ENERGY OPTIMIZATION OF A CONCENTRATED SOLAR POWER PLANT WITH THERMAL STORAGE

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"*You miss 100% of the shots you don't take*" - W. Gretzky

"*Start by doing what's necessary, then do what's possible, and suddenly you are doing the impossible*" - Francisco de Assis

"*Fall down seven times, get up eight times*" - 七転び八起き

"*My Sun sets to rise again*" - E.Browning

Energy Optimization of a Concentrated Solar Power plant with Thermal Storage

Abstract

One of the most relevant problems to solve at a planetary scale is the access to an affordable clean source of energy as CO_2 equivalent emissions should be reduced significantly. Some authors aim for a zero emissions target for 2050. Renewable energies will play a leading role in this energy transition, and solar energy with storage is a promising technology exploring a renewable and worldwide available resource.

Within the present thesis component development like a new thermal storage thermocline tank design or having latent heat storage capability are technological developments that have been pursued and analyzed on a system perspective basis, focusing on reducing the LCOE value of a commercial STE plant using TRNSYS software. Material research with molten salts mixtures and cement based materials has been performed at lab scale. A fully validation should occur through a 13 partners pan-European H2020 project called NEWSOL which has been developed supported on the laboratory data obtained.

Moreover, incorporation of local available material, “modern slag” from an old mine of Alentejo region, was also studied. The material could be used as an aggregate incorporated into calcium aluminate cement (CAC) or as filler. This would help to solve a local environmental complex problem related to soil, air and water pollution due to heavy metals and mining activity in Mina de São Domingos, Southeast of Portugal.

The integration of these results underlies a broad energy transition model, a proposal is presented in this thesis, with the aim to foster development towards a sustainable usage of resources and promote clean technologies especially in the energy sector. This model can be locally adapted depending on the pattern of existing industries. The goal is to achieve a smooth transition into a clean tech energy society in line with the target of achieving zero emissions for 2050.

Keywords: Solar Thermal Electricity; Energy Storage; Molten Salts; Cement based mixtures; Thermocline tank design

Optimização Energética de uma Central de Concentração Solar com Armazenamento de Energia

Resumo

Um dos problemas mais relevantes a resolver a uma escala planetária é o acesso, com um custo moderado, a fontes limpas de energia considerando que as emissões equivalentes de CO2 derão ser reduzidas drasticamente. Alguns autores ambicionam mesmo um objetivo de zero emissões em 2050. As energias renováveis irão desempenhar um papel preponderante nesta transição energética, sendo que a energia solar com armazenamento é uma tecnologia promissora que aproveita um recurso renovável e disponível em boa parte do Planeta.

Na presente tese foi realizado o desenvolvimento de componentes nomeadamente o design que um novo tanque do tipo termocline, ou de novos elementos recorrendo ao calor latente, desenvolvimentos tecnológicos que foram analizados de uma perspectiva de sistema, dando o enfoque na redução do custo nivelado da electricidade (LCOE) para uma planta Termosolar usando o software TRNSYS. Foi também realizada investigação em laboratório ao nível dos materiais com várias misturas de sais fundidos inclusivé em contacto directo com materiais de base cimenticia. Uma validação completa deverá ocorrer no projeto NEWSOL do programa H2020 que reúne um consórcio de 13 parceiros europeus e que foi preparado e submetido tendo por base os resultados laboratoriais obtidos.

Adicionalmente, incorporação de material disponível (escória de minério) de uma mina abandonada da região do Alentejo foi outro dos aspectos estudados. Verificou-se que este material poderá ser utilizado como agregado num ligante do tipo cimento de aluminato de cálcio (CAC) ou como *"filler"*. Este re-aproveitamento resolveria um problema ambiental complexo derivado do elevado conteúdo de metais pesados resultantes da actividade de mineração e que actualamente provocam poluição do solo, água e ar na área da Mina de São Domingos, Sudeste de Portugal.

Estes progressos deverão ser integrados num modelo de transição energética mais amplo. Na presente tese, uma proposta concreta é apresentada, com o objectivo de incentivar o desenvolvimento na direção de uma utilização sustentável dos recursos e a promoção de tecnologias limpas nomeadamente no sector da energia. Este modelo poderá ser adaptado localmente dependendo do padrão de indústrias existente. O objectivo é atingir uma transição suave para uma sociedade de energias limpas em linha com o objectivo de atingir zero emissões de CO_2 equivalente em 2050.

Palavras chave: Energia Solar Termoeléctrica; Armazenamento de Energia; Sais Fundidos; Misturas de base cimenticia; Concepção de tanque termocline

Acknowledgements

This thesis is a landmark.

It was a trigger to connect to extraordinary people, to an extraordinary place beyond the Tagus (Alentejo), in a tremendous UNESCO heritage place (Evora) and following the path of megalithic builders who in 4000BC were already looking to the Sun and to the starts (Cromeleque dos Almendres).

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I also acknowledge the support of the Portuguese National Science and Technology Foundation, also for supporting key research activities in Portugal like the Research Infrastructure Program, that will give an important contribution to the EMSP – Evora Molten Salt Platform, a bright landmark in Alentejo.

Finally, my most warm affection towards my family, Bruno, Carla, Pa^2, Ma^2, Du^2, they are the reason for this path, its beginning and its end.

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Nomenclature

E_{TES}	Total thermal energy storage capacity [Wh]
$\eta_{Cycle,OUT}$	Cycle efficiency at design conditions [-]
P_{OUT}	Power output [W]
Δt_{TES}	Thermal storage capacity [h]
$\rho_{TES,\max}; \rho_{TES,\min}$	Specific volume of the TES medium [g/m^3]
$c_{TES,\max}; c_{TES,\min}$	Heat capacity of the TES medium [W/g* m^3]
$T_{SF,return}$	Return temperature of the solar field medium [◦C]
$T_{SF,in}$	Inlet temperature of the solar field medium [◦C]
f_{HE}	Heat exchanger efficiency factor, solar loop / storage loop [-]
c_p	Specific heat capacity of the molten salts [J/kg*K]
T_{in} ; T_{out}	Receiver temperature inlet / outlet [◦C]
$E_{gain}; E_{TH\_loss}; E_{OPT\_loss}$	Energy: gain / thermal loss / optical loss [kWh]
P	Specific mass [kg/m^3]
ε	Bed porosity
T	Temperature [◦C]
t	Time [s]
$\dot{m}$	Mass flow [kg/s]
A	Bed transversal area [m^2]
H	Volumetric heat transfer coefficient [W/(m^3.K)]
v	Fluid flow velocity (in axial direction) [m/s]
w/c	Water cement ratio [-]
c/s	Cement sand ratio [-]
Rcomp	Compressive strength [MPa]

C	Heat-cycle number [-]
E	Dynamic elastic modulus [GPa]
cp	Pulse propagation speed [m/s]
ρc	Density of concrete [kg/m^3]
ν	Poisson coefficient [-]

Abbreviations

BAU	Business as usual
BAT	Best available technology
BFS	Blast furnace slag
CAC	Calcium aluminate cement mix
CAC+	Calcium aluminate cement mix plus slag
CAES	Compressed air energy storage
CAL	Calcareous based
CAPEX	Capital expenditures
CAT	Calcium aluminate based
CH	Calcium hydroxide
CLFR-EM	Compact linear fresnel reflector concentrator etendue matched
COP	Coefficient of performance
CPV	Concentrated photovoltaics
CSH	Calcium silicates hydrates
CSP	Concentrated solar power
DNI	Direct normal irradiation [kWh/m^2*year]
DSC / TGA	Differential scanning calorimetry / Thermogravimetric analysis
DSG	Direct steam generation

ECV	Electrical car vehicle
EMSP	Evora molten salt platform
FA	Fly ash
GDP	Gross domestic product
GHG	Greenhouse gases
HAZOP	Hazard and operability study
HSM	Heat storage material
HTF	Heat transfer fluid
HTLT	Hybrid thermocline layer tank
IAMT / IAML	Incident angle modifier Transversal / Longitudinal
IEA	International energy agency
IMF	International monetary fund
ITZ	Interfacial transition zone
JCESR	Joint center for energy storage research
LCA	Life cycle assessment
LCOE	Life cycle cost of energy
LPG	Liquefied petroleum gas
LTG	Limits to growth
MS	Molten salts
OECD	Organisation for economic co-operation and development
OPC	Ordinary portland cement mix
OPEX	Operational expenditures
PCM	Phase change materials
PSA	*Plataforma Solar de Almeria*
PTC	Parabolic trough collectors
PV	Photovoltaic systems

SCA	Silicone calcareous composition
SSA	Slag aggregate
SEGS	Solar energy generating systems
SEM / EDS	Scanning electron microscope / Energy dispersive spectroscopy
SF	Silica fume
Si O	Silicious based
SO4	Sulfate
SP	Superplasticizier
SPEC	(Technical) Specifications
STE	Solar thermal electricity
TES	Thermal energy storage
TG / DTA	Thermogravimetric / Differential thermal analysis
USD	United states (of America) dollars
UPV	Ultra pulse velocity
XRD	X-Ray diffraction

Contents

Chapter 1. Introduction

1.1 Motivation

Energy plays a central role in today's world. Apart from the very basic heating and cooling needs, industrialization has had a big impact on society with machines producing all sorts of goods, a food industry where food is deep frozen and later stored in refrigerators through the whole supply chain, massive daily transportation based on private car usage, long distance passenger transportation based on airplanes and intercontinental freight using large vessels. The growth seen on the transportation sector has been fueled by agreements on free trade, leading to global factories that deploy millions of goods anywhere on the Planet. This has an impact on raw material extraction, on Energy resources with associated negative effects (fossil fuels extraction and burning, CO2 eq. emissions); a fact that many people are not aware of its real dimension and impact, because of the globalized decoupled energy system where coal can be extracted for instance in South Africa, transported by train to a harbor, shipped to the USA, where electricity is produced in a coal fired plant far away from the end user consumption location, who is then very far from feeling the environmental burden of 1 kWh consumed. In addition, depending on the end user appliance there are many cases where more than 90% of the primary energy is wasted in the whole chain of production, delivery and device losses [1].
Energy production has been rising steady, primary energy of 6106 Mtoe in 1973 to 13371 Mtoe in 2012 [2] which corresponded to a total final consumption of 4672 Mtoe in 1973 and 8979 Mtoe in 2012, that is, energy consumption more than doubled in 40 years. Worldwide, in relative terms of fuel share, oil decreased from 48% to 41%, Coal decreased from 14% to 10%, Biofuels and waste constant at 13%, Natural gas increased from 14% to 15%, while electricity has had a significant increase from 9% to 18%.
Electricity as a noble energy form is more and more in use, with a total of 22728TWh generated in 2013. Renewables correspond to 22% of the total generation, already appear with a significant impact in the global mix, the biggest share coming from Hydropower and Windpower. Electricity from renewables is predicted to increase from 5000TWh in 2013 to 7310TWh in 2020 and 10225TWh in 2025. The rise will mainly be achieved with new Windpower, Biomass and Solar Thermal Energy [2].

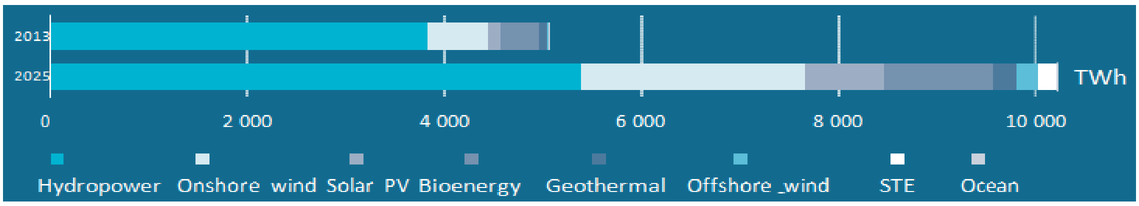

Fig. 1-1 – Renewable Energy used in Electricity Production in 2013 and prediction for 2025 [2]

In 2012, worldwide, 28% of Energy was being consumed in the Industry sector, 28% in Transportation sector, 35% in Others (Commercial, Residential, Public Sector, Agriculture, Forestry, Fishing, etc.) and 9% in non-energy usages.

In the Industry, energy-intensive sectors, that is, chemicals and petrochemicals, iron and steel, cement, pulp and paper, and aluminium, make up 67% of total industrial energy use. Especially in these industries, process innovation is a key issue. The target [2] is that savings of 4.5 Gton of CO2 eq. emissions (representing 54% of industrial direct emissions) can be achieved in 2050 through: energy efficiency measures, deployment of today's best available technology (BAT), switching to low-carbon fuel mixes and enhanced material recycling.

In the transportation sector, transitions to alternative liquid or gaseous fuels such as ethanol or hydrogen would require new production, storage, and distribution systems, with major infrastructure new investments that refrain their interest and delay their deployment. In fact, the expansion of the retail infrastructure for alternative fuels may pose greater issues than fuel costs, resources, or production capacity. Thus, a low CAPEX alternative is needed, possible paths include: massive modal shift, increase of occupation rate, changes in passenger behavior and higher renewables incorporation.

It is of major importance to notice, the existence of fossil fuel subsidies, which lead to inefficient use of energy and introduce market distortions, should be phased out as soon as possible. With 550 billion USD in 2013, total fossil fuel subsidies exceeded the subsidies for renewables by a factor of four [3], a fact that usually is not at all highlighted by mass media. A recent study from the IMF reports that if air pollution and associated health problems are accounted, the cost is much higher, estimated to be 5250 billion USD in 2015 [4].

All in all, if all energy subsidies would be removed (namely the ones for drilling exploring activities, gas and oil pipelines, LPG conversion plants), there would be no need to have direct subsidies for Renewables since they would be immediately competitive.

Carbon pricing and removal of fossil fuel subsidies are a necessary measure, but should additionally be complemented with a broader range of policy instruments (e.g. energy standards for buildings, vehicles, electrical appliances; eco-innovation design) to decarbonize the economy at a pace where GHG emissions are effectively reduced in a way to refrain global temperature rise. IEA has defined scenarios for 2050 with 2ºC, 4ªC and 6ºC average temperature increase comparing with 2014 level, that would implicate a shift from current Business as Usual (BAU) moving towards clean tech with a global estimated investment until 2050 ranging from 318 to 358 $x10^{12}$ USD for the 6ºC and 2ºC scenarios respectively. This investment would represent less than 1% of cumulative GDP and would enable 115 $x10^{12}$ USD savings in fuel costs [2], thus a transition seems achievable just from an economic resource availability perspective.

Furthermore, to decouple economic growth from energy consumption has been a central issue of energy policies and for many the solution that would enable a so called green economy and sustainable consumption patterns. Plenty of scenarios address this issue [5], however historical data shows, that:

a) worldwide steady growth of energy consumption in absolute terms has never stopped,

b) to be successful with reducing energy absolute consumption, energy intensity levels should decrease more than the double of the historic rate ever registered.

This leads to the central question, in a sustainable society, which variables (GDP output, life expectancy, health and education indicators, leisure time, etc.) are really necessary to growth? Is there a need for continuous economic growth?

Many authors claiming that the Earth has finite resources, state that re-usage, re-cycle is a must and that developed societies need to turn to degrowth strategies and higher efficiency usage, in order to be able to reach long term prosperity respecting the ecological limits, by means of [6].

a) imposing clearly defined resource/emissions caps,

b) implementing fiscal reform for sustainability,

c) promoting technology transfer and international ecosystem protection.

To address the above mentioned issues, a new approach towards energy issues is needed, one that fosters R&D, energy efficiency increase, a global model that enables a massive shift towards cleaner/clean energy, together with demand side management introduce incentives towards real energy savings and to closed loops of resource usage. All of this can and must be combined with Renewable energy resources, as these fit the double bill of being clean and inherently sustainable.

1.2 Statement of the Problem, the case for STE- Solar Thermal Electricity with Thermal Energy Storage

The global problem is the need for a CO2 emission free source of energy if possible at a lower LCOE- Life Cycle Cost of Energy than today's LCOE mix. From a base level of 32Gton CO_2 eq in 2012, some authors aim for a 0 emissions target for 2050, others are less ambitious in the range 5 to 20 Gt in 2050.

All of them agree that additional major joint efforts need to be performed to avoid BAU expected of 56 Gt in 2050. With the share of electricity gaining relevance, having a 100% renewable electricity production could be a first but very relevant step towards solving the problem.

A significant barrier for large scale deployment of renewable energy is the intermittency of the resource. This can be overcome having storage, a feature that makes Hydropower reservoir dams a valuable asset for managing electricity demand at any given time. The availability of suitable sites for new dams is very limited in Europe and in many parts of the World. From an economic point of view the next available renewable technology with storage in the MW range is Solar Thermal Electricity. It has a very interesting growth potential to produce electricity in a centralized way, since it has a high dispatchability value, is suitable for peak shaving and can have a high capacity factor depending on the solar field and storage sizes.

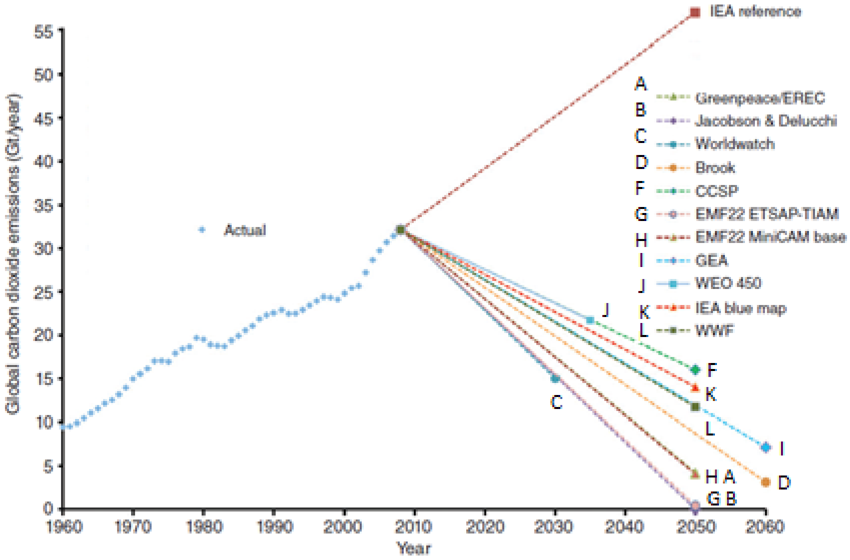

Fig. 1-2 – Scenarios for global CO2 eq emissions up to 2050 and 2060 [5]

For decentralized production with local consumption, typically residential and small businesses, PV and CPV is more adequate since transmission losses are avoided as well as grid capacity costs.

Within the STE-Solar Thermal Electricity area, the technology that has still the greatest technological development ahead and currently has the lowest potential CAPEX/MW installed is Linear Fresnel. Research on optimization of the concept has been pursued in the last 30 years, with interesting applications for STE appearing recently like the CLFR-EM concept [7]. For the current work, this was the base technological concept chosen for further development and system optimization.

Currently, the heat transfer fluid (HTF) used in standard STE plants is thermal oil that starts to degrade at 400ºC, apart from several environmental problems. Additionally there is an indirect system, since molten salts are usually used as storage media. Therefore, there is a clear path for innovation, using molten salts (MS) as the sole media both as heat transfer fluid in the receiver and as storage medium, thus enabling a higher conversion efficiency from the power block. They also have a positive LCA impact on the environment since they are not toxic and can be easily recycled as fertilizers.

From a cost benefit perspective, the established 2 tank MS storage system was developed in the 80s, with several optimization possibilities identified, among them the 1-tank thermocline, a system that deserved special attention in this research.

Moreover, a global problem shall consider solutions that can be adapted locally, solving if possible additional local problems. In current work, waste products from Alentejo (south of Portugal) region were analyzed, in order to find a solution to re-cycle or re-use them, in order to improve local sustainability within resource usage.

Finally, sustainability of resource usage associated with energy supply should have a global and integrated approach; during the development of the present thesis it became evident the need for a broad model that could become a framework to enhance and accelerate the necessary

energy transition (the so called *Energie Wende* in german).
In order to come up with solutions for the above named research issues, several research questions (RQ) were formulated and addressed:

RQ1: Can a new STE plant concept be optimized to achieve a lower LCOE than current LCOEmix for the south of Europe?
RQ2: Which could be the heat transfer fluid and storage media of such a plant?
RQ3: What progress is needed in terms of material science development and validation to enable new storage concepts for STE applications?
RQ4: What type of local materials could be used thinking on resource sustainability and closed loop systems?
RQ5: How could such concepts be validated taking advantage of the existing *Evora Molten Salt Platform* (EMSP) facility in order to enable a fast technological deployment?
RQ6: How could a transition to an integrated sustainable global energy system take place, and which energy policies could be implemented?

1.3 Worldwide Potential for Solar Thermal Electricity

All renewable forms of energy have a direct or indirect link to the Sun. From a useful energy point of view, there are some minor effects, induced gravity ones due to its mass, others resulting, for instance, from its magnetic field, but very large and main ones come from solar radiation that heats the Earth, inducing thermal currents of different fluids and temperature gradients that shape the Earth's climate. Solar collectors used for hot water production transfer the energy received to the fluid used, mainly constituted by water.
High concentration of solar energy however, uses direct solar radiation (DNI) since the solar beam will be focused into a receiver tube with a Concentration factor (~25 x or more), so that, much more energy can be delivered per m^2, and thus higher temperatures in the range 250-600ºC can be obtained using adequate heat transfer fluids.
STE plants will then convert direct normal radiation into electricity, the higher the resource, the higher the yearly energy production for a certain location and for the same investment cost. Thus, choosing a prime location is a major issue. Currently, as a rule of thumb it is considered that at least 1800 - 2000 kWh/m^2 a year of beam radiation are needed in order for a STE plant to be economically competitive, the best sites being the ones that receive more than 2800 kWh/m^2 a year like in northern Chile where LCOE can be 35% lower than in the south of Spain [8]. The majority of the regions suitable are located in the tropics, namely the North American "sunbelt" area, north of Africa, Middle East, Tibet, Australia, Southern part of Africa and northern part of Chile, as it can be seen in Fig.1-2, on the basis of satellite. Most of these areas are desert areas with very low availability of water, which makes STE ideal to be integrated with desalination plants. It should be noted, that for locations where potable water is a high valuable resource, using STE plants to focus primarily on potable water is an in indirect way of storage.

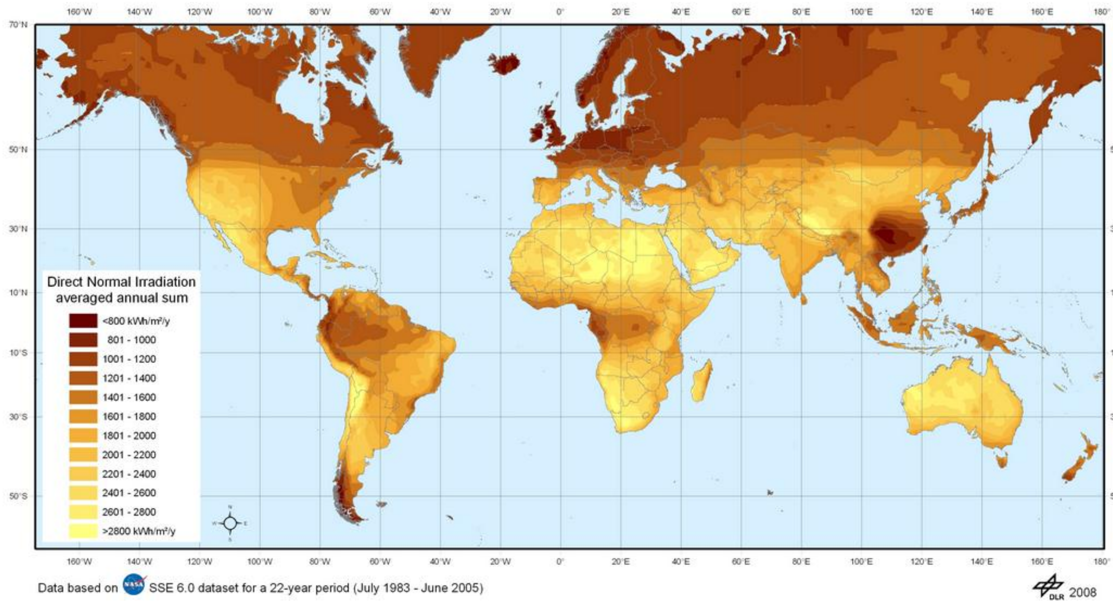

Fig. 1-3 – Solar Direct Normal Irradiation Map [9]

From a baseline of 4 GW of STE worldwide capacity in 2014, IEA estimates STE could have an installed capacity between 1000GW and 1500GW in 2050, only in Saudi Arabia 25GW are envisioned to be deployed until 2032. Other authors are event more ambitious, of 8000GW [10] of installed solar (PV+STE) capacity worldwide in 2050.

Land area for STE plants is usually not a problem, since locations where solar resource is the highest tend normally be arid or desert regions. It should be highlighted, that for instance in USA, a square of 153*153 km in the sun belt region (Arizona, Nevada, California) with state of the art STE would be enough to deliver all electricity needs in USA. [11]

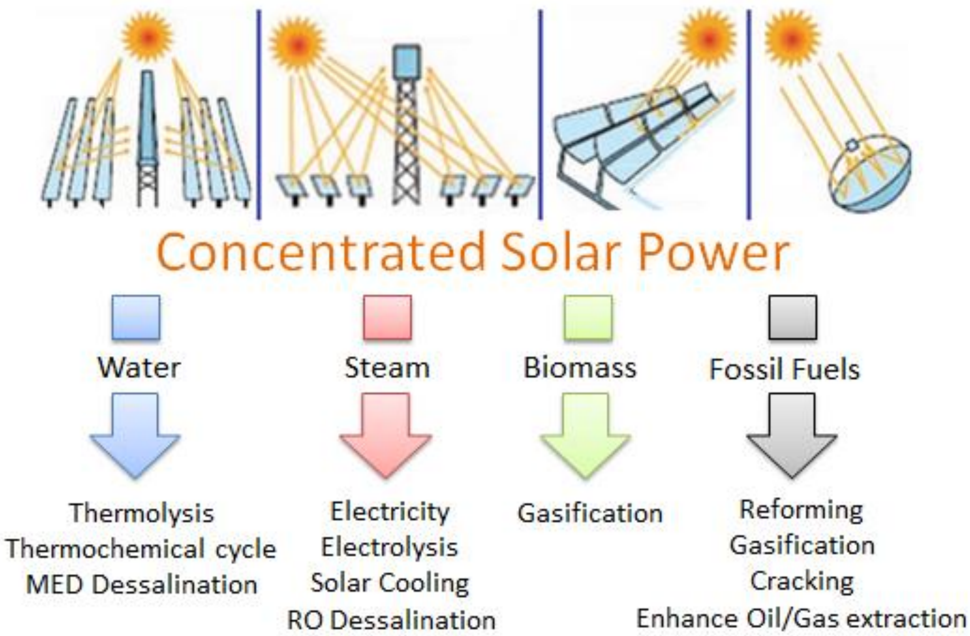

Fig. 1-4 – Process Applications using Concentrated Solar Power as an Energy source

Apart from producing electricity via thermal (STE), concentrated solar power is a highly interesting R&D topic since it can be used for several other applications when coupled with water, steam, biomass and fossil fuels, Fig.1-4. An interesting example is oil and gas enhanced extraction by means of introducing solar generated steam in the reservoirs to increase its pressure in order to further extract fossil fuels. A demonstration Project in Oman shows that both from a technical and cost perspective for this application it makes more sense to use solar energy than the also locally available gas [12]. Many other interesting applications can be thought of, including processes that need temperatures above 1000ºC, a feature possible today with focal point systems.

1.4 Worldwide Energy Storage Perspectives

Energy storage is a key issue on a dynamic energy system where supply permanently has to meet the oscillations of a variable demand load. For mobility purposes, most vehicles use fossil fuels (gasoline, diesel, LPG, av-jet, etc.) that come from refineries by pipeline or lorries, are stored in gas stations, and later on as chemical energy in the tank of cars, boats, trains and airplanes. This fossil fuel network with large storage facilities (for raw material 90 days consumption is the usual stock) was a large investment made in the past in most OECD countries.

Energy storage technologies available for large-scale applications can be divided into four types: mechanical, electrical, chemical, and electrochemical.

With the “electrification” trend in the industry, transportation and heating (e.g. heat pumps) sectors, for efficient grid management, storage that can be integrated into the electricity grid is becoming an important asset. Reverse-pumped hydropower accounts for 99% of the worldwide storage capacity of 127 GW of discharge power, and Compressed air storage (CAES) comes with 0,44 GW in a distant second place. These two technologies dominate in the MW range. In Europe, 10% of the total electric power delivered uses some form of energy storage, in Japan 15%, while in USA only 2,5% [13]. The trend is showing a clear need for additional storage in order to give stability to the grid, enable peak shaving and stabilize energy acquisition costs. Electrochemical storage shall play a more relevant role in the future, going along the growth in sectors like residential PV and ECV broader usage. In this field several technologies are competing, both from a cycle charge/discharge efficiency as well as cost. Current energy density for Li-ion batteries are ca. 250Wh/kg, with a forecasted increase up to 400Wh/kg. Solutions with Lithium and air batteries could achieve up to 1000Wh/kg, however major technical constraints seem difficult to by-pass. Other solutions at a lower cost like $Na\text{-}O_2$, might become an interesting alternative.

For Windpower parks, CAES has been studied and some projects have been implemented, however only seldom is a geological site available with suitable location nearby, making it difficult to become a mainstream solution.

For STE, 90% of the commercial plants that have storage use molten salts, up to now a binary mixture of 60%NaNO2 and 40% KNO2 is the current standard, however ternary and quaternary mixtures which have been formulated and validated at lab scale, may present an alternative for the future, especially if the whole system is optimized and a lower LCOE is achieved.

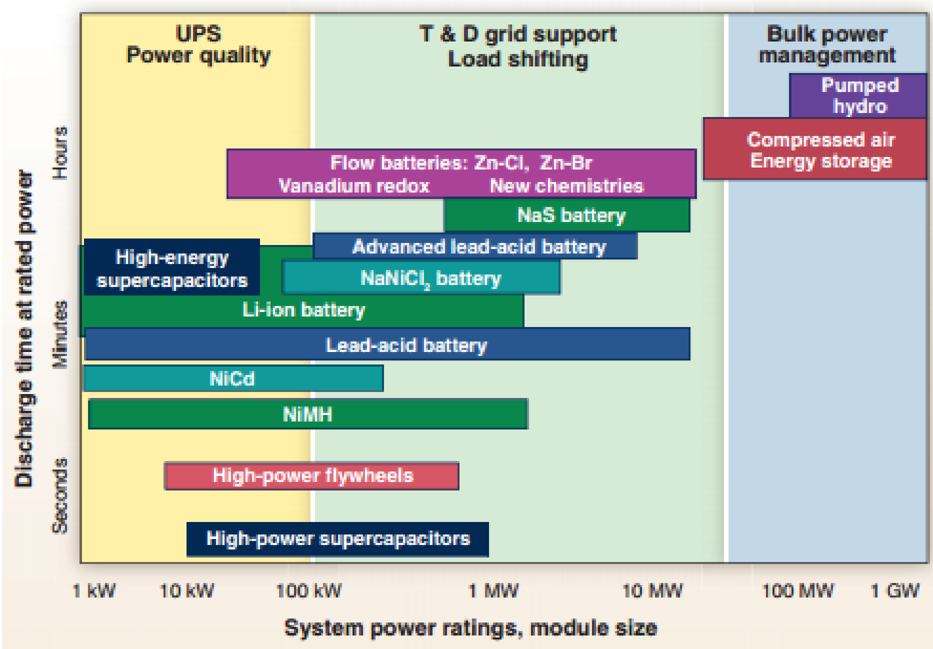

Fig. 1-5 – Energy Storage Technologies, discharge time and power ratings [13]

1.5 Objectives and Methodologies

A general objective of this Thesis is to find ways (technologies, operation guidelines, fast market deployment) to increase the attractiveness of STE technology, to make it an interesting and even a natural choice in many parts of the world where solar energy is abundant. To achieve that aim, several objectives have been pursued:

<u>1st main objective:</u> Designing a new STE plant with a lower LCOE

To make STE more competitive against other technological options, LCOE should decrease by means of technical component improvement as well as an overall new plant design/concept.

As a starting point, the Fresnel concept was selected due to the potentially lower CAPEX/MWe and for its good potential of performance increase.

Methodology: Several technical features have been studied namely:

- Optical optimization of the primary mirrors, starting from the LFR basic concept (a topic pursued by another researcher [7]) at the University of Evora (RE Chair)
- Optical optimization of the secondary mirrors, developing new concepts as the CLFR-EM and SMS XX (a topic pursued by another researcher) [7]
- Increase of the operating temperature validating the usage of molten salts up to 565ºC
- Develop operating strategies for the usage of molten salts as a HTF in a Fresnel type collector

These technical features have been simulated and evaluated using specific simulation software (ray tracing and TRNSYS), in order to predict the energy output, capacity factor and overall plant efficiency. Meteonorm weather data for Faro-PT and Hurgadha-EGP was used. For the techno-economic evaluation, SAM interface by NREL was used, to calculate the LCOE value.

2nd main objective: Storage material development

Existing heat storage material (HSM) were analyzed. Considering the requirements for the material thermo-physical characteristics, a short list of alternative materials was elaborated. It became clear that to increase the concept sustainability, usage of local materials should be considered as part of the storage mix concept.

Methodology: HSM literature review, followed by an analysis of local suitable material that could be used as part of the overall concept. Selected materials included several molten salt mixtures and solid material (rocks). A binder was developed to create a new material that would be in contact with molten salts. The materials selected went through a process of testing simulating thermal cycles in the range 290-550ºC, and finally, from the experimental work, several techniques were used to characterize the findings, namely:

- Compressive strength
- Ultra pulse velocity
- Microscopy SEM/EDS
- XRD analysis
- Chemical analysis
- DSC and TGA
- Mass loss and mass change
- Thermal conductivity, diffusivity, heat capacity

3rd main objective: Incorporation of local materials to solve an environmental problem

Renewable energy should be supported by a strong commitment of preserving local resources (clean air, water, raw material), in order to become both a global solution and to have a significant local impact. For this reason local available materials that could be used as a HSM were analyzed, namely materials that had no longer an economic value, which could become a twofold advantage. On one hand re-using a material no longer needed and, besides, with a substantial contamination potential and, on the other hand when the acquisition cost is zero (or, even belter, when there is a price a price to pay for environmental impact) it would contribute towards the LCOE reduction objective. In Alentejo, south of Portugal, there are several quarries which have produced a significant amount of residues (on average 70% of the material extracted) as well as mine residues from former extraction of Copper, Gold, Zinc, Sulphur.

In the Alentejo region, south of Portugal, cartography of old mine sites and quarries was studied specially in the Iberian Pyrite belt geological zone, which included visits and sample collection to several of them (Lousal, Canal Caveira, São Domingos, Beringel). After a first analysis it became clear, that the most severe environmental problem of all locations was in São Domingos, a mine that was closed in 1966 leaving behind several million ton of residues in an extension of more than 10km polluted soil and water streams, and thus the material selected for deeper analysis was a local abundant residue identified as “modern slag”.

Methodology: samples from three different locations within the São Domingos area were collected. All of them corresponded to “modern slag”, however dumped at a different time and place. These samples were then separated according to its grain size, and different incorporation rates were tested, in order to use it as an aggregate of a new mixture using a CAC base cement. Cylindrical samples were casted and put in contact with molten salts for thermal cycles in the range 290-550ºC. To characterize the mixture, several techniques were used, namely:

- Microscopy SEM/EDS
- Chemical analysis
- Thermal conductivity, diffusivity, heat capacity
- Crack analysis

4th main objective: Development of a scalable concept with fast deployment into the market

A new concept is more relevant, as it is scalable and easy to be implemented globally. That focus was there from an early stage, which led to a modular concept, where capacity can be easily increased with time and CAPEX can be divided into several years. A broader energy transition model was also developed, where technological improvements like the ones dealt in this work, are just a small part of a bigger and global framework.

Methodology: Discussion with industry partners about which solutions could be implemented on a real power plant, and what steps would be needed for a fast technology deployment. With this aim, a consortium was put together, with all necessary expertise in order to develop an extensive project with the aim of validating the new storage concept.

1.6 Structure of the Thesis

The work developed in this thesis is organized in the following way:

Chapter 1, Introduction: describes the motivation that led to the development of this work, stating the problem as well as the research questions dealt with.

Chapter 2, State of the Art: A technical review concerning STE technology and energy storage is performed, identifying the main technological constraints and current innovation areas.

Chapter 3, Energy Transition Model: The energy transition model is explained with its different mechanisms, as well as giving application examples

Chapter 4, Fresnel SMS XX Plant Simulation: A new plant Fresnel type with optimized optics, Molten Salts as HTF is simulated using TRNSYS/SAM considering storage and two locations

Chapter 5, Molten Salt loop validation: Experimental values (temperature, flow, pressure) are analyzed from a research campaign performed at an R&D Parabolic Through loop

Chapter 6, New storage concept: A new thermocline tank concept (HTLT) is presented to be coupled to STE plants using direct Molten salts both as HTF and HSM

Chapter 7, Material development - slag incorporation: The reasoning and technical background for the incorporation of old mining residues from *Alentejo* region is discussed

Chapter 8, Material development - new cement based mix: New mix development and tests performed is presented, based on cement CAC type with and without the incorporation of slag

Chapter 9, Material development - new mix in contact with Molten Salts: Tests performed using the new mix in direct contact with molten salts are presented

Chapter 10, EMSP loop development: Projects (HPS-2, PreFlexMS, INNOVLFR, LATENT, STOREMAT,) related to foreseen future developments of the EMSP site are presented

Chapter 11, Conclusions: Overall achievements and answers to the research questions are presented, as well as an outlook of future research topics

For the above work to be possible, many contributions were highly valuable, namely the ones enabling experimental work relevant for the content of different chapters. Therefore, I shall acknowledge and express my gratitude to following entities and persons for the meaningful discussions and support provided throughout this thesis: LNEG (T.Diamantino, A.Vieira, J.Cardoso, R.Tarouca, S.Casimiro, P.Azevedo), UniEvora (D.Canavarro, J.Marchã, A.Correia), DLR (M.Wittmann, M.Grünefeld, T.Bauer), ENEA (W.Gaggoili, A.Primo), CSIC (M.Alonso), ETH (A.Steinfeld, R.Castro), SENER (J.Burgaleta), SINTEF (H.Justnes), YARA (E.Iglesias, W.Franke), ACCIONA (J.Vera).

1.7 Publications

The work developed along the chapters in this thesis resulted in a number of publications which included conference presentations, journal and policy papers, as well as several R&D projects and patent application, all summarized in the following table.

