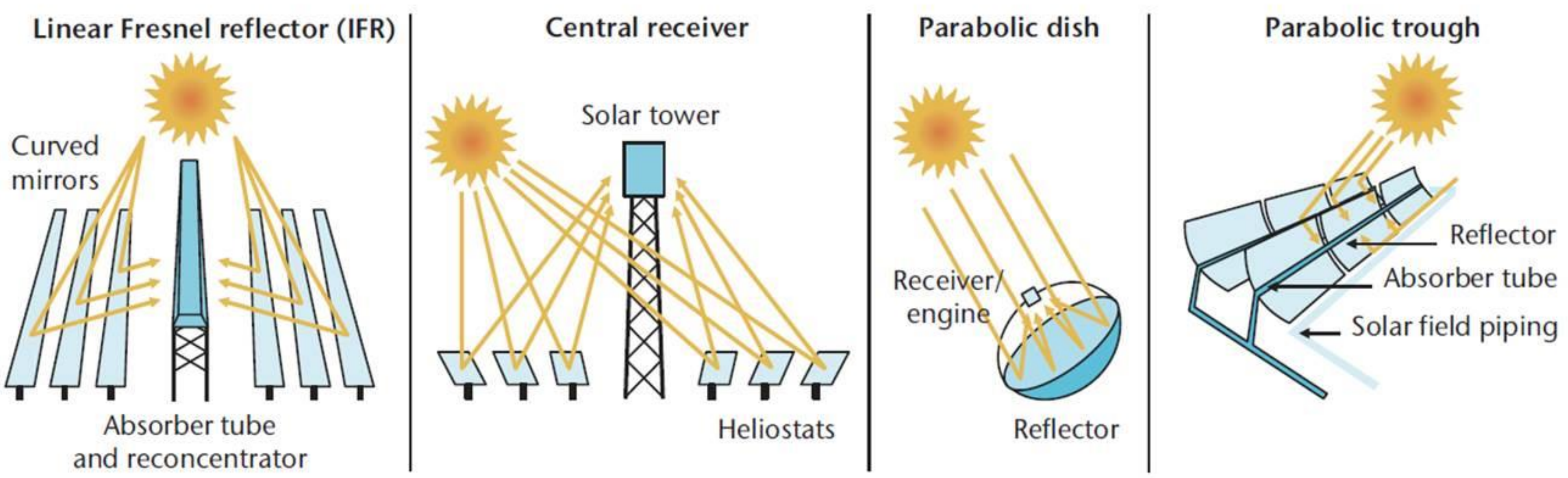
Compatibility of structural materials with molten salts and liquid metals for CSP applications

Marta Navas
Structural Materials Division
CIEMAT

MatISSE/JPNM workshop on cross-cutting issues in structural materials R&D for future energy systems

CSP Technologies

- Concentrating Solar Power (CSP) technologies convert solar irradiance into useful heat by means of concentration using different technologies
- Most current CSP plants are based on trough technology, but tower technology is increasing.
- CSP deployment has been slower than expected. The EU roadmap objective of 147GW of cumulative capacity by 2020 is now likely to be achieved 7 or 10 years later

