Figure 11. Walls and bottom temperatures of the tank

The thermal behavior of a tank of salt is very conditioned by two factors; the thermal losses through walls or foundations and thermal distribution inside the tank that occurs due to these losses. These temperature losses have been translated into thermal losses [36] reaching a value of 80 W/m^2 in the walls, 73 W/m^2 through the cover, 61 W/m^2 in the bottom (Table 3).

Table 3. Comparison of heat losses values, in W/m2

	Experimental data	EES model	According to Herrmann et al. 2004
Top	72.70	72.25	-
Walls	79.13	79.6	76.00
Bottom	61.00	-	-

5.3. Journal paper

Solar Energy 135 (2016) 518–526

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Temperature distribution and heat losses in molten salts tanks for CSP plants

Cristina Prieto [a], Laia Miró [b], Gerard Peiró [b], Eduard Oró [b,1], Antoni Gil [b,2], Luisa F. Cabeza [b,*]

[a] Abengoa Research, C/Energía Solar 1, 41012 Seville, Spain
[b] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

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A B S T R A C T

Solar power plants have been deployed in the last 20 years, so the interest in evaluating their performance is growing more and more. In these facilities, thermal energy storage is used to increase dispatchability of power. The two-tank molten salts storage system with "solar salt" (60 wt.% $NaNO_3$ and 40 wt.% KNO_3) is the one commercially used today. To be able to achieve a deep understanding of the two-tank solar storage systems with molten salts, in 2008 a pilot plant was built at the University of Lleida (Spain) and the experimental evaluation of the temperature distribution inside the tanks and their heat losses are presented in this paper. Therefore, this pilot plant is equipped with several temperature sensors inside the tank as well as in the different layers of external insulation. As expected, temperature is lower at the external part of the tank (near the cover, at the bottom and near the walls) and no stratification is seen. It is found that the influencing parameters in the temperature distribution of the salts inside the tank are: insulation, and the existence of different electrical resistances and the orientation and surroundings of the tank. Heat losses were measured and compared both with a simulated 1-D steady state model and previous literature. Measured heat losses were from 61 W/m^2 through the bottom to 80 W/m^2 through the walls (with 73 W/m^2 through the cover).

The pages from 56 to 64 contain the submitted article:

- Cristina Prieto, Laia Miró, Gerard Peiró, Eduard Oró, Antoni Gil, Luisa F. Cabeza. "Temperature distribution and heat losses in molten salts tanks for CSP plants". Solar Energy 135 (2016) 518–526.
  http://dx.doi.org/10.1016/j.solener.2016.06.030

6. P3: Thermal storage in a MW scale. Molten Salt solar thermal pilot facility: Plant description and commissioning experiences

6.1. Introduction

The double tank of molten salts represents an optimum system for the trough technology because it matches perfectly the thermal sensible behavior of the thermal oil used currently. Thermal oil operation temperatures used to be between 290ºC and 390ºC approximately, being nitrate molten salts efficient and operable enough within this range of temperatures. Optional thermal storage systems can also be added as it happens in almost totality of the under-construction parabolic trough solar plants [31].

As it has been explained previously, the UdL pilot plant of 66kWh$_{th}$ had given significant information related to material compatibility, emissions, blockage, instrumentation and it has put in relevance the significant effect of the heat losses in the efficiency of the plant.

Later, in a second step, part of this information where used to make the construction of a demo plant in Abengoa (scale higher than 100/1 with pilot plant). The relevant scale of the demo plant was 8.5 MWh$_{th}$ that also means a ratio near to 1/70 with the capacity of a commercial plant of 50MW with 6h of storage.

In this design, the solar field was constituted of a loop of parabolic trough collectors, with thermal oil as heat transfer fluid and a steam generation system. All the systems of a commercial indirect TES system were evaluated in the demo plant. The molten salt operability was studied at the much more relevant scale, with a TES system integrated in a real solar field. The MS-TES pilot plant was an indirect double tank storage system with 450 Ton of molten salts inventory, coupled to an oil parabolic trough solar field. The salt mixture used was the so-called "solar salt" [37] [38]. This is a non-eutectic mixture of 40% wt. KNO3 and 60% wt. NaNO3 that melts at 204ºC solidifies at 220 ºC, and it is stable up to nearly 600 ºC. The plant had a real external preheating system and an external furnace for melting the salt like in commercial projects.

MS-TES molten salt demonstration project, developed by Abengoa Solar in Solúcar Solar Complex in Seville (Spain) arose as a result of the continuous Abengoa Solar's efforts to reach dispatchability in their oil parabolic trough commercial plants. The evolution from the design to the operation can be seen in the Figure 12.

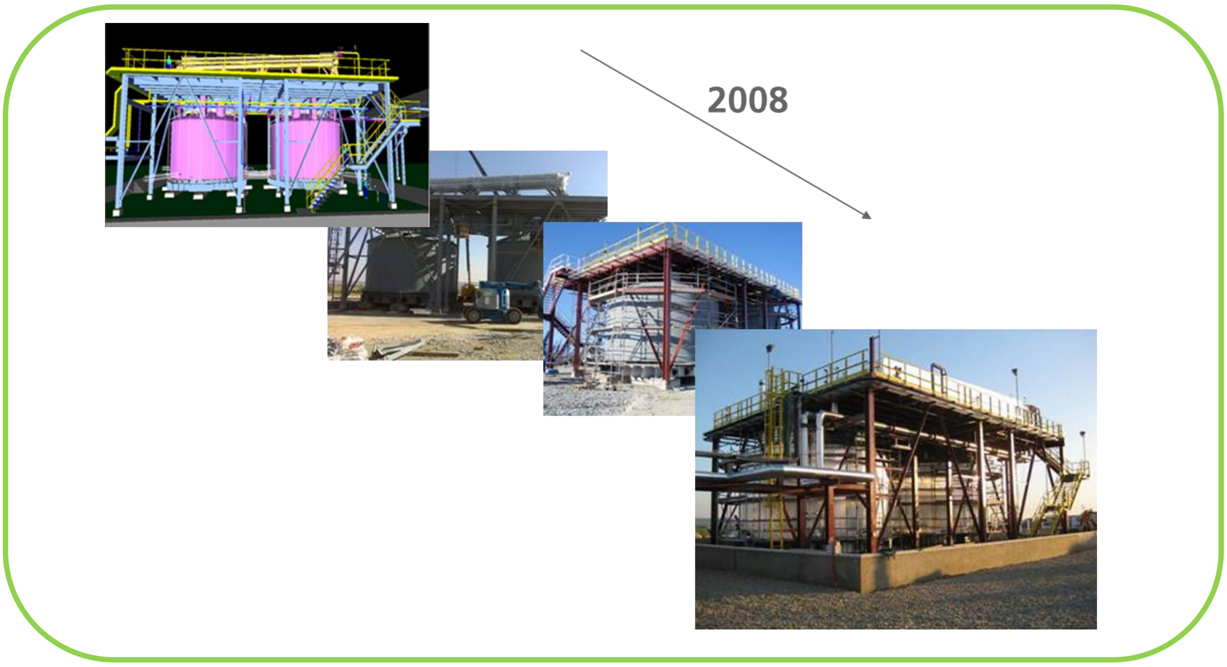

Figure 12. Demo plant TES_MS in Solúcar platform (Abengoa)

For Abengoa this technological milestone represented the needed technology maturity prior to the design, engineering and construction of the Solana plant [39].

Prior to the MS-TES pilot plant the experience in CSP with molten salts storage was rather limited. Even though Solar Two was using an inventory of molten salts able to provide 107 MWh_{th}, it was not confronted with the need of an oil-molten salts heat exchanger and the operational hours were not surpassing 1800 hours [40].

The system here described, with a representative scale with the commercial plant (1/70), was designed and built from 2008 to 2009 and started its operation at the end of January 2009. In operation till December 2012 it has accumulated more than 32000 hours in operation during those four years. It was the first worldwide experience of a CSP oil trough pilot plant with molten salts storage achieving a technology readiness TRL-9 (system proven in operational environment).

The efficiency of this storage system was a critical parameter in the specific cost of energy produced. The study of factors associated with losses of performance is critical throughout the demonstration phase of the technology. Now, an evaluation study has been done in a more relevant size demo plant, analyzing operational data for commercial plant design. With this target the process had four main steps: charge, storage, drainage and discharge. It has to bore in mind that the charging and discharging processes cannot occur simultaneously and the whole process is considered to be cyclic.

6.2. Contribution to the state-of-the-art

The contribution to the state-of the art is the parametric studies undertaken to determine the preferred design parameters for an indirect thermal storage system with molten salts. The experimental results and details about this research are presented in:

- Cristina Prieto, Rafael Osuna, A. Inés Fernández, Luisa F. Cabeza. "Thermal storage in a MW scale. Molten Salt solar thermal pilot facility: Plant description and commissioning experiences". Renewable Energy 99 (2016) 852-866.