Table. T1-1 – Publications resulting from work developed in this thesis

Chapter	Paper	Title	Published in / status
2	XII	Storage Technologies challenges and opportunities for CSP	In preparation*
3	V	Resources and Energy LTG Whitepaper	LTG Proceedings 2013
3	XIII	Energy Transfer Model, a new global energy framework beyond 2020	In preparation*
3	IX	Energy and Environmental reform in EU – path after 2020, a Policy Paper to ALDE	ELF 2015, ALDE Congress, Nov.2015
4	I	Increasing cost effectiveness of CSP technologies through the development of a new CLFR “etendue matched” collector	ISES Proceedings 2011
4	II	Increasing the efficiency of conventional LFR Technologies: A new CLFR “Etendue Matched” CSP collector	Solar Paces Proceedings 2011
4	III	Modeling Thermal Losses in a new CLFR-EM non-evacuated collector cavity	Solar Paces Proceedings 2011
4	IV	Energy storage for CSP plants, overview and detailed discussion of a storage system for a new Fresnel Plant	INNOSTOCK Proceedings 2012
4	VII	Efficiency improvement and potential LCOE reduction with an LFR-XX SMS plant with storage	Energy Procedia 2015 – Vol. 69, p.868-878
5	VI	Energy output and thermal losses in a PTC molten salt test loop	Solar Paces Proceedings 2014
6	XIV	The Hybrid Thermocline Layer Tank (HTLT): A novel concept to improve Thermocline type tanks	In preparation*
6	Patent ap.	Hybrid Thermocline type tank w/ well defined solid and fluid layers	submitted to INPI, 2015

6	Patent ap.	Thermal Storage with hybrid sensible and latent heat modular units (encapsulated PCM type)	submitted to INPI, 2015
7	X	New Materials for thermal energy storage in Concentrated Solar Power plants	Energy Procedia 2016 – Vol. 88
8	VIII	Calcium aluminate based cement for concrete to be used as thermal energy storage in solar thermal electricity plants	Cement and Concrete Research, vol.82, p.74-86
9	XI	Energy Storage for Solar Thermal Electricity using Molten salts and Calcium aluminate based cement concretes	submitted to Solar Energy, 2015
10	Projects	HPS-2, PreFlexMS, INNOVLFR, LATENT, SOLSTICE	submitted to BMWi and H2020, 2015

NB: * Papers XII-XIV in preparation, include research performed during PhD period

1.8 Applied Research. The Renewable Energies Chair of the University of Evora – a comment on the background support

An essential part of work done in more fundamental research, is to produce bright ideas and concepts that can be further pursued and developed to a stage that companies find attractive enough to invest in their commercial application. All work done at the Renewable Energies Chair of the University of Evora aims at achieving that broad goal.

From the start the Chair understood the need to create the proper R&D infrastructure to be able to carry out work in the solar Concentration area.

Essential to the motivation for the work done in this thesis, is an important part of the Chair's plan, the Evora Molten Salt Platform (EMSP) located 10km south of Evora, belonging to the University and aiming at becoming a reference research facility in Europe, for Solar Thermal Electricity and thermal energy storage technologies. Currently the framework of a trans European cooperation in this area is being discussed in the EU-Solaris platform.

In order to enhance the value and research capability of the EMSP, the Renewable Energies Chair with the important help of the work described in this thesis, has defined, organized, and submitted several projects to the relevant financing institutions. Some of them involve as many as 15 partner institutions among universities, companies and research laboratories, meaning there is a broad team that needs to be coordinated and research aims harmonized. These projects are part of an expansion plan for the EMSP and its capabilities, in order to make it a world class research facility and a worldwide reference within Solar Energy. In Fig.1-6, the participation and own contribution in the projects elaborated is described. The author would like to express its gratitude for all the Partners involved in the different projects, for their professionalism and commitment, specially to DLR, ACCIONA, CSIC, LNEG and ETH, who made it possible for such big challenges to become a reality.

As a final and important note, while the work in this thesis was being carried out, the Chair managed to establish very important R&D agreements with top R&D institutions like DLR (D-Köln) and Fraunhofer ISE (D-Freiburg) and created a National Research Infrastructure for Solar Energy Concentration, INIESC, in collaboration with LNEG-*Laboratorio Nacional de Engenharia e Geologia* and selected for funding by FCT-*Fundaçao de Ciencia e Tecnologia*.

CLFR-EM Test Plant (2nd phase concluded in July 2012) 2011/2
Main Player: EDPi
Aim: design and simulate a new STE plant
Own contribution (6MM, 30%): thermal losses, storage impact simulation, NPV

Concentrator Test Platform (concluded in Sep 2015) 2012/3
Main Player: Fraunhofer Institut
Aim: design, specify and built a test platform 18*13m
Own contribution (4MM, 5%): oil loop technical spec, technical procurement

Parabolic Trough Oil Test Loop (FCT funding not approved) 2012/3
Main Player: Martifer Solar
Aim: commisioning of a 24m long oil test loop
Own contribution (2MM, 90%): oil loop quality check, project funding application

Molten Salt Test Loop (tests concluded in November 2013) 2013
Main Player: ENEA
Aim: validate operating conditions in a Molten Salt loop with 1 tank storage
Own contribution (3MM, 90%): test definition, result analysis

HPS-2 (waiting for BMWi funding) 2013/5
Main Player: DLR
Aim: finish Parabolic Trough Molten Salt loop (EMSP) with 2 tank storage
Own contribution (12MM, 80%): IP and CFA agreements, project funding application

LATENT (H2020 funding not approved) 2014
Main Player: Acciona
Aim: design, validate and build a concrete module storage
Own contribution (3MM, 90%): system design, test definition, project funding app.

INNOVLFR (H2020 short list approved, waiting for funding) 2014
Main Player: Solar EuroMed
Aim: design, validate and build a Fresnel XX SMS molten salt loop
Own contribution (4MM, 40%): adapt EMSP loop, thermal losses, project funding app.

PreFlexMS (H2020 funding approved, started June 2015) 2014
Main Player: Alstom
Aim: design, simulate and built a new Steam Generator for STE plants
Own contribution (2MM, 90%): test period definition, project funding application

STAGE (H2020 funded, started 2013) 2014/5
Main Player: ENEA
Aim: WP7 – Test and validate high temperature storage materials
Own contribution (2MM, 10%): test plan, material tests, state of the art

SOLSTICE (H2020 1st stage ok, waiting for 2nd stage) 2014/5
Main Player: Acciona Ing.
Aim: design, simulate, built a new Thermocline Tank and concrete storage module
Own contribution (10MM, 90%): test plan, material tests, project funding app.

SOLMAT (waiting for FCT funding) 2015
Main Player: LNEG
Aim: material research, design and build a dynamic test loop
Own contribution (2MM, 90%): design dynamic test loop, project funding app.

Fig. 1-6 – Project Participation in the period 2011/2015

1.9 References

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Chapter 2. Solar Thermal Electricity and the need for Solar Thermal Energy Storage

2.1 Solar Energy

Energy consumption more than doubled in the last 40 years, from all renewable energy sources solar energy has the highest potential do deliver energy both in the form of heat (heating or cooling systems) or in the form of electricity. Worldwide solar photovoltaic (PV) capacity grew by an estimated 40 GWp in 2014, slightly more than the previous year. Growth was strong in China (10 GWp) and Japan (9 GWp), with Asia alone responsible for 50% of the new solar PV capacity. United States accounted for 6.5 GWp installed, in Europe leading markets were Germany (2GWp) and UK also with 2GWp installed [1], capacity installed in Europe was 39GWp at the end of 2011 [2]. This progress is explained by a number of reasons: falling prices of PV systems (60% reduction in the last 5 years), feed-in programmes in several countries to foster initial market development, technological improvements.

On PV, the leading technology in making solar cells is crystalline silicon due to its high efficiency, which reaches 20% or higher in the case of mono-crystalline cells developed using the Czochralski process. However, due to cost reasons, researchers focus on reducing material costs using thin film technology (amorphous, CIS/CIGS, CdS/CdTe), since it uses less material and the layers are much thinner compared to mono- and polycrystalline solar cell thus lowering the manufacturing cost. In lab scale the best thin film technology achieved as much as 19%, silicon crystalline 25% and multi-junction cells with 236x concentration factor as high as 40%. Using Fresnel lens, concentrating the solar radiation in photovoltaic cells (CPV) is a way to reduce the amount of silicon while delivering more energy per area.

Solar heat has also been growing in Europe, however at a more moderate pace. In 2014, EU27 had 28GWth installed, representing 40 million m2 of solar thermal collectors mostly in small size systems up to 10kWth. District solar heating systems represent just 12% and are most used in counties like Denmark and Germany. Solar collectors have seen also interesting developments in recent years, like the Compound Parabolic Concentrator (CPC) collector, the evacuated tube collector, polymeric collectors with new features like transparent insulation and selective glazing.

Another promising field is Solar Thermal Electricity (STE), which has the advantage of being a dispatchable way of producing electricity since it can have storage facilities (being molten salts the most used media) for several hours of operation with very low losses in the storage system.

2.2 Solar Thermal Electricity

Parabolic trough technology is the dominant (>90% market share) solar thermal technology for power generation, that has proven long term (>30 years) commercial references since 1984 with the parabolic trough power plants commissioned in the USA, the SEGS plants of Krammer Junction and Harper Lake in California. These power plants were operating successfully from the beginning and were optimized to a high level within years. After a long period where there were no new commercial plants, since 2008 also new parabolic trough power plants have been put in operation (i.e. Andasol I-III, Alvarado I), specially in Spain because of a set of stable conditions that enabled long term planning and investment. Other technologies like Linear Fresnel or Central Receiver (tower) concepts were not as much developed on a commercial scale mainly because of nonscientific/technical reasons, i.e reasons connected with the capacity to get the right financing on the market, taking advantage of the past experience (Luz projects in the US, in the late eighties and nineties) and the reputation of reliability already associated with them. The situation is slowly changing and a larger percentage of the most recent projects use these other technologies.

At present several other solar thermal power plants are in the planning, design or construction phase, in markets as Morocco, South Africa, UAE or USA. From a historical and experience reason most concepts focus on thermo-oil as heat transfer fluid in the solar field. The maximum working temperature of the thermo-oil (usually VP-1) is limited to 395°C due to the thermal stability of the oil, which starts to degrade at that temperature. Therefore the live steam temperature is limited to about 375°C so that at a steam pressure of 104 bar a net efficiency of about 37% can be achieved in the power block.

In contrast to most other players the Italian industry has focused its research activity on the concept of molten salt as heat transfer and storage medium. Experiences from the “Solar Two” tower project built in the 80’s in Dagget, California in which this concept was technically demonstrated between 1996 and 1999 at a 10 MW scale have shown a certain vulnerability to technical failure but also indicate solutions on how problems can be solved. In 2011, a consortium with the name Gemasolar started to operate a technically revised follow-up plant (19MWe electric power, 16h energy storage, 3 times larger solar field than Solar Two) using Solar Salt as the heat transfer. In 2012, a 5MWe parabolic through plant was developed in Priolo Gargalo, Italy coupled to an existing combined cycle plant. In 2013, an Italian/Japanese consortitum inaugurated a molten salt test loop in Massa Martana, Italy, where new receivers specially for molten salt will be investigated and further developed. In 2015, the design of a test loop using Fresnel collectors and molten salts as a heat transfer medium is being planned in USA by Sandia, confirming the broad interest that molten salt technology is achieving.

2.3 Energy storage

Energy storage emerges as an obvious need, to enable a more dependable energy delivery from an energy source that varies during the day / night cycle, with season, and with the local climates and their random impacts on the available sunshine.

In particular for the topics addressed in this thesis related to the production of Solar Thermal Electricity, Energy Storage emerges as a very powerful way of generating true dispatchability in conjunction with solar thermal systems, at a potentially low cost. In this respect it creates an advantage (rather a true complementarity) when compared with PV (photovoltaic) today.

There is a wide variety of Energy Storage systems. Generally can be dived into the following categories:

- Mechanical storage systems (e.g. compressed air);
- Thermal storage systems (e.g. ice storage);
- Electrochemical storage systems (e.g. batteries);
- Chemical storage systems (e.g. hydrogen);
- Magnetic storage systems (e.g. superconducting magnetic);
- Biological storage systems (e.g. glycogen);

2.3.1 Mechanical storage

Energy storage using compressed air CAES is a well established technology, the first utility-scale project in Huntorf, Germany started in 1978. It is a 321MW plant which takes 8 hours to charge. The energy stored allows its generators to run at full capacity for 2 hours. At peak hours the air is drawn out and combusted with natural gas before passing through a turbine to generate power. The plant reports a cycle efficiency of 42%. In USA, McIntosh, Alabama there is a similar plant with 110MW capacity and an efficiency of 54%. At both plants compressed air is stored in existing underground salt caverns, which is a very limiting fact for further deployment of this technology. Nevertheless in the USA, there have been built several installations coupled to wind power sites.

2.3.2 Thermal Energy storage

For solar energy systems, the most used technology is thermal energy storage. This can be done in three different ways: sensible, latent heat (phase change) and thermo-chemical storage. Sensible heat storage, supplying heat to a fluid or a solid which is then well insulated is the most used, however, research is being performed in order to achieve a more compact way of storing energy.

	Sensible	Latent	Chemical	
Volume	120	60	12	m^3
Density	110	250	500-3000	MJ / m^3
	31	70	140-830	kWh / m^3

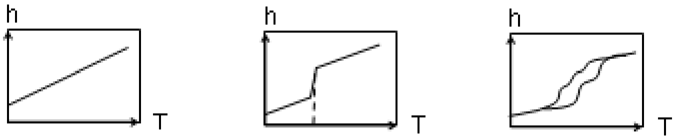


Fig. 2-1 – Heat storage principles: sensible, latent and chemical heat with typical volume and density

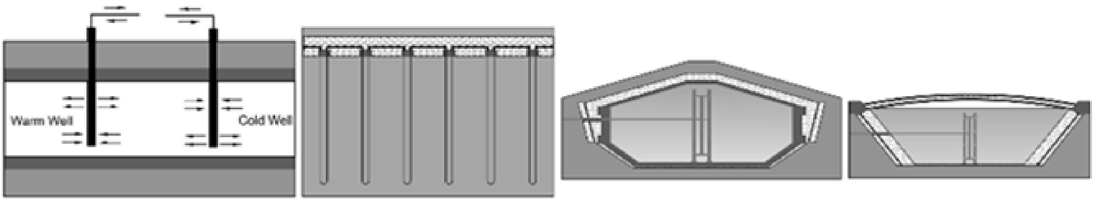
The specific application is depending on the functionality namely the following criteria:

- Charging and discharging Power;

- Temperatures;
- Storage capacity;
- Storage density;
- Efficiency (heat transfer, heat loss, auxiliary energy);
- Resource availability;
- Load;

The majority of recent improvements has been done in the fields of basic material R&D improving the material fit to a specific application, as well as in the testing of components such as reactors, heat exchangers and encapsulation. Additionally, at system design level planning and demonstration projects have been built and monitored in the last 20 years. specific investment cost of water seasonal storage systems has been decreasing from 450 Euro/m^3 down to 50 Euro/m^3 for installations built in Germany, main examples include Friedrichshafen (158 Eur/MWhth), Neckarslum (172 Eur/MWhth) and Crailsheim (190 Eur/MWhth). [3]

Storage technology	Advantages	Disadvantages
Aquifer TES	Based on a natural aquifer layer	Needs confining layers (top, bottom)
Borehole TES	Modular design	Lower heat capacity than water Drilling costs (30-200m deep)
Water tank	Independent of geological conditions Good thermodynamic	Construction costs Thermal losses
Water / gravel pit	Low influence of geological conditions	High cost for sealing the pit



Aquifer TES Borehole TES Water tank Water / gravel pit

Fig. 2-2 – Sensible heat systems: large seasonal storage

2.3.3 Electrochemical Energy storage

Batteries, depending on its chemistry can be divided into: aqueous, non-aqueous, Lithium or Sodium based. They great advantage is that they are rechargeable, storing energy within the electrode structure through charge transfer reactions.

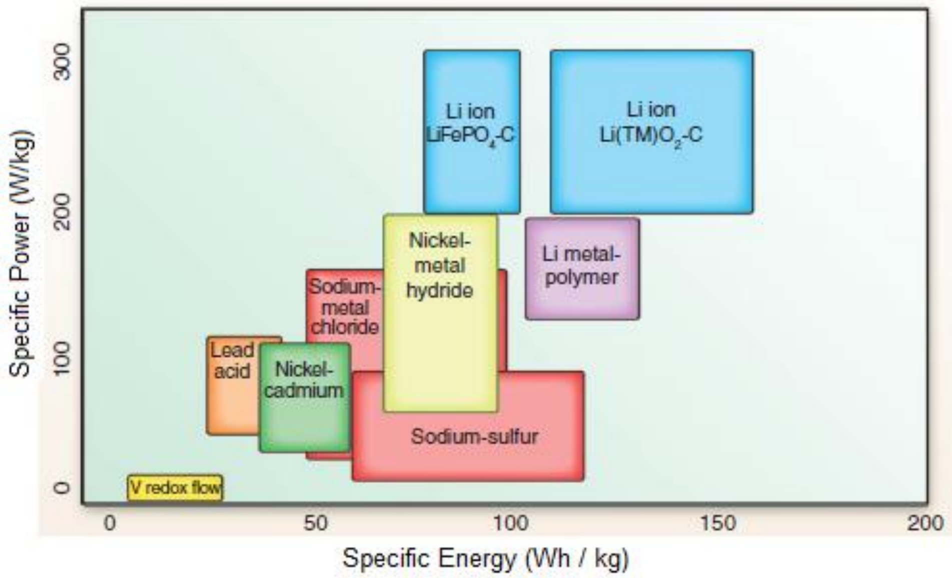


Fig. 2-3 – Energy and Power density for batteries [4]

The current prevailing technology is Li-ion battery technology based on the use of Li-intercalation compounds: Li ions migrate across the electrolyte located between the two host structures, which serve as the positive and negative electrodes. Li-ion batteries outperform, by a factor of 2.5, technologies like Ni−metal hydride, Ni-cadmium and Pb−acid) in terms of delivered energy and with a high specific power. The merit comes from its low molecular weight; small ionic radius, low redox potential (E°(Li+/Li) = −3.04 V) and a long cycle life. Li-ion batteries have experienced further technological development by controlling particle size in addition to composition, structure and morphology in order to design better electrodes and electrolyte components. Additionally, carbon-coating approaches to achieve core-shell morphologies has led to new directions in electrode materials. Currently energy density lies under 200 Wh/kg, however for electrical vehicles applications a target of 400 Wh/kg to be achieved by 2017 was set by JCESR. One way is using super computers to simulate the innards of possible new batteries, trying to find a combination of electrodes and electrolytes that will allow other elements like magnesium to pass through more easily.

A more ambitious target of 1000 Wh/kg is said to be possible to be achieved via oxidation of lithium with oxygen drawn from the air. Such beyond of technology batteries have an enormous weight advantage over other types, because they do not have to carry one of the main ingredients. A lithium–oxygen (Li–O) battery could eventually, store energy as densely as a petrol engine, that is more than ten times better than today's car battery packs. However, up to now, there has been no way to overcome one of the unwanted side reactions: carbon in the electrolyte and electrode material react with the lithium and oxygen to form lithium carbonate, so that in every cycle, some 5–10% of the battery capacity is lost.

2.3.4 Energy storage with Molten Salts

Mollten Salt as an alternative heat transfer media for linear systems shows an interesting potential for lowering the levelized cost of electricity (LCOE). [5, 6] described that a reduction of LCOE greater than 10 % depending on the temperature range and salt mixture is possible.

Current plants that have storage capability, have a hot and a cold tank which is connected via heat exchangers to the primary loop where thermal oil flows up to 400ºC. A further development would be the existence of only one tank, where thermal stratification would occur so that in the same tank both cold (in the bottom) and hot fluid (in the top layer) co-exist. Several tanks have been modeled, however only the Solar One facility in Degget, USA has performed experimental research that is currently used to validate such a solution.

Oils for heat transfer and storage have been used in the past, but these fluids suffer from a number of disadvantages including high cost, flammability, low boiling points and environmental hazard (including explosion risks). MS are more viable HTFs as they can operate at temperatures of up to 450-600 °C. In addition, MS are cheaper than synthetic oils, non-flammable, and non-toxic, but there is a lack of experience using MS both as Heat transfer and Storage media.

Currently, the maximum temperature allowable is one of the current limitations to the increased potential of CSP-storage plants. For example at Andasol (Spain) a non-eutectic MS mixture with 60wt% sodium nitrate (NaNO3) and 40wt% potassium nitrate (KNO3) is used. There is limited information about long term durability and the extent of the problems that could arise after 30 years of operation. Potential alternative candidate salts include the ternary reciprocal system K,Na/NO2/NO3 (including a mixture called Hitec Tm ~140 °C) and the ternary additive systems Ca,K,Na/NO3 (including a mixture called HitecXL Tm ~130 °C). Experience of the HitecXL mixture is limited to labscale experiments, where advantages in terms of costs and toxicity have been identified. All new molten salts mixtures need to be fully characterized in terms of its thermal stability and thermo-physical properties, namely to define the temperature range in which they operate without degradation.

In order to reduce costs of the storage system the thermal stability should be as high as possible and the melting temperature should be as low as possible: A high thermal stability not only increases the usable temperature range (proportional to the storage capacity) but also increases the efficiency of the conversion of thermal energy into work. A low melting temperature is required to increase the usable temperature range as well and additionally prevents freezing of the salt which could destroy the system. Therefore the development of alternative molten salts is essential. The incorporation of LiNO3 or CsNO3 has been identified as being beneficial for the overall mixture stability with a lower fusion point. However they are considerably more expensive than the Solar Salt, in the case of LiNO3 the cost per mass unit is about 10x higher than solar salt.

Other materials have been investigated in the past like liquid sodium of solid materials like concrete. Relevant issues to consider are container thermal stress durability and chemical induced attack of MS to the container. In the past OPC based concrete, as solid storage media, has been developed and validated up to 400ºC by DLR [8]. Recently, concrete based on CAC was investigated achieving stability at temperatures above 500ºC [9]. OPC and CAC concretes with inclusion of mineral admixtures have been tested up to 580ºC even in direct contact with MS. CAC concretes for structural components of the MS tank container showed good stability, tests in presence of MS have been positively evaluated.

$LiNO_3$	$NaNO_3$	KNO_3	$Ca(NO_3)_2$	-	Liq. T	
mol %	mol %	mol %	mol %	mol %	°C	
	50	50			223	Eutectic $NaNO_3$-KNO_3
	66	34			237	Hitec® Solar Salt
	7	44		49 $NaNO_2$	141	Eutectic comp. Hitec® HTF
	21	49	30		133	Eutectic comp. Hitec® XL
30	18	52			120	Eutectic $LiNO_3$-$NaNO_3$-KNO_3
31		58	11		117	Eutectic $LiNO_3$-KNO_3-$Ca(NO_3)_2$
31-27	20-11	38-50	12		<95	US 7,588,694
15	10	30	15	30 $CsNO_3$	65	J. W. Raade and D. Padowitz (Solarpaces 2010)

Fig. 2-4 – Molten Salts mixtures investigated for STE

Storage Medium	Sand-rock Mineral Oil	Reinforced Concrete	Nitrate salts	Carbonate salts	Liquid sodium
Temp. (cold) (°C)	200	200	265	450	270
Temp. (hot) (°C)	300	400	565	850	530
Avg. density (kg/m^3)	1700	2200	1870	2100	850
Avg. thermal conductivity (W/m K)	1.0	1.5	0.52	2.0	71.0
Avg. heat capacity (kJ/kg K)	1.30	0.85	1.6	1.8	1.3
Volume specific heat capacity (kWh/m^3)	60	100	250	430	80
Cost per kWh (US$/kWh)	4.2	1.0	3.7	11.0	21.0

Fig. 2-5 – Storage Media for STE plants [7]

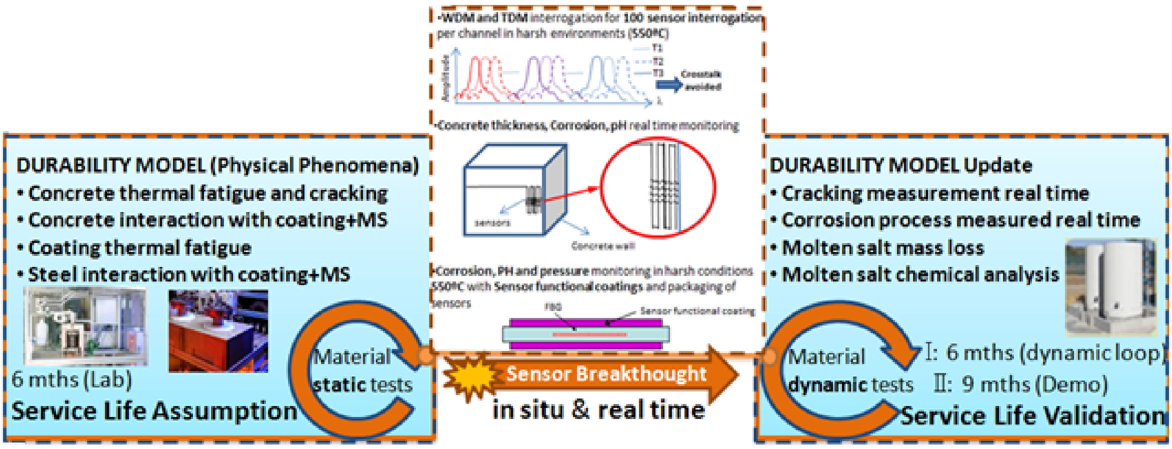


Fig. 2-6 – Durability Model scheme

For higher temperature applications chloride mixtures and halogen salt mixtures are suitable candidates as an alternative which feature thermal stabilities in the range up to 1000°C. However, the melting temperatures of reported mixtures exceed typically 400°C or contain expensive salts such as LiCl. Therefore the above mentioned chloride mixtures cannot fully replace nitrate mixtures in the common applications such as the two tank molten salt system with steam cycles.

In order to study in detail the advantages of an hybrid storage system (molten salts and solid material), the boundaries of a durability model have been established coupled with numerical analysis and also including static and dynamic tests. For this study to be performed, new developments in sensor and monitoring technology need to be performed. The result of this investigation will be applied at the future storage facilities of the EMSP, being storage a very important feature of the research facility.

2.4 Conclusion

The need for energy storage as a key element of renewable energy systems is explained in detail in this chapter. Energy storage emerges as an obvious need, to enable a more dependable energy delivery from an energy source that varies during the day / night cycle, as well as with the season and with the local climate.

There is a wide variety of energy storage systems. To produce solar thermal electricity (STE), molten salts are a suitable heat transfer media as well as heat storage media. STE plants with storage provide true dispatchability, at a potentially low cost. In this respect it creates an advantage when compared with photovoltaic systems.

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Chapter 3. Energy Transition Model

3.1 Transition is inevitable

Currently the carrying capacity of the Earth in terms of resources and energy usage is in danger due to the rate at which non-renewable resources are being depleted. Globalization of trade goods and persons fuels a further energy consumption increase. Due to population growth, finite availability of resources, and emissions associated to fossil fuels, in the long-term renewable energy sources are the ultimate source for energy, and for that reason Humanity will see a strong transition into renewable based energy systems. Transition is inevitable, but when?

A transition implies a strong increase on energy efficiency usage, and a drastically reduction on the reliance of fossil fuels. In addition, the existing stock of minerals must be used in the most efficient manner, emphasizing recycling and reuse, to minimize depletion. This will lead to a state where no more raw materials are extracted, but rather all the materials on the lithosphere are reused.

This change will need major and sustained investment in clean technologies: the increase in public and private investment in EU is calculated to amount to € 270 billion annually for the next 40 years [1]. On the other side, energy efficiency and low carbon economy shall reduce EU's average fuel costs by a value estimated in the range 175 to 320 billion Euro per year[1], thus, savings could eventually set aside enough resources to finance the transformation.

3.2 Simulating the World

Starting in the 1970s, a number of world-scale models about the world economy were developed. Perhaps the most famous is “The Limits to Growth” (LTG) by Dennis Meadows in 1972 [2], aimed at describing limitations to economic growth imposing environmental constraints and on resource availability. The so called World3 model was developed with 13 sub-sectors. It included detailed aspects of human society and its interaction with a resource limited planet, updates to the model were done in 2004 and 2012. In 1977, Leontief [3] developed a model to evaluate ways of closing the gap in material well-being between rich and poor countries. The close relation between linear models and the economic theory had been described in the 1950s, in fact for every linear program where the decision variables have a physical interpretation, there is a dual program whose decision variables, one for each constraint have a price interpretation. One can solve these programs for optima to linearly constrained problems, in particular identifying the lowest-cost allocation of resources among competing uses, for instance on international trade flows. Later, the World3 model was adapted into Modelica environment and different LTG scenarios have been tested and compared with historical data [4].

In this version, both natural resources and pollution models were upgraded by including changes in technology as factors influencing the depletion of resources and the release of pollutants. This is meaningful as improved technology may enable us to use the available resources more efficiently, and may also make it possible to produce goods in a cleaner way and delay a depletion scenario. In World3, the formula for calculating the amount of time left for a resource with constant consumption growth is [1]:

$$y = \frac{\ln((r \times s) + 1)}{r} \qquad \text{(Eq. 3-1)}$$

y = years left

r = 0.026, the continuous compounding growth rate (2,6%)

s = static reserve, ie. = R/C

R = reserve

C = annual consumption

This leads to consumption exponential growth curves, followed by a peak and collapse. Meanwhile, some authors tracking the LTG BAU scenario with historical data 1970-2010 (Fig. 3-1) argue that the collapse is imminent [5]. How could it be avoided? According to the World3 model, an option is an aggressive technology development and fast market deployment plan:

• Increased industrial resource efficiency, i.e., a reduction in the use of non-renewable material and energy, a 4% resource decrease/year.

• Arable land protection, e.g., to decrease and prevent land erosion

• Agricultural yield: a 4% increase/year.

• Pollution reduction: a 4% decrease/year.

This scenario (nr.9) assumes a capital cost to implement these technologies, and that 20 years are required for their full implementation.

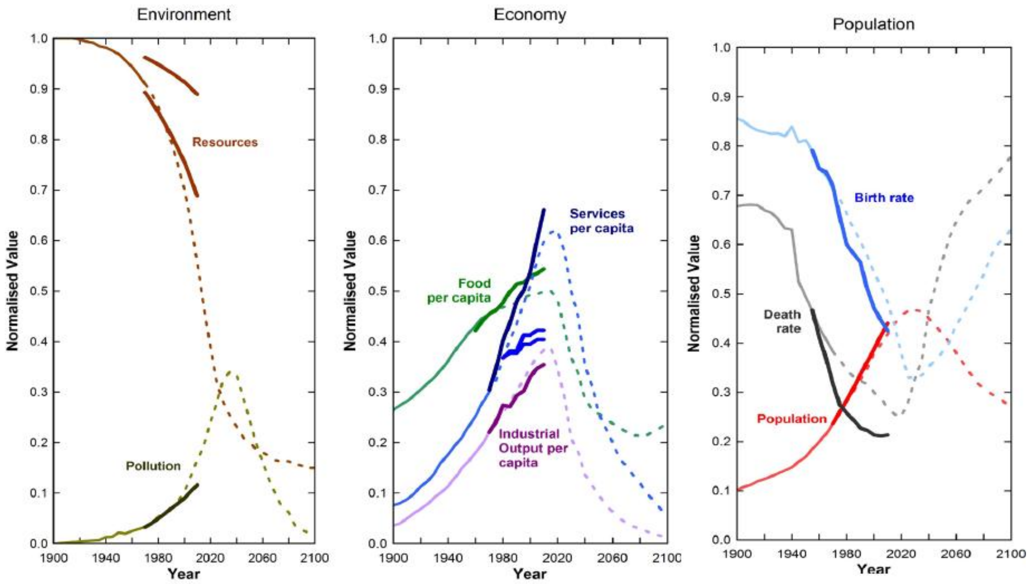

Fig. 3-1 – LTG scenario BAU versus historical data 1970-2010 [5]

3.3 Policy Scenarios

From the model outputs, many alternatives might be taken, since one overall goal like having zero CO_2 emissions in 2050 has many alternative scenarios that need to be implemented according to specific policies. For a global decarbonization process, four main scenarios can be thought:

1. Top–down scenario-based back-casting e.g. begin by selecting a proposed target for final decarbonization, then pre-select a portfolio of eligible low-carbon technologies.
2. Top–down integrated assessment modeling approaches utilize integrated models of the climate and economic systems of varying detail
3. Bottom–up energy systems modeling approaches use relatively detailed representations of the energy system to construct scenarios capable of achieving normative decarbonization goals.
4. Bottom–up technical or techno-economic assessments start with comparative rankings of various decarbonization technologies (ranked by cost) and/or opportunities.

Choosing one or the other approach is more a political than a technical choice.

3.4 The moment for a change is now

In terms of non-renewable resources, current extraction levels lead to a depletion of several raw materials and fuels within the next decades. Apart from a physical limit, due to increasing demand there is also a cost issue, making resource unavailable *“de facto”* to many entities much before its depletion moment.

Nowadays, a sense of crisis is spreading mainly in the developed societies, where the economy stagnates after years of remarkable GDP growth, while emergent economies like China or India (still) show high growth rates. Commodity prices rise significantly endangering current living standards. Environmental concerns rise in a global world, which faces tremendous difficulties to address global problems like the greenhouse gas emissions, deforestation or water scarcity. This crisis can be the decisive moment for a change into the way of thinking, and the move into a transition mode.

At COP15 in Copenhagen, Dec.2009, world leaders agreed that global average temperature should not rise more than 2°C, accordingly the IEA established technological plans and roadmaps until 2050 to fulfill that goal. Today, countries representing more than 80% of global emissions have pledged domestic targets in line with COP15, COP16 Cancun and COP21 Paris agreements, however a common overall agreement how to implement it is still lacking.

3.5 Pillars of the Energy transition model

After evaluating which parameters are relevant for several scenarios, a transition model based on a holistic strategy of resource and energy efficiency was developed during the course of this thesis. It is based in 3 pillars:

(a) per capita pricing category caps of resource use (demand side management)

(b) industry transition into clean technologies (supply side management)

(c) technological efficiency improvements (supply side management)

The aim is to become an effective system to achieve a sustainable level of usage of existing natural resources, together with the development of new sources based in renewable energy, and addressing the rebound effect, while improving human wellbeing equitably.

A possible path is proposed using three mechanisms:

(a) Societies determine and implement optimal levels of resource use per capita (a pricing cap system), taking into account socio-economic (defining a country base well being line and a poverty line) and political considerations at all levels wherein inefficient resource consumption leads to a redistribution of economic wealth towards disadvantaged groups within society (with the possibility of trade). A top down approach to contain global consumption and avoid waste.

(b) Economic incentives to environmental beneficial projects would enhance corporate transition towards clean production technologies, determined by a system-wide analysis of environmental, social and economic impacts along the life cycle, on a bottom up project perspective

(c) Investments into increasing production efficiencies shall be done by using a combined environmental burdens approach to assess production and use of products tied to caps for each with revenue being redistributed towards “low-impact” goods.

All these mechanisms are based on closed loop systems, in a way that the resources generated are clearly identified where the investment will be made. These are no new taxes, they should be seen as energy transfer investments, collecting resources from poor energy efficient performance products and industries into clean tech.

3.5.1 Pillar 1: Pricing caps of resource use

Identify heavy consumers. Then, make a reduction plan with monthly targets. Heavy consumers will pay more per unit consumed, money that will flow into the area below the poverty line:

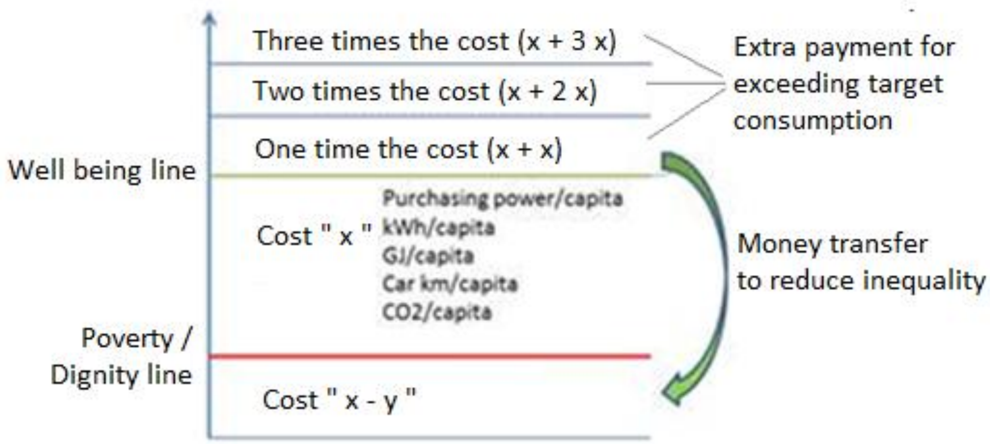

Fig. 3-2 – Pillar 1: Resource re-distribution

This system can easily be applied into energy bills, water consumption. A more challenging target would be to implement such a pricing per consumption level strategy towards the number of kilometers per polluting vehicle.

3.5.2 Pillar 2: Industry transition into Clean Tech

First of all, within each region (or country) it is necessary to Identify heavy consumers / industries that have a negative environmental impact. Examples can be in Norway or Nigeria the oil industry, in Brazil the Cement industry, in South Africa and Australia the mining industry. All environmental impact relevant industries from each country shall be analyzed and considered. Next, funds will be collected on a % of the revenues from those traditional industries, a 3% GDP reference is to be used as a default value, since according to IEA, this would collect enough funds for a decarbonized economy in order to achieve the 2ºC scenario. Clean tech projects (e.g. solar PV rural) would be financed in the same country/region using the collected funds, an example is shown in the next figure.

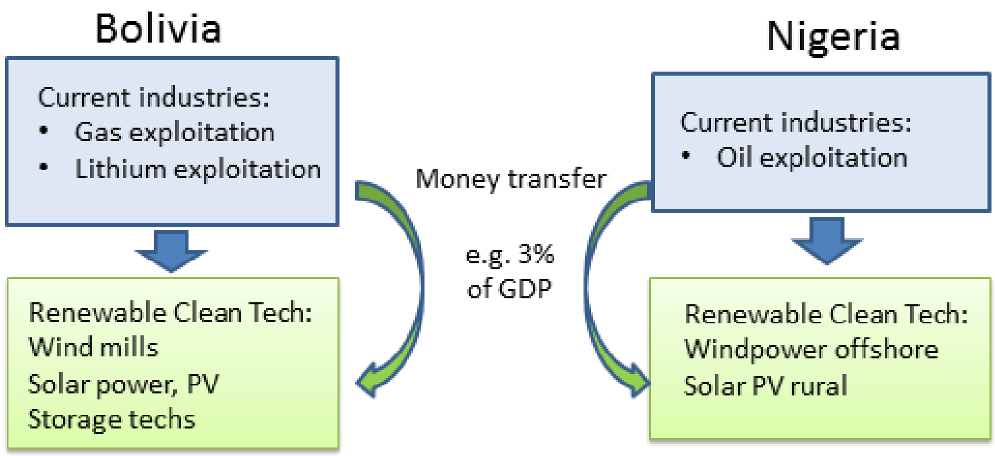

Fig. 3-3 – Pillar 2: funds transferred to clean tech projects, two national examples

The money transfer would be 3% charged of the revenues of the established industry (e.g. cement, pulp, oil). These industries are selected among those that have a higher negative impact on the environment and have a certain dimension. Project selection would be decided upon merit, on a bottom up perspective. Clean tech local projects (e.g. a solar thermal hot water unit in a pavilion that was previously using gas) would be financed this way, incorporating local materials and fostering local employment. Traditional companies can also create new companies that will be active within renewable energies and are eligible to be a project promoter, thus motivating established companies to join the investment in clean tech.

Considering the example of the oil sector in Nigeria which accounts for 11% of its the GDP, this is estimated to be 56320 Million Euro in year 2015, with a 3% money transfer 1690 Million Euro would be collected. These funds could be locally invested in Clean Tech projects like 675 MWp of PV installed or about 700MWe [6] in several Solar Thermal Electricity Plants.

3.5.3 Pillar 3: Technological improvements

The third pillar is related to technological improvements able to be achieved by manufacturers that invest in research and development. There will be limits, MEPS – Minimum Energy Performance Standards, both on the production as well as on the usage level side. These will be revised every 5-years after evaluating technological achievability on both axes depending on technological developments and resource re-usage availability.