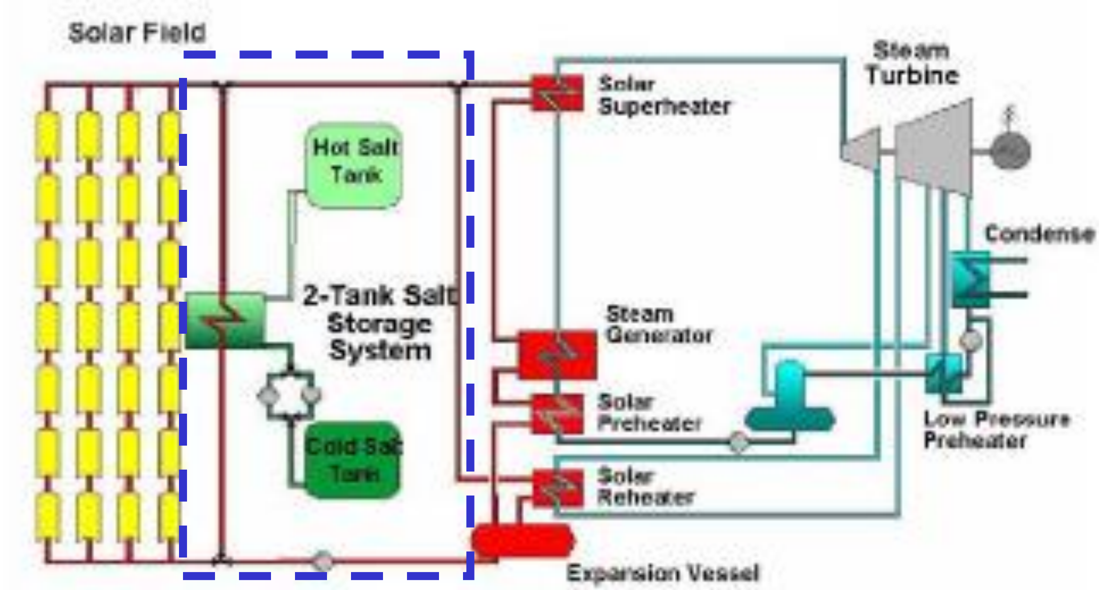


Parabolic trough plants

Reference plant: Parabolic trough plants with organic oil as HTF

Thermal Energy System: Sensible heat with two indirect tanks with molten nitrate salts

- Heat Storage Material: Binary salt: 60% $NaNO_3$ + 40% KNO_3
- Operation temperature of hot tank: 390 °C
- Main components: Tank, pipeline, tube, plate and shell of heat exchangers

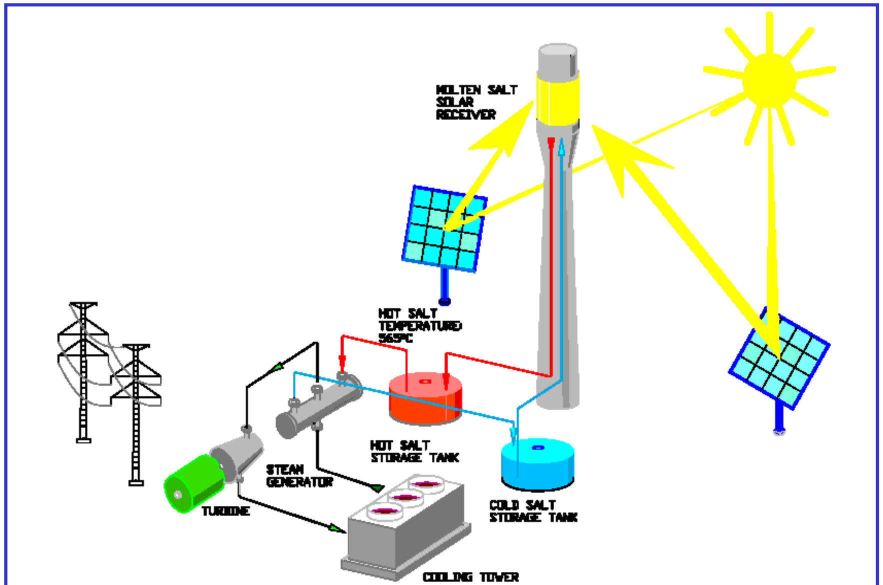


Central receiver

Molten salts used as HTF represent the most cost effective technology for electricity generation CSP

Central receiver: Solar Two Project, GEMASOLAR, Crescent Dunes

- Main components: Tanks, Steam generator system (Superheater, evaporator, preheater) Pipeline, Receiver System…
- Operation temperature of hot tank: 560 ºC