The plant TES-MS has been the first demo plant of a parabolic trough solar field with molten salt storage at MWh_{th} scale (see Figure 13) that has accumulated more than 32000h of operation in the world. This unique accumulated experience has allowed the implementation of relevant improvements in the commercial molten salt storage facility built by Abengoa.

Figure 13 Solúcar Solar Platform of Abengoa (Sevilla, Spain)

To guarantee the correct design and construction of the commercial plants, a full evaluation of the key component were developed in this demo facility. The lessons learn at relevant scale were from the design, construction, commissioning and startup of the plant to the evaluation of key performance indicator [41] and the final postmortem analysis.

In this paper, the description and the main lessons learnt in commissioning and startup is described in detail. A full monitoring system based on thermocouple at different level has been installed to evaluate the temperature distribution and the heat losses in a tank with molten salt. It is relevant the location of the thermocouple to study correctly a thermal distribution. The new study carried out now provides interesting data to take into consideration in the state of the art. It has detected a decrease of temperature in sensors that were closer to the walls or foundation. This drop in temperature is associated with a number of parameters among which the insulating material used and its correct assembly, the filling of the tank or tanks own orientation. A temperature reduction in the upper surface of salt in contact with the atmosphere of the tank is also detected. As the effect are detected in the beltway surface, this effect will be lower at higher tank dimension were the ratio volume of salt- surface of tank is lower. This study and the implemented improvement have guaranteed commercial tanks with losses lower than 1ºC per day.

Other tests developed to be implemented as new procedures and lessons in the state of the art were:

- Definition of key aspects and recommendations mainly focused in the start-up process (preheating, melting process, filling up the storage tanks, heat tracing systems and equipment used).

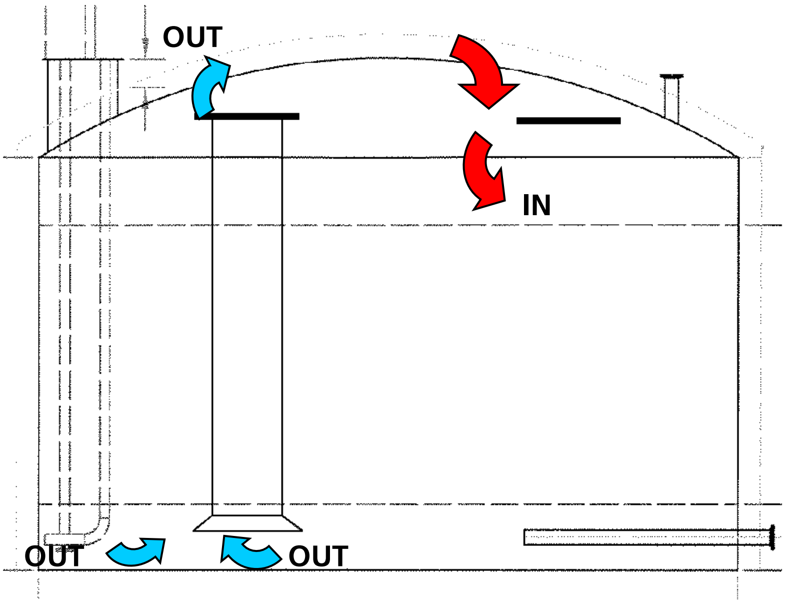

Figure 14 New preheating process suggested

- Definition of a design methodology for the molten salt tank, that don't have specific code. In absence of specific code for the cold and hot molten salts tanks the API 650 [18] appendix-M code (requirements for tanks operating at elevated temperatures) was used, understanding that this one is limited to the operational range (90ºC to 260ºC). The allowed tension for A516Gr.70 material was decreased by a factor of 0.7 due to an extrapolation done following the elastic limit reduction factor listed in appendix M. This hypothesis was validated in a test described in the paper made by C. Prieto et al. "Thermomechanical testing under operating conditions of A516Gr70 used for CSP storage tanks". Submitted to Solar Energy.

- Detailed procedure for molten salt pump selection is described. The longer shaft appear as one of the most critical problem from the point of views of vibrations.

- Definition of criterion for the heat tracing system configuration and internal heater is explained in detail. Problems associated to longer circuits are identified.

- Molten salts-HTF heat exchanger thermal behavior when operating with two different heat transfer fluids (HTF).

Focusing in the TES system design and start-up, this study compiles the most important start-up recommendations such as the filling up of the tanks with solar salts and how to the mixture, the need of a heat tracing system along the piping and the importance of the insulation. These processes were not evaluated in the pilot plant.

Regarding the operation of the TES system, the temperature distribution inside the tank, the heat losses to the surrounding and the behavior of the heat exchanger has been widely discussed previously. These recommendations had a huge impact in the new commercial CSP plants built by Abengoa around the world. This work has demonstrated that the use of pilot plants not only helps in a more successful commercial deployment of a technology, but also helps in the reduction of costs of such deployment.

In order to develop an optimum solar plant design, it is also important to conduct a detailed design analysis that accounts of costs, economics, and plant performance in order to determine the optimum TES configuration and solar field size [42].

The plant has been operating automatically for more than four years and, consequently, taking the implemented control system as a reference, the operation manuals to be used as a reference in commercial plants have been drawn up and optimized. The DSC screen used for the control is shown in the Figure 15 .

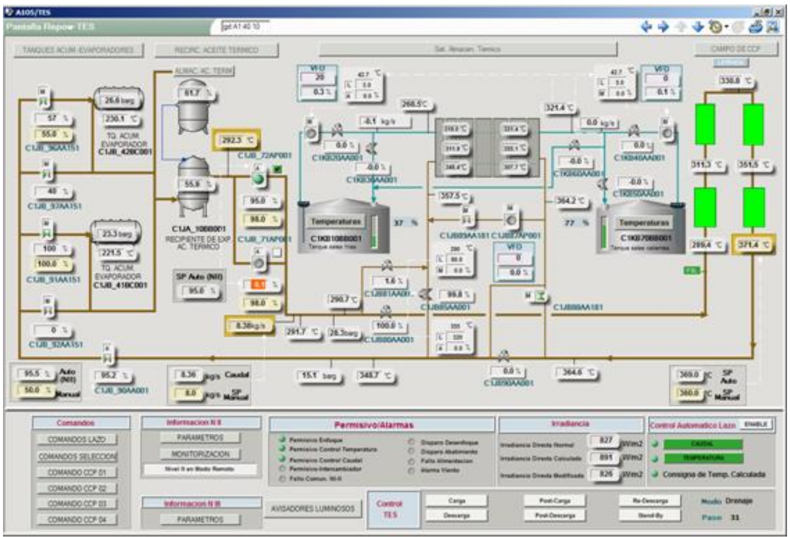

Figure 15 Control screen of the demo plant

6.3. Journal paper

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Thermal storage in a MW scale. Molten salt solar thermal pilot facility: Plant description and commissioning experiences

Cristina Prieto [a,*], Rafael Osuna [a], A. Inés Fernández [b], Luisa F. Cabeza [c]

[a] Abengoa Research, C/Energía Solar 1, 41012 Seville, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[c] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

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In 2008, following its R&D strategy roadmap for Concentrated Solar Power, Abengoa designed, built and tested a unique Molten Salts pilot plant at the representative scale of 8 MWh_{th}, coupled with a trough oil loop. The objectives of this project were based on evaluating the technology at a scale at which the results are sufficiently representative of the real circumstances facing a commercial plant that utilizes this storage technology. To this end, the MS-TES plant was brought into operation on January 19th, 2009, been the first demo plant of indirect double tank storage in operation in the world. Key points such a material corrosion, analysis of possible leakage points, calculation of performance or true efficiency of the storage (including a thorough assessment of thermal losses) and analysis of plant operation are the lines that have been analysed at this plant. Operational aspects such as the mechanical assembling, the pre-heating, the filling up and plant performance were deeply addressed. Key components as the storage tanks, the heat exchanger, the molten salts pumps, the heat-tracing systems or valves and instrumentation were tested. In this first paper, the description and commissioning of the plant is presented together a set of lessons learnt to be applied at the commercial plant scale.

The pages from 70 to 84 contain the submitted article:

- Cristina Prieto, Rafael Osuna, A. Inés Fernández, Luisa F. Cabeza. "Thermal storage in a MW scale. Molten Salt solar thermal pilot facility: Plant description and commissioning experiences". Renewable Energy 99 (2016) 852-866.

  http://dx.doi.org/10.1016/j.renene.2016.07.053

7. P4: Molten salt facilities, lessons learnt at pilot plant scale to guarantee commercial plants. Heat losses evaluation and correction

7.1. Introduction

As it has been mentioned previously in this thesis, the two-tank indirect system is the most usual commercial technology in CSP, with significant advantages in terms of operability and the ability to provide very large thermal storage capacity. However, the cost of the energy from the storage system depends on the efficiency of the system. The heat losses in the heat exchangers, in the tanks or piping produce a reduction of the efficiency and a significant increment of the energy cost.