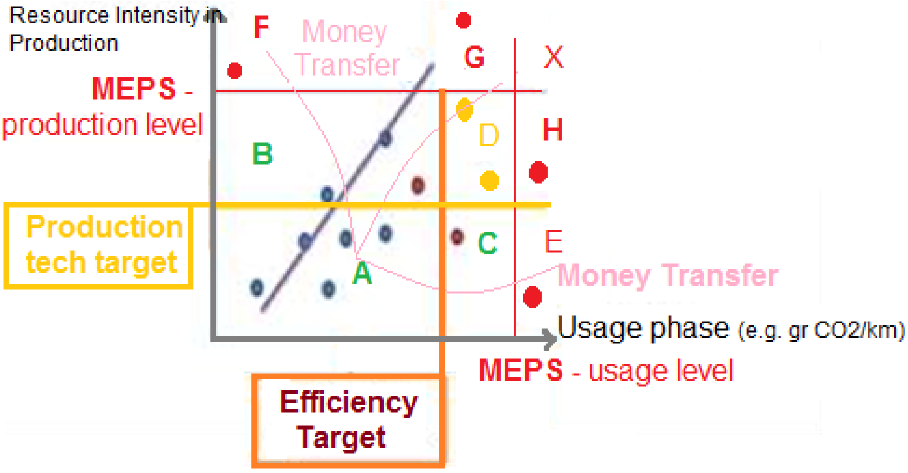

Fig. 3-4 – Pillar 3: technological MEPS with energy targets

In the mechanism proposed the efficiency should be achieved not only during the usage phase (like in the Top Runner [7]), but also on the Production side. An example for the car industry is shown for the usage phase (Fig.3.4, gr/CO_2 km), in this case a target which is already part of the EU CO_2 emissions target, and in line with the eco-innovation and super credits policies [8]. Above MEPS lines, standards are not met, and technology developments should take place or else, the products will tend to fade out of the market. There will be a money transfer (Fig 3.3, ie. a reduction in the acquisition price of products in region "A") of funds coming from an increase on the sales price of products in areas "D", "E", "F", "G", "H". Areas "B" and "C" meet one of the efficiency targets and thus are not subject to money transfer. Products in area "X" will be totally banned from the market within 6 months after last target revision process. This money transfer amount would be updated per category every month, so that price reductions on products from area "A" would be calculated with the funds made available from previous month. This way, a closed loop of revenues from a low performing into a high performing product is guaranteed avoiding new schemes of taxation. On the long run, only the best technological products survive, this analysis is to be performed by independent institutions and simulating real operating conditions. It shall be applicable to all products (imported or locally manufactured), only then would in the EU area the CE mark be given.

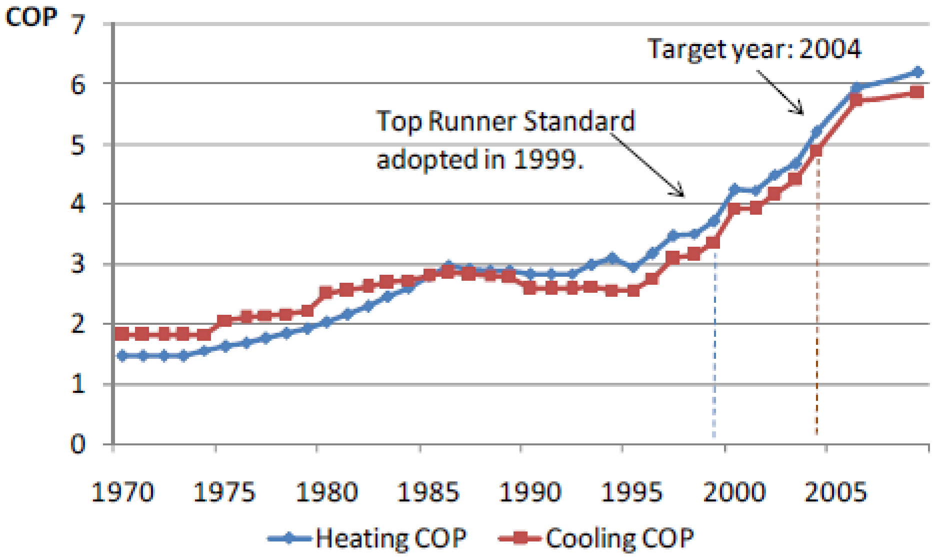

Fig. 3-5 –COP standard for heating and cooling applications, Top Runner Program [7]

3.5.4 STE as an example

A technological transition to occur via pillar 2, would make funds available for clean tech projects. These projects are selected within the clean tech area, according to its environmental and energy merit, but also the marginal cost of the technology, so that it can become mainstream technology.

One of the promising areas in energy production within renewables is solar thermal electricity (STE) with storage. By means of concentrating solar energy (by optical means), it is possible to achieve high temperatures in a stable way (550ºC or more) making it possible to use that available heat to make a turbine work with higher efficiencies than the ones considered at normal operative temperatures. This thermodynamic advantage of increased temperature (550ºC instead of 400ºC) by itself represents a gain of efficiency in the power block efficiency from conventional 35% to a value above 40%.

This field of research is recently being re-discovered after decades of R&D programs focusing on nuclear and fossil fuels. Research performed in recent years proved that it is possible to improve significantly the standard of the technique with recent discovered features for instance with developments in the field of the optics, material science and energy conversion.

This is the case of the evolution registered in the CSP field with the Linear Fresnel (LFR) concept. The initial simple focusing type of Linear Fresnel Collector, has evolved to advanced concepts incorporating second stage concentration (non–imaging optics) and an explicit concern for “etendue matching” for maximum optical efficiency, the CLFR-EM and the LFR SMS XX concepts [9].

This technological advance could lead to a lower LCOE cost. From an optical point of view a comparison made between Advanced LFR and PT (parabolic through) based systems, shows possible significant gains on energy collection and reduction of losses. For a detailed analysis, a study was performed in order to determine the energy production and LCOE of a LFR XX SMS 100MWe plant to be operated up to 550ºC. This study is reported in Chapter 4.

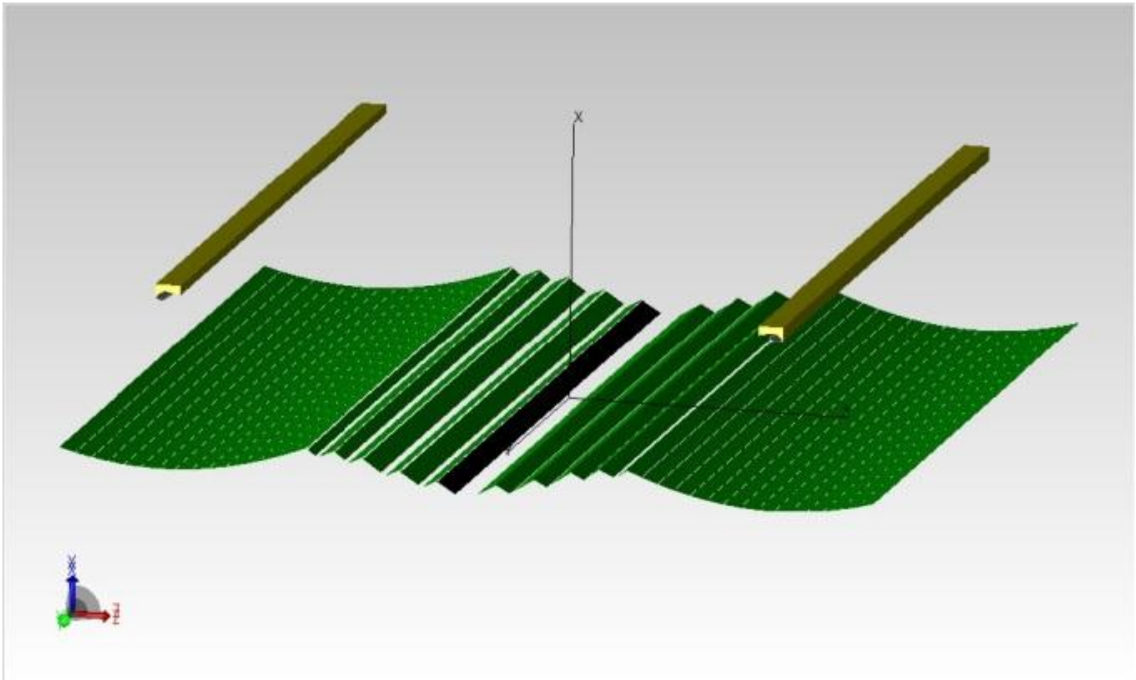

Fig. 3-6 – New CFLR-EM concept [9]

3.6 Conclusion

A smooth transition into a fully sustainable energy society is possible by means of improving energy efficiency, but also having limits on consumption in order to avoid the rebound effect. From the demand side management, this can be achieved by a pricing category with funds being internally transferred in a closed loop, that could refrain consumption of heavy users. Same methodology applies to industry transition and technological standards improvement towards energy efficiency and energy renewables development. These three pillars are part of an energy transition model proposed to be a force of change in current industry structure. This model to be most effective could be applied on a global scale or per economic blocks like EU, ASEAN, NAFTA countries. Levels would be adapted to each country specific situation with an update to be held every 5-year.
A new concept called LFR XX SMS is an example of projects that could be supported under such a mechanism. This concept will be studied more in depth in the next chapter.

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Chapter 4. Efficiency improvement and potential LCOE reduction with an LFR-XX SMS plant with storage

4.1 Linear Fresnel Systems using molten salts

For CSP plants with storage the most common storage configuration is the 2-tank indirect system which is connected to the solar field loop through a heat exchanger. This layout using thermal oil up to 400ºC in the solar side and molten salts on the storage loop became the standard not because it is an optimized solution, but for a risk aversion issue when planning recently built plants like Andasol in Spain, since there was knowhow on these type of systems in California, USA in the 80´s. For that reason and due to legislative 50MWe limitation in Spain, the design of most plants is very similar, as in the case of Andasol-1/2/3, as well as Termesol-1/2, Valle-1/2, Extresol-1/2/3 in Spain, Solana in the USA [2].

In Italy, the Priolo Gargalo 5 MWe plant is in operation since 2010, has a direct molten salt parabolic through system, using two tanks up to 550ºC. In Spain, Gemasolar with a direct molten salt tower system, up to 565ºC, in operation since 2011. Both plants show the possibility to successfully operate a plant with molten salt as the HTF at a considerable higher temperature than the standard 400ºC with thermal oil, which enables a higher conversion efficiency of the power block, increasing from 36-37% to 41-42% according to state-of-the-art turbines.

With the development of ternary and quaternary mixtures, in the future it is foreseen that molten salts will be more and more used as heat transfer fluid (HTF) also in the solar loop, both for Parabolic through collectors (PTC) and specially Linear Fresnel, since molten salts as a transfer media have a very interesting fit with Fresnel technology as presented in the following table.

Table 4-1. Comparison of Fresnel and Parabolic Through Collectors for usage with molten salts

Sub-areas	Fresnel – LFR	Parabolic – PTC
Heat Transfer	Usage of a secondary concentrator	Less impact of using a secondary concentrator
Concentration Ratio	Can be significantly increased by means of an optimized design primary + secondary (for instance the new LFR XX SMS)	Small efficiency increase possibility due to a higher impact of the shading effect of a possible second stage concentrator
Draining	Easy to drain since receivers are at more than 5m high	Difficult to drain since receivers are at a lower position and there are flexible movable parts
Joints	Receivers are fixed with no moving parts, easier Operation, less Maintenance costs	Receivers move according to solar tracking, higher Operation and Maintenance costs
Solar Tracking	Possibility to focus or defocus in small steps (move just a few primary mirrors) which enables a better control of the energy output and molten salt temperature	Only 3 modes possible: 1-full sun tracking; 2- partial following, 3- out of sun
Hydraulic circuit	Less receivers (higher concentration) and less piping (more compact) leading to lower losses	Higher pressure drop due to longer and more complex pipping system

4.1.1 Optical Efficiency Improvement

The field of Non Imaging Optics although it has been developed since the late 70's as a separate research field related to Solar Energy, still has a lot of potential for further improvement in solar related topics. One of the most promising areas is within Solar Fresnel Concentrating technologies, since conventional LFR is still far from the theoretical limits that can be achieved for the concentration factor. Developments from the conventional LFR include the Compact Linear Fresnel Reflector (CLFR) [3], the Etendue Matched upgrade (CLFR-EM) [4], and recently the LFR XX SMS Concept [1]. All concepts aim to have a primary reflector field where shading and blocking are reduced, and the concentration factor is increased in order to achieve a higher conversion efficiency. Using Ray Tracing Software, an optimization of the primary and secondary geometries was performed.

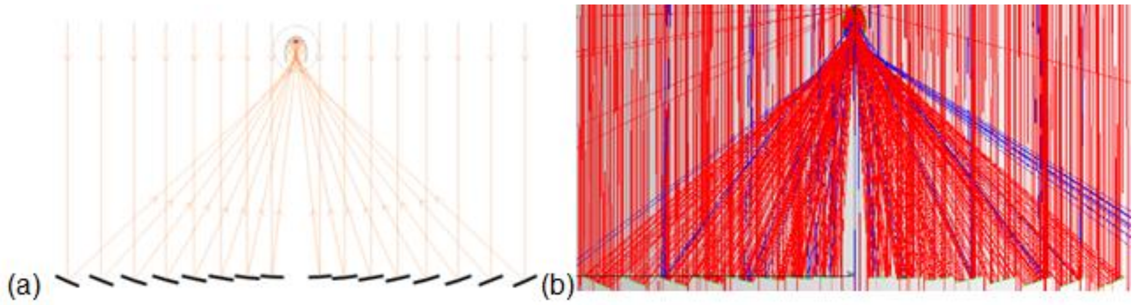

Fig. 4-1 – LFR XX SMS (a) concept (b) ray tracing [1]

In these new solutions, optical performance has been significantly improved for instance achieving a CAP of 0,57 and a concentration factor of 74x [1].

Additionally, to account for the performance loss due to different incident angles, a characterization of the Incident Angle Modifier (IAM) can be performed to yield results like the one in Fig.4-2. The mirror size and total area, the IAM curves and the material properties (reflectivity, absorptivity, etc.) are data used as input for the yearly energy simulation, which considers a Fresnel Plant of 50MWe in Faro (37º01'N, 7º93'W), Portugal.

	-180	-150	-120	-90	-60	-30	0	30	60	90	120	150	180
0	1	1	1	1	1	1	1	1	1	1	1	1	1
10	0,942	0,923	0,914	0,942	0,914	0,923	0,942	0,923	0,914	0,942	0,914	0,923	0,942
20	0,909	0,864	0,833	0,862	0,833	0,864	0,909	0,864	0,833	0,862	0,833	0,864	0,909
30	0,864	0,807	0,738	0,749	0,738	0,807	0,864	0,807	0,738	0,749	0,738	0,807	0,864
40	0,782	0,724	0,632	0,610	0,632	0,724	0,782	0,724	0,632	0,610	0,632	0,724	0,782
50	0,700	0,635	0,510	0,451	0,510	0,635	0,700	0,635	0,510	0,451	0,510	0,635	0,700
60	0,579	0,516	0,380	0,274	0,380	0,516	0,579	0,516	0,380	0,274	0,380	0,516	0,579
70	0,386	0,347	0,249	0,094	0,249	0,347	0,386	0,347	0,249	0,094	0,249	0,347	0,386
80	0,162	0,154	0,115	0,005	0,115	0,154	0,162	0,154	0,115	0,005	0,115	0,154	0,162
90	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 4-2 – IAM Matrix with the optical characterization

The final step concerning the increase in conversion efficiency is the usage of a molten salt heat transfer media that enables higher operating temperatures. The traditional solar salt (60%$NaNO_3$, 40%KNO_3) has been considered in the calculations, directly circulates in the receiver (see the discussion below). In the following figure, the main innovative features of the new Fresnel System are briefly described.

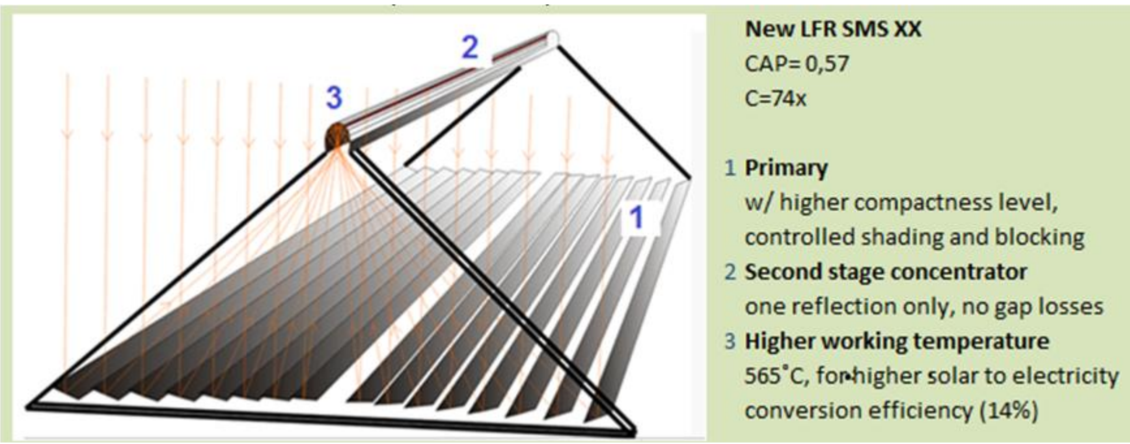

Fig. 4-3 – Main features of the LFR XX SMS concept

4.1.2 Heat Transfer Media

There are several heat transfer media being used in solar systems. Up to 400ºC the most common is the usage of mineral oils and synthetic fluids, however they are expensive and have a rather low temperature upper limit, for that reason molten salts are more and more used as an alternative, extensive research is ongoing.

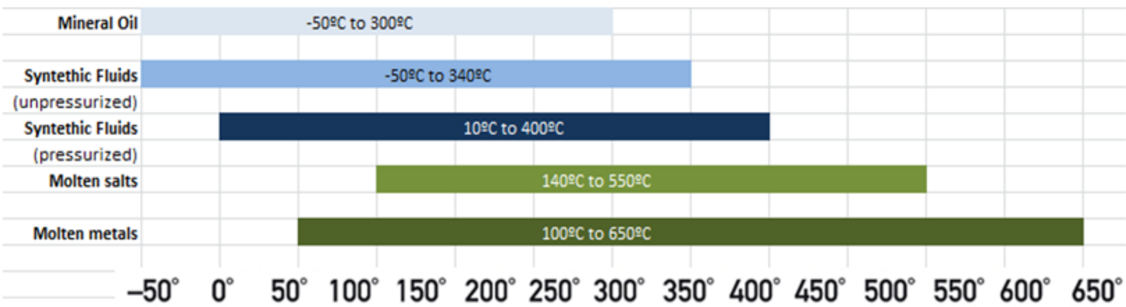

Fig. 4-4 – Heat Transfer Fluid in the temperature range -50ºC to 650ºC

Molten salts can be of two origins: extracted as a raw material from nature with a variable degree of impurities and as a result of industrial processes, which normally guarantees a lower level of impurities and better characterization. To choose a solar salt, apart from the cost, the following aspects are important: operative temperature range, thermal stability at high temperature, corrosion issues. Currently almost all commercial plants use the solar salt mixture, however there has been wide research to find alternatives, for cost reasons, or for lowering/increasing the operative temperatures, as presented below.

Table 4-2. Maximum and minimum stable operating temperatures for different molten salts

Molten salt	Minimum temperature	Maximum temperature
Salt 1: 60% Na NO_3, 40% K NO_3 (Solar Salt)	291ºC	600ºC
Salt 2: 7% $NaNO_3$, 53% K NO_3, 40%$NaNO_2$	170ºC	540ºC
Salt 3: 42% $Ca(NO_3)_2$, 15%$NaNO_3$,43%KNO_3	131ºC	560ºC
Salt 4: NaCl, Na NO_3, $NaNO_2$, KCl	140ºC	550ºC

4.2 Yearly Energy Simulation

4.2.1 Without Energy Storage

A calculation was made for solar to electricity efficiency using the assumptions presented in the following Table.

Table 4-3. Assumptions for the yearly calculation, case: no storage

Optics	LFR XX SMS as defined in [1]
Location	Faro (37º01'N, 7º93'W, 2234kWh/m2 Meteonorm data)
Receivers	Evacuated tubular receiver, 70mm, considering 800W/m heat loss at 565ºC
HTF	60% Na NO3, 40% K NO3, heat exchange (98% efficiency) design point at 565ºC
Steam Cycle	Steam generation design point at 545ºC and 100 bar, turbine efficiency of 0,41
Solar Field	210.000 m2: 13 rows of 933m length
Pipping	Connecting pipping length: 2300m considering heat losses of 130W/m

A detailed simulation, including hourly radiation and thermal losses, for operation at 565ºC was performed. The result for the overall yearly solar to electricity efficiency in these conditions is 14%. This result is significantly higher than the one obtained with conventional LFR designs and plants, which would show, for the same location, a value on the order of 9% or below [9].
Results of the yearly energy production are also presented in Table 4-5 for different solar multiples.

4.2.2 Thermal Storage Sizing with Energy Storage

Using salt mixtures proposed in the literature [5], it is possible to have a higher operative molten salt temperature close to 600ºC as well as a higher ΔT, which is a key factor in order to have an increase of the energy output of the plant, enabling a cost reduction also from the fact that a higher ΔT enables a reduction on tank size, for the same storage capacity.
When designing a CSP plant, a key relevant figure is the total amount of energy that can locally be supplied to the grid, which is associated to a limit on the installed power. If there is a storage possibility, than the total plant energy output can considerably be increased, and a production shift can occur from the peak solar radiation hours into the night within the defined power capacity. This production shift, which can occur at any given time of the day, increases the dispatchability level of CSP plants, thus increasing its market value, a considerable advantage of Concentrated Solar Power when compared with PV.
For that reason, the optimum sizing of the storage capacity for a given location is a quite important figure. For a certain plant, the total Thermal Energy Storage (TES) thermal capacity is given by,

$$E_{TES} = \frac{P_{OUT}\Delta t_{TES}}{\eta_{Cycle,OUT}} \qquad \text{(Eq. 4-1)}$$

With the stored energy calculated, Eq.4-1, it is possible to compute the total Volume of Thermal Energy Storage necessary,

$$V_{TES} = \frac{E_{TES}}{\frac{\rho_{TES,\max} + \rho_{TES,\min}}{2} \times \frac{c_{TES,\max} + c_{TES,\min}}{2} \times \left(T_{SF,return} - T_{SF,in}\right) \times f_{HE}} \qquad \text{(Eq. 4-2)}$$

In case the solar loop and storage loop media are the same, for instance using molten salts as both media, than,

$$f_{HE} = 1 \qquad \text{(Eq. 4-3)}$$

From an operational point of view, having 2 tanks, one “hot” (at the return temperature of the solar field) and one “cold” (at the inlet temperature of the solar field) has advantages, and thus, the total storage volume is usually divided into two tanks of equal size. Because of cost savings, a possible alternative could be the usage of just one tank thermally stratified, like thermocline storage.

4.2.3 Yearly energy yield for Fresnel XX SMS

Considering the new optics described, an yearly energy yield for a 50MWe Fresnel plant with storage has been simulated using TRNSYS. Besides the data used in Table 4-3, data input used also considers:

Table 4-4. Main Technical Data

Location	Faro – PT (38.57N, 7.91W, 2234 kWh/m2*year Meteonorm Data)
Total Primary Surface	Solar Multiple 2,0: 420 000m2
Optical Efficiency	0,69
Solar Resource design DNI for peak	950 W/m2
Turbine Full Load Efficiency	41%
Operating Temperature	290ºC to 565ºC
Storage	2 Tanks enabling 7h of TES (Direct system, 1010MWhth)

In the following figures the system yearly performance is presented: optical, storage and electricity output.

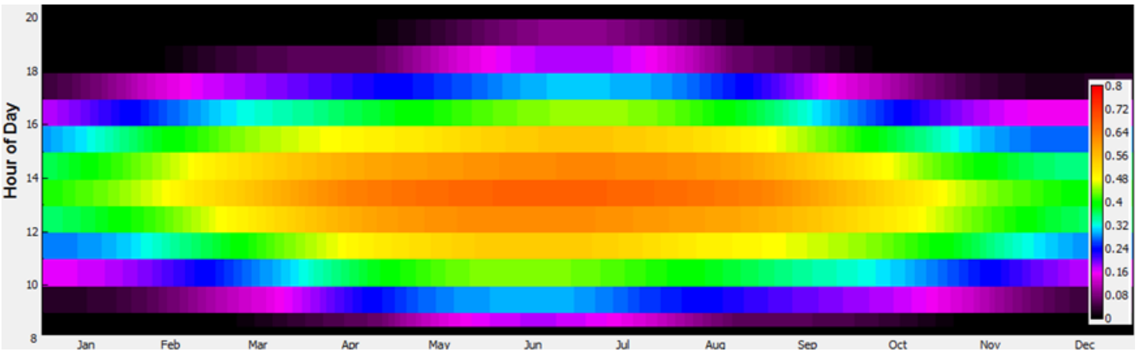

Fig. 4-5 – Yearly optical efficiency

The base case achieves a yearly net electricity production of 110 GWh for the mirror area considered (420.000m^2) and with 7h of storage. In order to understand the solar multiple and the storage effect impact on the net electricity production, a parametric analysis is presented in Table 4-5.

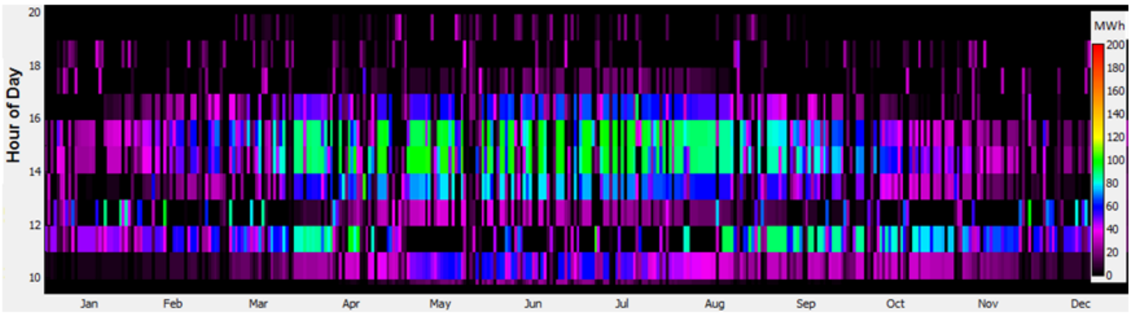

Fig. 4-6 – Thermal energy sent to storage tanks through the year

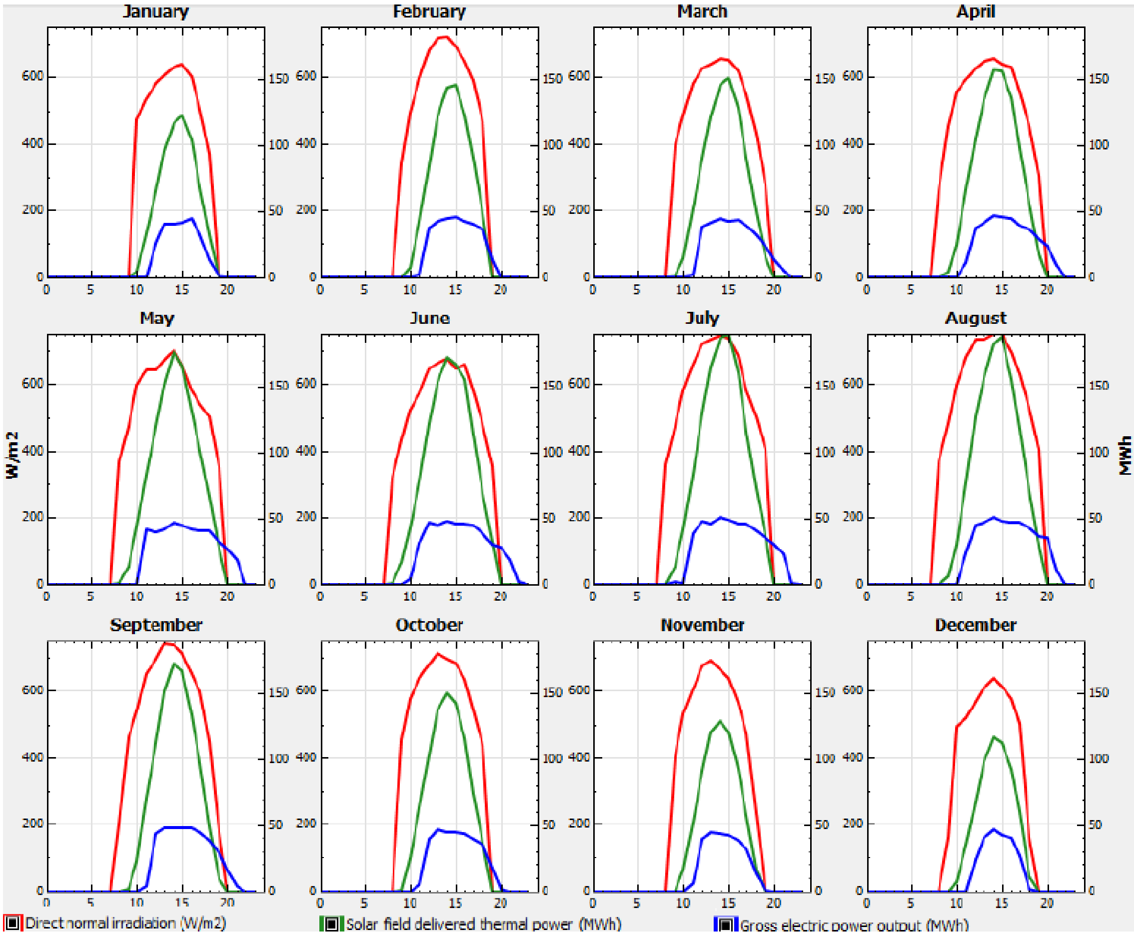

Fig. 4-7 – Yearly available resource, Thermal Power, Net electricity output

Table 4-5. Parametric analysis varying the solar multiple

Solar Multiple	Mirror Area [m^2]	Yearly Net [GWh] no storage	Yearly Net [GWh] storage 7h
2,0	420.000	92	110
2,5	525.000	107	147
3,0	630.000	115	172

4.3 Economic Valuation

Two cases were considered when calculating the LCOE for the plant.

- Case 1, considers a Solar Field (SF) cost of 150 Euro/m^2 which is a reference value for plants recently built in Spain [6,10].

- Case 2, takes into consideration the possibility that the SF cost might go down to 100 Euro/m^2.

Due to the significant reduction of the pipping, lower pressure drop in the circuit, the Balance of Plant (BOP) costs considers 25% savings when comparing with similar size PTC plants. The costs considered for the Power Block (PB), Storage (ST), HTF, Engineering/Procurement/Construction (EPC) are costs in line with the available literature [7,8,9,10], which in turn have a well identified cost reduction potential.

Table 4-6. Economic input data used for Levelized cost of energy (LCOE) calculation

Variable	Value
CAPEX-1 (case 1: SF 150Euro/m^2)	SF 63, PB 40, ST+HTF 50, BOP 24, EPC & others 18 = 195 MEuro
CAPEX-2 (case 2: SF 100Euro/m^2)	SF 42, PB 40, ST+HTF 50, BOP 24, EPC & others 18 = 174 MEuro
Economic Lifetime	25 years
OPEX annual costs	3,0 MEuro/year
Interest Rate	7%
Equity / Debt Ratio	50%

Table 4-7. LCOE calculation [cEuro/kWh.year]

Internal Rate of Return	Case 1: SF cost of 150E/m2	Case 2: SF cost of 100E/m2
IRR= 13%	12,6	11,4
IRR= 12%	12,3	11,1
IRR= 11%	12,0	10,8

These results show that the new LFR SMS XX, can achieve LCOEs approaching 10 euro cents/kWh with 7 hours of storage. In particular 10,8 cEuro/kWh.year for the minimum IRR considered of 11%, in a location like Faro. Although a very sunny European spot, it is still far from sunnier places in excess of 3000kWh/m^2.year or locations with lower latitudes, where much lower LCOE values can be obtained, with the same assumptions made above.

Further potential lower values can be obtained from performance increases (this can come through optimization of the proposed optics, still not yet at the limit of what is possible to achieve, in particular through further EM conservation to be done in future work). Besides, increasing the Solar Multiple to 3 which is a common value in order to take full advantage of the relative investment cost in storage facilities, it would lead to a further reduction of 1,7 cEuro, that is a LCOE of 9,1 cEuro/kWh.year. This figure indicates that if an optimization of the solar field size is performed together with other cost saving measures (e.g. one tank system) values below 10 cEuro/kWh.year are possible for a sunny European location with this new concentrator and associated technology.

4.4 Conclusions

In this chapter, a new Fresnel concept called SMS XX was presented, showing that there is a good theoretical potential for optical improvement (C=74x) of the Fresnel collectors currently in use for STE. For a sunny European location (Faro - Portugal) the total energy produced is 110 GWh with 7h storage, considering a solar multiple of 2,0. This could, in principle, be achieved with an LCOE of 10,8 cEuro/kWh.year. This value can still be reduced, with a further optimization of the optics itself and jointly with the rest of the solar field, power block and storage size.

As described, the combination of high performance new LFR concentrators with molten salts as HTF and storage fluid, can lead to a truly interesting low cost for electricity production. However it is clear that several aspects of the concept, from the new concentrators to many yet untried operational issues, must be practically investigated and implemented, to establish their true worth. Therefore, a broad R&D Project called INNOVLFR (see chapter 10) has been proposed to the H2020 program, in order to solve the open questions.

The new LFR concept achieves high concentration and high temperature because of the efficient coupling with molten salts as HTF fluid. Linear Fresnel concentrators with their fixed receivers, are naturally suited for the consideration of drain down techniques, eliminating some of the most serious draw backs of using molten salts as HTFs, something that should indeed be developed.

Concerning the operation with salt it is crucial to test them for the first time jointly with this new Linear Fresnel concept, extending the research also to new operational and control technologies for the concept as a whole. This was the motivation behind chapter number 5, where experience gained with a molten salt test loop is described.

4.5 References

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Chapter 5. Molten Salt test loop

5.1 Molten Salt Loop

Commercial Solar Thermal Plants with storage have a so called 2-tank indirect type, since the Heat Transfer Fluid (HTF) in the collector field is usually a thermal oil, normally limited to 400ºC operating temperature. It is connected by means of a heat exchanger to the storage circuit which uses molten salts. However, from an operational point of view there are several advantages for the use of molten salts also in the solar loop, in a direct system. A future match between Advanced Linear Fresnel Concentrators and molten salts as HTF was the reason behind the definition of a test plan in order to gain direct experience with molten salts loop operation by taking advantage of the work and facilities available in Italy, where there are two demonstration loops and a 5MWe commercial loop coupled to an existing power plant in Sicily. Since 2004, at ENEA (Rome, Italy) several research tests like the one reported in this article have been performed on a 2*50m PTC loop with a storage tank of 9,5m^3 and a backup boiler.

The circuit was designed to validate the usage of molten salts as the heat transfer fluid for a solar concentration power plant. In this case Parabolic Through Collectors with a east-west orientation (north of Rome, Location: 42°03′N 12°18′E) are installed using molten salts that can be stored in a non pressurized tank. In this loop it is possible to test molten salts under different operating conditions, as well as to measure a variety of parameters like: inlet and outlet receiver temperatures, collector positioning, flow, tank level and auxiliary power.

Fig. 5-1 – Test Loop, detail of the Collector field

In order to evaluate thermal aspects of the loop and its losses, a range of tests was performed in Autumn 2013. During these tests all the relevant parameters were measured for a 2 week period under very different irradiation conditions which varied from 150W/m^2 up to 950W/m^2. Thermal losses in the tubes were measured, a very important result in order to confirm the merit of operating at a higher temperature (550ºC) than the current standard (400ºC) using synthetic oil. This chapter analyzes energy gain and energy losses in the receivers, making it possible to have an understanding of the real conversion efficiency under operative temperatures in the range 350-550ºC.

Table 5-1: Test Loop main characteristics

Item	Characteristics
Collector Type	Parabolic Through
Optics	Aperture 6m, Focal Length 1,8m; Mirror Reflectivity 95%
Loop Dimensions	Collector in line extension = 100m, orientation east-west
Receivers	Evacuated Tube with selective coating, outer diameter 70mm, ca. 4m long
Tank	1-Tank with 9m3 capacity
Other Components	Centrifugal Pump 18m3/h@2900 rpm; 600kW electric heater; 2 Fan coolers
Heat Transfer Fluid	60% $NaNO_3$, 40% KNO_3, operating temperature: 290-550ºC

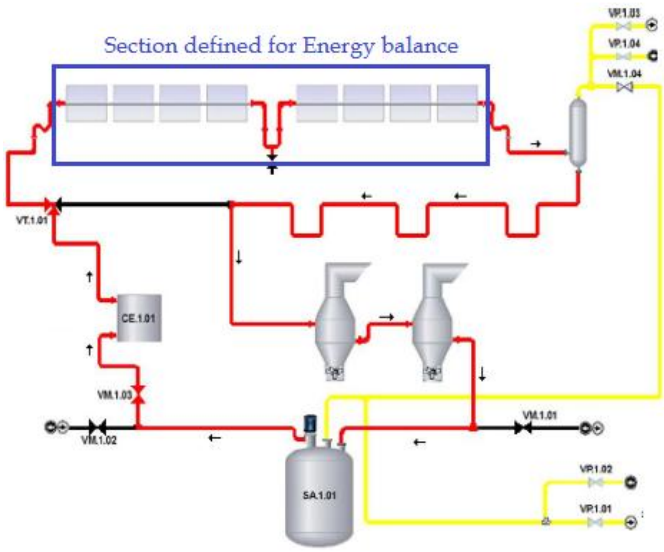

Fig. 5-2 – Test Loop, layout

5.2 Test Plan

5.2.1 Merit of using molten salts

With the development of ternary and quaternary mixtures, in the future, it is foreseen that molten salts will be more and more used as heat transfer fluid (HTF) also in the solar loop, both for Parabolic through collectors (PTC) and specially Linear Fresnel, since molten salts as a transfer media have a very interesting fit with Fresnel technology.

Table 5-2. Merit of the usage of molten salts

Past successful experience as HTF in concentrated solar plants (Gemasolar-SP, Priolo Gargalo-IT)
Enables operation at higher temperatures (565ºC and above) with higher efficiency conversion than synthetic oils
Stable composition and stable properties (density, viscosity) within temperature operation range
High innovation potential since wide research is being made concerning the development of new salts
It is not flammable neither toxic
When solid can be later used in agricultural activities
It is easy to pump and to store in the temperature range appropriate for energy capture in collectors

A fundamental topic is the increase of the upper temperature limit, which increases the efficiency conversion (from 37% to 40-41% of turbine efficiency) and also reduces investment amount (reduced tank size) because with a higher temperature, the same energy content can be stored in a much smaller volume.

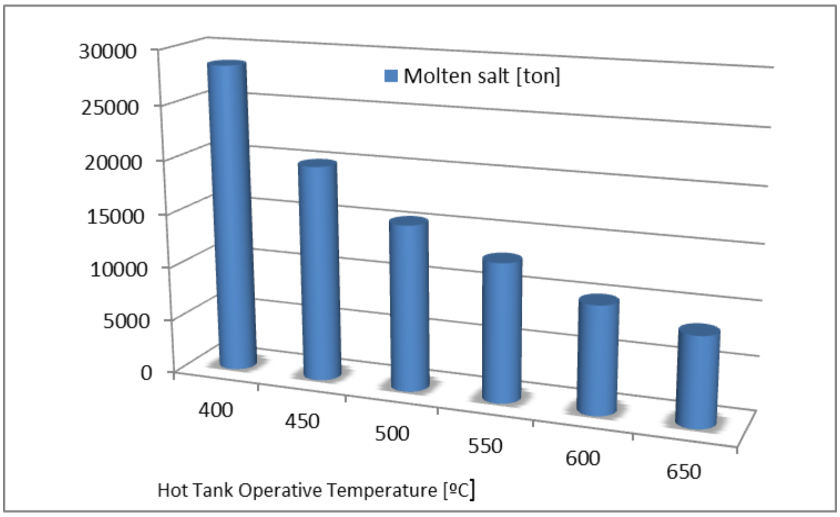

Fig. 5-3 – Storage Volume for different operating temperatures

Table 5-3.Energy Storage for different operating temperatures

Max operating Temp [ºC]	Nominal Tank size	Molten salt [ton]	Energy Stored [MWh]
400	1	28500	1010
450	0,7	19950	1010
500	0,54	13965	1010
550	0,45	9776	1010
600	0,35	6843	1010
650	0,29	4790	1010

5.2.2 Test Plan definition

In order to test and validate different operating strategies, a test plan varying mass flow, fluid temperature and duration was elaborated.