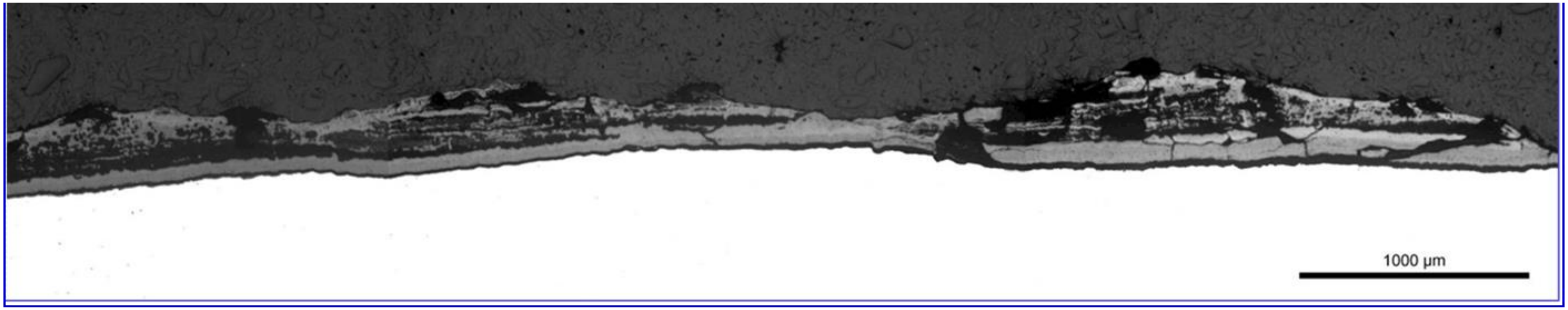
Burgaleta SolarPaces 2011

Molten Salt Technologies

- Nitrate molten salts (60% $NaNO_3$ + 40% KNO_3) are used as HSM, for sensible heat of TES system, but also as HTF in central receiver plants.
- CRS with MS technology allows working at high T with a reduction in size and cost of the TES system.
- High receiver efficiency can be achieved by reducing the receiver size, forcing it to operate with very high flux levels.
- Feasibility of these technologies relies on the compatibility of structural materials and nitrate molten salt.
- Structural materials must present a good behaviour against thermal transients, thermal cycling and corrosion
- Key aspects of nitrate molten salts aggressiveness
  - Chemistry composition
  - Thermal degradation due to nitrite formation

Molten salt corrosion

- Metallic alloys exhibited uniform corrosion depending on the protective oxide layers formed on nitrate MS.
- Corrosion behaviour relies on the material type, chemical composition/quality of molten salt and operating conditions
- At high T, a double oxide layer was obtained with Fe oxides in the outer layer and Cr and Ni oxides mixture in the inner one.
- The absence of Cr in the outer layers can be due to its solubility in molten salt under some working conditions
- Intergranular or preferential attack has been obtained at high T.
- Thermal cycling can produce mechanical damage in the oxide scales



Structural material requirements

- Materials recommendations are mainly based on the corrosion resistance due to the peak temperature of the component.
  - Carbon steels: at temperature below 400ºC
  - Ferritic steel (low Cr and Mo) up to 500ºC
  - SS or Ni base alloys at the highest temperature (600ºC).
- Some components can suffer important thermal transients and thermal cycling: possibility of LCF and thermal fatigue.
- Durability: Effect of material agging at high T → Changes on the alloy microstructure (precipitation or phases)
- Microstructural changes can alter: Mechanical properties, creep, fatigue and corrosion resistance

EERA Roadmap

- The CSP EERA community has established a 10 year RTD roadmap for the improvement of STE technologies.
- For short-medium term research activities:
  - More effective and less expensive systems
  - Reduce the TES cost (50%) by some technological breakthroughs and by improvement of actual technologies.
- For long-term activities:
  - Increasing of temperature regime with new HTF (Heat Transfer Fluid) and HSM (Heat Storage Materials).
- The structural materials compatibility with the actual and new materials will play an important role.

SFERA-II Project

Solar Facilities for the European Research Area - II

- Funding scheme 7th FRAMEWORK PROGRAMME
- Capacities Specific Programme Research Infrastructures
- Integrating Activity - Combination of Collaborative Project and Coordination and Support Action
- EU financial contribution: €7 million
- Duration: 48 months (2014-2017)
- 12 Partners
- The purpose is to integrate, coordinate an further focus scientific collaboration among the leading of European research institutions in solar concentrating system

SFERA -II Project

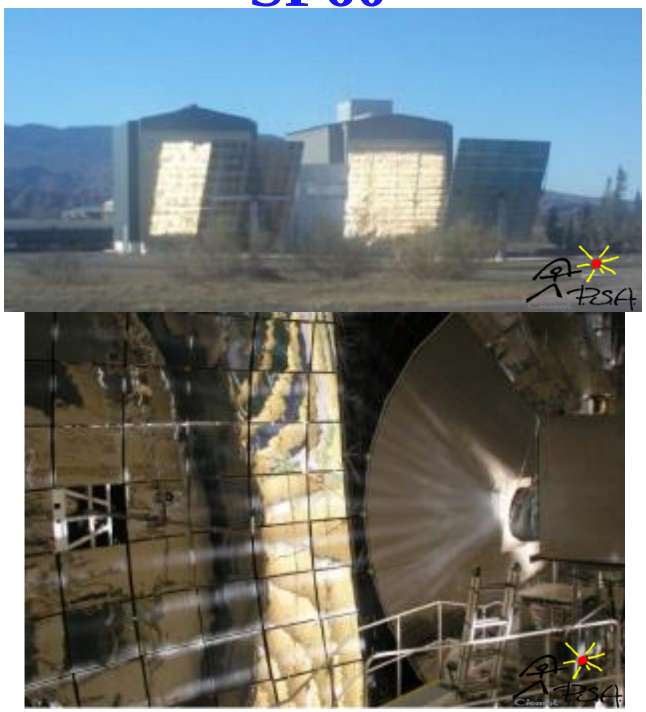
- WP 1 Management
- WP 2 Dissemination and publicity
- WP 3 Promotion of Innovation in CSP based on SFERA activities
- WP 4 Educational outreach activities
- WP 5 Exchange of best practices for harmonization of approaches
- WP 6 Joint Management of 'Transnational Access' activities
- WP 7/10 Transnational Access to PSA/PROMES/PSI/ENEA facilities
- WP 11 Development of Joint Calibration Procedures and Facilities for Sensors
- WP 12 Pyrometric Temperature Measurement Methods
- WP 13 Determination of physical properties of CSP materials under concentrated solar irradiation
- WP 14 Characterization of solar concentrators and interconnecting elements
- WP 15 Characterization of heat transfer fluids and heat storage materials