Increase heat losses in the tank causes a drop in the temperature of the salts, moving away the plant of its nominal conditions. In turn requires an oversizing of the tank heaters which increases the parasitic of the plant. Thermal losses associated to exchangers produces a loss of efficiency in the exchange forcing to oversize the solar field, with a direct impact on the cost of plant. Finally losses in the pipe force the oversizing of heat tracing systems.

Having established the criticality of the thermal losses in the performance of the plant, it was decided to conduct a comprehensive study of the thermal losses in the demo plant TES-MS in order to feed back the new designs with the lessons learned. A thermographic camera is used for this study. Thermography measures surface temperatures by using infrared video and still cameras. These tools see light that is in the heat spectrum. Images on the video or film record the temperature variations of the wall skin, ranging from white for hot regions to black for cooler areas. The paper presents results of a field survey that used this technique to develop a better understanding of how the construction meets the design requirements in order to fulfill the performance model of the facility.

The relevant data obtained due to the relevant size of the demo plant has allowed making a reengineering process of some critical components.

7.2. Contribution to the state-of-the-art

The main contribution to the state-of-the art is the evaluation of the performance of a two tank storage system from the point of view of the heat losses. Deep evaluations of conventional system such as insulation, mechanical assembly or foundation have been carried out. Different scenarios were performed and based on experimental results; decisions for reengineering of the pilot plant were taken to improve commercial storage plants as is shown in the following publication:

- Cristina Prieto, Rafael Osuna, A. Inés Fernández, Luisa F. Cabeza. "Molten salt facilities, lessons learnt at pilot plant scale to guarantee commercial plants; heat losses evaluation and correction". Renewable Energy 94 (2016) 175-185.

During the evaluation some conclusions have been obtained for the state of the art.:

A deep study of heat losses with thermographic camera has been carried out (see Figure 16).

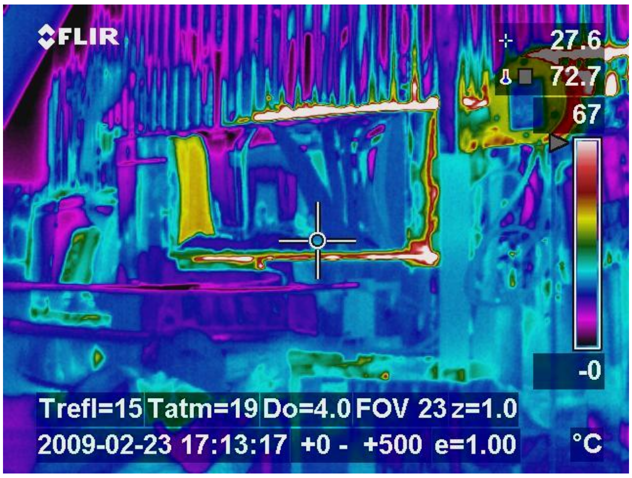

Figure 16 Foundation heat losses study with thermographic camera

The relevance of the heat losses through the foundation is a key factor to be evaluated. A methodology to optimize the foundation design has been developed in the paper. Different scenarios have been simulated (see Table 4 Considered scenarios for the reengineering process Table 4). Thanks to this study new commercial design are being implemented in the commercial plants.

Table 4 Considered scenarios for the reengineering process

#	Tank temperature [ºC]	Floor temperature [ºC]	Ambient temperature [ºC]	Time [hrs]	Thermal behavior within the cold grading	Auxiliary heater
1	370	20	40	8	Stratified air (conduction)	No
2	370	20	40	8	Air convection (1 and 10 $W/m^2{\cdot}K$)	No
3	300	5	0	100	Air convection (1 $W/m^2{\cdot}K$)	No
4	300	5	0	100	Radiation screen	No
5	300	5	0	100	Thermal insulation	No
6	300	5	0	100	Air convection (1 $W/m^2{\cdot}K$)	Yes
7	300	5	0	100	Radiation screen	Yes
8	300	5	0	100	Thermal insulation	Yes

This study has also shown the relevance of the heat losses in the walls of the tanks or in the pipes due to the displacement of the insulation material layers. Optimized assembly procedures have been also defined in this paper.

Other lessons learnt were:

- Tank insulation: Higher thickness in the insulation and better material in the first layer near the wall. We have selected a better insulation material in the tank surface because we noticed a degradation of mineral wool on piping insulation. Joints of each layer cannot be placed at same position around the tank.

- It shall overlap all wall insulation layers with the top insulation layers (1 m minimum). It is critical to take into account the thermal expansion during the heating of the system.
- Insulation of the spacers' aluminum protection with 3 mm thickness insulation (fiberglass, Microtherm®, ...). Another option could be to build the spacer from ceramic material.
- Heat exchanger insulation: Same specification than in the tanks. Improve the insulation on the legs of the skid to avoid the freezing of salts inside the heat exchanger.
- Higher losses than calculated because of non-insulated surfaces. Pipe supports need special attention, well defined criteria is needed to avoid thermal bridges in piping supports.
- Heat losses have to be defined to do a good design of heat tracing system.
- Reductions of thickness have to be forbidden (take care of distance between pipes, beams...)
- Where the section changes (valves, equipment...) insulation has to be overlapped.
- Possible leakage points (valves' body, vents, drainages...) have to have easy removal insulation.
- A good supervision of insulation works is necessary. Criterions well defined.
- Enough space between lines, equipment, it is necessary to guarantee a good insulation and maintenance.
- Tank foundation: The significant losses due to an inadequate design obliged to take the decisions for reengineering of the pilot plant on base on experimental results. The heat losses were modeled considering a semi-infinite model and different scenarios have been set to optimize insulation material or the use of radiation screen.

7.3. Journal paper

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Molten salt facilities, lessons learnt at pilot plant scale to guarantee commercial plants; heat losses evaluation and correction

CrossMark

Cristina Prieto [a], Rafael Osuna [a], A. Inés Fernández [b], Luisa F. Cabeza [c, *]

[a] Abengoa Research, C/Energía Solar 1, 41012, Seville, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[c] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

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ABSTRACT

This paper presents the importance of the thermal losses in the performance evaluation of thermal storage systems. In order to reinforce this statement, an evaluation of a pilot plant whose size is sufficiently representative for the extrapolation of results at larger scales has been carried out. The evaluation of the heat losses of a molten salt pilot plant with 8.1 MWh_{th} built in Spain by Abengoa is presented. While the storage materials development has attracted a lot of attention from the researchers, the performance of a two-tank storage system has not been evaluated in detail. The relevance of the design of conventional systems such as insulation, mechanical assembly or foundation, are found to be the key for the feasibility of a TES system. Different performance scenarios were performed and based on experimental results, decisions for reengineering of the pilot plant could be taken to improve commercial storage plants.

The pages from 89 to 99 contain the article:

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8. P5: Thermomechanical analysis

8.1. Introduction

Initially, for the hot-tank in the demo plant TES-MS and due to the higher operational temperatures, it was considered using an alloy steel with higher percentage of Cr (to increase the corrosion resistance) and Mo (to increase mechanical resistance) avoiding potential oxidation and creeping issues. Finally, and based on preliminary material tests made by Abengoa, this option was discarded and Steel A516Gr.70 steel was used to manufacture the storage tanks in the pilot plant of nitrate molten salts with 8 MWhth built by Abengoa [43] [44]. It is well known that the mechanical properties of steels as the yield strength or the modulus of elasticity decrease with increasing the temperature. In our study, this change is of extremely importance because during operation of both storage tanks, the cold one is designed to operate at 288 °C and the hot one at 388 °C. In that case, parameters used for the design were those of the Appendix M of code API 650, although it gives the requirements for working temperatures between 90ºC and 260°C. In particular, from appendix-M the following design guidelines were selected:

a) The temperature difference between the base of the tank and the inferior ring.

b) The allowed thermal expansions of the tank base that can be influenced by the molten salts filling temperature.

c) Temperature gradients between different parts of the tank as for example between wall and ambient.

In the design one of the most important parameters to be evaluated is the yield strength. The allowed strength for A516Gr.70 material is expected to decrease with temperature. Preliminary tests have been carried out to evaluate the elastic limit reduction factor with molten salt. The study of the reduction of mechanical properties with temperature has been tested at laboratory scale performed with a specific testing device adapted for such purpose; in which steel specimen is mechanically tested while it is in contact with molten salts at 380°C.

8.2. Contribution to the state-of-the-art

The main contribution to the state-of-the art is the development of an experimental setup designed and built to perform the mechanical testing of steel A516Gr70 under operational conditions at 380ºC in contact with molten salts. A deep evaluation of device has been carried out in the following publication:

- Cristina Prieto, Mónica Martínez, Camila Barreneche, Luisa F. Cabeza, A. Inés Fernández. "Thermomechanical testing under operating conditions of A516Gr70 used for CSP storage tanks". Submitted to Solar Energy.