Table 5-4.Test Plan defined

Concentrated Power Test	units	Nr. 1	Nr. 2	Nr. 3	Nr. 4
Temperature, Solar collector inlet	°C	450*	450*	500**	500**
Mass flow	kg/s	3,5	7	3,5	7
Full Sun Tracking		ON	ON	ON	ON
Test time	h	3	5	4	4

Concentrated Power Test	units	Nr. 5	Nr. 6	Nr. 7
Temperature, Solar collector inlet	°C	OFF	400	550
Mass flow	kg/s	OFF	6,5	6,5
Full Sun Tracking		OFF	ON***	ON
Test time	h	96	0,5	1

NB: * Inlet Collector Temperature variable (backup heater off)

** Minimum Inlet Collector Temperature variable (backup heater ON)

*** Test with defocused concentrator

There are two main cases, the first one when the system is in full sun tracking and there is no backup system, and the second case when the backup system is ON in order to maintain a certain minimum inlet temperature in the first receiver. Whenever the solar energy captured is not enough, in case the pipelines reach the set point temperature for the heat tracing, this one is automatically switched ON, so that, the fluid inside the pipes never reaches the solidification temperature.

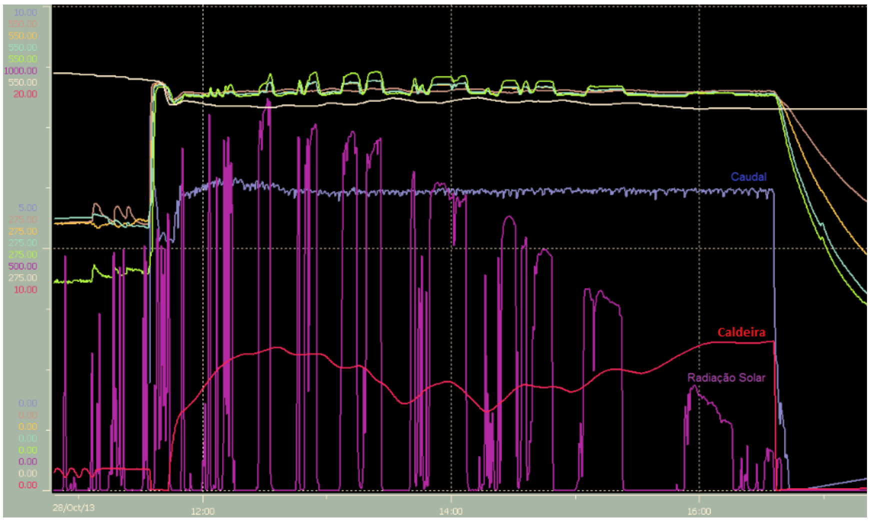

Fig. 5-4 – Main Parameters measured for 8h period on 28/10/2013

5.3 Results Discussion

Results obtained during two weeks were analyzed. Energy captured by the receiver (DNI), part of it is absorbed, the rest are losses. The Energy absorbed can be computed trough the temperature difference between receiver outlet and inlet temperatures. For the calculations presented, day 23/09/2013 (Test nr.2) with particular good DNI was selected.

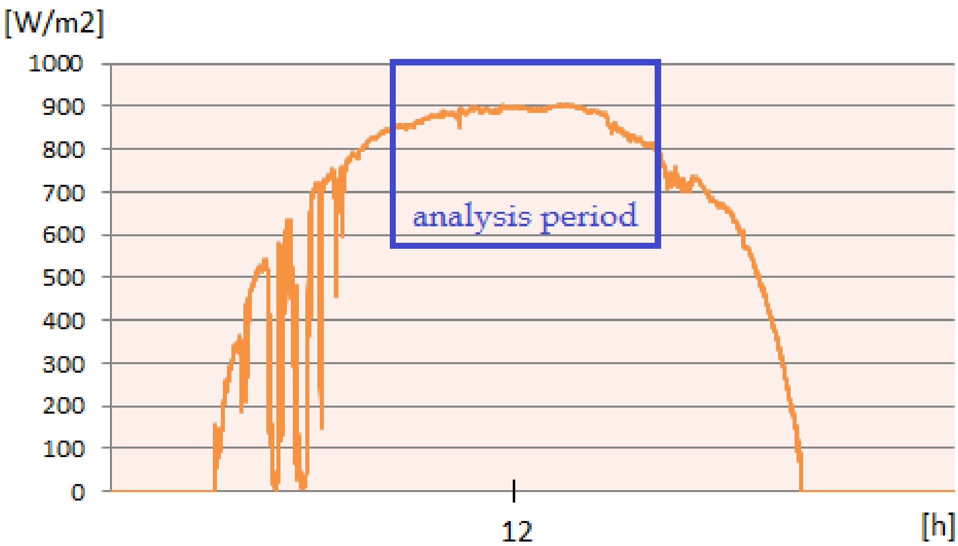

Fig. 5-5 – Direct Normal Irradiation (DNI) data during the test day, 23/09/2013

The heat capacity for the solar salt mixture (60% $NaNO_3$, 40% KNO_3) considered is given by the formula:

$$c_P = 1443 + 0{,}172 \times T_{in} \qquad \text{(Eq. 5 -1)}$$

A section of about 100m tube length was defined for the energy balance calculation. Measured values for the Direct Normal Irradiance (DNI) are compared with computed result for the Energy gain. To calculate the energy gain, the inputs used were measurements of both temperatures, mass flow and computed specific heat capacity.

$$(\Delta T)_i = (T_{out} - T_{in})_i \qquad \text{(Eq. 5 - 2)}$$

$$\sum (E_{gain})_i = \sum (m \times c_P \times \Delta T)_i \qquad \text{(Eq. 5 - 3)}$$

$$\eta_{SOL\_TH} = \frac{E_{gain}}{DNI} \qquad \text{(Eq. 5 - 4)}$$

Additionally to the Energy Gain calculated, an hourly conversion efficiency was calculated in the period 10am-3pm, where the DNI values are very stable and always above 800 W/m^2. Since the DNI has a very slight variation, the hourly efficiency curve shape is quite similar to the energy gain. The maximum hourly efficiency measured was 45% in conditions that can be seen as stationary (constant radiation and mass flow). The maximum obtained was at solar noon, when the IAMT = IAML ≈ 1.

The characteristic longitudinal Incident Angle Modifier (IAM) curve of the Parabolic Collector was considered in order to calculate the optical losses. Thermal losses are indirectly calculated from the measured DNI, energy gain, and from the calculated Optical losses (Eq.5-5).

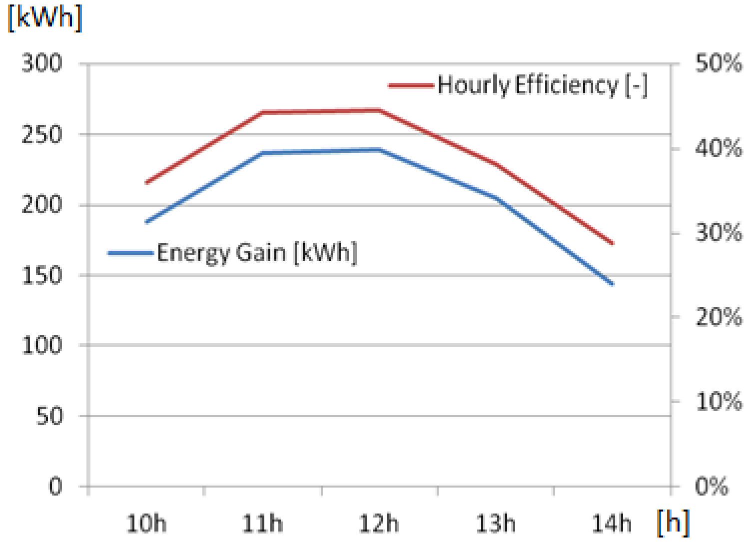

Fig. 5-6 – Energy gain (left axis) and hourly efficiency (right axis)

$$E_{TH\_losses} = DNI - E_{OPT\_losses} - E_{gain} \qquad \text{(Eq. 5-5)}$$

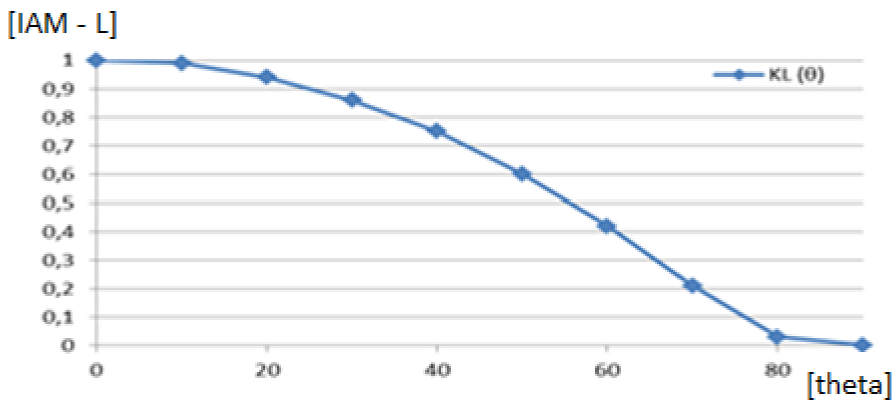

Fig. 5-7 – IAM longitudinal for the Parabolic Trough Collector

Results obtained show that optical losses present an expected minimum at solar noon, representing 108kWh for the 100m receiver. Thermal losses (including receivers and flexible tubes) increase proportionally with the increase of the inlet temperature in the receivers, from 324ºC at 10am to 473ºC at 3pm. Total energy gain was 1013kWh for the analysis period of 5h.

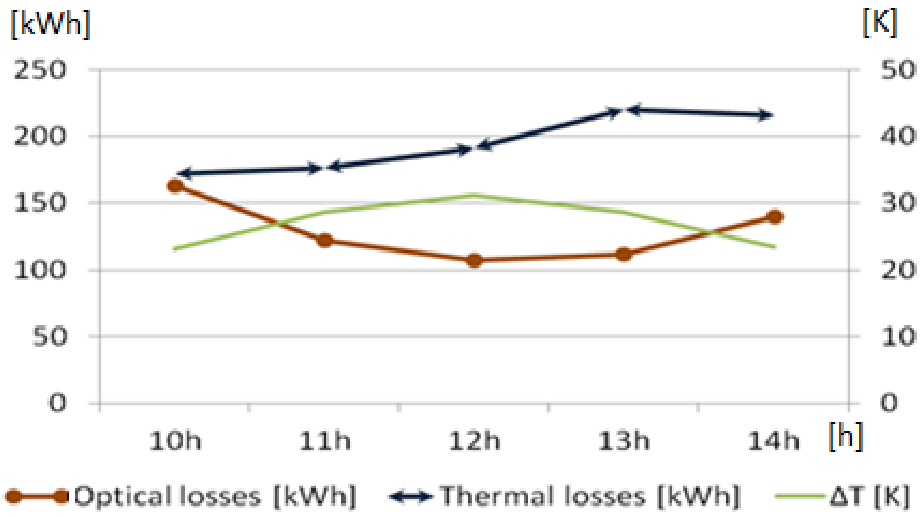

Fig. 5-8 – Optical, thermal losses (left axis) and temperature difference (right axis)

5.4 Conclusion

Molten Salts are foreseen to become in the near future the most successful Heat transfer fluid for Solar concentrated plants, which operate at temperatures up to 600ºC, which is the case of the successful STE Tower plant (Gemasolar) inaugurated in 2011. Until now, concerns about draining the facility at night and costs with the heat tracing system have prevented a broader usage of molten salts in commercial plants.

Nevertheless, with the energy gain and losses results that were measured in the experimental loop, the authors think that this solution is a very good match to Linear Fresnel Technology, due to the fact that the receiver tubes are fixed (non-movable parts, joints or flexible hoses) and are placed in a high point (8 to 10m high), facilitating solutions of the drain back type. A potential low LCOE is to be expected from Advanced LFR collectors combined with several hours of energy storage, using molten salts as HTF and storage medium [2].

The next phase of this technology is to test different salts and operating strategies in order to validate a range of design options, to optimize a future Fresnel linear STE commercial plant.

Higher concentration Advanced LFR technology [3] is being proposed to operate with a molten salt mixture as HTF at 565ºC at the EMSP (Evora molten salt platform), with a full implementation plan already elaborated, the project INNOVLFR (see chapter 10).

5.5 References

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Chapter 6. Hybrid Thermocline Layer Tank (HTLT)

6.1 Merit of a Thermocline tank

As described in Chapters 2 and 4, having a high efficient storage capability is the key advantage of STE plants when comparing with other renewable like PV.

Currently, the most common storage system for STE plants is the 2-tank indirect system which is connected to the solar field loop through a heat exchanger. Primary loop in most CSP plants uses a synthetic oil which operates at a maximum temperature of 400ºC, because above this level oil degrades quite fast, thus, current storage facilities operate only up to this temperature. However, since 2011 there are two commercial plants, Gemasolar in Spain with 20MWe and Priolo Gargalo in Italy with 5MWe which operate directly with molten salt using a binary mixture operating at temperatures up to 565ºC. With the development of ternary and quaternary mixtures, in the future it is foreseen that molten salts will be more and more used as HTF in the solar loop, not only in Tower systems, but also in parabolic through collector fields (see chapter 5) and specially in Advanced Linear Fresnel collector ones [1]. In fact molten salts usage has a very interesting fit with Fresnel technology, due to the fixed receiver at a higher position and with no moving parts like in the case of PTC. With salt mixtures proposed in the literature and validated at laboratory scale, it is possible to have even a higher ΔT, increasing the efficiency of the plant.

Concerning thermal storage technologies, there are currently three commercial possibilities: 2-tank MS indirect system, 2-tank MS direct system, steam accumulator.

Having two thermal storage tanks, results in higher system thermal storage investment costs (higher CAPEX). Tested for the first time in the early 80’s in the USA, single-tank thermal storage system is an alternative, also known as thermocline thermal storage, because there is a significant thermal gradient inside the tank with hot fluid laying in the top, and colder fluid in the bottom of the tank which is always full.

Having just one tank, with the HTF being the same as the fluid in the tank, savings related to storage CAPEX can be in the magnitude of 40% to 50% of the total investment costs referred to a standard 2-tank Storage System, since:

- Just one tank to be built;
- The heat exchanger oil/MS is not necessary since the same fluid is the heat transfer fluid and at the same time the heat storage fluid;
- Between 50% and 70% of the tank volume can be substituted by a filler at low or no cost at all;
- 2 Pumps less (same pumps for solar loop and tank).

Therefore, for a 50MWe STE plant, saving 40-50% of the investment costs for the storage system can represent up to 20-25 MEuro in CAPEX savings. This means there is a clear motivation and opportunity to make STE more interesting and competitive.

6.2 Historical background

A Thermocline tank is a single tank of cold and hot fluid facing a vertical temperature gradient, by means of a thermocline layer (Fig. 6-1b, also known as the thermocline). Buoyancy forces help to maintain a stable thermal stratification between hot and cold fluid in the same. With the tank always full, this layer shifts position inside the tank during charge and discharge procedures. During the SEGS development in California, USA, there was high interest in Concentrated Solar Power. Back then, Thermocline type tank was one of promising technologies with a test facility being built in the early 80's as part of the Solar One facility in Barstow, California. [2]

This thermocline tank of 170MWh$_{th}$, apart from having a synthetic oil, Caloria HT-43, also had solid material known as filler, with good heat storage capacity at a significant lower cost than molten salts. This filler was placed as a rock-bed inside the tank, with a bed void fraction of 0,22. Modellation of this concept has been performed by several authors [3, 4], who used the available experimental data from the 80's to elaborate on their model performance. In the case of Solar One, starting at the bottom of the tank, there is a base layer of sand, followed by rocks (quartzite) of selected size, rock mixture (quartzite) and sand, and finally a top layer with rocks.

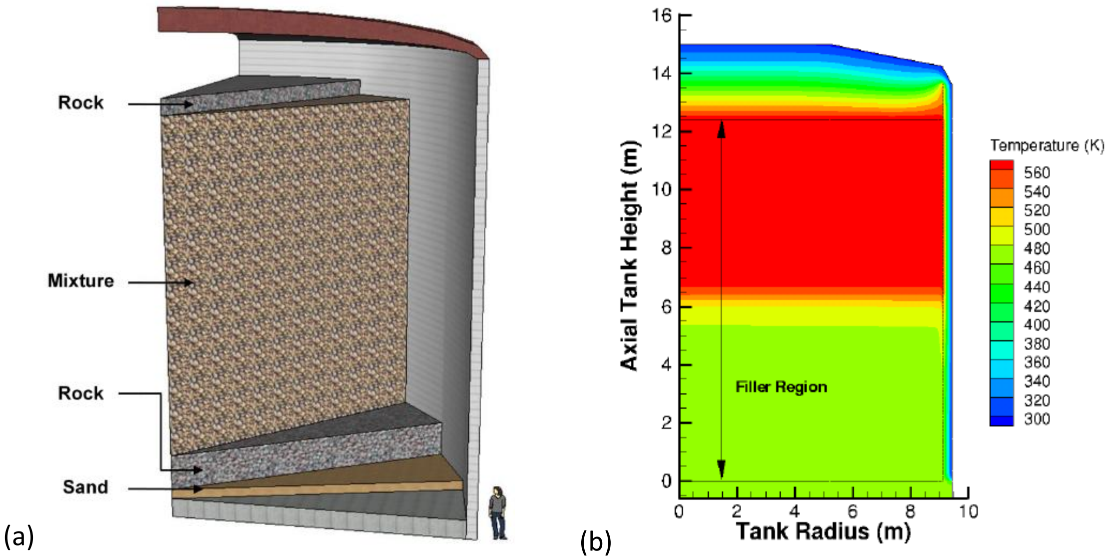

Fig. 6-1 – Solar One, Thermocline Tank (a) vertical section (b) temperature profile & thermocline layer [2]

Results reported in the literature refer the degradation of thermocline effect [2] as a matter of concern during operation. Other issues to be solved back then were:

- retching at the tank containing walls due to the thermal expansion coefficient of the filler material;
- unwanted particles moving inside the tank;
- outlet filter clogging among other issues.

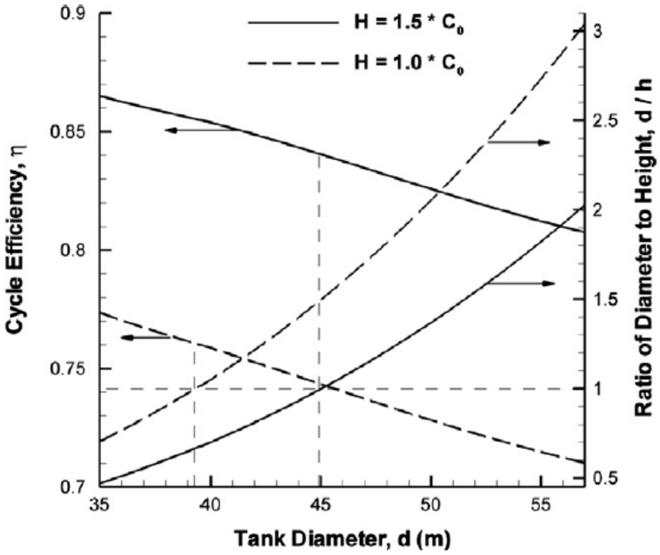

Fig. 6-2 – Thermocline Tank, efficiency depending on the ratio diameter to height [5]

The cycle efficiency of a thermocline tank is related to several factors. A taller tank has higher efficiencies, as well as higher height to diameter ratio, and smaller particle size. For a 53m height tank with 35 m diameter, filler particle size 0,1 m, a 86% efficiency is reported [5].

In the early 2000's a small scale 2.3 MWh_{th} thermocline using molten salt as heat transfer fluid was tested by Sandia. It is a carbon steel tank, height of 6.1 m and a diameter of 3 m insulated with 23 cm of fiberglass insulation on the sides and with 20 cm of calcium silicate ridged block insulation on the top [6]. The tank was full with 50 ton quartzite and 22 ton of quartz sand (filling the voids) in several layers: 3 cm sand, 20 cm quartzite, 5 m of several 5 cm layers of quartzite and sand. For the overall 41 hours testing period, total energy extracted was approximately 2.4 MWh_{th}, with a final hot salt temperature exiting the tank of 361 °C. The average heat loss was measured to be approximately 20 kWh_{th} [6]. Temperature measurements exhibit significant scattering, nevertheless the promising result is that the thermocline profile was still well pronounced and could yield useful energy extracted at a reasonable temperature potential.

After the Spanish developments from 2007 onwards, STE become again a popular research topic, especially in Europe. A thermocline tank of 3 m height and 1 m diameter to be filled with oil was built at CEA, France [7]. As filler a mixture of silica gravel and silica sand has been used with a mass proportion of 20% of sand and 80% of gravel, with a void fraction in the range 0.27-0.3. From the tests performed, in discharge mode, an almost constant tank outlet temperature and discharged heat duty were obtained for 3 h and a total energy extracted of 230 kWh_{th}. Moreover, measurements performed on the thermal oil flowing through the storage tank in direct contact with the rock-bed in cyclic operations show no specific properties modifications. This indicates that no specific oil/rock interaction occurred, a factor that could lead to oil alteration.

6.3 Concept variants

Most STE power plants built in Spain have storage facilities. The same applies to the ones being planned or built in the USA, Morocco and South Africa. However, none of them decided to go for a thermocline tank, perhaps because of the lack of long term experience with this technology. However, new concepts have been recently investigated and proposed.

One of them proposes a new design of the interior of the tank, introducing barriers in order to enhance and maintain the stratification effect inside the tank. There are baffles inside the tank that orient the flow inside the tank from the top middle towards the middle bottom. With only one way in and only one way out, the fluid has a preferred way to flow.

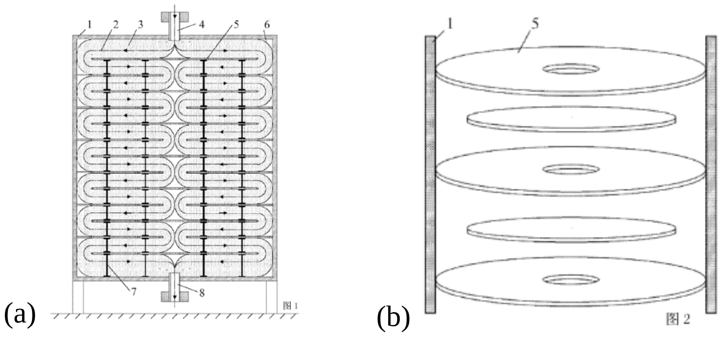

Fig. 6-3 – Thermocline Tank, new design cross section (a) with internal baffles (b) [8]

Another proposed concept is the design of one single tank with the interior of the tank having a separating barrier in order to enhance and maintain the stratification effect inside the tank. There are two separate chambers and the fluid from the lowest chamber does not contact the fluid in the upper chamber, since the barrier isn't permeable. The floating barrier uses the effect of different densities between the hot and cold fluid, in this case molten salts. A demonstration unit was built in the Spanish plant of Valle and if successful will be introduced at larger scale.

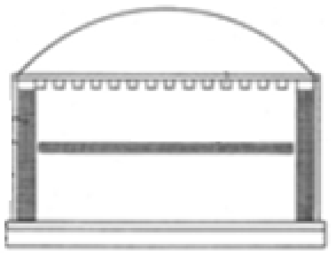
Fig. 6-4 – Thermocline Tank with an internal floating barrier [9]

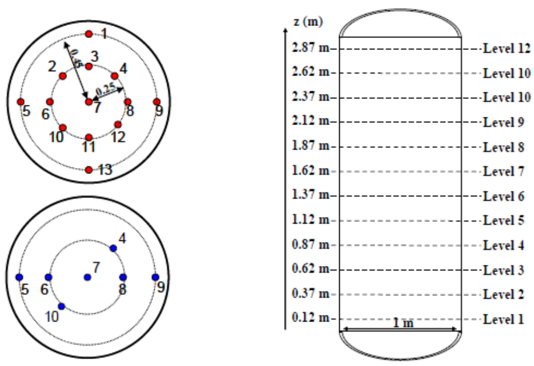

Fig. 6-5 – Thermocline Tank using oil as the heat transfer media [7]

Knowing that higher tanks achieve higher efficiencies, a tank with a ratio height, diameter of 3 was built and is being tested with oil, where the stratification effect should be easier to maintain due to the superior H/D ratio [7].

6.4 1-D tank modelling

As mentioned previously, a filler material is used in order to decrease the investment cost and to improve the thermal inertia of the storage facility, but this filler material must meet some criteria such as sturdiness in order to be subject to a large amount of charging/discharging cycles (raising and lowering its temperature to maximum and minimum) without presenting appreciable degradation nor cracking under structural demand. As such, one of the major problems to this technology is to find the proper materials to last several years at an affordable cost. Some of the identified disadvantages of current thermocline tanks relevant for modelling are:

- It is more difficult to separate the hot and cold HTF;
- Maintaining the thermal stratification requires a controlled charging and discharging procedure with appropriate devices to avoid mixing;
- Design of storage system inlet and outlet is complex.

In order to tackle some of the identified problems that hinders the spread of thermocline technology, results from 1D model based on the Schumann equations' are presented (Fig.6-6).

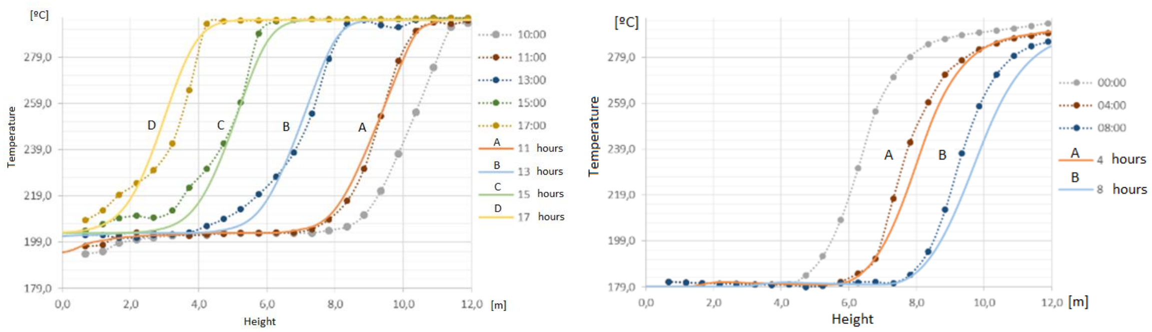

Fig. 6-6 – 1-D simulated thermocline tank cycles when charging (left) discharging (right) [11]

Analyzing the charging and discharging curves, it became clear that the degradation of the thermocline layer is one of the main problems to be solved, a very important aspect since storage capacity is reduced when degradation of the stratification occurs. This behavior appears to be related to the fluid thermal diffusivity and thus results in a smaller storage capacity. Moreover, the thermal energy storage tank is not always performing charging or discharging cycles. Thus, the thermal diffusion phenomena in stagnation conditions (when the tank has no inflow/outflow) must be addressed as well as in the charging and discharging cycles. A possible approach is to improve the design of the tank to reduce this problem.

6.5 New tank design

Having only one storage tank has a lower cost and also high heat storage efficiency advantages. However, despite the economic advantages of a thermocline tank, there are several potential difficulties with a standard thermocline design which has been shortly presented above, namely:

- the thermal ratcheting of the tank wall during the charge / discharge cycles, which remains a significant design concern;
- the stratification effect is easily lost after several charging and discharging operations;
- having oil as a heat transfer fluid is a potential environmental hazard;
- in some cases there are filler particles moving inside the tank which might be a problem for the piping system due to clogging risks;
- unknown filler temperature and long term degradation.

In order to address the concerns reported above a new concept has been developed, the so called Hybrid Thermocline Layer Tank (HTLT). This new concept is a thermocline solar thermal tank, comprising a thermal storage tank made of steel or concrete, where there are multiple layers arranged in a way that fosters temperature stratification. The fluid considered, a binary molten salt mixture, enters the tank by means of specific openings placed one per each layer. At the other end of each layer there is one opening where the fluid leaves the tank. All flows are controlled by a specific algorithm that enhances stratification, depending on a predictive model that considers DNI data (real time and 10min forecast) as well as real historic data, for inlet and outlet openings to be properly controlled. Inside the tank, there is a multilayer liquid / solid hybrid thermal storage system (Fig.6-7). Each of the layers is hybrid, i.e. composed by two different materials, the bottom part is a solid material (filler) suitable to be used as thermal storage material, and the upper part is the fluid used as heat transfer fluid. The layers have a geometry defined by means of supporting structures where wire meshed boxes are placed and inside the filler material will be placed.

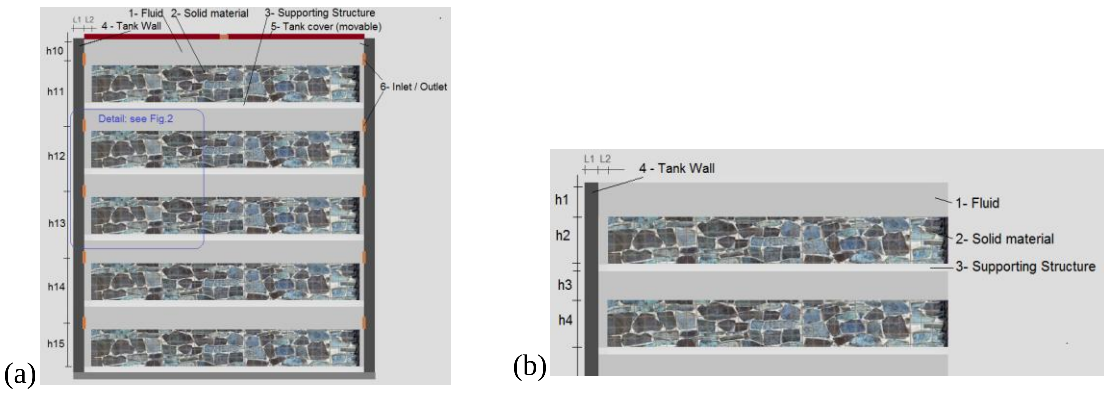

Fig. 6-7 – HTLT cross section (a), cross section detail (b)

The fluid can flow through the porous material placed in a metal wire meshed box (Fig.5) filled with aggregates or any suitable solid medium, meaning a solid heat storage medium like sand, ceramics, concrete, slag from industrial or mining processes (Fig.6). These solid materials are all well contained inside this wire meshed box, a feature that prevents thermal ratcheting of the tank wall (Fig.6-8). The tank cover will be able to be easily movable, so that it can open. By means of a crane it is easy to put or take out the solid material content of the tank. Layers' size can also be easily adapted.

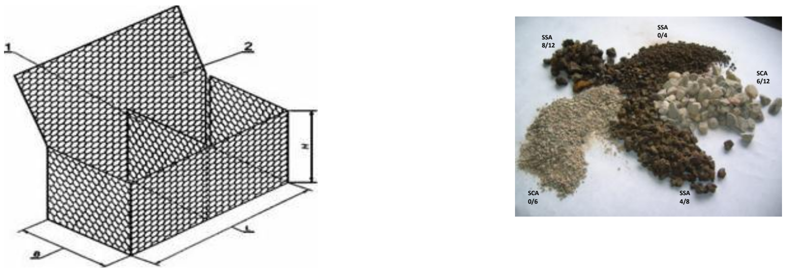

Fig. 6-8 – Filler material (a) container (b) aggregates used as filler

The thermal storage concept is based on alternating horizontal layers of solid and fluid material, the number of layers and its thickness are to be optimized through simulation and as a function of the tank size, minimum and maximum heat transfer fluid operating temperatures. In the case of binary mixture, the temperatures considered are in the range 220-550ºC. The system has a specific control to be able to automatically mix fluid coming from different openings in order to achieve the desired inlet and outlet temperatures. This algorithm (fuzzy logic type or similar) receives weather data including DNI data (real time and forecasted data like 10-minute gap), and according to parameters characteristic for the facility, will provide the right mass flow to all inlet and outlet openings to take maximum advantage of the stratification principle using sensible heat both from solid and liquid material. This concept was subject to a patent application, for details see annex 2.

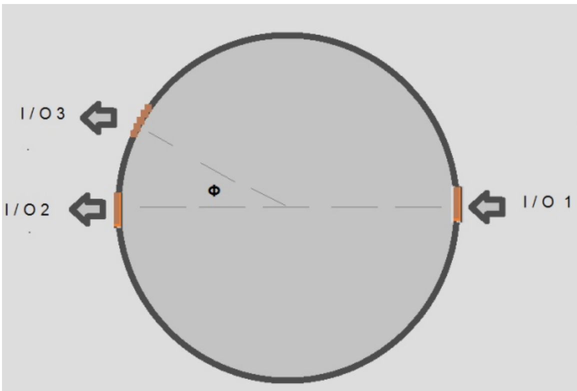

Fig. 6-9 – HTLT top view

Another interesting feature of this tank is that it can also store heat in the latent form, being thus an hybrid tank. Inside the tank and in direct contact with the media (molten salts) there are several containers with PCMs inside the tank placed in several vertical tubes (for details annex 3). Containers may move upwards or downwards to release heat taking advantage of the different temperature levels in the tank at a given time.

6.6 Merit of the HTLT

In order to be able to implement control strategies that can operate the HTLT concept, a real time measurement of several parameters like vertical temperature profile of the storage media, temperatures in the filler, temperatures at the wall, and also degradation mechanisms need to be monitored. For this, state of the art technology solves part of the task. Specially if the tank walls are built in concrete, crack formation, pH and temperature are parameters that need to be monitored. This requires intensive research and development on topics like increasing the sampling rate up to 2,5MHz for crack monitoring or real time corrosion monitoring. These tasks will be performed using FBG (Fiber Bragg Grating) sensors, which measure the variation in the reflected wavelength as a sensing parameter. A tensile strain over the fiber changes the FBGs spatial frequency and therefore the wavelength of the reflected light. The optoelectronics required for the measurements are known as interrogators and include a tunable laser source and a detector that determines the wavelength of the reflected light. These tasks have been integrated into a 18 month research plan to be performed in project SOLSTICE (2016-2017).

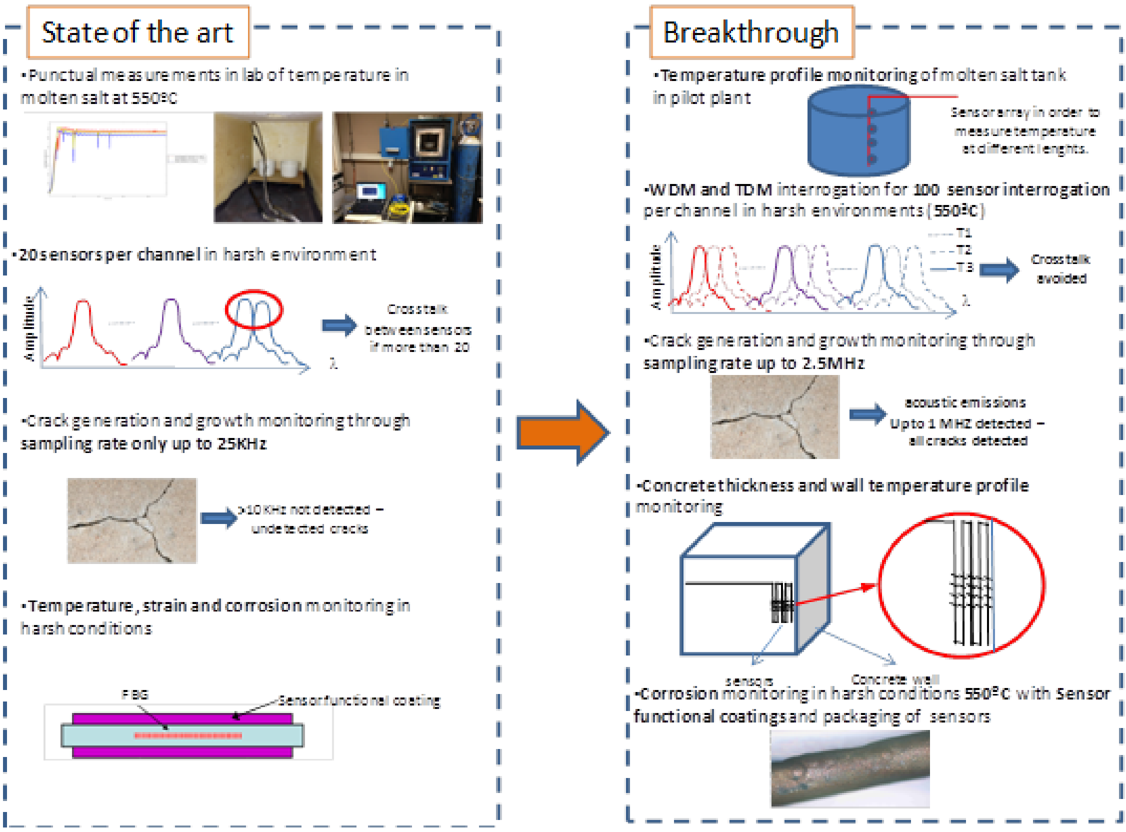

Fig. 6-10 – Monitoring technologies: state of the art and breakthroughs

As an overview, the main features of this tank comparing with the state of the art are:

- it has layers solid / fluid / solid material with thicknesses that can be easily adapted;
- it has metal wire boxes where the solid material is placed and cannot escape;
- fluid can flow through the boxes where the solid material is placed;
- boxes which contain the solid material prevent thermal ratcheting of the tank wall;
- there are metallic supporting structures where the wire boxes stand. The position of these structures can be easily adapted by means of a crane;
- it has several inlet and outlet openings, whose flow is controlled by a predictive model.

6.7 Conclusion

The advantages of the HTLT concept are a one hybrid thermocline thermal energy storage system with a lower cost and superior thermal energy efficiency, due to its stratification and control strategies coupled to weather data forecast and real time monitoring of critical parameters. This new concept can also incorporate “modern slag”, a waste material as part of the filler, which represents an environmental merit on its own. This will be explained in detail in the next chapter.