CIEMAT-PSA Facilities: Solar furnaces with high fluxes are suitable for use in Advanced Materials R&D

CIEMAT PSA-Solar Furnaces

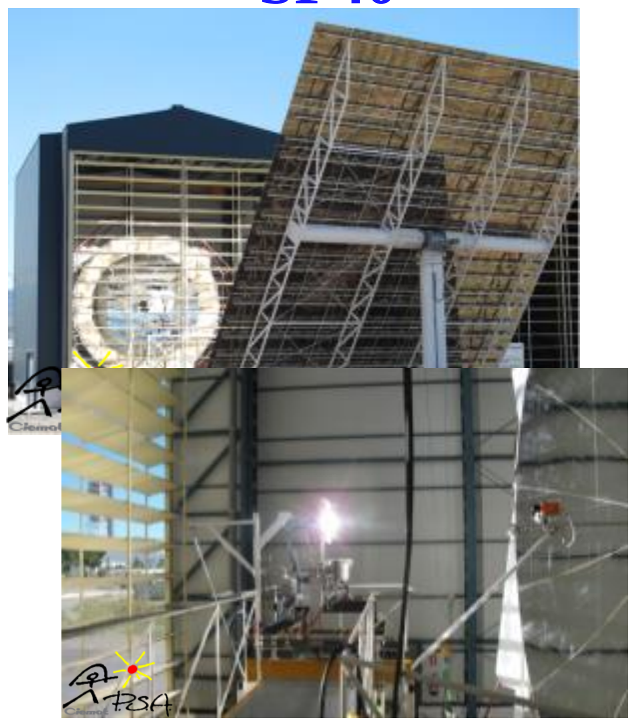
Horizontal SFs:

SF60



Power	60 kW
Peak Concentration	3000 kW/m^2
Focus Size	Ø 25 cm
Focal Distance	7.45 m

SF40



Power	40 kW
Peak Concentration	7000 kW/m^2
Focus Size	Ø 10 cm
Focal Distance	4.5 m

Vertical SF:

SF5

Power	5 kW
Peak Concentration	7000 kW/m^2
Focus Size	Ø 2,5 cm
Focal Distance	2 m

PSA Ciemat Solar Furnaces

Direct application of highly concentrated solar radiation to materials

Flux density up to 7000 kW/m^2 (and more)

Very high temperatures >2000°C

Extreme operating conditions

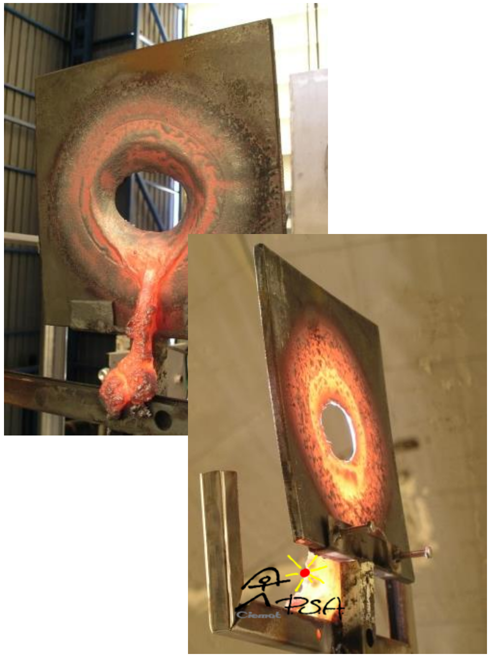
Materials testing
Thermal shock tests
Accelerated Ageing of Materials
Processing of metallic and ceramic mat
Surface materials treatment