A small furnace was designed and built at University of Barcelona to perform the tests at the desired temperature (in this case 380°C), having the specimen in contact with nitrate molten salts during the mechanical testing. The mixture selected was solar salt. The device was made of quartz, with a cylindrical shape and dimensioned to ensure that all the length of reduced section of the specimen is within the device. A specific opening was designed to introduce a thermocouple to monitor the molten salts temperature as shows the scheme of Figure 17 (a). The top and the bottom of the device are designed so that a refrigeration circuit using water as heat transfer fluid may be coupled, to prevent molten salts leakage. Furthermore, it also has the central part with a reduced section in which an electrical resistance was coiled around, see Figure 17.(b), and then fully thermally insulated, see Figure 18.

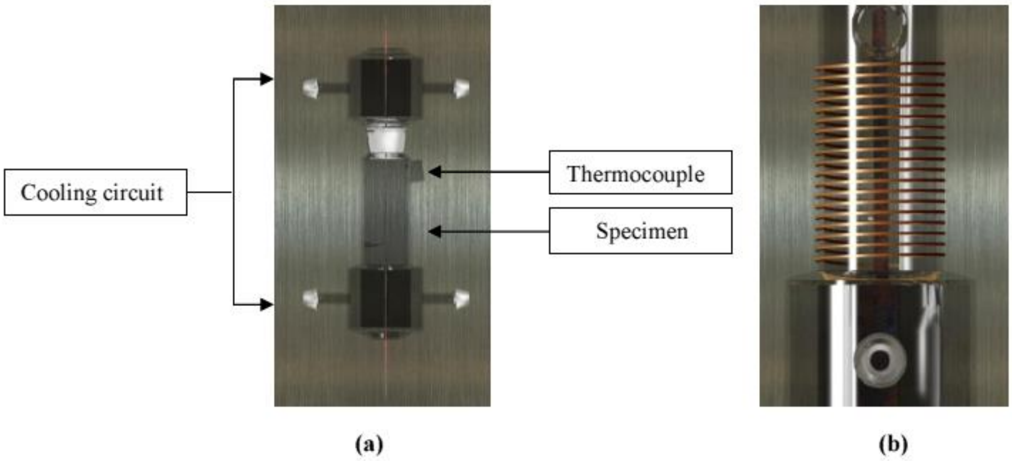

Figure 17 (a) Small furnace device; (b) Heating source

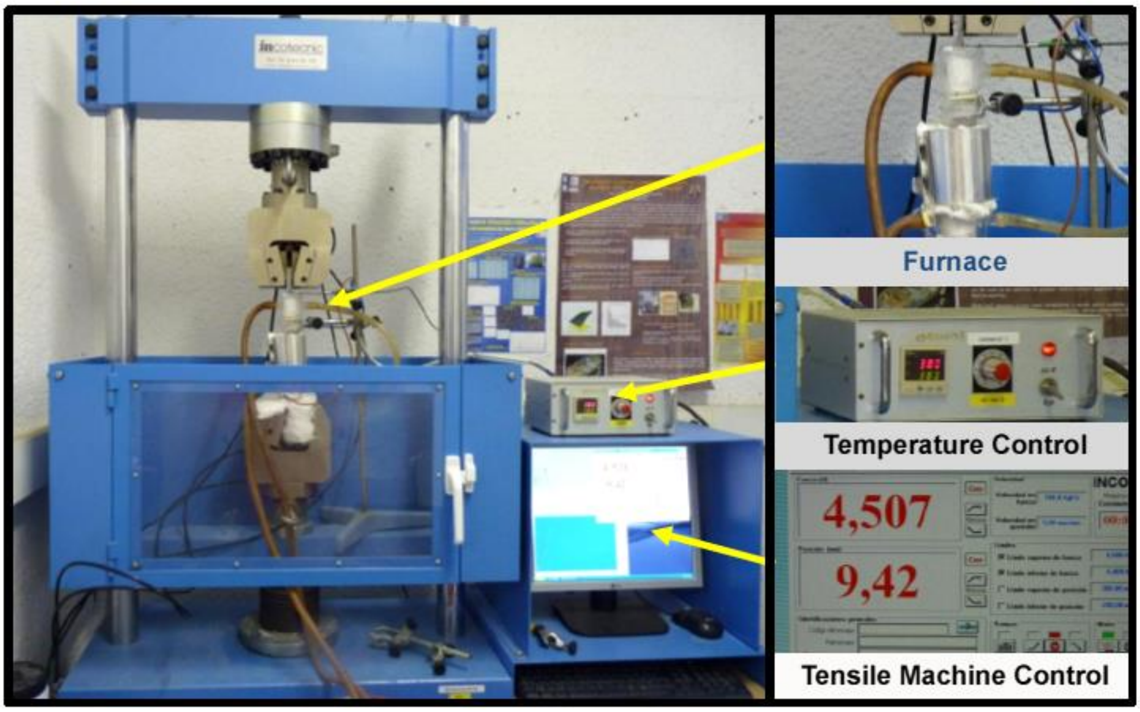

Figure 18 Picture of the experimental set-up

Finally, the mechanical behavior of the steel tested changes when working at elevated temperature. In order to determine a possible variation of the properties under service conditions (load, temperature and contact with molten salts) a specific experiment is designed. It consists in applying a load and keeping the specimen in molten salts for 7 days at a constant elongation. The experimental procedure was to apply an initial load below the measured yield strength at 380°C, to a specimen immersed in molten salts at 380°C. Therefore, to perform thermo-mechanical experiments a safety factor of 1.25 was used, which is commonly used for exceptionally reliable materials used under controllable conditions [45].

Mechanical testing under operational conditions confirmed the reduction of yield strength and Young Modulus as well as the increase of elongation compared with the testing at room temperature. Measured yield strength and elongation are above the limit defined in the ASTM standard. The elongation goes from 17% at the room temperature to 33% at 380ºC that is above the minimum value of 21%.

The test has shown a reduction factor of the yield strength at 380ºC tof 0.8 versus the factor 0.7 used by API 650 Annex M. The device designed has allowed the validation of the design criterion used in the tank design of the TES-MS demo plant.

A study of the microstructure prior and after each step has been done to complement the results. The reduction of yield strength and the increase in elongation is attributed to the annealing of the sample and this fact is corroborated with the metallographic study.

The device can be used to perform the mechanical behavior of different container materials when working at elevated temperature.

8.3. Journal paper

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Title: Thermomechanical testing under operating conditions of A516Gr70 used for CSP storage tanks

Article Type: Regular Paper

Section/Category: Concentrating Solar Power & high temperature processes

Keywords: thermomechanical properties, concentrated solar power(CSP), thermal energy storage(TES), molten salts

Corresponding Author: Dr. Ana Ines Inés Fernandez, Ph.D

Corresponding Author's Institution: Universitat de Barcelona

First Author: Cristina Prieto

Order of Authors: Cristina Prieto; Mònica Martínez, PhD; Camila Barreneche, PhD; Luisa F. Cabeza, Professor; Ana Ines Inés Fernandez, Ph.D

Abstract: Thermal energy storage (TES) in molten salts is the dominating technology in solar power applications today. In two-tank molten salt storage systems it is achievable energy density ranges from 30 to 70 kWh/m3. Salt system used is a binary system, composed of 60% $NaNO_3$ and 40% KNO_3. In the 8 MWhth pilot plant built and tested by Abengoa, the storage tanks were made of steel A516Gr.70 using the Appendix M of code API 650 for their design. A specific testing device was developed to evaluate thermo-mechanical properties. Therefore, a study was conducted in order to evaluate tensile properties of A516Gr.70 specimens under operation conditions for the hot tank at the pilot plant that is in contact with molten salts at 380 °C. Results confirmed the reduction of yield strength and Young Modulus as well as the increase of elongation compared with the testing at room temperature. Moreover, changes in mechanical properties after 7 days testing under operational conditions are confirmed. The reduction of yield strength and the increase in elongation is attributed to the annealing of the sample and this fact is corroborated with the metallographic study.

The pages from 104 to 118 contain the submitted article:

- Cristina Prieto, Mónica Martínez, Camila Barreneche, Luisa F. Cabeza, A. Inés Fernández. “Thermomechanical testing under operating conditions of A516Gr70 used for CSP storage tanks”. Submitted to Solar Energy. Reference number SE-16-00604.

9. P6: Study of corrosion by Dynamic Gravimetric Analysis (DGA) methodology. Influence of chloride content in solar salt

9.1. Introduction

Trough and tower technologies use molten salts as heat transfer and/or storage fluid in order to produce high temperature steam for electricity generation. Although high purity salts are used for solar thermal electricity (STE) applications, some impurities such as chlorides, magnesium, sulphates, carbonates, nitrites, among others, are involved in the chemical composition coming from the manufacturing process [46].