6.8 References

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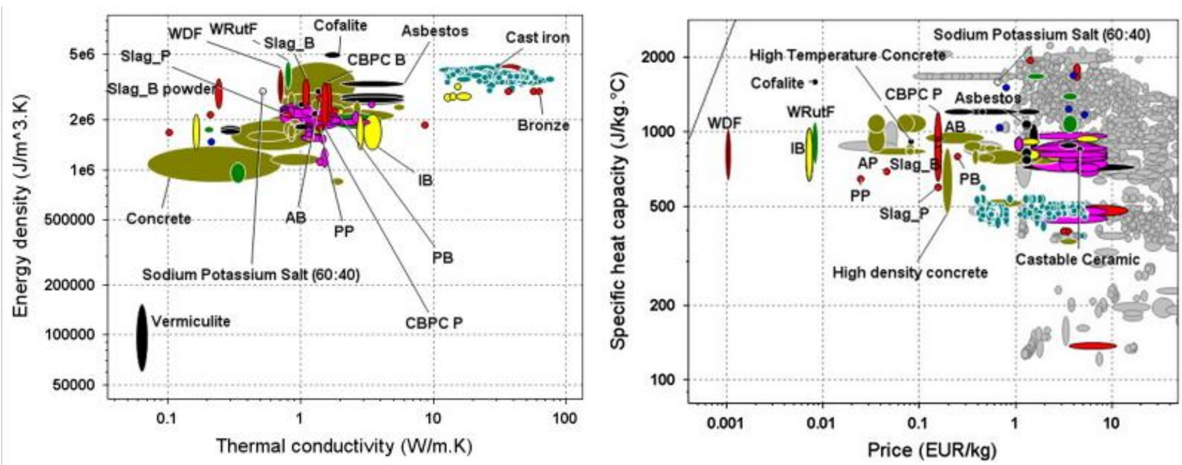
Chapter 7. New Materials for Thermal energy Storage

7.1 Material Research

In recent years, research has been performed, on direct MS systems [1], since it has several advantages like modularity and the possibility to combine with other (solid) thermal storage materials. This is one of the strategies for achieving a lower investment cost as well as a lower LCOE [2], which would make STE plants more competitive. Several alternative materials and systems have been studied in this research. Storage materials were identified with thermo-physical data being presented for different rocks (e.g. quartzite), super concrete, and other appropriate solid materials. Among the new materials being proposed like rocks from old quarries, an interesting option is the incorporation of solid waste material from old mines belonging to the Iberian Pyritic Belt [3]. These are currently handled as byproducts of past mine activity, and can potentially constitute an environmental hazard due to their chemical (metal) content. These materials are part of a broader study to improve the current concept of solar energy storage for STE plants, having the additional merit to become a valuable solution for environmental protection related to re-use of mining waste.

In order to find materials with a lower investment cost when compared with molten salts, several alternatives have been studied in the past [4]. Characterization of these materials has been performed and work has been done both at lab scale and at demonstration levels using for instance cofalite, an inert ceramic by-product originated from plasma treatment of asbestos [5]. The way to use these “low cost” materials in new systems has also been subject of research for instance using concrete as a binder to agglomerate selected aggregates [6].



(a) (b)

Fig. 7-1 – Overview of solid material selection (a) thermal conductivity, (b) cost

However, up to now, the subject of the selection of the suitable solid materials, even when cost and thermal performance is known has not been optimized in a system to achieve the best output with current and future operating conditions of STE plants, which operate at temperatures up to 400ºC (Parabolic Through plants) or 565ºC (Tower plants).
Additionally, material validation and durability are also issues that need to be deeply investigated before these materials can be seen as an alternative or a complement to the current molten salt storage technology.
Possible candidates for this quest are rocks as a by-product from old quarries and SLAGs as a by-product of mining activity. On average between 30 and 70% of the material extracted from quarries is dumped as a residue, most of it without any subsequent valorization. In the case of mines is even worst, thus in this paper this second option is explained and studied for the case of south of Portugal.

7.2 Slag, a by-product of mining activity

The South west area of the Iberian Peninsula is rich in metals, especially in the Iberian pyrite belt. Already during Roman times the extraction of metals became permanent with metals like copper, sulphur, silver and gold having the greatest demand. Main mines in this area are: São Domingos, Aljustrel, Neves Corvo, Lousal (all in Portugal) and Rio Tinto (in Spain). Modern times of exploitation re-start at both locations by English companies, in São Domingos during 1857-1966 and in Rio Tinto during 1873-2001. Open Pit with either the gallery or the cut and fill method were the two main methods used. The residues of the ore pre and post-processed material, were accumulated in mining landfills in open air over a large area. These landfills have different materials, all with relevant content of heavy metals [7]. If this material could be suitable for energy storage, it would create a benefical situation both from an environmental point of view, as well as from an energy point of view.
One of the aims in the 19th century was the extraction of elemental Sulphur, to produce sulphuric acid from mineral sulphides for the chemical industry. The decomposition of pyrites into pyrrhotite and elemental sulphur on heating has long been recognized as the potential basis for a process, with several furnaces being built in the mid 19th but with poor results. One of the obstacles were the impurities (like Arsenic) in the pyrite which created problems. Orkla, a mining based company originally set in 1904 to exploit a huge pyrite mine in Norway, developed important production processes related to the exploitation of the mine. The most important technological development was its patented industrial Orkla-process to make pure sulphite out of the pyrite [8], a process that was applied in several mines like the Rio Tinto and Sao Domingos mines. The process includes smelting of cupreous pyrites in an enclosed blast furnace, designed to prevent ingress of air at the top, to recover both matte and elemental sulphur. Pyrites, fluxes and coke are fed through double bells, similar to those used on the iron blast furnace. Hot gases leaving the furnace are cleaned by electrostatic precipitators and cooled to condense the Sulphur. The first gas filtration stage was to remove impurities such as lead, zinc, arsenic, iron and silica and the second to remove uncondensed sulphur mist before

discharging gas to atmosphere. Due to the technological evolutions which had an impact on the cooling rate of the slag, there are batches of material with characteristics significantly different. In any case, SLAG is a product left over after a desired metal has been separated.

(a) (b)

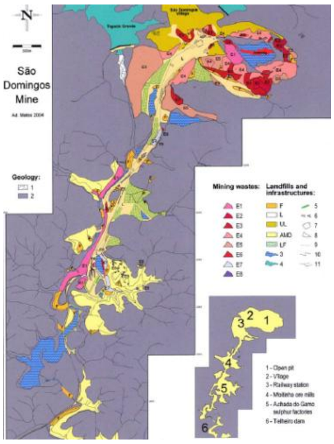
Fig. 7-2 – São Domingos mine, (a) Main pit cross section (“iron hat”), (b) Main pit, slag

The European Union (EU) estimates that in EU alone, the total amount of rock waste as a result of past mining activity is 8,976 x 10^9 ton [9]. This material has been disposed either because it had no ore content, or its content was lower than the commercial threshold. Additionally, within EU the ratio between production and ore can vary by a factor 10 or more, within EU, taking Copper as an example ore grades in European mines vary from 0,4 to 5% underground mines which genera less waste.

7.3 Environmental issue

Mining activities took place in São Domingos until 1966 in a total surface area of 450 ha. From all the residues currently at the surface, 653.571 m^2 is occupied by industrial landfill and leaching tanks, while 544.046 m^2 by waste with mixed rocks [7]. The total volume estimated is ca. 27 Mt which are laying around the main pit and on both sides of a water stream that flows southwards into the Chança River. As a result of this long mining activity at Sao Domingos, large volumes of residues were produced and dumped at several locations accumulated in different thicknesses varying from 14m near the open pit to less than 1m at the locations furthest downstream. All these piles contain significant amounts of metals, which might be either a source of pollution (of soils, surface and groundwaters), or a potentially valuable by-product.

Further use of this SLAG which currently is a by-product with no economic value is of great importance, for instance for the manufacture of aggregates (fig 3b). A detail study of the different slag batches apart from characterizing its composition, might point out that it makes sense to perform a re-smelting operation or other alternative chemical handling to obtain valuable and metal concentrates, amounts that have been estimated by previous research [7]



(a) (b)

Fig. 7-3 – (a) Sao Domingos site map (b) slag incorporated in aggregate mix to produce concrete mix

Weathering effects are observed in a considerable extend of the slag deposits, denoting significant chemical reactivity of their glassy component, which makes these slag pile deposits (fig 7-2b) a potential source of metal pollutants. The main problems are:

- leakage of heavy metals into the soil and ground water
- high emissions due to Acidic Mine Drainage (PH 1,5 – 2,5 in superficial groundwater)
- low pH water flowing into the Chança and Guadiana rivers
- aquifer contamination

A recent study indicates that as much as 5400ton of SO4, 38 ton of Arsenic, 9 ton of Copper are being emitted to the water in São Domingos area every year. It terms of Human toxicity it represents 400 Daly with an estimated damage cost of 3,8 MEuro/year [10].

7.4 Characterization of the slag

SLAG piles at São Domingos represent 8% of the mine residues accumulated in that place, recording discarded outputs of the ore smelting carried out in different periods of the massive sulphide and its "iron hat" exploitation. The major constituents of a well identified waste named as "modern slag" (produced between 1934 and 1962) are crystalline silicates (mostly olivine and pyroxene), magnetite and glass; with accessory amounts of sulphides and metal alloys. According to the literature. modern slag is iron-rich (30-40%) and contains up to 1.7% Zn, 0.9% Pb and 0.5% Cu. [7]

SLAG characteristics reflect mainly the chemical composition of the ores and additives used in smelting, also being strongly influenced by the temperature and cooling rates of the melts produced and, subsequently, discarded. During the smelting process, however, the density and viscosity of the molten slag has to be kept low enough to ensure the gravity separation of metal-rich liquids (sulphide matte). Under ideal conditions, silicate slag should float on to the surface of the sulphide matte, concentrating the oxide components of the silicate gangue and additives. Nonetheless, metal-rich droplets unable to decant in time will be incorporated in slag. The relative abundance of Fe-olivine (theoretically formed at 1100-1177ºC) strongly suggests that the temperature reached in the furnace must have been no less than 1200ºC. The melts produced were poor in Calcium. The prevalence of these crystalline silicates together with the absence of melilite, indicate also that the slag was cooled and quenched quickly or under a fairly fast rate; this is consistent with the observed textures [11].

It should be noticed, that the piles of weathering slag since they can have quite a large volume, also have unweathered SLAG under it. The exterior zones are characterized by alternate silica and iron rich zones, with the composition of different phases of slags varying considerably. Major elements vary in composition within the ranges presented in the following table.

Table 7-1: Elemental characterization of the slag in weight (%) [12]

Component	Unweathered slag	Weathering silica rich products	External iron rich products
SiO2	35,2 – 45,2	65,4 – 70,2	1,2 – 2,9
CaO	1,1 – 12,6	0,1 – 0,3	0,02 – 0,04
FeO	37,9 – 54,8	4,8 – 12,2	33,7 – 71,5
S	1,1 – 2,6	0,5 – 3,1	1,4 – 7,3

Furthermore, on a SEM/XRD analysis it is possible to identify in the outer area of the slag, the presence of iron, lead, zinc, plomb and arsenic rich deposits (Fig.7-4)

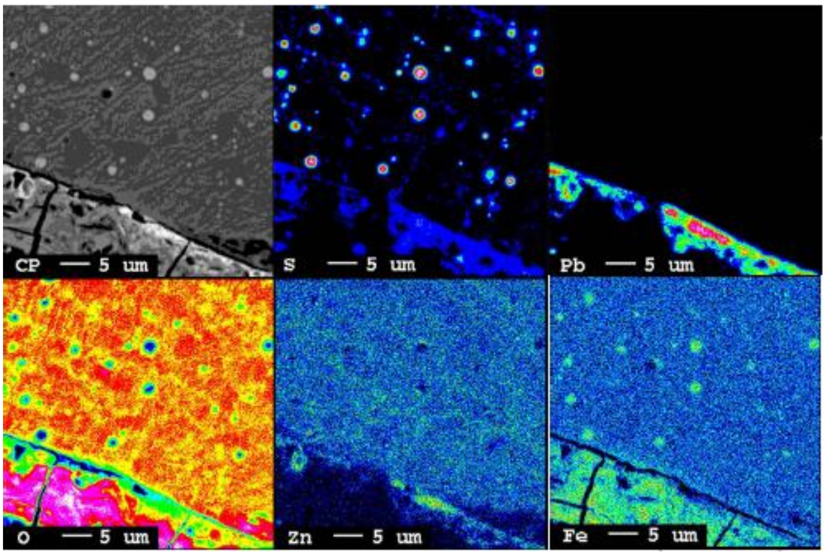


Fig. 7-4 – SEM / XRD Analysis of “modern slag” [12]

7.5 Valorization scenarios for the slag

From the existing SLAG piles at *São Domingos*, 3 samples were taken and different valorization scenarios for the slag were analyzed:

- Extract existing valuable metals in the SLAG
- Use the slag as aggregate material in the construction industry (e.g. road pavement)
- Use the slag as filler material for energy storage
- Use the slag as aggregate material for energy storage

7.5.1. Extraction of valuable metals

As for the first valorization scenario, economically relevant grades of Sb (above 1%), Bi (above 0.2%) and Re (until 3.4 mg kg-1) together with other minor metals were found in the *Achada do Gamo* waste pile in a Cu-rich pyrite ore. In this gossan dump, interesting Au concentrations (1 to 4 mg kg-1) can still be found [12] and could be subject to extraction for instance using a high concentration 3D central receiver concept with a CPC type second stage concentrator reactor that would be able to extract the small quantity of metals in the slag using only solar energy as a power source, thus a sustainable reconversion process. Samples were collected in 3 different locations of *São Domingos* area and a test plan with a specific sequence was defined. Experiment using solar radiation will take place in the future when weather conditions allow, the aim is to evaluate if this process is suitable for the purpose of extracting valuable metals.

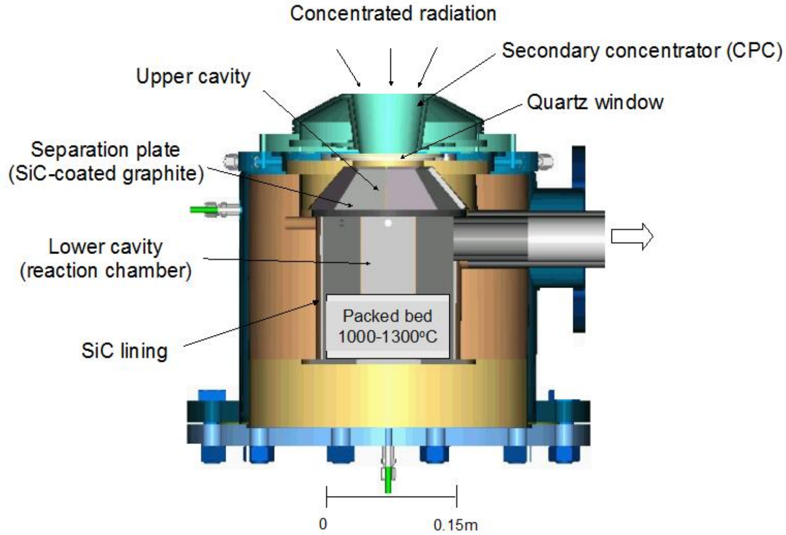


Fig. 7-5 – CPC type second stage concentrator reactor [15]

7.5.2. Usage in the construction industry

As for the second option, the construction sector is currently on a down turn making it difficult to compete with low cost aggregates from quarries which have a well defined origin and characterization. Usually, specific studies with different binder mixes and studying non-homogeneity effects are needed to check compatibility, a topic which is out of the scope of present work.

7.5.3. Usage as filler material

To evaluate the interest of being used as a filler material, the requisite is that a solid material has to withstand well thermal cycles in contact with molten salt without degradation. Three different samples were collected at *São Domingos* mine waste piles and representative grain size was selected (Fig.7-6). After 24h of exposure, via SEM analysis there was no degradation identified on the surface of any of the 3 samples, thus it was defined that long term tests should be performed, with a final chemical analysis of the salt indicating if the system is stable.

Fig. 7-6 – Samples selected as filler (from left to right ref: L1, L3, L4)

From a minearologic point of view these samples had already been characterized [11]. The next step was the immersion into a molten salt (solar salt) bath for 500h, that is direct contact between molten salts and each filler was performed. Data analysis (DSC, colligative properties method) shows that the onset in all samples is lower than the onset of the samples with filler material suggesting that the filler material (ref.L1) slightly degrades and gets dissolved into the molten salt. However the degradation process can be reduced very much by utilizing appropriate filler materials: The sample with the filler "ref.L1" only shows a minor shift (1,31º) in the onset temperature, Fig.7-7. This shows that – by screening different filler materials (ref: L1, L3, L4) the degradation was reduced successfully.

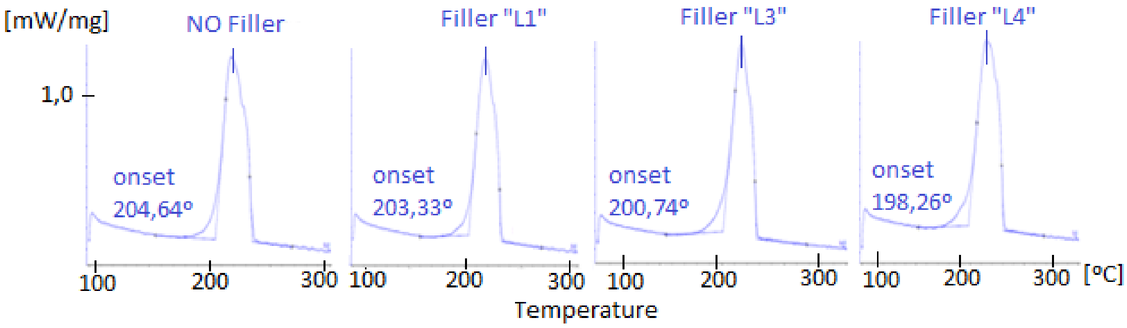


Fig. 7-7 – DSC Analysis: Filler testing in contact with Molten Salts (500h for 500ºC)

This is a promising application field, in the sense that for this application particle size can vary and non-homogeneity can be a relevant issue. Preliminary results are encouraging, pointing out that these materials can be used in direct contact with MS without chemical or physical degradation. However a final conclusion will be reached only once long term compatibility test results will be known.

7.5.4. Usage as aggregate material for energy storage

For the fourth scenario, a new solid material was elaborated (next sub-section) using slag as a substitute of aggregate and a cement as the binder. A CAC mortar based, with different mixes was prepared in order to compare the performance of different types of cement and aggregates among them the SLAG. Using concrete as a binder for high temperatures is a recent research field, thus there is not yet a single preferred mixture. Both CAC, OPC cement types as well as a mix of both are possible to find in the literature [13]. For the current study, a CAC based binder was used because of its superior performance at high temperatures (ca. 550ºC). BFS was included as an additive to the CAC mix considering a w/c ratio of 0,5. One OPC mix was used as a comparison.

Table 7-2: Samples, mix chemical composition

Mix	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	SO_3 %
OPC	17,4	4,7	5,1	60,3	1,8	0,2	0,3	3,2
CAC	4,4	40,3	15,2	37,4	0,5	0,2	0,1	0,1
70CAC / 30BFS	36,6	10,4	0,3	45,5	7,5	0,4	0,5	0,1

Apart from the binder selection, the type of aggregate is another fundamental parameter for concrete thermal stability.

The current study aims at identifying which changes occur to the aggregates, namely:

- chemical transformations related with mass losses as occurs with calcareous aggregates, (most transformation of $CaCO_3$ into CaO and CO_2 occur above 600ºC while the heat cycles were limited to 550ºC)
- volume stability, since while most aggregate tend to expand (siliceous aggregates more than carbonates), the cement paste suffers dehydration which leads to a shrinkage process and thus decreasing volume

Table 7-3: Samples analyzed with different types of aggregates

Sample	Mix type	w/ c ratio	SiO agg.	CAL agg.	SLAG agg	CAT agg
1	OPC	0,5	yes	-	-	-
2	CAC	0,5	yes	-	-	-
3	70CAC / 30BFS	0,5	yes	-	-	-
4	70CAC / 30BFS	0,5	-	yes	-	-
5	70CAC / 30BFS	0,5	-	-	yes	-
6	70CAC / 30BFS	0,5	-	-	-	yes

7.6 Thermal resistance evaluation

To validate the option of using SLAG as aggregate material for energy storage, an evaluation of its heating resistance incorporated in mortars and in aggregates was performed. Samples were exposure to thermal heat cycles (1, 10 and 25 cycles) inside an electric furnace with a periodicity of 24 h each. In order to simulate real conditions of a plant operating with 2 MS tanks, the maximum temperature defined for the cycle was 550±5ºC, constant for 8h and the minimum 290±5ºC constant for 16h in order to simulate a day cycle.

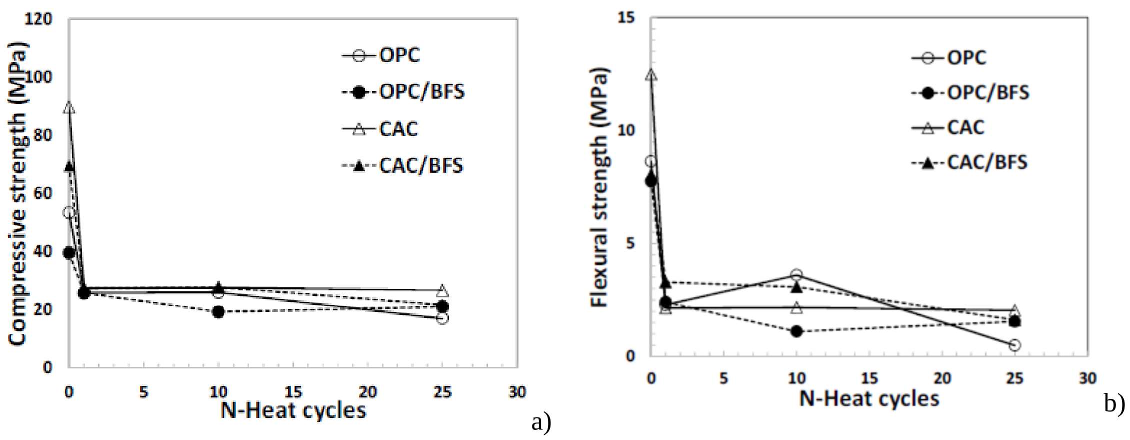


Fig. 7-8 – Mix subject to heating cycles (a) compressive (b) flexural strength

Analyzing samples subject to 1, 10 and 25 cycles it is possible to verify a decrease on the strength of all the samples already on the first cycle performed. In the cases analyzed, a decay in mechanical properties in the order of 50% or more from the initial state is observed, due to the dehydration process occurring in the cement paste.

However after the first cycle, no relevant changes are appreciated for CAC mix after 10 and 25 heat-cycles while a progressive decrease is observed in the case for OPC. One explanation can be that it is a consequence of progressive swelling risk has reported in [14]; this phenomenon is observed both in compression and in flex resistances. In order to understand the possible influence of BFS, an additional sample was made of OPC with BFS, (Fig. 7-8). Results indicate that the effect is that this sample has a performance lower than CAC but significantly better than the OPC alone. This indicates that a CAC mix shall be preferred to an OPC mix.

Concerning aggregate composition, mass losses with mortar of the same cement type (CAC with BFS) and 4 different aggregates (table 3) were tested, namely using Silicious (SiO), Calcareous (CAL), and Calcium Aluminate (CAT) and additionally the slag (SLAG) intended to be validated.

The most stable is SiO, probably because higher mass losses occurs in the calcareous based samples due to progressive decarbonation. Slag samples have a very similar behavior to SiO which is clearly a very positive result for its usage as an alternative aggregate.

Another analysis was performed using an ultra-sound velocity measurement technique (Fig.7-9b). It can be observed that the ultrasonic velocity followed a sharp decrease after the first heat-cycle. Additionally it can be seen that repetitive heat/cool cycles penalize more strongly the samples with SLAG and SiO aggregates, which means that CAT and CAL shall be preferred when internal cohesion is an important issue.

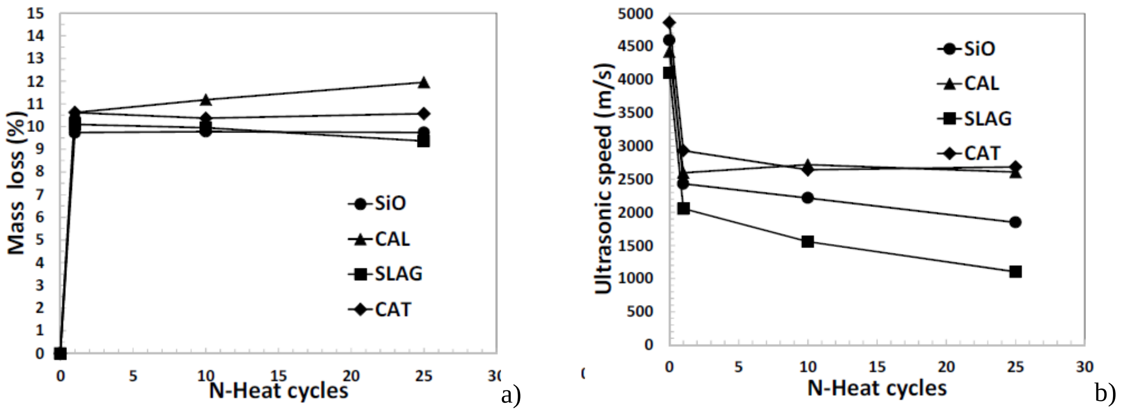


Fig. 7-9 – Heating cycles (a) mass loss (b) ultrasonic speed

Concerning mechanical properties changes (fig.8), and analyzing after the first heat cycle, there is a decay in all cases independently of the aggregate type. The dehydration is in this case the controlling parameter. With further heat-cycles Slag samples and SiO samples are the most penalized aggregates particularly in the case of flexural strain forces, which can induce more fatigue damages than the samples with CAT and CAL aggregates.

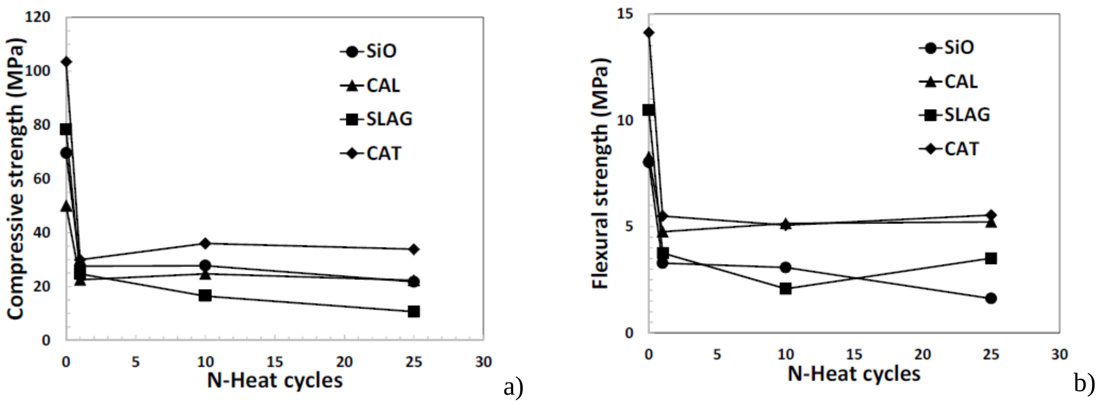


Fig. 7-10 – Mechanical resistance (a) compressive (b) flexural

To be conclusive, further studies using the optimum mixes are needed, using appropriate cement/aggregate balance. Present study recommends CAC base cement suitable for its refractory stability at repetitive heat-cycles. As for the aggregates CAT and CAL perform best, especially from a mechanical point of view, however SLAG can be an alternative if this parameter is not the most relevant one, as it is the case with energy storage. Overall, slag performs better than the SiO analyzed, meaning that it is a more suitable choice.

Furthermore, long term durability tests and chemical analysis to the salts are scheduled, so that a more complete picture will be obtained for a possible final recommendation concerning the usage of SLAG as a new solid storage material for STE plants.

7.7 Conclusion

The usage of new options for solid materials suitable for high temperature energy storage, is in line with the search of alternatives to more conventional options, in view of decreasing storage costs. In this chapter it is reported a preliminary analysis of the SLAG, a material which is highly abundant in many old mines and is handled as a waste material up to now.

SLAG from mining activities in *São Domingos* has been studied because of the possible environmental impact reduction associated with its reuse, with 4 different alternatives being proposed. All of them have merit, and will be further detailed in the future, for now the usage as aggregate for energy storage seems a promising one.

Additional analyses of the usage of SLAG being incorporated into cement based mortars were performed. The conclusion is that as a binder, CAC base cement is recommendable for its refractory stability at repetitive heat-cycles and should be selected. The aggregates CAT and CAL showed the best performance from a mechanical point of view. However SLAG can be an alternative if this parameter is not the most relevant, as it is the case with energy storage. A broader validation will be reported in future work, after conclusion of long term durability tests.

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Chapter 8. Calcium Aluminate Cement for energy storage

8.1 Cement for high temperature applications

The temperature requirements of cyclic loads between 200 and 550ºC in a STE storage unit are very demanding for any material. Using cement, a refractory concrete special design has been developed with the target to be exposed for long periods above 500ºC.

Refractory concretes in the past were used primarily as a protective lining, as a consumable material that needs to be replaced after an appropriate service life. In recent years, refractory concretes for large load-bearing structures were developed, as for nuclear power plants [1].

Actually, many different materials can be used for refractory purposes and some of them are based on the use of hydraulic cements: OPC allows limited refractory applications and the refractory properties are mainly provided by the use of appropriate aggregates in the mix. Calcium silicates hydrates (CSH) from the hydrated OPC decompose at temperatures above 105ºC and calcium hydroxide (CH) at temperatures around 450ºC, both forming CaO as main dehydrated residue [2]. After cooling, the CaO can be easily rehydrated again by absorbing moisture from the atmosphere with the consequent swelling of the hardened paste, increasing cracking and also causing powdering of the cement paste after been exposed to temperatures above 500ºC. Therefore, thermal cycling could result in severe disruption and damage [3]. Blended cements, using blast furnace slag or natural pozzolans as mineral additions generate more CSH and less CH than plain OPC, so that dehydration follows similarly as in the Portland case except for CH and then, the residual strength can be higher after cooling than in the case of pure OPC.

Therefore, for the reasons mentioned, attention is focused on high alumina cements (CAC type). It is a hydraulic cement that combines water to harden and increase strength. At normal temperatures and moisture the first hydrated phases are CAH_{10} and C_2AH_8 and colloidal aluminium hydrate CH_3. Hydration takes place very rapidly allowing high mechanical strength after 24hr. However these initial hydration phases are chemically unstable and conversion reactions to more stable hydrated phases take place, C_3AH_6 and AH_3 [4]. The density of this last cubic phase is higher (2,5 g/cm^3) than that of the initial hexagonal phases (1,7 g/cm^3). But this increase in density occurs with a reduction in volume, thus there is a porosity increase of the paste, which is considered to be the main cause of the strength decay. Several actions have been considered to retard or completely eliminate the conversion of hexagonal phases to cubic one. More commonly used solutions are based on the incorporation of mineral blends containing high silica content, as BFS, fly ash (FA) or silica fume (SF) to avoid the C_3AH_6 transformation from early hydration ages from the formation of hydrogranet calcium aluminates, which contains silica in its structure that are more stable, and also promote the formation of Afm phases [5], even mixes with OPC/CAC can control the conversion.

There are relatively few studies on CAC dehydration compared with the ones available for Portland cement paste. Research [6] shows that above 105ºC the chemically combined water of CAC paste is gradually lost from hydrated aluminates. Most important changes occur up to 300ºC: dehydration of CAH_{10} and CH_3. At temperatures between 400-500ºC the dehydration of aluminate hydrate should be completed. As occurs in case of hardened Portland cement paste, the density and porosity of CAC pastes change due to dehydration on exposures above 100ºC. Porosity of CAC concrete can increase by about 25% up to 500ºC. These changes in porosity and density affect the strength of CAC paste. From 200 to 600ºC CAC paste strength might decay 50%. At higher temperatures no significant changes occur until melting above 1300ºC. Additionally, the dehydrated CAC is more stable after cooling reducing swelling risk.

One additional importunate characteristic to consider is that CAC type concretes are considered to show also higher chemical resistance in aggressive environments than OPC concretes [7], being this aspect relevant if concrete structure have to resist to aggressive environments at high temperature like molten salts in case there is a direct contact concrete mix to the molten salts.

Studying the suitability of the refractory concrete for TES in STE plants is the topic of this chapter, with the development of a high temperature resistance CAC based concrete stabilized with BFS. Aggregate composition and size influence is considered, and mechanical and microstructural properties analyzed after air treatments at temperatures in the range 290 to 550ºC in different number of thermal cycles: 25, 50 and 75, corresponding roughly to 1,2 and 3 months of STE plant operation.

8.2 Experimental Set-up

Calcium Aluminate Cement (CAC) was blended with blast furnace slag (BFS) to stabilize the conversion process, with a binder mix of 70 % CAC plus 30% BFS. The chemical compositions of both components are included in Fig. 8-1. Accordingly to standards [8], for special refractory concretes the total alumina content shall be no less than 32% and the ratio of the percentage by weight of alumina (Al_2O_3) to that of lime (CaO) should be no less than 0.85 or more than 1,3. The CAC used has 40% Al_2O_3 and Al_2O_3/CaO ratio=1, so that complains with this basic requirements as hydraulic binding agent in refractory concrete. In addition the iron content also has a relevant role, a content of 15% Fe_2O_3 limits the maximum temperature usage to 1370ºC.

	%SiO_2	%Al_2O_3	%Fe_2O_3	%CaO	%MgO	% SO_3	%Na_2O	%K_2O
CAC	4.40	40.30	15.20	37.43	0.47	0.06	0.16	0.14
BFS	36.57	10.39	0,29	45.50	7.46	0.05	0.42	0.49

Fig. 8-1 – Chemical composition of CAC cement and BFS (weight %)

	Particle size distribution (%)					Mean particle size (µm)
	10	25	50	75	90	
CAC	0.71	3.68	9.89	23.34	36.40	15.10
BFS	1.11	2.20	3.74	7.50	17.59	4.19

Fig. 8-2 – Particle size distribution, CAC and BFS

The mean particle size of BFS is three times lower to that of CAC cement. In Fig.8-3a, XRD analysis shows the mixtures main components, the main crystalline component of CAC is calcium monoaluminate ($CaAl_2O_4$, CA), other phases are $C_{12}A_7$, C_4AF and Al_2O_3. The BFS shows massive presence of amorphous phases together with some crystal phases as calcite, gehlenite (calcium aluminosilicate) and calcium-magnesium aluminosilicates.

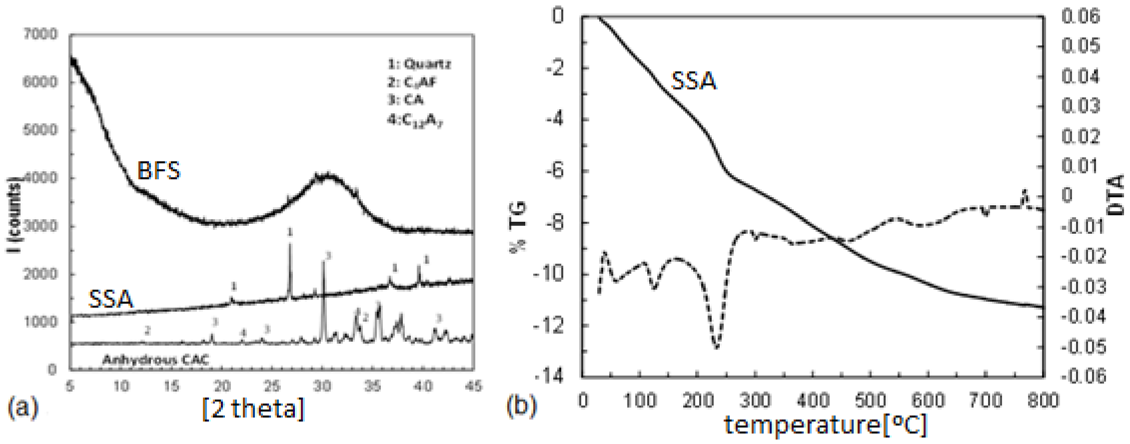

Fig. 8-3 – XRD of anhydrous CAC with BFS and SSA aggregate (a); TG/DTA of SSA aggregate (b)

Mortar and concrete specimens were prepared with the binder (CAC+BFS). Mortar samples of 4x4x16 using standard siliceous sand (1-4mm), c/s= 1/3, w/c=0.44 and an additive (1% sikament-180), were prepared with a fluidity of 17mm. For concrete design, two types of aggregates were used, from 0 to 12 mm size:

1) Natural aggregates from crash stone with silicone-calcareous composition (SCA) mainly constituted by quartz and calcite
2) Aggregate from industrial waste slag from ore processing (SSA, details in chapter 7) with a partial crystalline structure, with quartz (SiO_2 content variation 25-40%, Fe_2O_3 (40-60%), with Al_2O_3 and CaO content residual (less 3%). The TG/DTA data shows that SSA follows progressive mass loss at high temperature, the more relevant occurring at temperatures below 300ºC, probably associated to iron components and loss of bound water and oxidation at high temperature. Crystalline transformation of the quartz component from α to β-quartz occurring at 550ºC is also detected.

Two different concrete dosages were prepared maintaining the same type and content of CAC+BFS binder, but varying the type of aggregate. CAC samples refers to concrete prepared with 100% of SCA, while the CAC+ refers concrete made with a mix of 75% SCA+ 25% SSA. The adjustment of aggregates dosage for CAC+ concrete was made following a Bolomey curve. It can be seen that the introduction of SSA gives more homogeneously to the distribution of all ranges of aggregate particle size. Final dosages of CAC and CAC+ are presented in Fig.8-5.

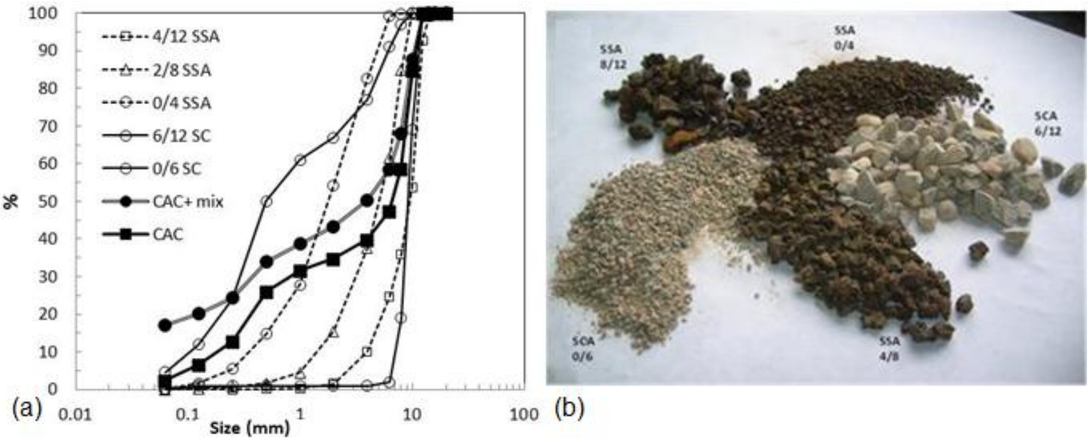

Fig. 8-4 – Bolomey curves for CAC and CAC+ mixtures (a) SCA and SSA aggregate type (b)

	Water	w/b	CAC	BFS	SCA 0-6	SCA 6-12	SSA 0-4	SSA 4-8	SSA 8-12	SP (%)
CAC	200	0.5	280	120	805	845	-	-	-	0.8
CAC+	228	0.57	277	123	698	698	190	149	111	0.8

Fig. 8-5 – Components of CAC and CAC+ mixtures (kg/m^3)

After several trials the water cement ratio (w/c) was chosen, w/c = 0.5 for CAC and w/c= 0.57 for CAC+, because SSA needs more water to maintain same fluidity without concrete bleeding. The cone of both type of concretes varied between 5.5–6cm. With these two mixtures, cylindrical concrete samples of 7.5cm in diameter (Ø) and 15 cm in height were prepared and cured for 7 days under standard conditions (22±2ºC, 100%±5%RH) in a chamber. After curing each concrete sample was cut in two halves allowing a Ø/H=1.

Compressive and flexural strength was measured after 7 days of curing, followed by XRD and TG/DTA to determine initial hydrated phases, as well as mercury intrusion porosimetry.

8.2.1 Pre-conditioning and heating protocol

After the curing process, concrete samples were pre-dried before exposure to heat cycles to minimize risk of spalling during the first heating cycle. The drying protocol was 3 days drying at

60ºC to eliminate most of the water in capillary pores, but without affect significantly the hydrated solid phases. In this phase water loss of both CAC and CAC+ was 3.54%±0.23.