Studies about corrosion in steel concluded that the impurities typically contained in commercial grades of alkali nitrates have relatively small effects in corrosion of stainless and carbon steels in molten salts prepared from these constituents [47]. Thermal cycling generally aggravates high temperature oxidation, but the degree to which a particular material may be affected in any given environment is difficult to predict.

In applications where exposure to nitrate salts can be limited to 400ºC or less, the use of carbon steels should be considered. The corrosion in carbon steels (used to make the two tanks) was studied under the point of view of effect of dissolved impurities, such as chloride and sulphate, on corrosion as compared to pure nitrate melts. Results of short-term corrosion tests of carbon steels in molten salts show that the corrosion of mild at 400ºC increased approximately as the logarithm of the chloride concentration [48]. At 0.6 wt.% NaCl, the corrosion rate increased by a factor of about three compared to a chloride-free melt, during an 8 hours test. Corrosion rates increased by about a factor of four during a 25 hours test, when the chloride concentration was 0.7 wt.% compared to a chloride-free melt. The effect of dissolved sulphate in nitrate melts on corrosion of mild steel results in corrosion rates increased by 20% when 7.5 wt.% Na_2SO_4 was added to the pure molten salt [49].

Corrosion rate measurements are usually performed under ASTM G31 [50] standard, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals". The initial total surface area of the specimen (making corrections for the areas associated with mounting holes) and the mass lost during the tests are determined. The procedure involves an intensive sample manipulation because of the manual brushing the technician must to do, and thus, the results are dependent on the ability the technician has to perform this operation several times.

With regard to corrosion, this thesis focuses on the development and demonstration of the dynamic gravimetric methodology at laboratory scale, and it has been studied carbon steel tanks with three compositions molten salt where the chloride content varies. It is assumed that the loss of total weight undergone by tested samples is only due to generalized corrosion and not to local corrosion phenomena.

A large study of corrosion rate values was also obtained from base coupons installed in the molten salt tanks of TES-MS demo plant. For each material and exposure conditions the obtained corrosion rate value was the average of descaled test coupons. Corrosion coupons were analyzed for 5 different exposure times in the life of the plant and significant data were obtained from this study. But the results of these tests are scope of a full independent thesis.

9.2. Contribution to the state-of-the-art

The main contribution to the state-of-the art is a new methodology (Dynamic Gravimetric Analysis, DGA) developed and used to determine the corrosion produced in carbon steel A516Gr70 samples induced by different salt mixtures commonly used as molten salts containing different amounts of chloride, at working temperatures conditions.

In order to minimize the handling of the sample a new methodology has been developed, showing that the higher is the content of chloride in molten salts the greater is the steel loss produced by corrosion and makes the corrosive kinetics to be highly increased when it is overtaken. A deep evaluation of this methodology has been carried out in the following publication:

- Cristina Prieto, Juan Gallardo González, Francisco Javier Ruiz, Camila Barreneche, Mónica Martínez, Mercè Segarra, A. Inés Fernández. Study of corrosion followed by the Dynamic Gravimetric Analysis (DGA) methodology. Solar Energy Materials & Solar Cells 157 (2016) 526–532.

During the evaluation some conclusions have been obtained for the state of the art:

- To determine the corrosion on a metal plate, ASTM Standard-G1-03 procedure is usually applied, in which the corroded metal sample is submitted to several cycles including: attack by a chemical solution, washing, cleaning, drying, and weighing. In order to minimize the handling of the sample, a new methodology (Dynamic Gravimetric Analysis, DGA) has been developed and used to determine the corrosion produced in carbon steel A516Gr70. After the thermal treatment with the three different compositions of molten salts, the amount of corrosion products formed on the surface of each metal sample was determined by using the new methodology developed at University of Barcelona named dynamic gravimetric analysis (DGA).

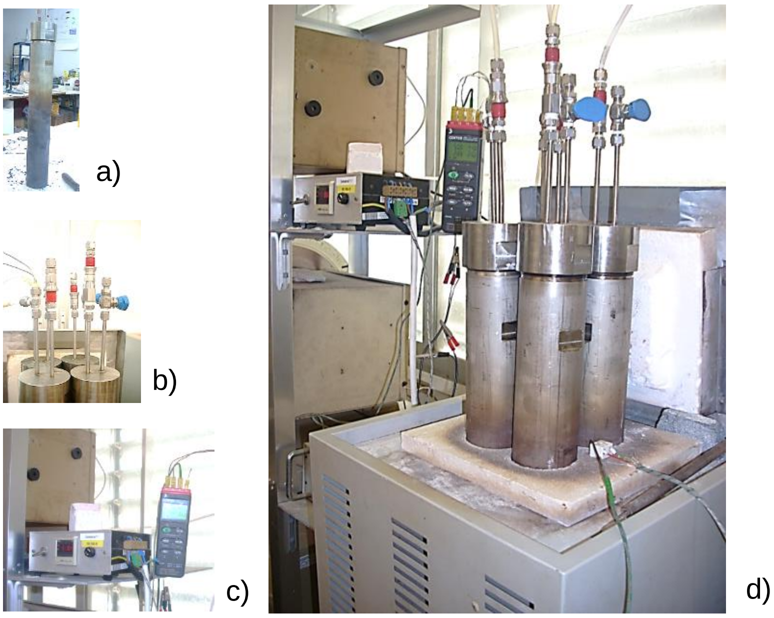

Figure 19 Thermal-corrosive treatment: parts of the experimental set-up a) tubular reactor, b) atmosphere controller, c) temperature controller and data-logger, d) general view of the experimental set-up

- To determine the amount of oxide layer removed by a cleaning solution with accuracy, the mass of the sample is plotted versus time during the DGA.

- The kinetics processes observed through this study clearly show no linear tendency due to the complex mechanisms appeared when the thermal-corrosive treatment is proceed at 400 ˚C and under N2 atmosphere. Thus, corrosion is affected only by the time factor when molten salts contain low chloride percentages. Under this condition, only after 30 days of exposure time the steel loss increases, reaching a maximum 30 days later.

- The amount of oxide formed during corrosion in molten salts is expected to be different for each sample, so the change in the slope should be found at different times, depending on the amount of scale formed during the immersion in molten salts.

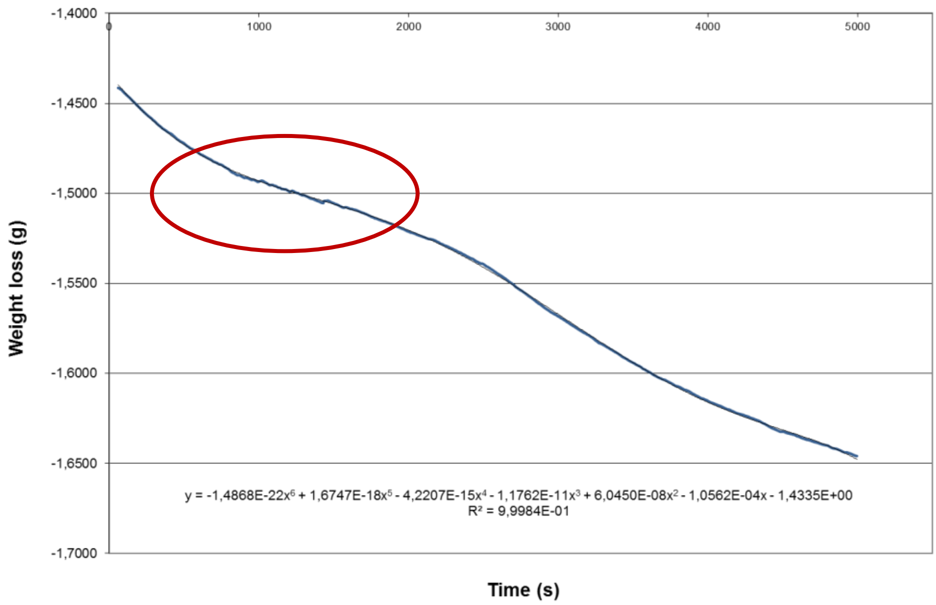

Figure 20 Mass loss of a corroded sample during DGA cleaning procedure and adjusted polynomic curve.

- The point on the graph in which the slope changes, as it can be seeing in Figure 20 will correspond to the final value where all corrosion products have been removed.

- An increase in the chloride content produces changes in the scales formed, and the formed oxide layer shows delamination and higher porosity. the presence of chloride at the metal–scale interface confirms the corrosion mechanism, involving iron chloride that had a key role in the corrosion process.

9.3. Journal paper

Solar Energy Materials & Solar Cells 157 (2016) 526–532

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Study of corrosion by Dynamic Gravimetric Analysis (DGA) methodology. Influence of chloride content in solar salt

CrossMark

Cristina Prieto [b], Juan Gallardo-González [a], Francisco Javier Ruiz-Cabañas [b], Camila Barreneche [a], Mònica Martínez [a], Mercè Segarra [a], A. Inés Fernández [a,*]

[a] Department of Materials Science & Physical Chemistry, Universitat de Barcelona, Martí i Franqués 1, Barcelona 08028, Spain
[b] Abengoa Research, C/ Energía Solar n° 1, Palmas Altas, 41014 Sevilla, Spain

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ABSTRACT

When a system for thermal energy storage (TES) is designed, many factors must be considered: storage time, dimensions, material to store heat, etc. Usually, molten salts are selected as TES materials because of their great thermal properties at high temperatures. When the whole TES system is going to be built, the material to be used for containing the thermal storage material becomes an important issue. It must have proper mechanical properties, withstand high temperatures and, above all, resist corrosion due to storage material, being in most of the cases, highly corrosive molten salt mixtures. To determine the corrosion on a metal plate, ASTM Standard-G1-03 procedure is usually applied, in which the corroded metal sample is submitted to several cycles including: attack by a chemical solution, washing, cleaning, drying, and weighing. In order to minimise the handling of the sample, a new methodology (Dynamic Gravimetric Analysis, DGA) has been developed and used to determine the corrosion produced in carbon steel A516Gr70 samples induced by different salt mixtures commonly used as molten salts containing different amounts of chloride, at working temperatures conditions. The results show that the higher is the content of chloride in molten salts the greater is the steel loss produced by corrosion and makes the corrosive kinetics to be highly increased when it is overtaken.

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10. P7: Review of technology: thermochemical energy storage for concentrated solar power plants

10.1. Introduction

For thermal energy storage systems it can be derived, that there is more than one storage technology needed to meet different applications. Consequently, a broad spectrum of storage technologies, materials and methods are needed. The overall target in designing TES systems is the reduction of investment cost, the enhancement of efficiency and reliability of the energy supply from it. In the previous papers a deep study has been done of the sensible storage in molten salt for large scale applications. However, TES system based on sensible heat offer a storage capacity that is limited by the specific heat and the thermal stability of the storage medium. Phase change materials (PCMs) can offer a higher storage capacity that is associated with the latent heat of the phase change. PCMs also enable a target-oriented discharging temperature that is set by the constant temperature of the phase change. Thermochemical storage (TCES) can offer even higher storage capacities. Thermochemical reactions (e.g. adsorption or the adhesion of a substance to the surface of another solid or liquid) can be used to accumulate and discharge heat and cold on demand (also regulating humidity) in a variety of applications using different chemical reactants.

TCES is proposed as a future alternative to molten salts technology to manage thermal energy storage in CSP plants. Unlike molten salts in which heat is stored as sensible heat, TCES allows solar energy to be stored (and subsequently released) in form of chemical energy by promoting a chemical process. Thus, a highly endothermic reaction is used for the charging step, while the reverse exothermic process allows releasing energy while closing the chemical loop for a new cycle. As chemical bonds are broken and formed during the process, a large amount of energy is absorbed /liberated within the cycle allowing high energy storage densities (800-2000 vs. 450 kJ/kg of molten salts) and, consequently, significantly less CAPEX intensive storage tanks compared to molten salts. Also, TCES allows higher discharge temperatures compared to molten salts, this potentially leading to superior efficiencies in steam turbines. In spite of these advantages, TCES has not been commercially developed so far. The literature reviewed suggests that the main aspects limiting commercialization of TCES technology in CSP plants are: (i) the lack of long-term thermal and mechanical stability of the solid materials employed and, (ii) slow kinetics for adsorption/desorption processes. These two aspects lead to poor recyclability (well below the high standards required by a CSP plant, around 10000 cycles) and unpractical time scales for charging and discharging processes. Consequently, lab-scale research is needed on low-cost, high surface area and thermally stable materials before TCES is commercially implemented in CSP plants.

R&D challenges are mostly related with the development of the proper thermochemical reactions, the characterization of the most promising material and the practical arrangement of the reactor, thereby resolving a number of problems connected with very high temperatures, high solar flux, chemical compatibility, and materials. But a STE thermochemical plant configuration also involves a central receiver (tower) plants and works based on gas-solid reactions able to capture the solar energy, namely the use of a pair of redox reactions involving multivalent solid oxides. The idea is to employ redox oxide materials, combining ceramic volumetric receiver and structured solar reactor technologies in order to develop an integrated receiver/reactor/heat exchanger configuration with enhanced heat storage characteristics. This is achieved through a series of innovations involving efficiently integrated systems within the plant configurations, new reactor/heat exchanger designs, enhanced incorporation of redox materials in the reactor structure and improved redox material compositions, and the power block. Power block is mainly composed by a turbine, a dissipate system, fluid pressurized system, a pump and an electricity generator. It could be an open or a closed power cycle.

10.2. Contribution to the state-of-the-art

The main contribution to the state of the art is a review that summarizes and compares the different TCES that are today being investigated for CSP applications. Those systems are based in three redox reactions, sulfur-based cycles, metal oxide reduction-oxidation cycles, and perovskite-type hydrogen production. Thermochemical storage, as it has been called, presents a substantially high storage density, which accommodates plant space constrictions, and a loss-free and long term storage option. Unfortunately, due to being in its infancy, the technology still presents several questions in terms of its cyclic stability and how easy it is to integrate it with concentration solar power.

A state of the art of the main thermochemical cycles has been conducted from a global vision to give the overall approach needed for the study of thermochemical systems. This study has been published in:

- Cristina Prieto, Patrick Cooper, A. Inés Fernández, Luisa F. Cabeza. "Review of technology: thermochemical energy storage for concentrated solar power plants". Renewable and Sustainable Energy Reviews 60 (2016) 909-929.

This review shows that all these cycles are promising, but none of them seems to have all the characteristics necessary to become the only one storage system for CSP.

The sulfur cycle has not been tested commercially yet but its simplicity and efficiency in storing energy, in the form of non-degradable chemical bonds, has launched large scale research initiatives. The system is quite versatile in terms of catalysts, storage materials (sulfur, hydrogen), and even the chemistry of the cycles used to produce them (electrolysis, disproportionation, halogen reactions). This technology, much like solar energy, seems to be evolving into an option to be tailored to the necessities and facilities of each storage system it is attached to, instead of acting as an overarching, ubiquitous method. Future developments still to be undertaken to ensure the proliferation of this technology will revolve around: preparing the Brayton cycles to run under the harsh and corrosive conditions of sulfur dioxide and trioxide; maximizing the selectivity in the *sulfuric* acid generation steps; increase the conversion in each step so as to reduce sizes and utility costs; and maximizing the flow rates through the reactor without punishing its performance.

Different redox cycles as manganese and calcium oxides have been evaluated. In the calcium carbonate cycle, the most important consideration for this system is increasing the carbonator activity; due to this limitation, the plant efficiency of 42.8% is still uncomfortably low for investment. More importantly, if after 20 cycles the activity rests below 19% and the system is optimized at present with 25%, this means that new CaO or CaCO3 will have to be inevitably replaced into the system, attributing operating costs to the sourcing of new raw materials. For an ideally closed cycle, this is oxymoronic.

The CaO/Ca(OH)2 cycle is an attractive system because of its simplicity: it utilizes simple raw materials such as quicklime and water; it can be integrated into the power block by looping a HTF around it; the reaction occurs within one reactor with no transport of solids anywhere; and, finally, the operating temperatures are high enough to be efficient but low enough to be attainable without involving complex mechanical engineering. Calcium hydroxide cycles have, to this effect, even been suggested for trough systems. The main setbacks with this cycle originate to the water reactant. The use of steam, to be more precise, is problematic for two reasons: first, it requires the addition of water to the system and second, its recyclability has not been proven.

The manganese oxide cycles are very easy and straight forward from an operability point of view: both reactions occur at roughly the same temperature and the reaction is run depending on whether sunlight is heating the reactor or if gas is coursing through it. The heat evolved, which is absorbed by the HTF, air, is high enough (at 900-1100ºC) to power a Ranking cycle through a heat exchanger further downstream. However, the chemistry of the reaction will still need work. Re-oxidations are still not perfect even with iron oxide doping and they stabilize, at best, at 90% after numerous cycles.

Finally, for perovskita structures, as catalysts for hydrogen production is still at an early stage of development. Only a few reactors have been tested and the entirety of them only at a laboratory scale. Its benefits are evidenced by the results: perovskites facilitate oxygen diffusion without deforming and so they can operate at high temperatures necessary for a catalyzed water-splitting reaction. Furthermore, they have eclipsed the production capacity of previous catalysts like Ceria by tripling thrice the amount of hydrogen produced in similar circumstances and even at, on average, 100ºC less of operation. Last, they are cheap, malleable and readily available.