The thermal resistance of concrete to cyclic loads was evaluated throughout the exposure inside an electric furnace of the samples to heating/cooling cycles. Each period last for 24 hours the maximum temperature set to 550±5ºC and the minimum 290±5ºC. A heat rate of 1ºC/min was selected for the first heating step, to minimize thermal damage and crack developing as consequence of strong temperature gradients in the bulk of the samples respect to the concrete surface, in order to guarantee that the changes were mainly consequence of dehydration of cement paste. For the next cycles it was used a heating rate 9ºC/min up to 550ºC followed by cooling to 290ºC at a rate <1ºC/min and staying at that temperature until starting the next heat-cycle. For each week, periods of 5 heating/cooling cycles of 24hr and 2 days constant at 290ºC plateau were considered until 75 cycles were completed. Samples were taken from the oven at 25, 50 and 75 cycles for analysis. During the heat-cycles the temperature inside the oven and at the surface level of the samples was recorded to continuously identify the thermal regime performance and evaluate the thermal inertia of concrete.

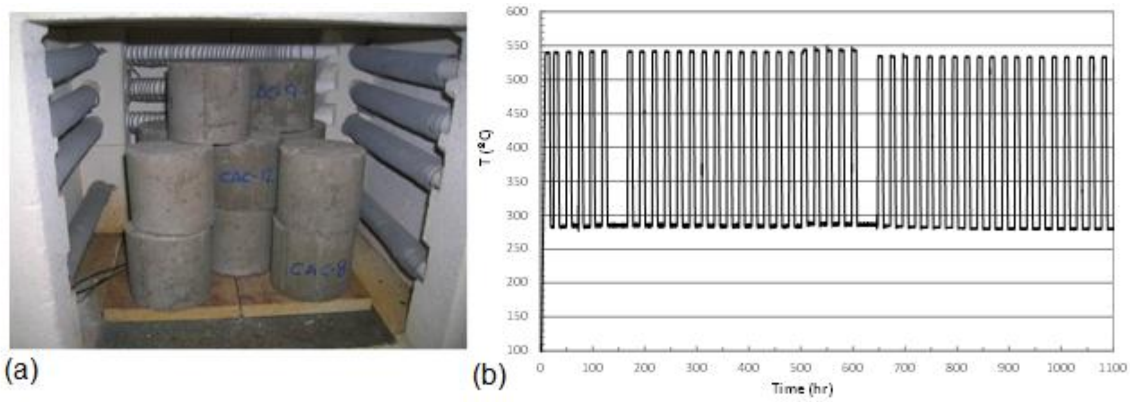

Fig. 8-6 –CAC and CAC+ cylindrical samples, in the oven (a), heating cycles (b)

8.2.2 Methodology

Samples subject to heat/cool cycled samples were characterized using different techniques from macro to micro level. At macro level, mass loss, ultrasound velocities, compressive and flexural strength were determined. At micro level, DRX (concrete and also mortar samples) TG/DTA (only mortar), mercury intrusion porosimetry, thermal conductivity and SEM/EDS back-scattering microscopy were done measured.

8.3 Results and discussion

8.3.1 Mass loss

It is relevant to point out that most of mass loss takes place during first cycle associated mainly to dehydration processes of cement paste. In an intermediate measurement it was found that after 5 cycles the mass loss is practically stabilized, with values in the range 6-9%. In the case of CAC+ higher mass losses were measured, probably associated to the progressive alteration of SSA aggregates, which agrees with the TG data (Fig.8-3b). To confirm this, powder from SSA aggregate was heated for 24hr at 550º and mass losses above 3% were detected.

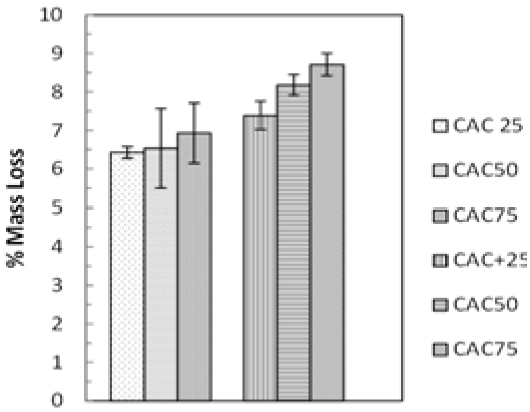

Fig. 8-7 – Mass loss after 25, 50 and 75 cycles

8.3.2 CAC stabilization due to BFS addition

As mentioned previously, CAC conversion phenomena of metastable hydrates, CAH_{10} and C_2AH_8, hexagonal structure, to C_3AH_6 cubic form can be avoided by introducing in the binder system a mineral addition with high SiO_2 content, like BFS. To understand this initial phenomena, CAC mortar was cured for 1 and 7 days. DRX, Fig.8-8, shows that the hexagonal forms associated to CAH_{10} and C_2AH_8 are present at the initial stage but after 7 curing days CAH_{10} and grossular-hidrogrossular solid solution with Si in their composition (hydrogranet type C_3AS_3-xH_2x) is detected. The formation of the Si-Hydrogranet is also confirmed with TG/DTA, with two singular exothermal peaks appear between 100-250ºC. More than 80% of the total mass loss takes place within this range of temperature due to the dehydration of these phases, which agrees well with the fact that CAC hydrates contain in their structure more bounded water that OPC CSH.

The control of the conversion process due to the incorporation of amorphous SiO_2 rich mineral addition with curing evolution due to hydration of CAC crystalline phases and BFS allows to detect an increase in mechanical strength, avoiding the strength decay associated to conversion evolution and C_3AH_6 formation due to its lower volume. After 7 days, for mortar samples, an increase of 47% was measured in compression and 37% increase in flexural strength, similar values registered in the concrete mixes.

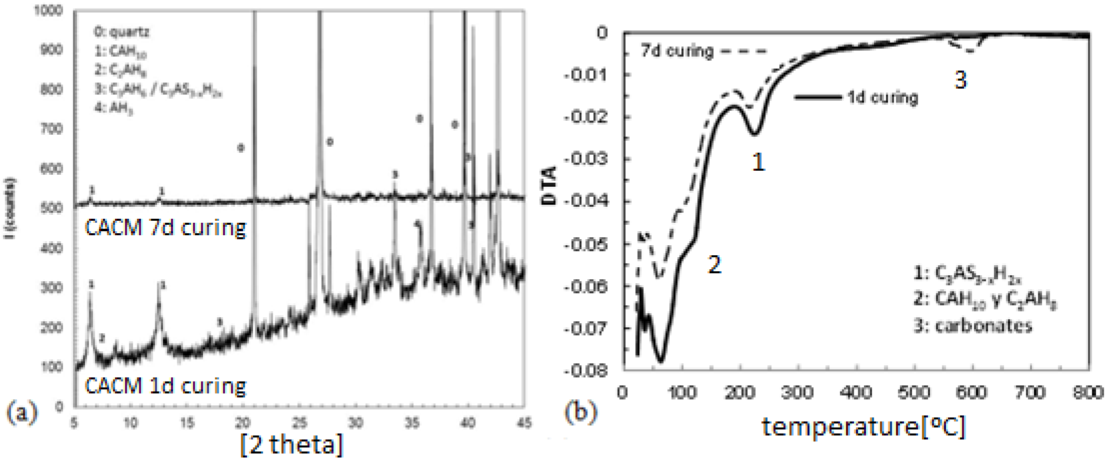

Fig. 8-8 – XRD (a) and TG/DTA (b) after 1 and 7 days of mortar curing

8.3.3 Thermal fatigue

The mechanical properties of CAC concrete mixes are affected due to heat up to 550ºC, Fig.8-9. This temperature level expected during normal STE operation is above the stability of CAC hydrates. Compressive strength decay up to 50% compared with the initial state, in agreement with results reported [9] with CAC concrete containing fly ash.

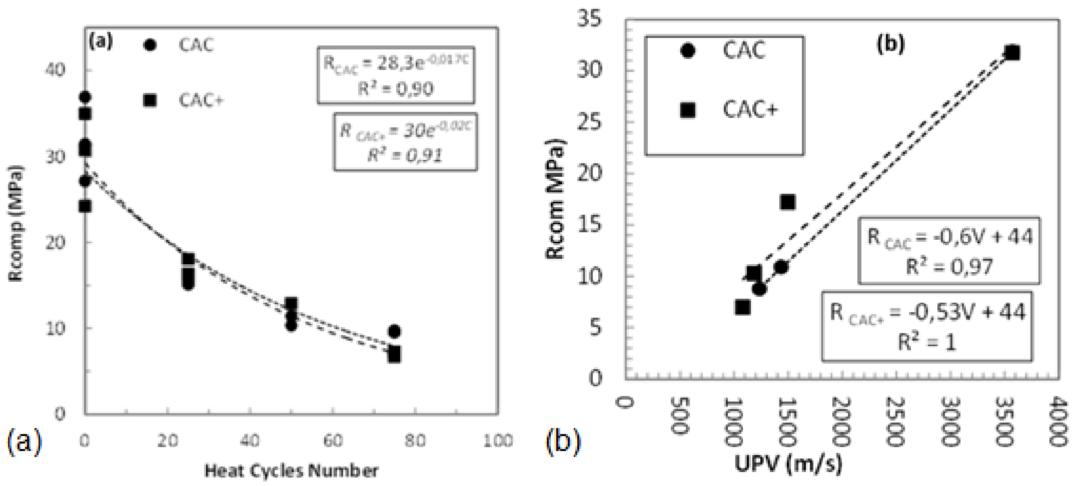

Fig. 8-9 – CAC/CAC+ samples after heat cycles, compressive strength(a) and its relation to ultra-sound (b)

It is noteworthy to point out that further heat-cycles do not follow the same trend decay, there is a stabilization effect, with the small size of aggregates (max. size 4mm) softening the effect of the fatigue due to thermal heat-cycles, a phenomena also reported in [10] using OPC+BFS.

Similar compressive strength decay values (Fig.8-9) are detected in both concretes mixes independently of the aggregate type, SCA or mix SCA+SSA, despite the additional mass losses occurring during heating with the SSA aggregate. The fatigue evolution with heat cycles is more pronounced in concretes mixes of higher aggregate size (max. 12mm). The repetitive expansions and contractions taking place during each heat-cycle can contribute to the crack propagation, which would explain the progressive decrease of ultra-pulse velocities (UPV) after heat-cycles. A good correlation between Rcomp and UPV has been found, Fig.8-9b. From the UPV values measured, dynamic elastic modulus of the concrete mix was estimated, Eq.8-1[11]:

$$E = \frac{Cp^2 \rho (1+\upsilon)(1-2\upsilon)}{(1-\upsilon)} \qquad \text{(Eq. 8-1)}$$

with: E: dynamic elastic modulus (GPa),

Cp: pulse propagation speed (m/s),

ρ: density of concretes (kg/m3)

ν: Poisson coefficient.

The Poisson coefficient for the initial state was assumed to be 0,2 as for normal concrete, however after high temperature exposure the ν value decreases even down to 0.08, values used for E estimation in present calculation.

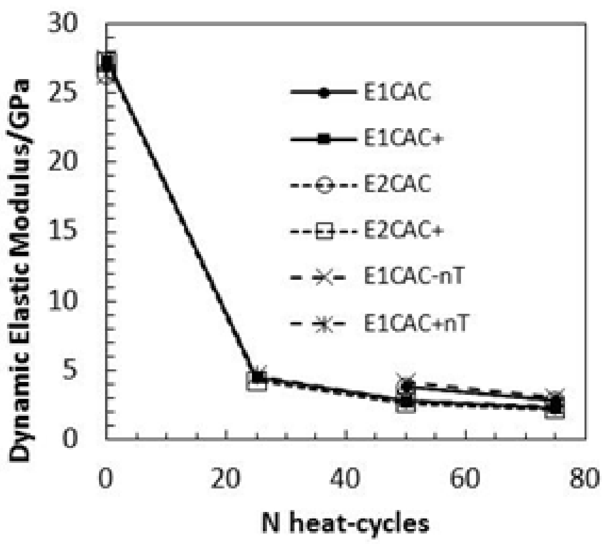

Fig. 8-10 – CAC/CAC+ samples after heat cycles, dynamic elastic modulus

In Fig.8-10 it is presented the evolution of E with heat cycles for 3 cases: “E1” using ρ calculated from mass and volume of sample, “E2” using ρ obtained from MIP and nT considering the influence of temperature in the calculation of the Poisson coefficient. All give very similar results showing the loss of E due to heating cycles.

The alteration of mechanical properties, in compression, flexion and elastic modulus, indicates that the concrete behavior both during pre- and post heating cycles should be analyzed in more depth, to guarantee the minimal performance requirements during the service life of the structure exposed to high temperature. The stabilization on progressive strength decay is fundamental, which suggests that additional measures to reduce the fatigue effect of heat cycles should be included in TES-concrete. To address this topic, a durability model with results from lab and a demo storage unit is foreseen to be developed during SOLSTICE project.

8.3.4 Changes in the microstructure

The reported changes observed at macro level should be a consequence of changes occurring at micro level. With XRD analysis similar crystal composition is observed in both concrete mixes. From a microstructural point of view, CAC+, with a high slag mineral admixture has allowed to control the conversion process, that is the initial hexagonal hydrates CAH_{10} and C_2AH_8 of a pure CAC have not evolved to the cubic C_3AH_6 and gibbsite (AH_3). Instead part of the hexagonal hydrates have evolved to the formation of members of the grossular-hidrogrossular solid solution with silica in their composition (C_3AS_3-XH_2X). Also quartz and calcite are identified as part of the aggregate composition.

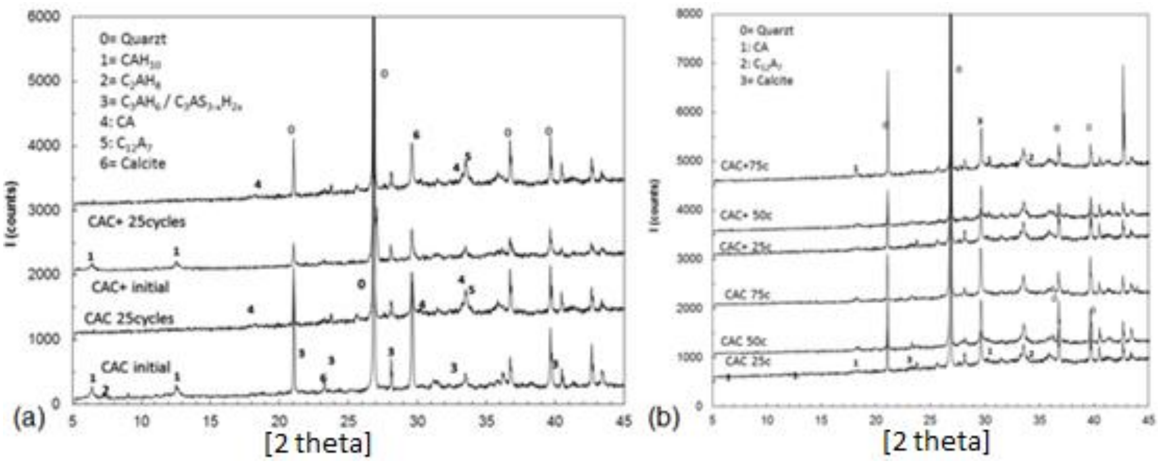

Fig. 8-11 – CAC/CAC+ samples, XRD (a) initial and after 25 cycles (b) 25, 50 and 75 cycles

After 25 heat-cycles, calcite and quartz are present (Fig.8-11), but also peaks near to the CAC cement anhydrous phases containing calcium and Aluminium are detected, together with phases containing silica in its crystal structure, such as Magenite, dehydration occurring at 500ºC. The chemical changes due to heating were also confirmed by an additional DTG test. It is important to notice that after the first heating at 550ºC all dehydration processes in CAH and CASH has been developed and further heat cycles are not inducing more chemical transformation, Fig.8-11b. Mass losses at this stage are more associated to progressive aggregate chemical transformations and alteration of dehydrated paste/aggregate interface.

Moreover, the heating cycles have induced changes also at pore level. The increase in porosity detected after 25cycles explains the decay in mechanical strength, both, the pore structure distribution and size are affected, Fig.8-12. A clear increase is observed in capillary pores below 3µm due to the dehydration of cement paste, the pore distribution and total porosity after 25 cycles (21%) is similar in both concretes, what explains the similar mechanical response found for both concretes. The main difference is in the initial porosity of CAC+ having less capillary pores (porosity 10.6%) but in the same pore region than CAC (porosity 12.9%), which might be a consequence of the distribution of aggregate size in CAC+ concrete using SSA, Fig.8-5.

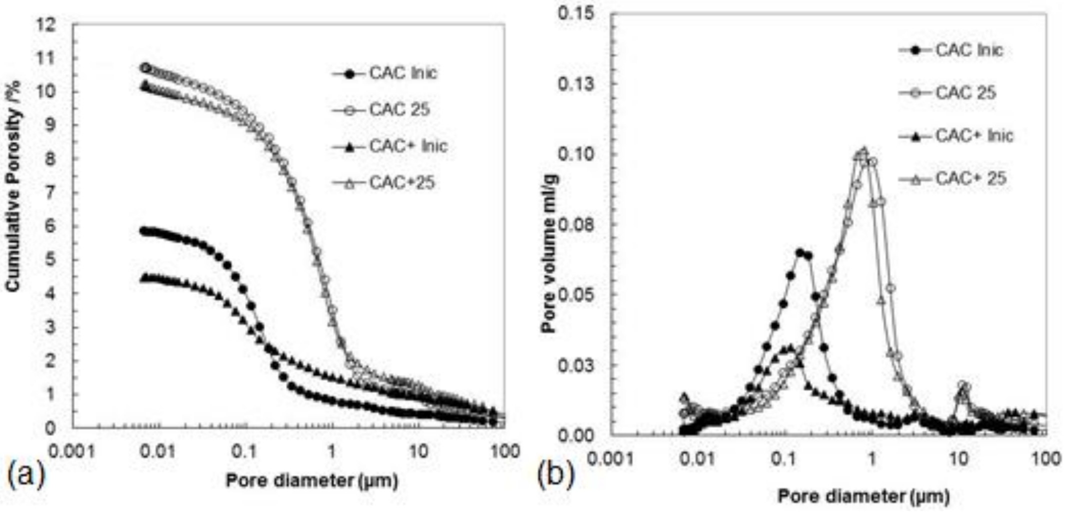

Fig. 8-12 – CAC/CAC+ samples (a) cumulative porosity (b) pore volume

All these transformations are confirmed through SEM and EDS. Changes in microstructure and density of the cement paste can be observed, Fig 8-13 8-14. Before heat-cycles a quite dense cement paste is observed in both mixes, containing some more crystalline zones and others with more amorphous shape. Zones with more amorphous aspect contain phases with higher Si/Ca ratio, associated to hydrogrossular incorporating Si as solid solution from the hydration of BFS with CAC. Zones more crystalline contain higher Al/Ca ratio and low Si content.

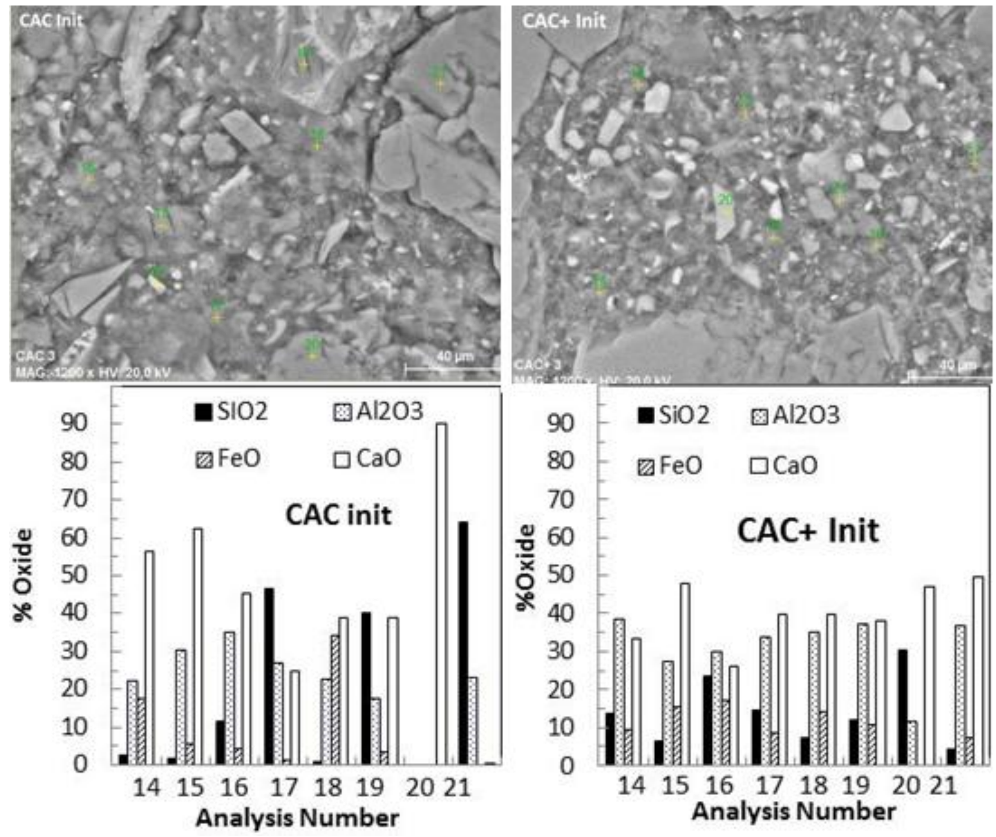

Fig. 8-13 – Microstructure before heat cycles (up) cement paste (down) oxide composition

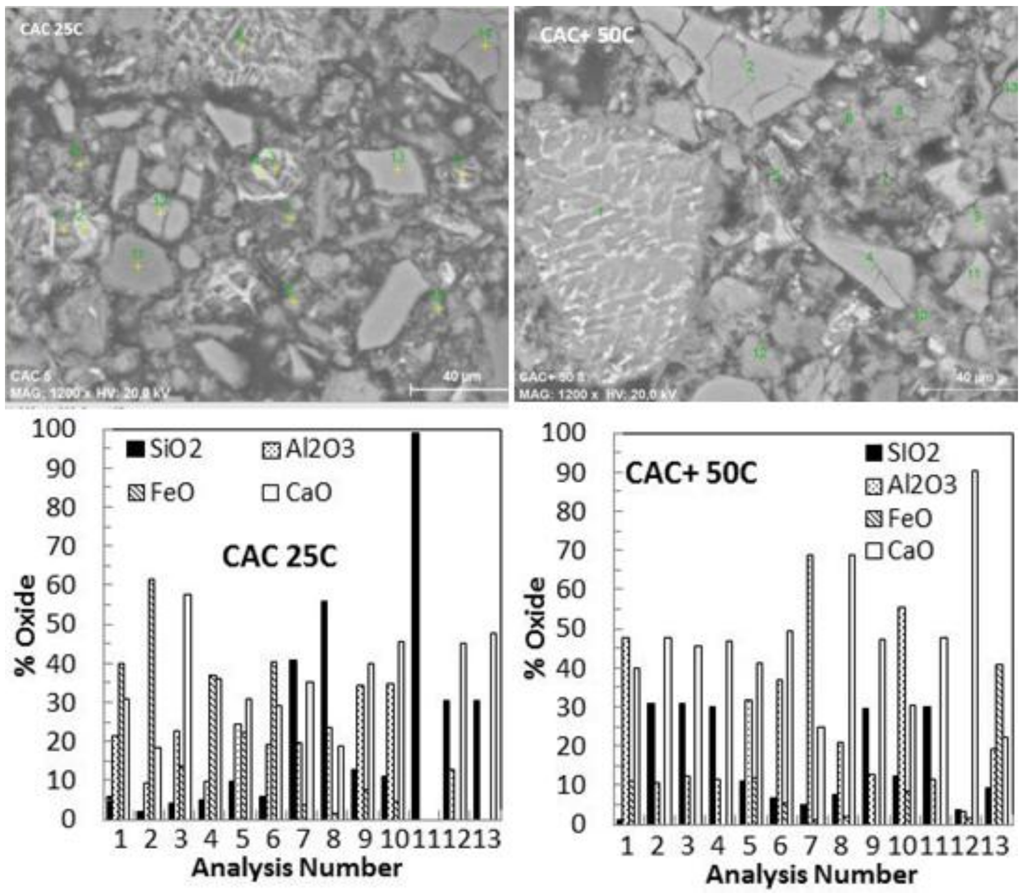

Fig. 8-14 – Microstructure after heat cycles: (up) cement paste (down) oxide composition

After the heat-cycles, cement paste is less dense due to dehydration of aluminates, but also solid regions with more geometrical form are observed (Fig.8-14), in a composition indicating presence of quartz and/or BFS. Other phases that bring back the CA anhydrous composition, were confirmed with EDS and XRD analysis.

Another important aspect to be analysed through SEM are the interfaces of cement paste with aggregates (interfacial transition zone, ITZ). Differences in thermal expansion between the aggregates and the cement paste favor cracking generation of the paste that surrounds the aggregates and also grow towards the dehydrated cement paste. These microcracking both at the interface between the aggregate and the cement paste, as well as in the bulk region are contributing factors to the damage evolution and the loss of mechanical properties found in Fig. 8-9 and 8-10, even after the first heat-cycle. The thermal compatibility of these two main components of concrete, cement paste and aggregate, in relation to thermal deformation is of significant importance for concrete resistance at high temperature. It is therefore not surprising that the concrete mixtures containing coarse aggregates exhibited the highest reduction in compression strength subsequent to elevated temperature exposure. This effect of the aggregate size in microcraking generation and evolution has been detected measuring the gap in the Interfacial Transition Zone (ITZ) in various aggregate sizes, results shown in Fig.8-15. Small aggregates (< 0.5mm) show less ITZ than higher aggregate size (1-2mm in Fig. 8-14). After heat-cycles the ITZ increses 3 to 5 times from its initial size.

	Type of aggregate	Aggregate size (mm)	Interface size µm
Initial	SCA	0.5	1-2
Initial	SCA	1-2	2-3
Initial	SSA	0.5	1-2
Initial	SSA	≅1	2-3
25 Cycles	SCA	≃1	16.5-18.2
25 Cycles	SSA	0.5-1	9.3-13.6
50cycles	SSA	1-2	11.3-15.3
50cycles	SSA	0.5-0.7	2.3-4.6

Fig. 8-15 –Paste aggregate interfacial zone size depending on aggregate type and size

A final aspect to consider is the shrinkage of cement paste during dehydration, which is overcome by the volume increase of the aggregate at high temperature. The repeated heat-cycles affect the paste contributing to the development of microcraking.

8.3.5 Thermal response

One main interest of concrete use in TES is the ability to store sensible heat. The heat capacity of a concrete varies with the composition of concrete. Concrete with a heat capacity of 0.8 kWhth/m3ºK is possible and adequate for TES and have been developed in the past [10]. Another relevant thermal parameter is the thermal conductivity (λ), a typical value is 2W/mK. The concrete used in present study has a $\lambda_{0cycles}$=2.05 W/mK and $\lambda_{25cycles}$=1.16 W/mºK. To control this decay after heat cycles, additional components for the concrete mix that enhance thermal conductivity of concrete are needed, for instance: silane, steel fibers, carbon fibers, carbon nanotubes, graphene, graphite powder. An alternative during the TES module construction phase would be the application of additional heat transfer structures, graphite or aluminum foils placed between the layers of the precast concrete [10].

8.4 Conclusion

In this chapter two new cimentitious based mixes were developed. These could conduct and store heat at high temperatures, namely with thermal cycles in the range 290-550ºC. The main results can be summarized in the following way:

- ✓ The incorporation of blast furnace slag to CAC mix controls the conversion phenomena and Si-Hydrogranet phases, type CASH, are formed.
- ✓ CAC concrete with conversion control also suffer dehydration at high temperature, accompanied by decay in mechanical strength
- ✓ The use of correct grading of aggregates (max 12 mm) is fundamental for resistance under high temperature heat-cycles for TES-concrete.
- ✓ High thermal expansion aggregates must be limited (siliceous alone or calcareous), as they can significantly affect the mechanical resistance under high temperature environments and also under thermal fatigue cycles.
- ✓ Concerning the size distribution it is important to compensate concrete volume changes due to thermal expansion and dehydration reactions of the cement paste.
- ✓ SSA waste from ore mining production used as aggregate for concrete has shown similar mechanical performance as SCA. Additionally, using aggregates with different thermal stability can be a benefit for the overall paste adaptability to thermal stress.

- ✓ The ITZ is significantly affected with the aggregate size. Higher aggregate size increase the thermal fatigue of concrete during heat-cycles.
- ✓ After first heat-cycle the CAC concrete evolve to stabilize the thermal fatigue induced by heat-cycles.
- ✓ Concrete based on blended CAC with appropriate design can be employed for TES up to 550ºC in CSP plants and is more appropriate than OPC to resist thermal cycles.

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Chapter 9. Molten Salts and CAC based cement concrete

9.1 Cement based mixtures for Energy Storage

Most of the past developments in the field of solid material to be used for high temperature thermal storage have been validated only at lab scale. Knowledge in the field of solar concentrated systems has been used in order to define the material requirements and to validate its usage specially taking into consideration the cyclic thermal load. Concrete is a composite material with great versatility in the selection of the components to improve its performance, adapting to the requirements in service. The selection of adequate cement type, mineral additions, aggregate (size distribution and composition) water/cement (w/c) ratio, additives to design the optimal concrete mix in order to fulfil certain criteria, in this case, improving thermal conductivity, diffusivity and thermal cycling resistance.

Some research to validate the usage of concrete for thermocline systems (a one tank solution with a thermal gradient inside the tank) has been performed [1]. Both OPC and CAC mixtures were investigated in different formulations. It was found out that compressive strength of concrete and mortars thermally cycled and in direct contact with molten salts present a significant reduction of compressive strength. However strategies like prior temperature conditioning or the introduction of additional materials i.e. mineral additions, such as Fly ash (FA), silica fume (SF) or blast furnace slag (BFS) improved the refractoriness [1,2,4].

Results presented in chapter 8 showed that a CAC mixture with BFS due to its thermal behavior is a suitable solid energy storage material for STE applications when exposed to charge/discharge heat cycles. All in all, at high temperatures CAC is more adequate than OPC.

At a demonstration scale, the most developed and validated concept using a concrete mix to store heat was developed by DLR based in OPC plus BFS [2] using steam as the heat transfer media. In the project WESPE running between 2001 and 2003 [2,3], storage temperatures of 325ºC have been reached. Some years later, a new Project by DLR was realized having 400ºC as the target operation temperature. A concrete module with 1,7x1,3x9m dimensions was built and operated for 23 months. With a 120K temperature difference, a total of 1518 kWh were transferred during 37-h charging and 950 kWh (thermal losses of 9.5 kW) were extracted during 23-h discharging (thermal losses of 7.6 kW). This lead to an average value of 1148 kWh stored energy, with an energy density of 0.63 kWh/(m^3K) [3].

The main advantage of this concept is that it is a modular unit, which can be easily implemented in power plants including existing ones as a capacity upgrade. The main finding for this concrete storage unit is that from a material point of view, such a solution is viable, however needs further research and optimization of the mix. The main problems detected were: thermal stress and fatigue due to the demanding thermal cycles, some of the binders tested were not appropriate for charging/discharging required rates and water dehydration was not fully achieved. Later, the mix has been tested up to 500ºC, with cycles in the range 450 to 500ºC and showed a decrease on compressive strength from 30MPa down to 15MPa.

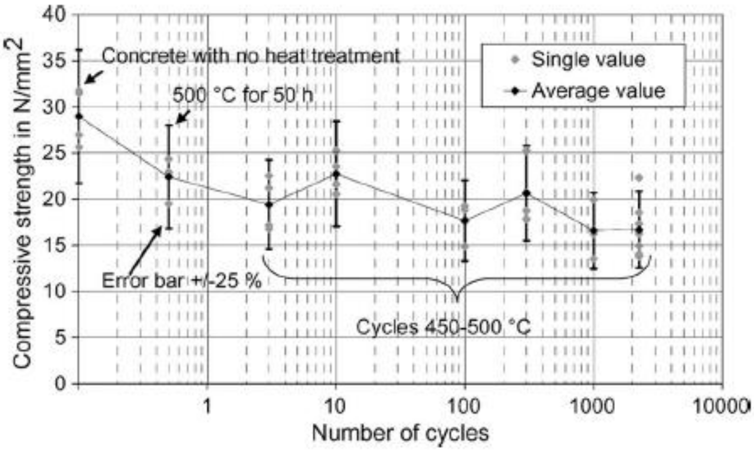

Fig. 9-1 – Compressive strength of a concrete mix tested up to 500ºC and 2250 cycles [3]

Table 9-1 Concrete mixes comparison [3,5,6]

Concrete Mix	Density	Thermal conductivity	Heat Capacity
DLR mix (OPC type)	2250 kg/m^3	1,20 W/mK @ 400ºC	0,66 kWhth/m^{3}K @ 400ºC
Heatcrete (OPC type)	2364 kg/m^3	2,2 W/mK @ 340ºC	0,75 kWhth/m^{3}K @ 340ºC
Heatek	4000 kg/m^3	not available	2,2 kWhth/m^{3}K @ 288ºC
UniArk	2278 kg/m^3	2,16 kWhth/m^{3}K @ 25ºC	0,16 kWhth/m^{3}K @ 25ºC

Table 9-2 Demonstration Projects [2,3,5]

Concept	Dimensions [m]	Thermal Storage Capacity [kWhth]
DLR – Almeria, WESPE	23 * 0,5 * 0,5	350
DLR – Stuttgart	1,3 * 1,7 * 9	474
NEST – UAE, Masdar	not available	1000 = 4 units of 250 each

In order to be a flexible solution for a broader STE storage system, this type of solution should be able to operate in the range of 290 to 550ºC which is currently the temperature range of plants recently built like Gemasolar in Spain, using molten salts both as transfer media as well as storage media.

The challenge addressed in this chapter was to understand how molten salts affect concrete mixtures in case they would be in direct contact with each other. A range of tests, including thermal stress due to cyclic loading has been designed in order to fully understand this phenomenon.

9.2 Experimental set-up

To validate the mixture, there was a need to decouple the thermal cyclic effect from the chemical impact due to the molten salts, therefore, tests were conducted for the concretes, both in contact with air (see Chapter 8) and in contact with molten salts (Chapter 9). Initial research was made to develop a suitable concrete mix starting with CAC (Calcium Aluminate Cement) as a base, with two different mixes being prepared.

The first concrete mix selected was named as CAC with a binder mix of 70 % CAC + 30% BFS

(Blast Furnace Slag) and water cement ratio was w/c=0,5..The second concrete mix, identified as a CAC+, was a CAC base cement designed to incorporate slag from old mines as partial substitution of the silicon-calcareous aggregate, as a way to have a positive impact on an old environmental problem, re-using material with high metal content, simultaneously making use of a low cost material with a potential of having the right thermo-physical properties to be used as a storage material for STE applications. In the second concrete mix, CAC+, aggregate content was 75% SCA and 25% slag, with a water cement ratio of w/c=0.57. To obtain a soft concrete 0.8% SP (superplasticizier) (Sikament 180) was used in both mixtures.

With these mixtures 16 cylindrical concrete samples of 7.5cm Ø and 15 cm height were prepared, and were cut into half, so that 32 samples were prepared. All samples went through a drying protocol for 3 days, drying at 105ºC to eliminate most of the free water in capillary pores, but without significantly affecting the hydrated solid phases. The water loss (in %) was similar for both mixtures,3.5 ± 0,23%.

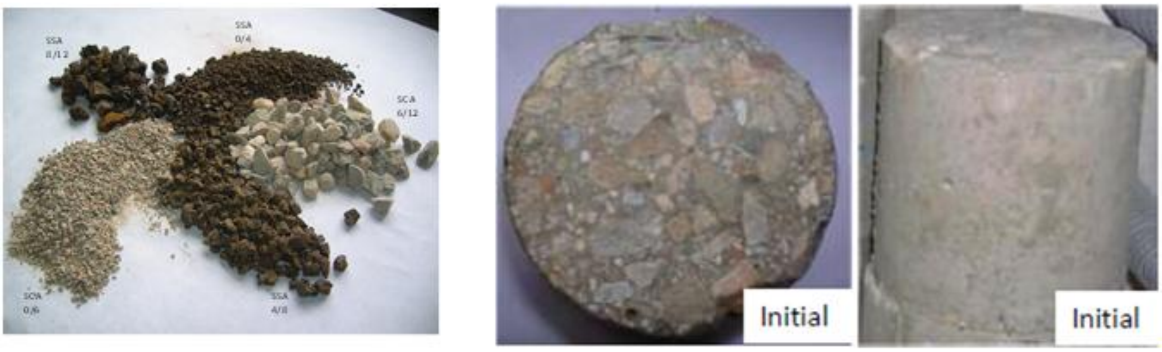

Fig. 9-2 –CAC+ concrete mix: (a) aggregate (b) (c) CAC+ concrete sample in initial state

9.3 Thermal Cycling and Methodology

The description of the testing protocol with air and the results obtained is described extensively in chapter 8. A resume of the number of samples used in the study is presented below.

Table 9-3 – Test Plan

	0 (initial state)	1 month (25 cycles)	2 months (50 cycles)	3 months (75 cycles)	Total nr. samples	Remarks
Compressive strength	2+2	2+2	2+2	2+2	16	
Ultrasounds	1+1	1+1	1+1	1+1	8	
XRD						
Microscopy, SEM	1+1	1+1	1+1	1+1	8	
Thermal Conductivity	1+1	1+1	1+1	1+1	4	
Crack measurement	4+4	4+4	4+4	4+4	32	16 tested w/ air + 16 with MS
Total	4+4	4+4	4+4	4+4	32	

The heating resistance of concrete has been evaluated throughout the exposure of the samples to heating/cooling cycles of 24 h length each, inside an electric furnace, as shown in figure 4-left, the maximum temperature being 550±5ºC and the minimum 290±5ºC. A heat rate of 1ºC/min. was selected for the first heating, to minimize thermal damage and crack developing as consequence of strong temperature gradients in the bulk of the samples in relation to the

surface, so that to approach that the changes are mainly consequence of dehydration of cement paste. For the next cycles an heating rate 9ºC/min up to 550ºC was used, followed by cooling to 290ºC at a rate <1ºC and staying at that temperature until the start of the next heat cycle. Periods of 5 cycles of 24hr followed by a permanence of 2-3 days at 290ºC were considered until the completion of 25, 50 and 75 cycles of temperature variation from 550ºC to 290ºC for CAC and CAC+ concrete mixtures simulating respectively 1,2 and 3 months of operating conditions in a STE plant.
During the heat cycles the temperature inside the oven and at the surface level of the samples was recorded to continuously identify the thermal regime performance.

Fig. 9-3 – Samples CAC and CAC+ set in the oven in direct contact with molten salts

Heat/cool samples were characterized using different techniques from macro to micro level. Compressive and flexural strength were measured, DRX, mercury intrusion porosimetry and SEM back scattering microscopy with EDS characterization, as well as the thermal conductivity in concretes. Mass loss after heat cycles was also determined.