Their major setback, nonetheless, is the efficiency. At a maximum efficiency of 32.2% and a yearly average of 25% it is severely lagging behind the Department of Energy's solar-to-heat target of 65%. In the current reactor construction, there are several mechanical parts which could be an avenue for wasted energy and technical malfunctions. In parallel, the membrane reactors are even less developed and suffer from a steady rate of less than 10% which is too wasteful. Efforts to improve the reaction by adding natural gas or carbon monoxide as a stronger reducing agent become contradictory to the self-touted nature of the project as self-sufficient and free from the volatilities of fossil fuels.

10.3. Journal paper

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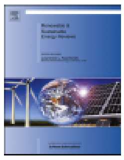

Review of technology: Thermochemical energy storage for concentrated solar power plants

Cristina Prieto [a,1], Patrick Cooper [a,1], A. Inés Fernández [b], Luisa F. Cabeza [c,*]

[a] Abengoa Research, C/Energía Solar 1, 41012 Seville, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain
[c] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

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ABSTRACT

To be able to extend the operation of a solar power plant (CSP) up to 15 h, thermal energy storage (TES) is necessary. But TES also provides more versatility to the plant and makes its reliance during operation hours more dependable. On the other hand, due to the different CSP configurations, a broad spectrum of storage technologies, materials and methods is needed. Sensible and latent heat storage are known technologies in CSP, but thermochemical storage (TCS) is still very much at laboratory level. Nevertheless, TCS has de advantage of nearly no losses during storage and very good volumetric energy density. This review summarizes and compares the different TCS that are today being investigated. Those systems are based in three redox reactions, sulfur-based cycles, metal oxide reduction–oxidation cycles, and perovskite-type hydrogen production, and metal oxide non-redox cycles due to their similarity. This review shows that all these cycles are promising, but none of them seems to have all the characteristics necessary to become the only one storage system for CSP. The main conclusion of the review is that the calcium carbonate is the cycle with most experimentation behind it to infer that it could be viable and should thus be attempted at a research plant scale once a reactivation cycle can be designed; and the manganese oxide cycle, while less developed, is fundamental enough to be a suitable application for desert climates over the rest of the water-frugal or even water-avoiding cycles.

The pages from 136 to 156 contain the article:

- Cristina Prieto, Patrick Cooper, A. Inés Fernández, Luisa F. Cabeza. "Review of technology: thermochemical energy storage for concentrated solar power plants". Renewable and Sustainable Energy Reviews 60 (2016) 909-929.

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11. Conclusions and recommendations for future work

11.1. Conclusions of the thesis

The transition of the new technologies, from the research stage up to the deployment stage in the market, is a risky step that often fails. The work carried out in this PhD thesis has made this transition in the thermal energy indirect storage technology. The thesis identifies strategies associated with the successful commercialization of molten salt technology though a deep analysis of the technology at different scale. In particular the focus has been on two R&D facilities of different size which present relevant problems to be solved before of guaranteeing the market feasibility of this technology.

After the design, the construction and 4 years of operation in the plant in Seville (8.5 MWhth pilot plant) and a similar period of operation in the plant in Lleida (66 kWhth pilot plant), key aspects were highlighted when working with TES and CSP technologies. The lessons learnt had high impact in the new commercial plants built by Abengoa with this technology, as all the components that were used later in commercials plants were successfully tested and optimized in both pilot plants. This work has demonstrated that using pilot plants helps to obtain a more successful commercial implementation of an emerging technology and had a significant impact in the new Abengoa commercial plants allowing a re-evaluation to optimize and integrate all aspects of the design from a system viewpoint, and to evaluate trade-offs in design to reduce complexities, increase performance and minimize costs. In particular the following system components and design requirements were included in this thesis:

- Piping System
- Freeze protection
- Operating temperature level
- Heat losses/parasitics
- Heat tracing
- Pumps/valves
- Molten salt tanks design
- Heat exchangers
- Instrumentation
- Control system

This thesis has identified the key indicators to guarantee the efficiency and capacity of the thermal energy concept with molten salt as indirect storage system in the oil parabolic trough collector technology. The main achievement and conclusion concerning the molten salt system analyzed in the pilot plants are:

- The tank temperature evaluation: In general, it has been seen that the higher temperatures are found in the middle height temperature sensors. This phenomenon is due to the heat losses through the foundation, wall and the roof of the tank. This effect is worse when the tank is not being completely filled. These losses depend on the assembly and the good design of the isolation system and the foundation selected. This problem is reduced in the commercial size due to they have a ratio volume / surface more favorable.

- Heat losses: The molten salt storage represents an optimum system for the parabolic trough technology because it matches perfectly the sensible thermal behavior of the synthetic oil used in the current parabolic trough solar plants. Thanks to the utilization of efficient heat exchangers the hysteresis between charge and discharge can be reduced to a few degrees (around 5 ºC), thus the system is able to generate higher efficiency than 95% of the nominal conditions and being able to maintain constant conditions during the whole discharge phase. These heat exchangers must be designed with small thermal approaches (in the range of 3 ºC to 10 ºC) in order to minimize the performance penalty of the Rankine cycle during the discharging. It is important to note that live steam temperature will be lower during the storage operation than during daytime, when steam is generated directly by the solar field. This leads to a slight decrease of the power block efficiency. The low thermal approaches also help to maintain a minimum oil temperature to return to the solar field during the charging. If heat losses appear in the system it affects to the approach in the heat exchanger reducing the efficiency of the power cycle in discharge. The blockage by freezing is a second effect of the heat losses that will affect the operability of the plant. Finally the heat losses reduce the storage capacity of the plant. This exhaustive study of the thermal losses at relevant scale in the demo plant TES-MS allows the design optimization in commercial plants, with tanks that lose less than 1ºC /day and systems exchangers with 99% efficiency.

- Foundation models: Thermal energy storage tanks are highly insulated in order to minimize the heat losses through the top and lateral walls and the foundation. In the thesis, an analytical model for the estimation of the tank's bottom heat losses in steady state at relevant scale has been developed, allowing a reengineering process that enhanced the thermal behavior of the foundation. The thermal model has improved the comprehension of the heat transfer mechanisms and has allowed the optimization of the final design of the commercial tank, considering the worse boundary conditions.
- Analysis of the heat tracing system and analysis of the main problems from leaks and solidifications of fluids. During the installation of the tracing systems, one should be aware of not damaging it. The housing of the resistance wire could be affected, which can turn out into break down of the electrical heating wire and its malfunction. Moreover, the areas where the salts have a higher probability of being solidified should be surrounded by a metallic mesh connected to the electrical tracing, helping to increase the heat transfer area. On a related point, photographs should be taken of all of the heat trace installations. Once the thermal insulation is in place, the plant operation and maintenance staff will not know where the cables are installed. This problem increases with the higher capacity of the facility as well as the pilot and demo plants have shown. As problems develop, the knowledge of where are located the cables and the thermocouples will be an important contribution to diagnosing the problem. The keys to a successful heat trace system are to 1) fabricate the cables only after the final equipment and piping arrangement has been defined, and 2) provide a good supervision for the cable installation.
- The storage system requires isolation valves downstream of each nitrate salt pump, and in each of the vent and drain lines. Based on the experience at relevant scale of the MS-TES project with ball, gate, butterfly, and globe valves, the recommended valves for the thermal storage system are gate valves with bellows seals. The principal failure mechanism for a gate valve in nitrate salt service is the formation of an oxide layer on the plug and seat when the valve is closed. The layers interfere with each other, and bind the plug to the seat. The solution is to exercise the valve on a regular basis to prevent the formation of a common oxide layer.
- From the point of view of the equipment and control systems, the main conclusions have been that in general, it is important to use an appropriate signal wire and it must be shielded in order to prevent noise as a consequence of the system disturbances. It is also important to protect the signal wire with a high temperature resistance coating to prevent it from burning. Temperature sensors are recommended to be installed far away from bifurcations and closer to the places where it is estimated that the temperature could be critically low as a consequence of operation and flowing of fluids. It is also recommended that temperature sensors should be located inside the tanks at a minimum height from the ground and not so close to the suction tube of the pump in order to get accurate values without disturbances. With these sensors, precise information must always be available so as to ascertain whether or not there are freezing salts in that part of the tanks (because of stratification or heat losses) and therefore the pump would be adversely affected.

  Two flow-meters were also compared: vortex and ultrasonic. So far, the behavior of the flow-meter has been found to be the more stable of the two types assembled. However, problems on the determination of the real flow rate have been also found, mainly due to the thermo-physical properties of the fluids evaluated (e.g. density and viscosity). For commercial plants, it is recommended to perfectly determine the thermo-physical properties of the fluids which are going to be evaluated and afterwards implement possible correction factors the reading of the flow-meter.

Several problems arose with pressure sensors, especially in the molten salts line. After solving this problem, a better assessment of the real load losses in the exchanger was performed. For future commercial plants, it is recommended on the one hand, not remove the manifolds of the pressure sensors and on the other hand, seek a possible solution in order to avoid the molten salts solidification inside them. One of the best solutions would be to install an electrical heat tracing to avoid freezing and maintaining the manifolds to keep this instrumentation in operation. A good pressure sensors functioning and a good characterization of the molten salts thermophysical properties, can lead to a more accurate measurements of the molten salts flow rate with an orifice plate.

- Mechanical design of the molten salt tanks: Other important issues detected in the design of the R&D facilities were the difficulties to design the molten salt tank. In absence of code, API 650 appendix-M and ASME VIII have been employed to estimate the yield strength behavior with the temperature. In this thesis an experimental device has been developed to validate the design parameters of the tanks. An experimental setup was designed and built to perform the mechanical testing of steel A516Gr70 under operational conditions at 380 ºC in contact with molten salts. Mechanical testing under operational conditions confirmed the reduction of yield strength and young modulus as well as the increase of elongation compared with the testing at room temperature. A 7 days experiment maintaining the sample under operational conditions and tensile. Changes in mechanical properties, the reduction of yield strength and the increase in elongation are attributed to the annealing of the sample and this fact is corroborated with the metallographic study.
- Commissioning: The evaluation of commissioning processes like the preheating or the filling process in the demo scale have identified several problems like thermal expansion or death areas in the tanks during the preheating. Fluid-dynamic models and thermo-mechanical models are necessary to guarantee thermal and mechanical behaviors during these first steps.
- Finally, corrosion rate is not an issue working with molten salt at 400ºC and Cl^- lower than 0.3% (wt) [28]. In those conditions, a corrosion allowance of 4 mm is a safety value for commercial plants. If the content of Cl^- reaches values higher than 0.6%, non-protective oxide layer appears making not feasible the use of carbon steel as construction material. To make these measures, a new non-invasive methodology has been developed. The main contribution of this thesis is a new methodology (Dynamic Gravimetric Analysis, DGA) developed and used to determine the corrosion produced in carbon steel A516Gr70 samples induced by different salt mixtures commonly used as molten salts containing different amounts of chloride, at working temperatures conditions:

In order to minimize the handling of the sample a new methodology has been developed based on the mass of the coupons in the cleaning solution plotted versus time during 2 hours.

Once the scale is removed the steel will begin to be oxidized by the cleaning solution. These two processes (dissolution of scale and corrosion of steel) take place at different rates detected with a change in the slope of mass losses.

The results showed that the higher is the content of chloride in molten salts the greater is the steel loss produced by corrosion and makes the corrosive kinetics to be highly increased when it is overtaken.

As we have seen in this thesis, molten salts like storage medium have already been validated as commercial storage systems thanks to the analysis carried out in two different pilot plants. However TES technologies face some barriers to its market entry and parameters like cost, material properties or stability are key issues. R&D activities in thermal storage are still going on. This thesis shows as the research in thermal storage is currently focused on reducing the cost of high-density storage system as thermochemical energy storage. The thermochemical energy storage is proposed as a future alternative instead to molten salts in order to manage thermal energy storage in CSP plants. The main conclusions of the TCES state of the art made in this thesis are:

- TCES development is still in a fundamental, laboratory stage. The state of the art realized is based on three reactions: sulfur-based cycles, metal oxide cycle and perovskita but none seems to be complete to be ubiquitous in any field. The sulfur cycle has not been tested commercially but is one of the most advanced in research initiatives. This reaction feed a Brayton cycle that has to be prepared to run under very corrosive conditions.
- Different oxide cycles have been analyzed, being the manganese oxide cycle one the most promising development to power a Brayton cycle or Rankine cycle, but the rotary kiln used is one of the bottleneck to be solved.
- The perovskita structure as catalyst for hydrogen production is still in an early stage of development. The cost of perovskita is a handicap but it is most promising another catalyst like Ceria. Several developments are focused in the stability, heat recovery and efficiency of this material.

The review of the most explored reactions and reactor technologies have identified that more R&D activities are needed. Aligned with the work developed in this thesis, the design and evaluation of new pilot plants at different scales will be critical for the technology feasibility.

11.2. Recommendation for future works

The molten salt indirect storage system has been validated like a feasible storage technology for commercial purposes. At this point, it is important to result that more analysis should be done during the commercial operation. From the research carried out and presented in this thesis, some points arise which are not addressed in this work and are relevant for the future:

- Evaluate more in detail some risks identified: A small leak in the heat exchanger will allow limited quantities of thermal oil to mix with the nitrate salt. Thermal oil vapors will accumulate in one or both of the storage tank ullage volumes and the vapors will be periodically released to the atmosphere through the tank vacuum / pressure relief valves. Liquid thermal oil will need to be periodically added to the expansion vessel to compensate for the losses. If the thermal oil is in its original chemical composition of diphenyl oxide and biphenyl, the vapor pressures at the temperatures of the cold tank and the hot tank both exceed 1 atmosphere. As such, the potential for the thermal oil dissolving in the salt should be very low. However, some level of oil decomposition in the collector field is expected. The decomposition produces hydrocarbons which are lighter and heavier than the original composition. In principle, a slow leakage of thermal oil into the nitrate salt could deposit hydrocarbon compounds which have a vapor pressure less than 1 atmosphere, and the salt could accumulate some level of contaminants. The potential for hydrocarbon contamination, and the effects on the heat transfer or the storage characteristics of the salt, have yet to be studied.

- During the procurement of the nitrate salt, representative samples of the salt should be obtained from the successful bidder. The samples will be analyzed for unexpected impurities, and the samples will be melted to determine if unexpected reactions occur. For example, at the MS-TES demonstration project, the salt supplied contained 0.08% of magnesium in the form of magnesium oxide. On initial heating to a temperature of 375°C [51], the magnesium nitrate decomposed as follows:

$$Mg(NO_3)_2 \rightarrow MgO(s) + 2NO_2, (g) + O_2, (g)$$

  The magnesium oxide precipitated in the bottom of the storage tanks; however nitrogen oxides were released to the atmosphere as NO_x. Analyzing and melting the salt prior to delivery will provide the time necessary to incorporate any required changes to the environmental permits or the melting equipment.

Inorganic nitrate salt mixtures are the preferred storage medium due to a favorable combination of thermal and chemical properties. The indirect storage system is able to supply energy at constant conditions during the discharge, without having big concerns about corrosion phenomena or degradation of salts. However, it needs significant time to switch from charging to discharging conditions, not allowing the system as buffer storage or to protect the turbine against transients. This TES system is the most used thermal storage in solar thermal electricity plants, but its working conditions are limited by the synthetic thermal oil used in the solar field. Thermal degradation in the oil limits the molten salt temperature up to 400ºC The evolution in molten salt technology is to work with the molten salt as HTF with a direct storage system [52]. In that case the maximum operating temperature is fixed by the thermal stability of the salt (565ºC) [53] [54]. Or to develop new molten salts design which can operate in a wider range of temperature [11].

However, and to complement the corrosion study at 400ºC, the corrosion at higher operating temperature is still a no-conclusive work in the state of the art [55] [56]. Higher operation temperature in molten salt will produce higher corrosion rates due to two main issues:

- Corrosion phenomena are usually activated by the temperature following Arrhenius performance. Oxide ion concentration increasing coming from nitrite decomposition taking into account previous decompositions reactions: $NO_3^- \rightarrow NO_2^- + ½ O_2$; $NO_2^- \rightarrow O^- + NO$.
- A thermal decomposition will also start if we work at temperature higher than 565ºC (Molten salt tower temperature). A more detailed study of corrosion at temperature higher than 565ºC is recommended under up-scale conditions if we want to work near the thermal stability temperature of the molten salt.

Finally, thermochemical energy storage is proposed as the future alternative to molten salts technology to manage thermal energy storage in CSP plants with significantly less CAPEX intensive storage tanks compared to molten salts and superior efficiencies in power cycle (Rankine, Brayton, supercritical CO_2, and others). In spite of these advantages, TCES has not been commercially developed so far. Certain main aspects are limiting commercialization of TCES technology in CSP plants and pending development are:

- To guarantee the long-term thermal and mechanical stability of the solid materials employed.
- To solve slow kinetics for adsorption/desorption processes. These two aspects lead to poor recyclability (well below the high standards required by a CSP plant, around 10000 cycles) and unpractical time scales for charging and discharging processes. Consequently, more lab-scale research is needed on low-cost, high surface area and thermally stable materials before TCES is commercially implemented in CSP plants.
- The reactor design has to be optimized from the point of view of solar efficiency or/and reactor conversion. Key efficiency and feasibility factors for solar-thermal technology lays in reducing receiver re-radiation, reflection, and convective losses. For example, to increase the overall reactor efficiency a reflective cavity wall can be studied. Furthermore, it is very important to notice that heat transfer processes are affecting different depending on the reactor scale, thus at lab-scale conductive losses are more remarkable than radiation. But lab-scale reactors, as we have demonstrated in this thesis, are useful to investigate design issues.

The analysis and the evaluation of these technologies in pilot plant at different scale will play a key role for the final feasibility of these new developments.

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