9.4 Results and discussion

In the case of concrete the mass change measured is very similar for the periods 25, 50 and 75 cycles. There was just a small increase, probably associated to the progressive alteration of calcareous and slag aggregates. With the demanding thermal cycles from 290ºC to 550ºC, cracks start to appear and develop. This means that with the time, the salt can more easily penetrate into the samples. After 25 cycles, once the samples are taken from the oven, the salt solidifies inside the samples, leading to an interesting result: compressive strength increases from 30MPa up to 40 or even above 50MPa, something it was not to be seen when samples were exposed with thermal cycles just with air (decrease to 15 – 20 MPa) as shown in Fig. 9-4.
Increase in mass during heat cycles in MS is observed and explained due to the penetration of MS inside the concrete. Compressive strength and UPV evolution in heat-cycles in the presence of MS after several heat-cycles is represented. Initially the interaction with MS makes the concrete more dense and compensate the decrease in strength due to dehydration and sealing of thermal fatigue cracks, but at longer periods (50 and 75 cycles) in MS the concrete looses progressively mechanical properties (registered in the compressive strength measurements, Fig.6a, due to the progressive reaction of MS with CAC phases that are not stable and degrade the cement paste in such a way that there is a cohesion loss in the concrete as explain later.

This progressive cohesion loss can be detected both from the compressive strength as well as from the ultrasound analysis where an indirect correlation can be observed, fig. 9-5.

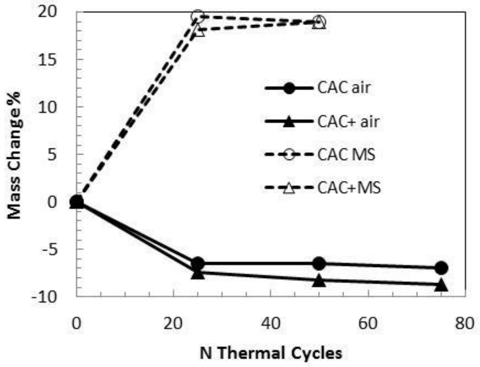

Fig. 9-4 – Samples CAC and CAC+, mass change

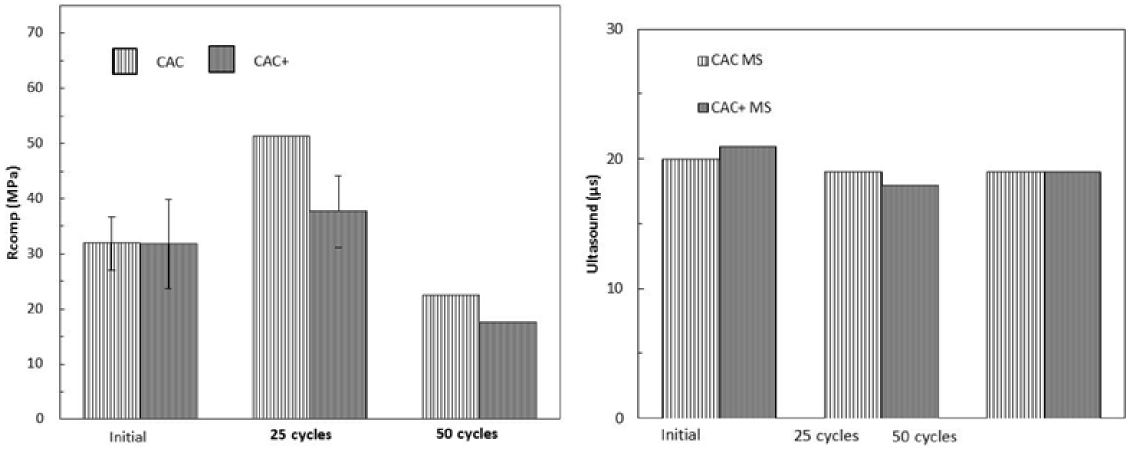

Fig. 9-5 – Samples CAC and CAC+, Compressive strength and ultra pulse velocity

Due to the thermal cycling, there is a thermal degradation that fosters crack development. This physical phenomena leads to a higher contact surface between the salts and the solid sample, which in turn accelerates the chemical reactions between the salt components and the elements present in the paste. With the chemical interaction, the samples tend to become more granular, less cohesive. The heating cycles have induced changes in pore structure distribution and size. A clear increase is observed in capillary pores below 3μm due to the dehydration of cement paste, the pore distribution is similar in both concretes.

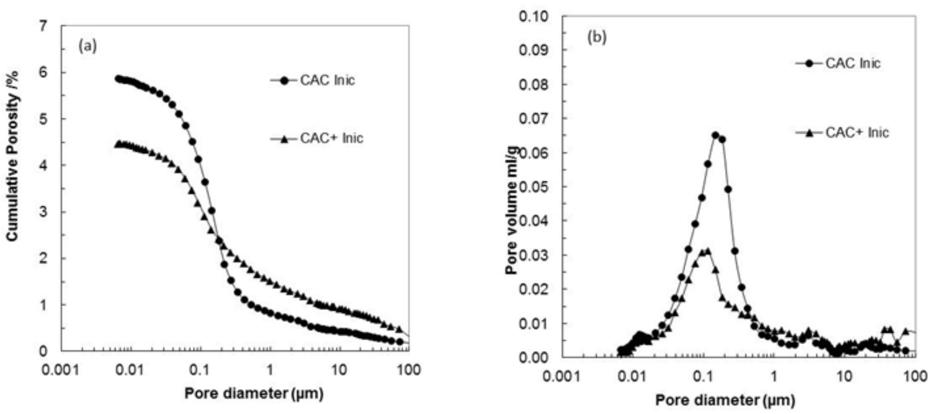

Fig. 9-6 – Samples CAC and CAC+, Pore Diameter

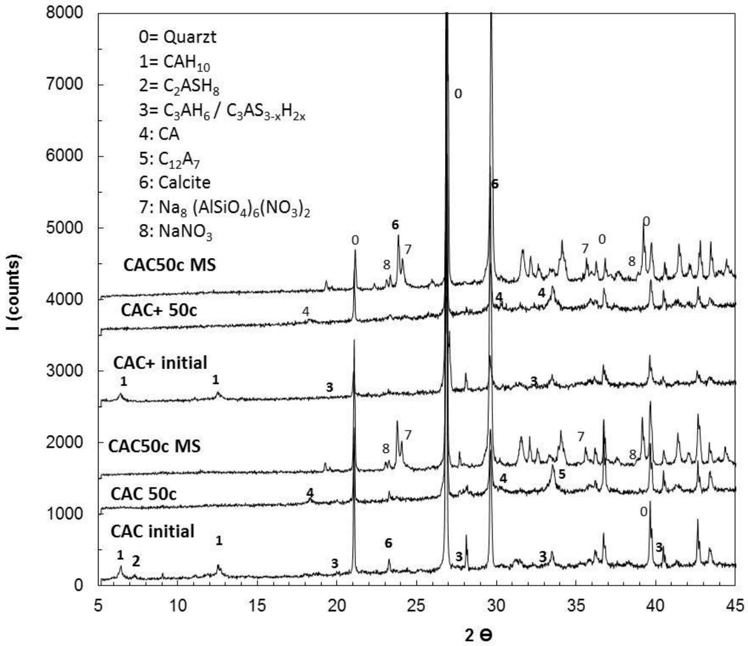

Fig. 9-7 – Samples CAC and CAC+, XRD analysis

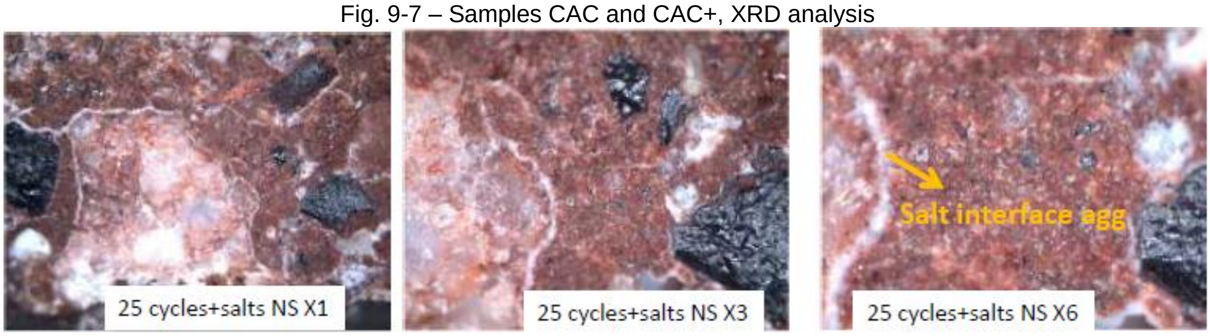

Fig. 9-8 – Samples CAC and CAC+, SEM after 25 cycles in direct contact with MS

X-Ray Difraction (XRD) analysis after 7 days of sample curing shows that hydrated phases associated with calcium aluminates hydrates (CAH_{10} and C_2AH_8) are present. Besides Si-hydrogranet, type (calcium silico aluminates hydrates, C_3AS_3-xH_2x) is formed that is a hidrogrossular solid solution containing Si in its composition due to the interaction with BFS. In a previous experiment (chapter 8) performed only with air heat-cycles, it came evident that peaks associated to anhydrous phases as Calcium Aluminates (CA) type ($C_{12}A_7$) ($Ca_{12}Al_{14}O_{33}$), are detected, together with phases containing silica in its crystal structure, such as Magenite. Also calcite and quartz from the aggregate are present. However, heat-cycles in molten salts show that both hydrated or dehydrated phases are not observed. New phases incorporating nitrates (NO3-) in their structure are formed as sodium aluminium nitrate silicates (Na_8 $(AlSiO_4)$ $_6(NO_3)_2$) which confirm the interaction of cement phases with MS. It is relevant to notice that calcium is not present in this new crystalline phase, it seems that Ca has been substituted by NO_3 and Na. Clearly the CAC components interact with molten salts.

It is relevant to point out that most of mass change takes place during the first cycles as a consequence of dehydration processes, after 25 cycles the process stabilized. However the MS penetrate through concrete pores and fill any gap and cracks of the dehydrated concrete samples and sealing the interfacial Transition Zones (ITZ) with aggregates, Fig. 9-10.

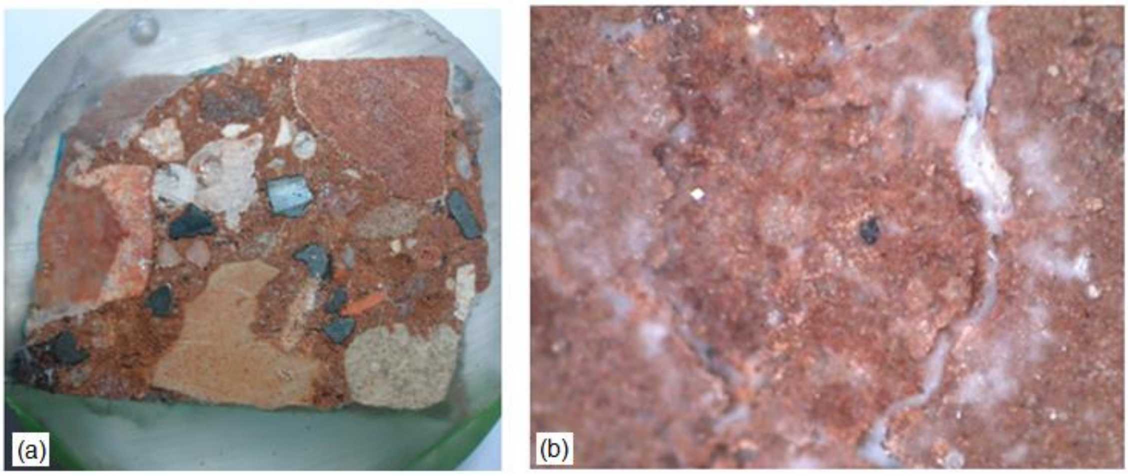

Fig. 9-9 – Sample CAC+, (a) being prepared for SEM, (b) SEM analysis

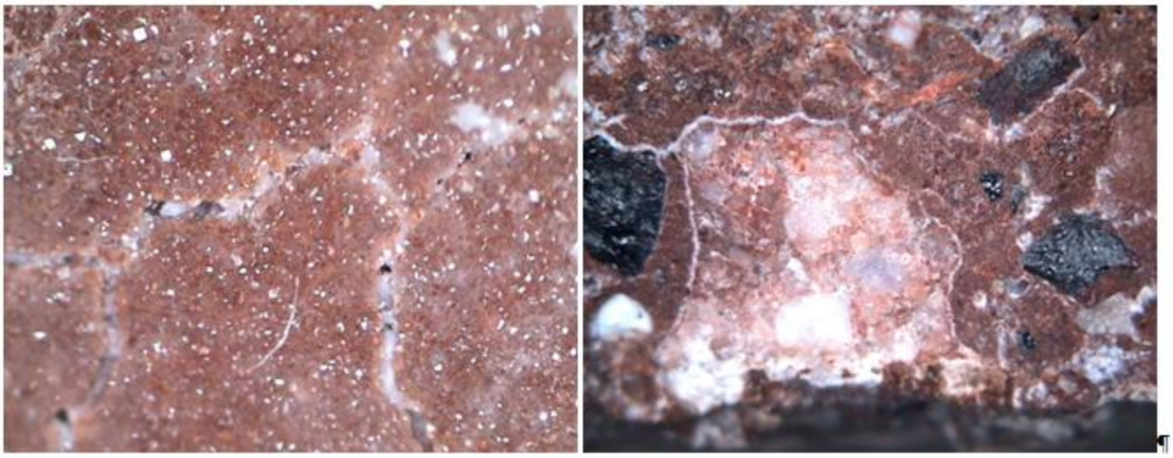

Fig. 9-10 – Samples CAC+, SEM after 25 cycles (MS filling the ITZ cement paste aggregate)

Molten salts penetrate in the concrete, filling the cracks formed during fatigue heat-cycles, but also fill the gap in the ITZ between cement paste/aggregate, both SCA and SSA. The aggregates used are stable in present of molten salts, are not altered.

In the initial state, cement paste is dense and different hydrated phases are observed with different crystalline structure. Also aggregates show a good interfacial zone (ITZ). After heating cement paste become more porous due to dehydration and increase the ITZ with aggregates and propagation of microcracks inside the cement paste. In molten salts, the cement paste changes completely the aspect, although it seems more dense and granular. This aspect changes with longer exposure to MS, at 50 heat-cycles the cement paste has loosed its integrity (cohesion loss), but the aggregate remained unaltered.

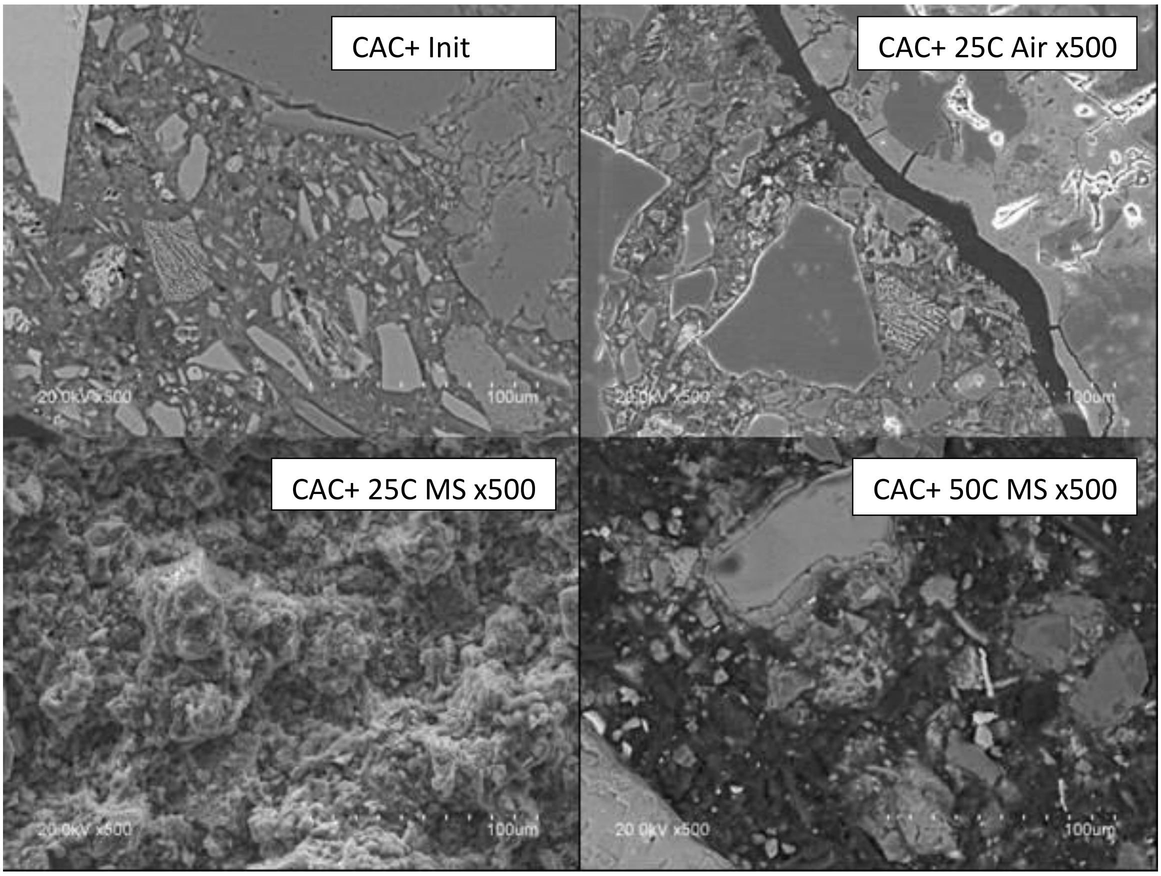

Fig. 9-11 – Samples CAC+: SEM Analysis (molten salts initial, 25 cycles, 50 cycles)

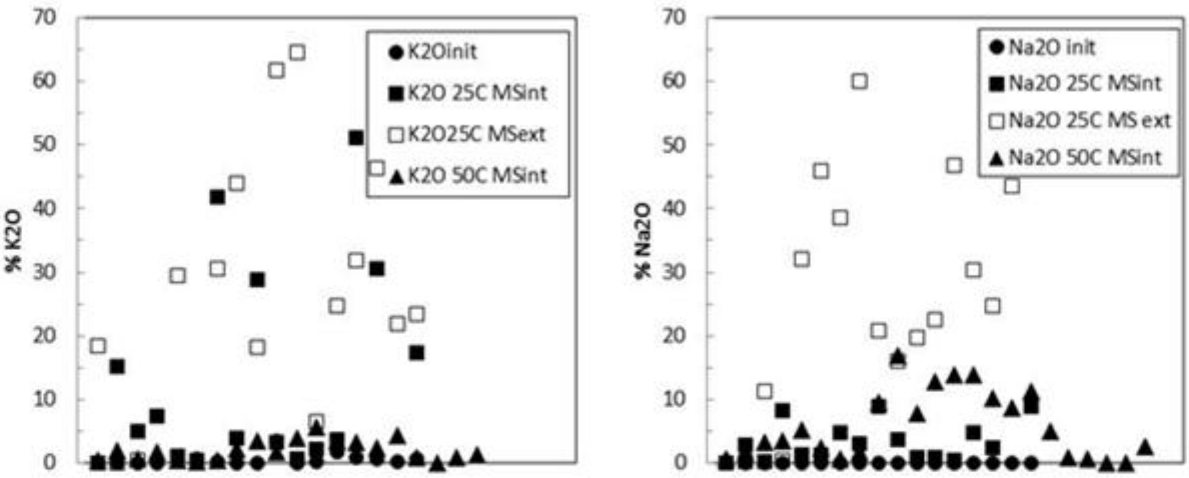

Fig. 9-12 – Samples CAC+ after MS exposure (initial, 25, 50 cycles): potassium and Sodium content

Analyzing figure 9-12, Sodium and Potassium content increase significantly inside the concrete, been higher towards the external sample boundary (<1cm from the surface) in contact with MS, respect to the interior (>5cm from the surface), confirming the penetration of the molten salt deep into the concrete.

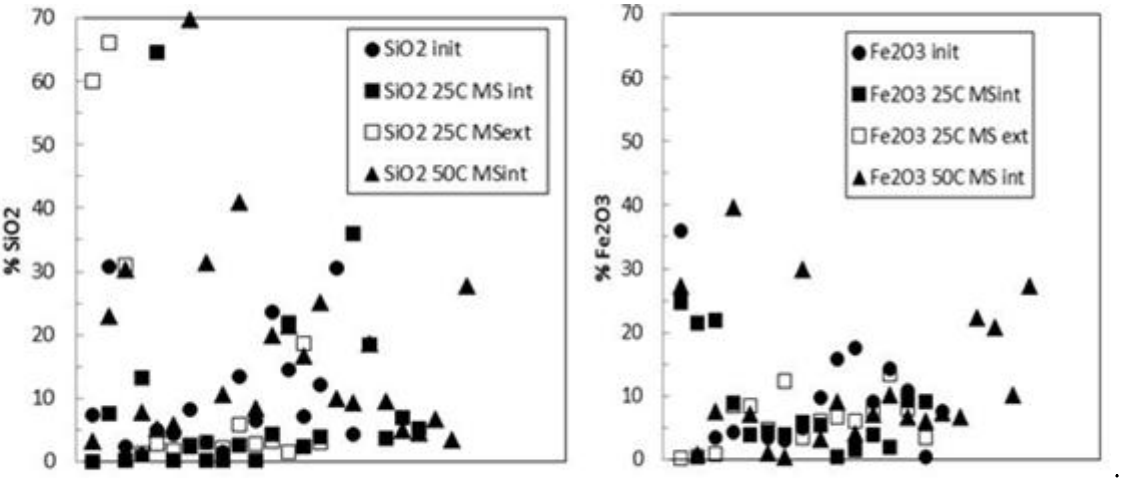

Fig. 9-13 – Samples CAC+ after MS exposure (initial, 25, 50 cycles): silicon and iron content

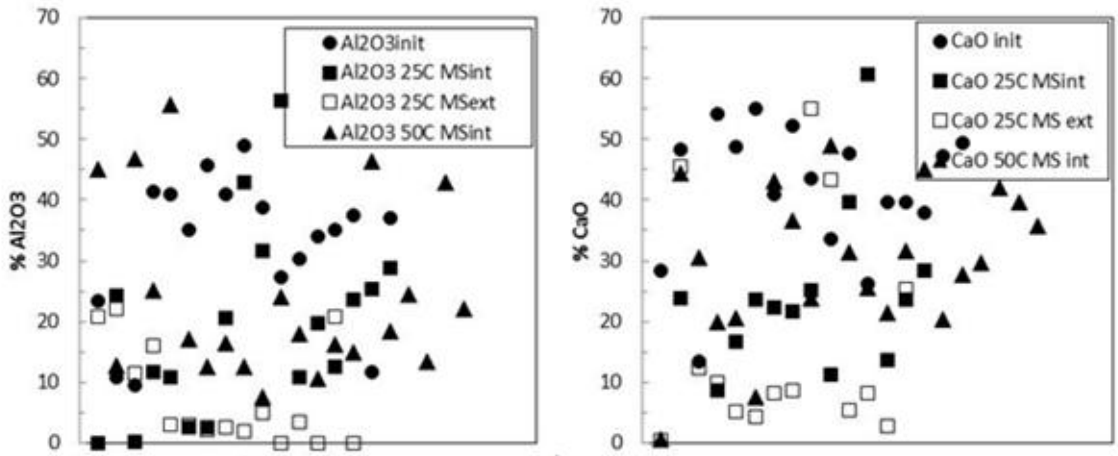

Fig. 9-14 – Samples CAC+ after MS exposure (initial, 25, 50 cycles): aluminium and calcium content

The main components of the cement paste change the content due to the heat-cycles in direct contact with the molten salts. Silica and iron oxide are the less affect, although Silica content at the more external part near the MS is lower in comparison with the interior, Fig. 9-13.

The most relevant changes were observed in the content of Aluminum and Calcium oxides. In both the content decreased from the initial state, although most relevant in case of CaO. That can likely explain the new phases detected in XRD (sodium aluminum nitrate silicate) which do not contain Ca in the structure, Fig.9-14 that above microphotographs represent the initial aspect of CAC+ (right) and after 25 cycles in contact with MS (left).

The mapping of Fig. 9-15 clearly shows the differences. In the initial the cement paste of the CAC+ contains mainly Al and Ca but in some places Si, in agreement with the hydration products identified with DRX of Fig 9-7. However after the cycling in MS a clear increase in alkalis, Na and K, is observed with a clear depletion in Ca and Al. The aggregates remained unaltered what indicates that both type of aggregates employed in the concretes are stable in contact with MS.

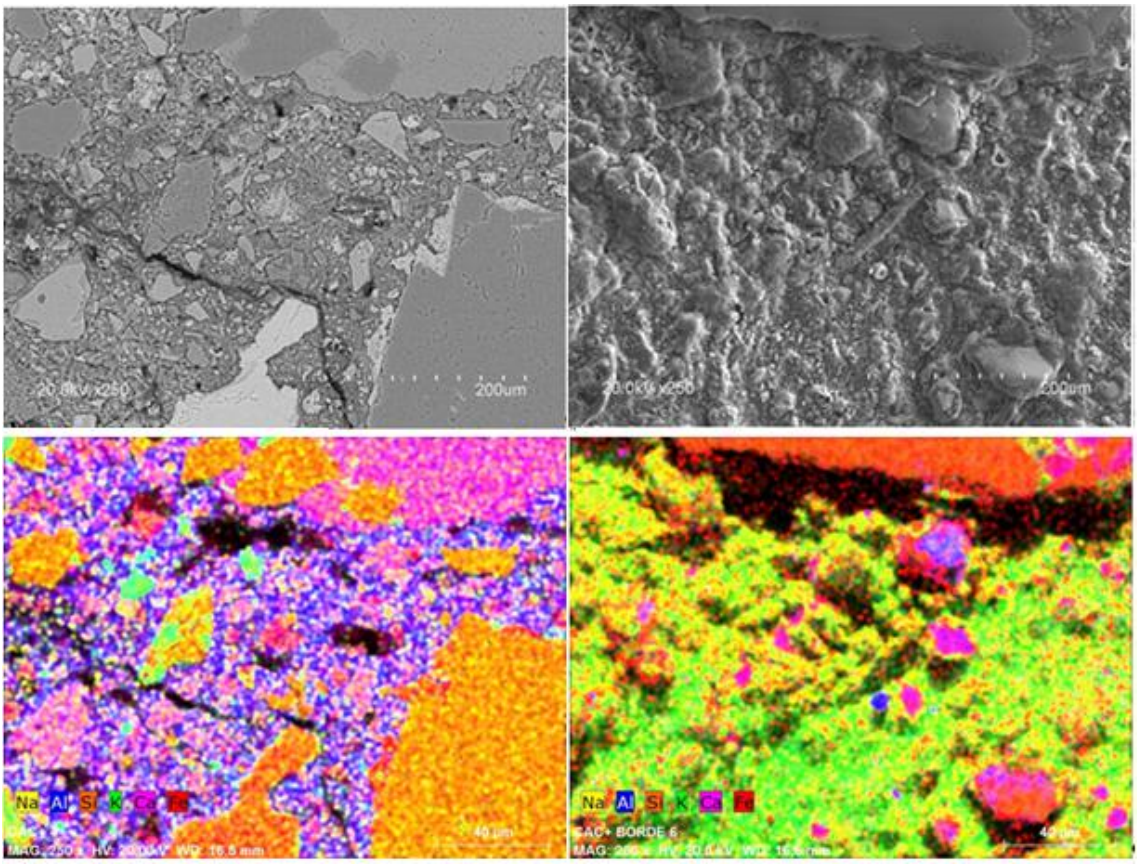

Fig. 9-15 – Samples CAC+ after MS exposure (25 cycles), SEM elemental analysis mapping

After confirming the penetration of the molten salt deep into the concrete MS and that this phenomena enhances crack formation, a protective layer was developed in order to protect the concrete surface. Several coatings were studied, a silica based sol gel coating was selected for experimental tests. Small coated and non-coated cubic 50mm samples of CAC type where brought to an oven to be in contact with molten salts in cyclic loads up to 550ºC. After that, samples were taken out of the oven and analyzed using DSG.

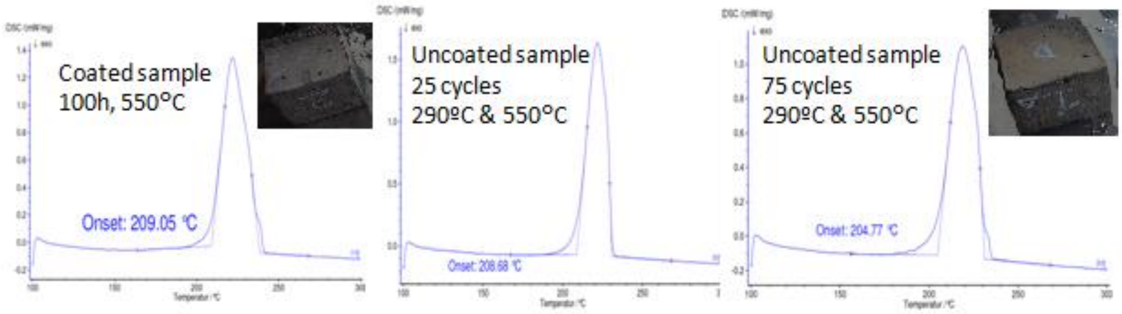

Fig. 9-16 – Sample CAC (coated and uncoated) after contact with MS, DSC analysis

The data, Fig.9-16, shows that a temperature onset in the coated sample is higher than the onset of the uncoated sample which can be explained by two effects:

- The uncoated samples were subjected to a longer period of high temperature 200h (25 cycles) and 600 h (75 cycles) versus 100h in the coated sample which enhances the thermal decomposition of the nitrate salt.
- The coating might have slowed down the degradation of the concrete sample in the salt, which is exactly the effect intended for applying this coating

This approach will be further investigated in the future in a project called SOLSTICE (see chapter 10), in order to define the best solution to achieve a long service life.

9.5 Conclusion

In this chapter experiments are reported concerning a new concrete mixture based on CAC blended with BFS set in direct contact with Molten Salts. The main findings were:

- MS penetrates inside the concrete mainly trough pores and thermal cracks and allocate in the interface between cement paste and aggregate
- Crack formation specially in the ITZ area
- Initially an increase of compression resistance takes place due to MS penetration through pores and ITZ past/aggregate. After prolong contact with MS a loss of compressive resistance due to the reaction with MS that leads to disaggregation in some cases. The reaction of dehydrated cement phases with lead to the formation of new materials as sodium aluminium nitrate silicate
- The binder lost resistance in a significant way, implying that direct contact is not recommended for CAC mix with MS and subject to this wide temperature range
- CAC/CAC+ mixtures need to be optimized from the thermal conductivity point of view
- Mechanical resistance was similar in CAC and CAC+ mixtures, having different thermal gradients is an advantage to the overall thermal behavior
- The idea of using slags from old mines has an added value potential to the concrete mix, that of reducing a clear existing environmental impact and, and at the same time, introducing old residues as a low cost or even zero cost material to contribute to the STE energy storage cost reduction goal. This has been identified as an interesting strategy to pursue in the future.

All in all, direct contact between Molten Salts and a concrete mix has a big impact on the solid material composition leading to progressive cohesion loss. The temperature effect needs to be decoupled from the chemical attack of the molten salts towards the concrete. An idea would be to introduce a protective layer to guarantee a longer resistance of the concrete mix, an idea for future research.

9.6 References

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Chapter 10. EMSP Storage upgrade, towards a new set of projects

10.1 Introduction

While the work on this thesis was being done, a strong development effort was taking place under the auspices of the Renewable Energies Chair (U.Évora). In particular a very important research infrastructure was being built, a large scale (industrial scale) infrastructure. EMSP is a molten salt test loop for research purposes (see Annex 1)) indispensable to the R&D efforts reported in this thesis and, in particular to the work that can and will be set up in the future, as a consequence. In this chapter there will be a brief description of the novel contributions to this effect.

This development involved a deep collaboration between the Renewable Energies Chair and DLR (Deutsches Zentrum für Luft- und Raumfahrt) from Germany, for both institutions to be in a condition to complete and operate the EMSP and then to carry on new projects using this facility.

10.2 Project HPS-2

The first action gave birth to the Project HPS-2 (High Performance Solar) Project in order to use direct molten salts trough the collector receivers of a linear solar concentration system.

During the course of this Thesis, work related to the HPS-2 Project was developed with the goal of making sure the facility would have full flexibility and capacity to accept projects for R&D on the topics: (1) solar plant operation (2) high temperature solar thermal energy storage.

Concerning the scientific goals, a detailed research Plan for 2 years was discussed, with the following scientific goals:

- Increase of the efficiency of solar thermal parabolic trough power plants
- Development of a solar field for molten salt operation
- Erection of the Ultimate Trough
- Development of molten salt solar receivers
- Demonstration of a highly flexible steam generator
- Investigation of different salt mixtures in operation
- Lowering of investment costs
- Reduction of electricity production costs
- Demonstration of a complete system consisting of solar field, thermal storage and steam generator
- Demonstrate alternative operating concepts for safe operation and handling

- Development of new measuring techniques (e.g. in line calorimeter)

In order to develop such an ambitious project, a joint consortium of industrial Partners, DLR and the University of Evora was established, a funding decision is pending.

10.2.1 Challenges and risks

There are well identified opportunities of molten salt systems, namely in the reduction of electricity production costs (levelized cost of electricity, LCoE) between 14,2 to 17,2% [1] to a level of 10-12 cEuro/kWh (see Chapter 4) in the South of Europe. However, there are some risks which have been identified and will be addressed in the course of the project:

- Difficult procedure for filling and draining of the plant
- High thermal effort to avoid freezing
- Danger of freezing in piping and absorber tubes
- System behavior during black out
- High requirement for corrosion resistance of the materials
- Performance of solar field at high temperatures
- Tightness and reliability of the flexible connections
- Possibility to prevent leakages (from experiences of Solar Two)
- Unknown maintenance procedures and disturbance handling
- Thermal stability of the applied salt mixtures

The experimental plant is designed to provide answers to the above mentioned questions. Furthermore the plant allows to test different operating strategies and therefore to identify the optimal procedure which can in the future be deployed to a commercial power plant.

10.3 Project PreFlexMS

Working with molten salts for solar concentration is a new process, can however profit from integrating other state of the art technologies. Project PreFlexMS aims at demonstrating and introducing into the market key enabling technologies to improve predictability and flexibility of a STE plant with molten salt energy storage.“PreFlexMS”, stems from the key words “Predictability”, “Flexibility” and “Molten Salt”.

10.3.1 Project goals

The PreFlexMS project wants to adapt and integrate available technology into a product ready for market introduction. The project is structured along three axes:

1) Technology integration of two key components:
    a) Once-through steam generator with molten salt as heat transfer medium

b) Weather forecasting and dispatch optimization

2) Technology evaluation (technical, economical, business), namely:
   a) Risk assessment
   b) Life-cycle analysis (environment, economy and society)
   c) Business case and exploitation
   d) Thermo/economic performance evaluation and benchmarking according to key-performance indicators
3) Technology demonstration including all activities for the implementation of the developed technology in a pilot installation at the EMSP working in real conditions, which will enable the market uptake

Within the project a functional specification of the final product for a utility scale will be elaborated. The reference plant (a requirement from the technology customer) is a tower-based STE power plant with molten salt storage in the 100 MWe class. The engineering concept will be developed including feasibility and pre-engineering tasks. Based on this, a down-scaling exercise will be carried out to produce concept-level engineering for the pilot installation. On this basis, a detailed engineering will be carried out, ready for execution at the demonstrator site in Evora. This approach ensures that the pilot design will be relevant for the demonstration of the actual technology as applied in the full scale plant product. This is especially critical in the STE market, where technology uptake always faces resistance if not clearly, univocally backed up by a relevant demonstration, like the one planned in this project using the power supplied by the collector solar field at EMSP.

10.3.2 Activities

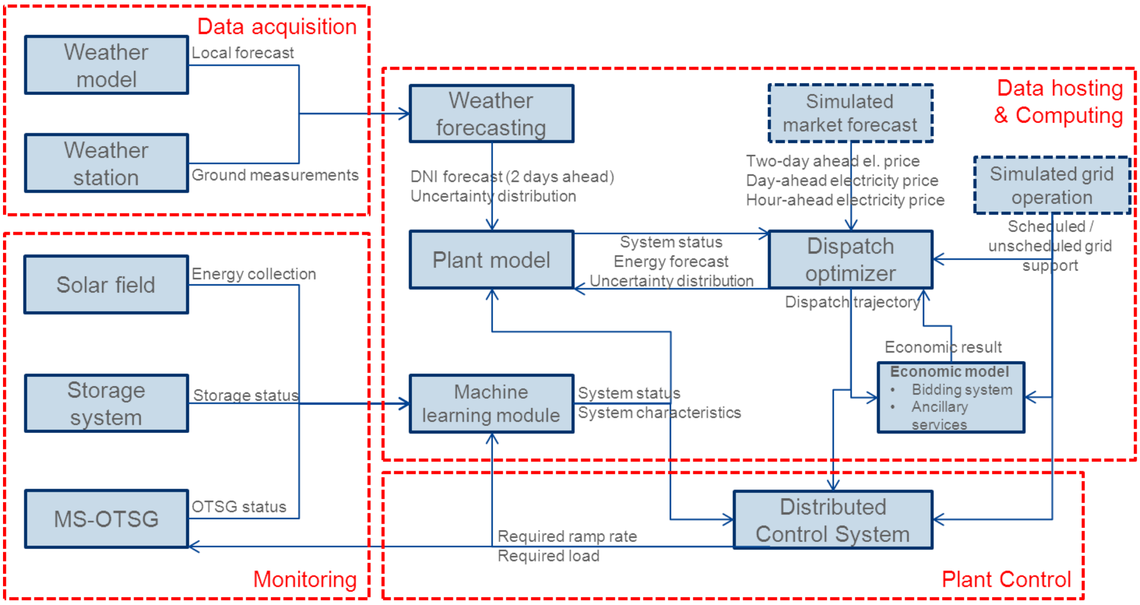

Fig. 10-1 – Project PreFlexMS, activities

The Demonstration activity will be performed at the EMSP, with the UniEvora scope by assuming the operation and monitoring of the demo plant. At the solar test site of Évora, an OTSG was erected during the HPS-1 project, but was never operated, a task scheduled for 2016. It will entail test trials to demonstrate the capability of the MS-OTSG to deliver high pressure and temperature live steam (140 bars/580°C). The power rating is 1.8 MWth nominal, with minimum load of 33%, admissible overload of 120%, and expected temperature gradient of approximately 15 K/min. The operation of the existing system will create a basis of knowledge and expertise at the demo site, which will serve this project, by ensuring a faster and smoother commissioning and test execution phase. The challenge at site will be the effective integration of the integrated hardware and software developed within the PreFlexMS, as a realization or even a demonstration of a weather forecasting system and dispatch optimizer connected to a steam generating system, an innovative feature which is an extra merit of the project.

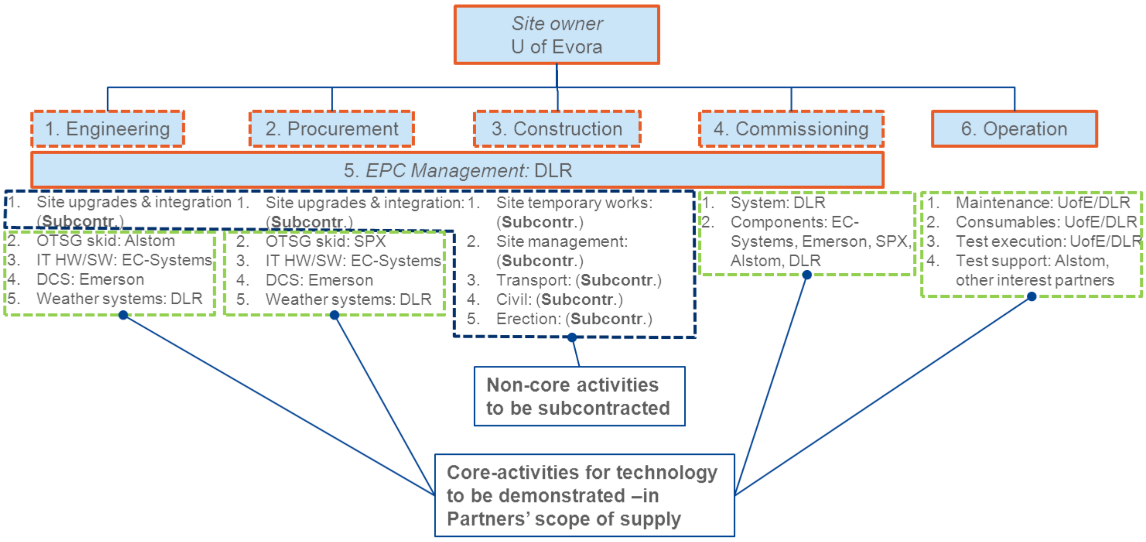

Fig. 10-2 – Project PreFlexMS, scope of UniEvora

For the final sizing of the OTSG, additional power is considered by enlarging the capacity of the storage tanks already available on site, task to be performed installing additional measuring and control devices, which will enable the usage of full capacity of both tanks. An additional possibility is the installation of a second solar field, based on Fresnel Technology (see Project INNOVLFR).

The are two possible scenarios: the energy collection system will match or not the thermal rating of the OTSG. In the first case, continuous operation of the OTSG will be possible, with the dispatch optimizer simulating a real time power plant operation and directly linking to the DCS system. In the second case, the dispatch optimizer will be run separately, and selected, interesting dispatch profiles will be implemented on the OTSG, for limited run-times. In both cases, the test facility will allow an unambiguous demonstration of the overall concept:

- Weather data sourcing and data streams
- Dispatch optimization
- Automatic performance mapping
- Integration in DCS

- OTSG operability and performance

And an extrapolation of the results to a full-scale power plant for the activities of evaluation and benchmarking.

Choosing the EMSP site (Evora Molten Salt Platform) is an opportunity to take advantage of the local knowhow using molten salt as a transfer fluid, and at the same time enhancing synergies with other ongoing research projects who focus more on optical improvement (INNOVLFR) and on storage (LATENT, SOLSTICE).

10.4 Project INNOVLFR

Conventional LFR technology has been developing at a lower pace than other technologies like those based on Parabolic Troughs (PT). Many reasons can be given for this fact, not the least relevant being the fact that the bankability of PT technology has been much more significant, thus leading towards an initial stronger expansion. Nevertheless several companies (e.g.Novatec Solar, Solar Euromed) have introduced in Europe the first commercial LFR plants to the market, incorporating solutions which accentuate the possibility of going down in cost by producing very large primaries (e.g. as Ausra proposed in the past or second stage concentration to raise temperature) and increase overall conversion efficiency.

A Project INNOVLFR was submitted to H2020 call, based on the fact that conventional LFR solutions are far from the limits meaning that with an optimized optical design LFR concentrators can be substantially improved, achieving higher efficiency, thus lower cost. The proposal can be summarized in the following way:

- A new LFR-SMS-XX concept already fully developed at a theoretical level by the researchers at the University of Evora [2] will be designed in order to become a demonstration facility
- The novelty lies in the number of mirrors, their aiming strategy, their ground coverage and the final shape of the second stage concentrator
- These evolutions lead to an increased concentration ratio for the same acceptance angle, thus reducing the number of receiver tubes required for the same field power delivery
- These modifications should correspond to a lower cost per mirror area, since the same mirror area corresponds to less receiver length
- Alternative draining concepts have been conceived in order to guarantee a safe operation
- The facility should be installed in a site which also has a parabolic through, thus enabling a direct comparison among line focusing systems

INNOVLFR was approved (2^{nd} stage approval) but did not get any financing. A renewed proposal will be presented in 2016. As part of the work for this Thesis, the scientific work related to the INNOVLFR Project was:

- Definition of the project challenges together with the other Partners and access its impact
- Definition of the operating strategies, namely the drainage concept of the molten salt solution
- Integration of the new molten salt pipelines in the circuit layout

10.4.1 New operating strategies

There are several advantages (environmental, safety, efficiency) of using liquid molten salts as heat transfer fluid when compared to thermal oil or direct steam generation.

Through the heated salts, steam is produced and high steam parameters are achievable, leading to a higher thermodynamic efficiency of the water steam cycle, higher than conventional solar thermal power plants. The salts are cost-efficient, can be stored directly and thus provide the possibility of a competitive electricity generation adapted to the varying demand of electricity (dispatchability advantage).

A significant drawback of the liquid salts comes from the fact that when they remain in the absorber tubes in the evening, after operation, there is the risk of solidification by freezing of the salt mixture. For this reason the liquid salts are normally being heated during the night to avoid solidification. However a continuous heating of large solar fields over night or on days with low solar irradiation is very costly especially in winter. To achieve this purpose existing facilities need to be upgraded in order to enable different operation strategies.

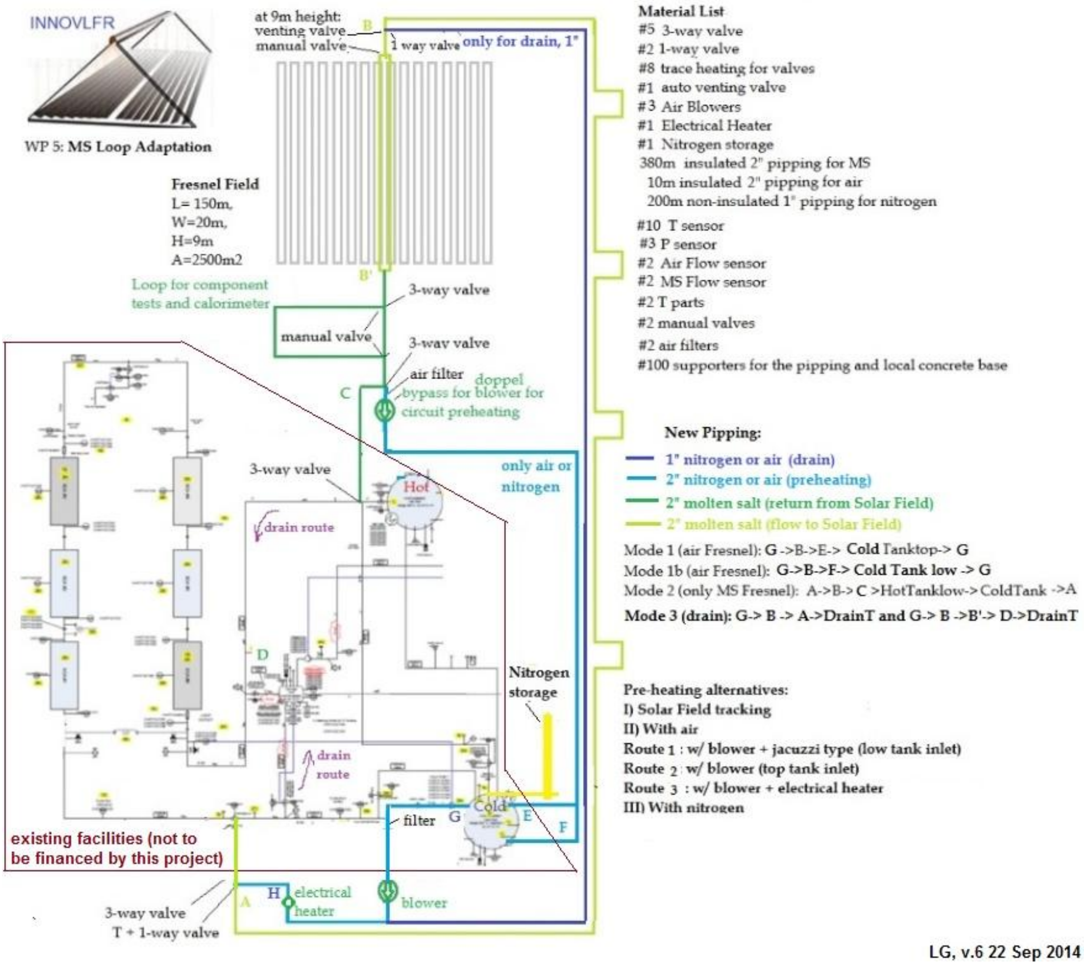

Fig. 10-3 – EMSP, detail of the pipping layout in the scope of INNOVLFR

In order to increase the operation flexibility, this project proposed substituting the heating concept by a new mode of operation called “vespertine draining and morning” solar preheating. This new concept includes draining of the hot liquid salts into a drainage tank (a feature of the molten salt loop referred above) and simultaneous filling of the absorber tubes with an inert gas (i.e. nitrogen) from the gas cushion of the expansion vessel. Subsequently, in the morning, the inert gas is used as a secondary heat transfer fluid for the solar absorber preheating process. A blower circulates the inert gas through the partially focused Fresnel collectors of the solar field until the absorber tubes reach the salts melting point temperature. Once reached the required temperature the liquid salts from the drainage tank can be pumped back into the absorber tubes without the risk of clogging by solidification. Simultaneously to the solar field refilling, the inert gas is being pushed back into the gas cushion of the expansion vessel.

This new operating strategy reduces the heat losses over night significantly. Especially Fresnel collectors are suitable for this operating concept due to two reasons. The first reason is because the elevated, very long and continuous, fixed (not moving), absorber tube of a Fresnel collector can be drained easily without salt remaining in interconnection tubes or flexible connections. The second reason is because the solar radiation is almost homogeneously distributed over the circumference of the absorber tube and can be modulated by partial defocussing of individual facets, thus avoiding problematic temperature gradients which might cause bending of the tubes during solar preheating.

10.4.2 EMSP Further Development: Projects LATENT and SOLSTICE

The two projects presented above (HPS-2 and INNOVLFR) have been designed from the technical point of view, in order to be a worldwide reference for any investor that is interested in Solar Thermal Electricity specially using Molten Salt technology. The successful implementation of these two Projects will turn the EMSP into a leading facility integrated in a broad European Infrastructure Network, which currently is being gathered under the EU-SOLARIS initiative. These projects had a natural interface with the work in this thesis, as explained, but the two being presented below in the area of thermal energy storage, are a direct consequence of this thesis and thus can be considered a true part of it.

10.5 Project LATENT

At the EMSP there are two tanks for storing molten salts plus a drainage tank. With this configuration, different operation strategies using molten salts as a transfer fluid can be used tested. However, solutions using low cost solid material for energy storage are a promising complement to molten salt technology, a topic addressed in the Project LATENT.

During the course of this Thesis, work related to the LATENT Project was developed, a project having in mind the upgrade of the EMSP storage facilities, namely:

- material selection and research for the solid module
- definition of the specific material requirements to comply with a STE plant
- pre-design the module
- selection of partners to join the consortium

- defining the working plan concerning the scope of activities of the University of Evora

Concerning the scientific goals, following items have been defined:

- definition of the requirements for the implementation of concrete solutions in a STE plant and developing of concrete mixes to comply with it.
- evaluation of the concrete performance under the thermal working conditions in contact with molten salts.
- optimizing the design of a solid storage system using the characteristics of the most promising mixture, in the fields of heat transfer and material behavior at high temperatures.
- Construction of a prototype that is integrated with a molten salt loop. Validation of the concept to be made through a detailed monitoring program, 9 months of operation is foreseen.

In order to develop such an ambitious project, a joint consortium of industrial Partners together with the University of Evora was established.

10.5.1 Challenges

As described in chapter 7, work was done in recent years in order to identify important characteristics of waste materials from past mining activity in Alentejo. This material was investigated in order to verify if it would be a suitable material to be part of a cement based storage facility. One of the materials identified that has a good potential is the usage of aggregates with a high content of several metals, a slag from São Domingos area. Currently this material is not used in any industrial activity and is considered to be an environmental problem, due to possible leakage to the underground waters.

Its most relevant physical properties (e.g. thermal conductibility, thermal capacity) have been analyzed in order to check the capability of using it as a thermal storage material, and promising results have been achieved pointing that it can be used together with cement as a binder. Several aspects are necessary to be optimized (e.g. granulometry, maximum content, homogeneous level), tasks that will be performed in the LATENT project.

This Project aims to develop a new plant design concept based on the advantages of both molten salt storage and solid storage with concrete based. The innovative concept design not only focus on new plants to be built but also in existing plants where an innovative concrete module could be built next to the existing tanks, thus increasing the thermal capacity storage of the system and reducing its cost per heat storage unit.

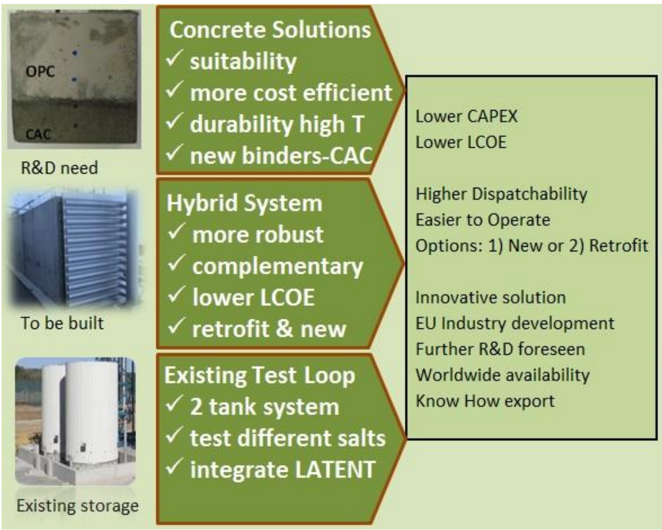

Fig. 10-4 – LATENT concept

Table 10-1 – LATENT objectives

Objective / Challenge	WP	Description of the activity		TRL ini. /end	
Innovative concrete mixes able to meet the requirements of a hybrid (concrete and molten salts) thermal energy storage system. It will be considered the durability properties under the thermal cycles conditions expected and under the chemical attack of the molten salts.	WP2	Up to 550ºC	Without salt interaction	4	6
			With salt interaction	3	6
		Up to 650ºC	Without salt interaction	3	4
			With salt interaction	2	4
Innovative concept design, evaluation and modelling	WP3	Hybrid storage system design. Heat transfer from liquid to solid.		3	6
Prototype construction, operation, monitoring and validation.	WP4	Prototype validation.			

10.5.2 Working Plan

With the aim of expanding the energy storage of the EMSP facilities, a working plan has been established dividing the research work into several working packages, namely:

WP 1 – Project management

The scope of the University of Evora will be: support the project Coordinator

WP 2 – Concrete mix proportioning design and characterization with following content:

- Definition of requirements for the energy storage using concrete solutions
- Concrete development
- Mechanical and thermal compatibility of concrete
- Durability and compatibility with molten salts

The scope of the University of Evora will be: support the requirement definition, perform compatibility tests with molten salts

WP 3 – System Design and Modelling with following content:

- Design of the concrete module

- ➢ System Modeling

The scope of the University of Evora will be: support the design and system modeling

WP 4 – Prototype Construction and validation with following content:

- ➢ Concrete up-scale
- ➢ Prototype Construction
- ➢ Operation and Monitoring.

The scope of the University of Evora will be: supervision of prototype construction, operation and monitoring activities

WP 5 – Techno-economic evaluation and exploitation with following content:

- ➢ Simulation of a STE commercial plant calculating the yearly energy output and LCOE for the optimized concept
- ➢ Technical, environmental and economic evaluation, including LCA and LCC.
- ➢ Towards Market Update: Exploitation plans and Business models.
- ➢ Risk Assessment and Mitigation
- ➢ Pre-normative research and standardization

The scope of the University of Evora will be: simulate an STE plant, support LCA studies, participate in risk assessment

WP 6 – Completion of the steam generator with following content:

- ➢ Finish the steam generator system

The scope of the University of Evora will be: onsite support

WP 7 – Dissemination Activities with following content:

- ➢ Dissemination, Training and Communication.
- ➢ Guidelines for Up-scale to a Commercial Plant.

The scope of the University of Evora will be: support dissemination and guidelines for up-scale

10.6 Project SOLSTICE

Following an extensive work on material research for high temperature applications reported in chapters 7, 8 and 9, a broad project called SOLSTICE was elaborated focusing on extended life in service of materials to be used in energy storage. One research line of the project is to develop new ternary salt mixtures and quaternary at lab scale, that can reduce operating problems, particularly durability issues with the aim to extend in service life and increase the usable ΔT, without having a significant cost impact. A concrete tank thermocline prototype made of a high temperature resistance concrete is foreseen to be built.

During the course of this Thesis, work related to the SOLSTICE Project, namely:

- overall Project Coordination
- selection of partners to fit into the consortium
- definition of Project managing structure
- material research for the concrete tank

- definition of the specific material requirements to comply with a STE plant
- pre-design the concrete tank
- definition of the project challenges together with the other Partners
- assessment of the project impacts
- definition of the scope of UniEvora within the activities planned
- defining the working plan concerning the scope of activities of the University of Evora

10.6.1 Project goals

SOLSTICE's main objective is to implement an innovative thermal energy storage design, validating new materials by real time monitoring of material degradation in order to increase the lifespan of CSP storage systems, increase system efficiency and operation flexibility. It aims for an estimated reduction of 15% in OPEX, and reducing CAPEX of the storage system in 40%. The approach presents two innovative storage solutions, a concrete module and a concrete tank. The implementation of advanced functional materials (concrete, coatings, aerogels, PCM incorporation) is coupled with new sensor development for in-site monitoring, that enable a new storage mix concept.

It is divided into two main ideas:

- For new Plants: to develop an innovative thermocline tank for the molten salts heat storage system with improved thermal and durability behavior
- Retro-fit of existing Plants: to develop a solid-media module to increase the thermal storage capacity of an existing power plant

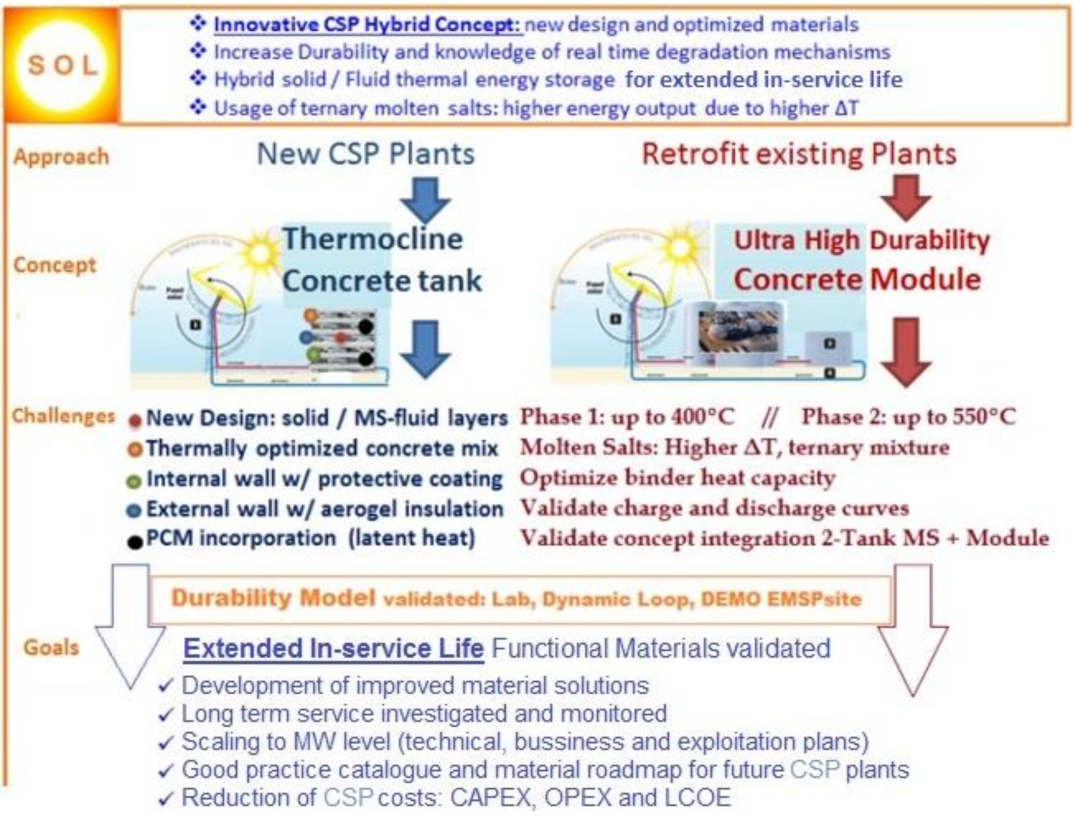

Fig. 10-5 – SOLSTICE, Concept

Table 10-2 – SOLSTICE, Challenges

R&D Challenges	Relevant WP	Material Development	TRL ini	TRL end
Concrete Mix	2.1 / 2.2 / 3.1 / 6.1	Concrete mix (at 550ºC) for tank	4	6
		Concrete mix (at 400ºC /at 550ºC) for module	5/4	6 / 6
Molten Salts and PCM	3.4 / 3.6	Molten Salt ternary mixture	4	6
		PCM encapsulation and incorporation	4	6
Insulation	3.2	Insulation (aerogel)	5	6
Filler Material	3.5	Filler Material incorporation (w/ salt)	5	6
Coatings	3.3 / 3.7 / 6.5	Coating for concrete (w/ salt and substrate)	3	6
		Coating for steel (w/ salt and substrate)	4	6

10.6.2 Project merit

SOLSTICE focuses on material research to enhance its durability over the life time of a STE plant. It has several advantages, namely:

- Lower construction and maintenance costs compared with current solutions, (2-tank indirect system) enabling lower CAPEX and OPEX values of STE plants:
  - The innovative high performance concrete functional material to be used maintains an integrity at high temperatures (up to 550ºC for the thermocline tank and up to 400ºC for the module). A durability model will be developed in order to evaluate performance degradation and identify ways to increase service life of STE plants at controlled maintenance costs, e.g. replacing the periodically the protective coating.
  - In STE plants with MS as heat storage fluid, the development of the innovative concepts proposed in this document will allow the removal of the 2 metallic tanks, thus decreasing the construction costs and the associated durability problems of high corrosion risk of metallic tank in MS.
  - Easy and in-situ constructability: the proposed advanced concrete technologies will have a high flexibility of application to different specific requirements of the thermal storage system. Moreover, considering the actual concrete technology innovations, they will offer an easy and fast (even ad-hoc) in-situ construction process for both the thermal storage core and the thermal insulating (w/ aerogels) concrete external layer.
  - Adaptability: Two new concept designs proposed, one optimal for new CSP plants to be built consisting of a 1-tank thermocline Ultra High Durability Concrete and one optimal for existing CSP plants consisting of a concrete module. The tank will be easy to open from the top and will have filler inside. This filler can easily be taken

out of the tank to be replaced. It is an innovative and highly durable concrete solution whose walls will act as hybrid energy storage together with the filler and molten salts inside, thus reducing the quantity of molten salt needed and thus the overall cost.

- To guarantee the service life of new and retrofitted CSP storage systems of at least 20-25 years by using tailored integration of longer service life functional materials: concrete + coating + MS, knowing the degradation of such materials and in-situ monitoring in the specified operation conditions.

- Increased efficiency: the higher temperature operation (up to 550ºC instead of the current 400ºC) of the proposed materials will allow the use of MS enabling higher efficiency on the thermal conversion, thus increasing the power block efficiency from 35-37% to 40-43%. On the other hand, the fact that the concrete inner walls and the filler act also as energy storage media will increase the overall flexibility and dispatchability of such an hybrid concept. Energy density also increases due to PCM incorporation.
- Advantages from an environmental point of view, a topic to be fully addressed in the Life-Cycle assessment, as well as additional specific actions:
  - A strong environmental merit of the project is the incorporation of waste by-products of past mining activity (industrial slag), which will be incorporated in the concrete mix and also used as filler inside the thermocline tank.
  - The materials present in these storage systems are extremely recyclable at the end of their service life: the concrete is recyclable and MS can be used as a fertilizer, thus increasing the sustainability of the system and reducing the environmental impact over the entire life-cycle.

10.6.3 Working Plan

The project working plan was established to have a logical sequence, starting with the definition of the requirements, material research, modeling, built up a concrete module and a thermocline tank, followed by up-scale and normalization studies.

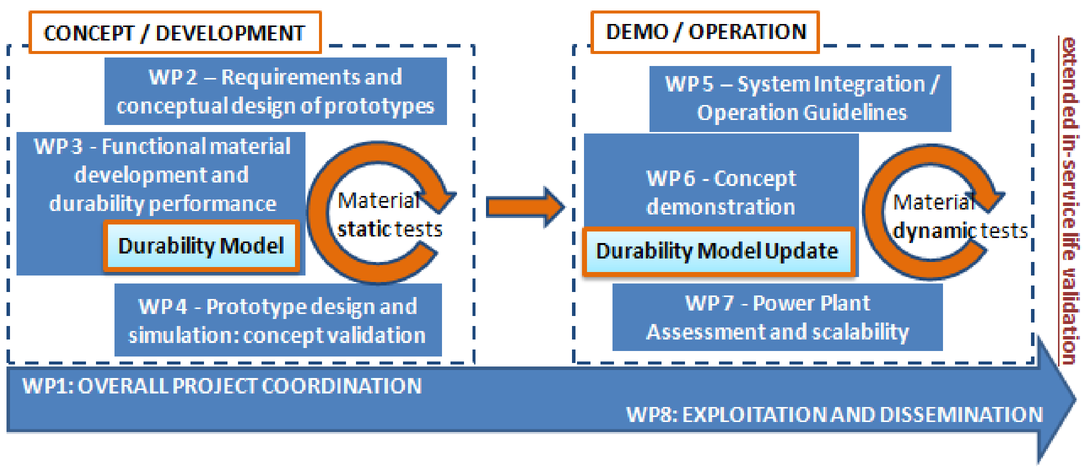

Fig. 10-6 – SOLSTICE, Activities

The work is divided into the following activities:

WP 1 Project Management with following content:

- Overall Project management

WP 2 Requirements and conceptual design of pilot facilities with following content:

- Thermocline Molten Salt tank (for new plants)
- Module (for plant retrofit)
- Preliminary screening of materials based on cost efficiency

WP3. Functional material development & durability performance with following content:

- High Temperature Heat Storage Materials
- Materials for Insulation
- Coatings developing for concrete tank
- Materials for Capture and Transmission: Molten Salts
- Materials for Energy Storage: Filler Material for thermocline
- Materials for Energy Storage: PCM selection and encapsulation
- Durability Model

WP4. Pilot Plant design, simulation: conceptual validation with following content:

- Thermocline MS tank simulation (new plant)
- Tank detail design (final SPEC)
- MS Module simulation (plant retrofit)
- Module detail design (final SPEC)

WP5. System Integration / Operation Guidelines with following content:

- Integration of prototypes w/ industrial facilities
- Sensor development for component/system monitoring
- HAZOP and Operation Guidelines
- PCM encapsulation preparation

WP6. Concept demonstration and extension in service life: material validation with following content:

- Concrete Mix Preparation
- Build Prototypes
- Operate
- Testing, monitoring
- Result evaluation
- Durability Model Update

WP7. Power Plant Assessment w/ new concept & materials

- Technical Model
- Economic Model
- Scaling issues
- Life cycle assessment – material flow
- Business Plan adapted to the reference case

WP8. Innovation Management, Exploitation and Dissemination

- Data and Innovation Management
- Business Plan w/ Market Analysis
- Exploitation Plan
- Dissemination and communication activities
- Pre-standardization research and Material Roadmap
- Catalogue of good practices

Fig. 10-7 – SOLSTICE Partners meetings (Evora, EMSP, Olivença) for in depth definition of the work plan

Following project structure is foreseen:

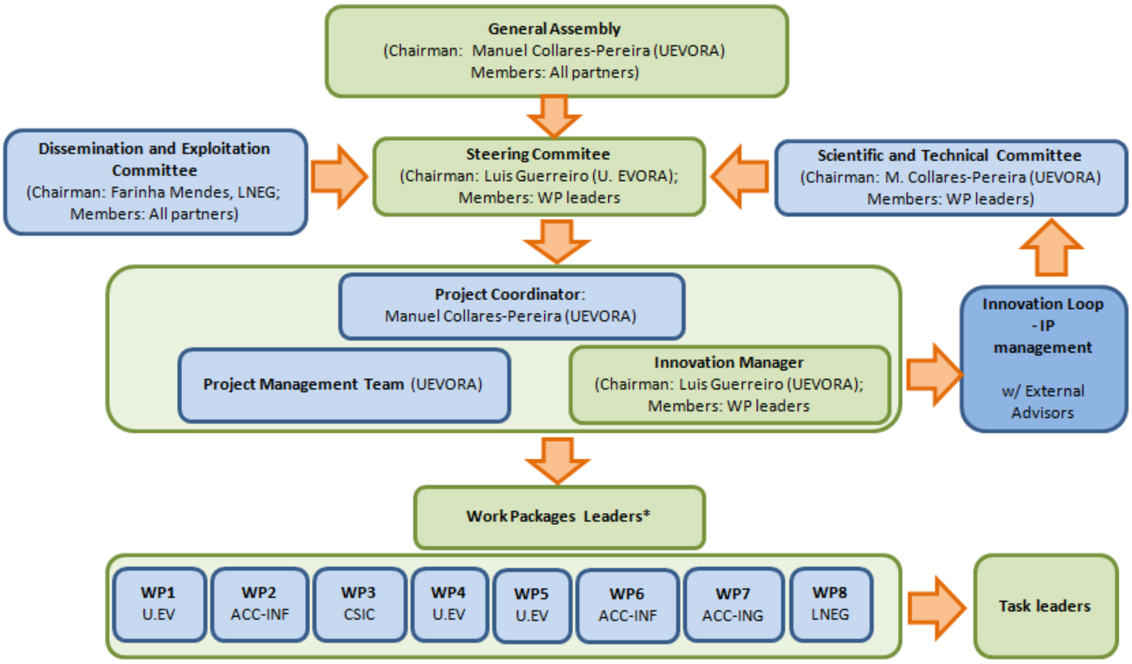

Fig. 10-8 – SOLSTICE, Organizational structure

10.6.4 Project mitigation measures

A detailed project risk assessment was performed, as presented below.

Table 10-3 – SOLSTICE, risks and risk mitigation measures

Description of technical risk	WP	Proposed risk-mitigation measures
Design of full scale tank involves more (or more complex) aspects than expected.	2 and 4	1- A supplementary time period between end of WP2 and start of WP4 was foreseen. 2- Supplementary resources shall be used in WP4 to evaluate the full scale design.
Overall real cost of the novel technologies added to the CSP plant are too high to make profitable business case under assumed scenarios	2, 4 and 7	The target costs under the pricing scenarios will be prescribed under WP2 and material screening will be done. Procurement tasks will be performed on WP4, to guarantee that the build up cost is within target, otherwise a cost reduction exercise will be initiated in WP4
Material validation not achieved after laboratory tests are performed	3	Several alternative materials will be studied in WP3 to define which one has the best in service life performance, e.g. for concrete protection, 3 solutions will be evaluated: i) refractory bricks; ii) silica sol gel coating iii) geopolimer coating
Optimization during tank and module simulation does not achieve the improvement target	4	An intermediate report will be produced during WP4, so that, additional resources can be allocated towards the 2nd half of the WP4
Unforeseen long time tests for sensor equipment development	5	1- Sensor development will have an early start, as soon as WP2 is finished. 2- Development reports every 6 months
Insufficient data input from Partners for LCA	7	1- Literature data has been gathered in addiction 2- Partners have contacts with LCA experts and databases outside the consortium
Insufficient data input from Partners for the technical model and business plan	7 / 8	1-ESTELA has agreed to support the project with Info 2- A prospective customer will cooperate in th project
Difficulty to disseminate project results to decision makers	7	1- A prospective customer has been contacted and will follow closely project achievements 2-An expert company will support in contacting worldwide investors through their offices in San Francisco, Singapore and China 3-Dissemination events will be organized as well as information will be made available at Solar Paces.

10.7 Conclusion

The research work performed during this thesis has provided a good background to plan current and future projects to be developed at the EMSP in Évora. Some like PreFlexMS have already started, others like HPS-2, INNOVLFR and SOLSTICE shall be a reality in the years to come, which will provide a solid basis for companies to develop R&D activities at the EMSP.

10.8 References

[1] A.T. Kearney and ESTELA, Solar Thermal Electricity 2025, ESTELA, 2010

[2] Canavarro, D. “Advances in the design of Solar concentrators for Thermal applications”, PhD Thesis, UniEvora, 2015

11. Conclusions

11.1 Energy storage is absolutely necessary

All available energy forecasts indicate that the share of renewable energies within the total final energy mix will continue to increase worldwide, in some regions Windpower will be the renewable leader in the mix, in others solar energy will become more relevant as the average investment costs continue to decrease, especially in photovoltaics. From 4GW installed global capacity in 2014, IEA forecasts STE power output to increase to 11% share in 2050 of the worldwide power supply with a capacity of 1000 GW in 2050 [1]. Most of STE plants will have energy storage capability because it is crucial for renewable energies to collect the advantages of being a flexible and dispatchable way of generating electricity, characteristics with intrinsic value *per se*. It should be noticed that STE plants with storage have a lower LCOE than STE plants without storage. From a system perspective, STE offers significant advantages over PV, mostly because of its built-in thermal storage capabilities. Both technologies, while being competitors on some projects, are ultimately complementary because mid-day peak shaving is well suited to the STE dispatchability.

In what concerns solar energy systems with storage, solar thermal electricity has the best technical solution (storage efficiencies higher than 95%) and the overall system is still far away from its technical limits, thus, an overall energy output improvement is expected to occur in the future [2] supported by research on new materials, new optical concepts, better weather forecast, optimized operation and control strategies.

This thesis contribution is focused on new materials (chapters 7, 8 and 9), techno-economical evaluation of a new optical concept (chapter 4), optimized operation (chapter 4 and 5) and a new storage design concept (chapter 6), all with the objective of contributing to the development of this technology and to its cost reduction.

11.2 Research questions

Along the chapters of this thesis, work was developed to enable new and direct answers to the research questions outlined at the start.

RQ1: Can a new STE plant concept be optimized to achieve a lower LCOE than current LCOE mix for the south of Europe?

Within the STE area, the technology that has still the largest potential for technological development ahead of it, together with the potential for the lowest value of CAPEX/MW installed is Linear Fresnel. Research on optimization of the concept has been pursued at a low pace in the last 30 years, with interesting applications for STE like the CLFR-EM concept. In chapter 4, a 50MWe with 7h storage plant using such a concept was simulated using TRNSYS. In the southwest part of Europe, Faro-PT (37º01'N, DNI=2234 kWh/m^2), 110 GWh would be produced with a LCOE of 10,8cEuro/kWh which is lower than any Parabolic Through plant in operation. An LCOE lower than 10cEuro/kWh was shown to be possible already in a first trial, for a sunnier location like Hurghada (27º26'N, DNI=3043 kWh/m^2) in Egypt.

RQ2: Which could be the heat transfer fluid and storage media of such a plant?
Currently, the maximum temperature allowable of 400ºC is a technical limitation of the thermal oil used as heat transfer fluid that starts to degrade at that temperature, additional drawbacks are its high cost, flammability, low boiling points and environmental hazard (including explosion risks) and certain (still low) thermodynamic conversion efficiency into electricity. To avoid these disadvantages, a variety of molten salts (binary, ternary and quaternary mixtures) have been validated at lab scale. Nowadays, at that temperature a non-eutectic molten salt mixture with 60% sodium nitrate ($NaNO_3$) and 40% potassium nitrate (KNO_3) is the most used media for storing energy. In chapter 5 tests have also been performed to use the receivers as a direct system. Moreover, molten salts have a good heat capacity and can be a good heat transfer fluid in hybrid systems using solid storage material (see chapter 9), they are also able to operate at much higher temperature for a much higher conversion efficiency.

RQ3: What progress is needed in terms of material science development and validation to enable new storage concepts for STE applications?
Material science research is a key issue for technological development since it enables new systems and higher conversion efficiencies. On STE applications, thermal stability of molten salts at operating temperatures (range 150ºC to 600ºC) as well as corrosion issues are characteristics that have been pursued for the best mixture, for instance including lithium and cesium nitrates. Solid materials to be used in storage up to 600ºC need to have a good stability and cohesion for the cyclic loads typical of an STE system. Selected samples have been tested (chapters 8, 9) and are foreseen to be fully validated on a much broader project called SOLSTICE (chapter 10) which gathers 15 partners among industry and research institutions.

RQ4: What type of local materials could be used thinking on resource sustainability and closed loop systems?
Think globally, act locally. Sustainable solutions should significantly rely on local resources. This is the reason behind an initial research held in 2011 and 2012 to screen which materials available in Alentejo region, Portugal could be used for energy storage applications at high temperature. Samples from quarries and from old mines were analyzed, the most interesting solution was a type of slag ("modern slag") from the old mines of *São Domingos* (see chapters 7, 8 and 9). Not only would local material be used, but also it would solve a big environmental

problem estimated at a cost of 3,8 MEuro/year due to air and water pollution. The re-usability of this material as an aggregate for a cement base storage was tested (chapter 7) with positive results, meaning the loop could be closed in a way that a current residue turns to be a valuable energy storage material due to its physical properties.

RQ5: How could such concepts be validated taking advantage of the existing *Evora Molten Salt Platform* (EMSP) facility in order to enable a fast technological deployment?
The research conducted during this thesis always had in mind, the usage and upgrade of the EMSP facility. This research platform is a key part of a validation process that needs to occur before new technologies are deployed to the market. Along the concept development and new findings, industry and research partners were selected and brought to a stage of common development focusing on different projects (see chapter 10): INNOVLFR (for optimization of the optical and system operation aspects), LATENT and SOLSTICE (for validation of new energy storage materials).

RQ6: How could a transition to an integrated sustainable global energy system take place, and which energy policies could be implemented?
A transition to an integrated sustainable global energy system could be achieved not only developing further clean technologies like the FRESNEL SMS XX with storage concept (see chapter 4), but also two other axes: I- fostering transfer of resources from old and pollutant industries into clean tech projects; II- have a demand side management approach that collects resources from heavy users (energy, water, etc.) and uses those to promote higher sustainable resource usage and poverty relief. This is the designated Energy Transition Model presented in chapter 3.

11.3 Thesis impact

The full impact of research can only be assessed on a long term perspective. However, a few dissemination indicators can be highlighted, namely:

- Articles published (peer reviewed): #11 which includes all articles with content developed in this thesis
- International Projects (H2020 and BMWi) application: #2 (leading role) and #4 (partial contribution)
- Patent application: #2 (to INPI)
- Awards: #1 (Young scientist award in the field of Energy, “Limits to Growth revisited”)
- Media: #1 (“The limits of growth”: interviewed for the german channel TVN-Hannover)

It should be highlighted that this work also gave an important contribution to the EMSP realization and its long term planning.

11.4 Future Perspectives and lines of investigation

During the course of this thesis, several research projects have been written and submitted (see chapter 1). One of them, in the framework of H2020 has been approved and started in June 2015, having the University of Evora a leading role in WP7 (demonstration). Another project is SOLSTICE which has successfully passed to the second stage of a very recent H2020 call (under evaluation). In this project, future investigation for a 3 year period (2016 - 2019) is well defined and divided into 8 working packages (see chapter 10), including areas like material research and validation, development of a durability model, system simulation, tank design, techno-economic analysis for a commercial plant, HAZOP and LCA studies, market research and technical guidelines.

In case SOLSTICE project becomes a reality, EMSP storage facilities will be upgraded in a way that will make it one of the World references in STE technology especially on what concerns thermal energy storage developments.

11.5 References

[1] IEA, Technology Roadmap: Solar Thermal Electricity, 2014

[2] ESTELA, SET-Plan, 2013

PARECER

Eu, João Farinha Mendes, Investigador Principal do LNEG e co-orientador da tese de doutoramento de Luís Filipe Lopes Guerreiro, para os devidos efeitos declaro que após a sessão pública de discussão realizada a 29/02/2016, o trabalho realizado está concluído e na sua versão final.

Lisboa, 30 de Maio de 2016

João Farinha Mendes