- Thermal Shock Tests
- Accelerated ageing
- Sintering
- Carburization
- Nitrurization
- Aluminium Foaming
- Tempering and Annealing

Solar tests in air, vacuum and in controlled atmosphere conditions (i.e. Ar, N_2, N_2/H_2)

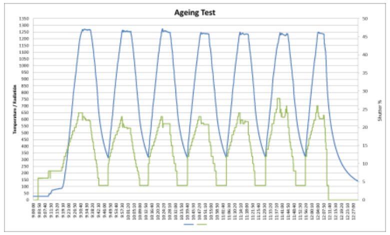
PSA Ciemat Solar Furnaces: Applications for structural materials at High Temperature

Thermal shock tests and accelerated ageing of materials

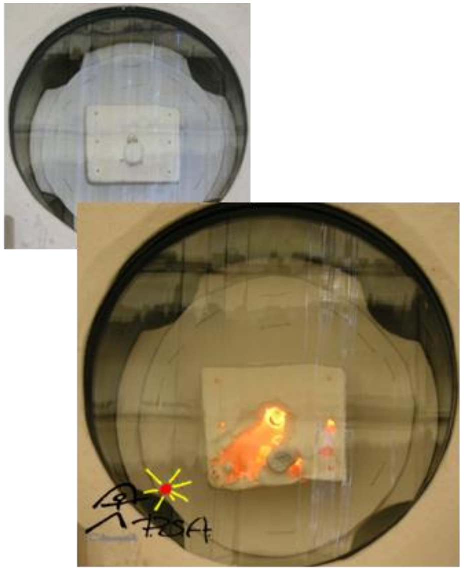


Oxi-reduction of carbon steel under solar thermal shock

CIEMAT



Material sintering



Solar Melting of YSZ and Sintering of Alumina ceramics

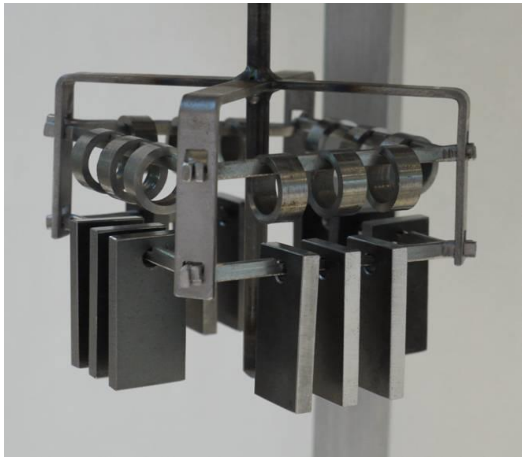
CIEMAT
(Fusion Tech. Division & SSC Unit)

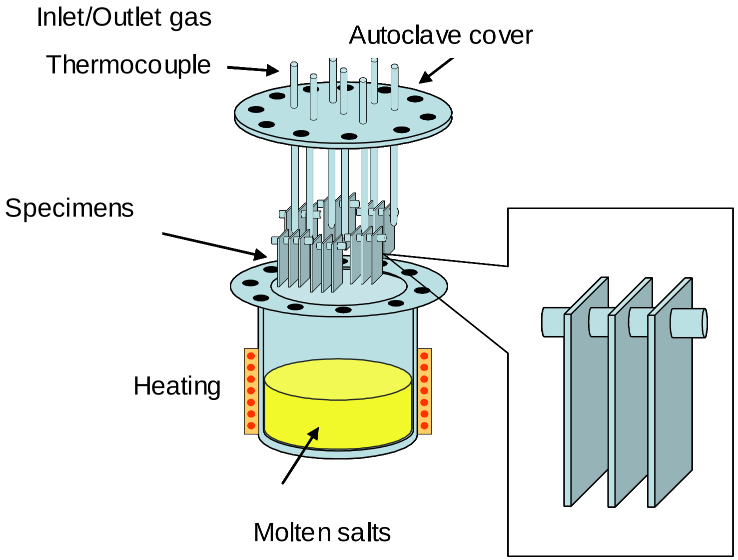
Inmaculada Cañadas CIEMAT PSA

MS Corrosion tests

Standardization of corrosion testing of structural materials by molten salt DEV 15.1 (June 2015) CIEMAT-SMD

- Long term corrosion immersion tests
- Working temperature: 390 ^{0}C/565°C
- Determination of corrosion rate:
  Weight and thickness losses
- Studies of oxide layers





STAGE-STE Project

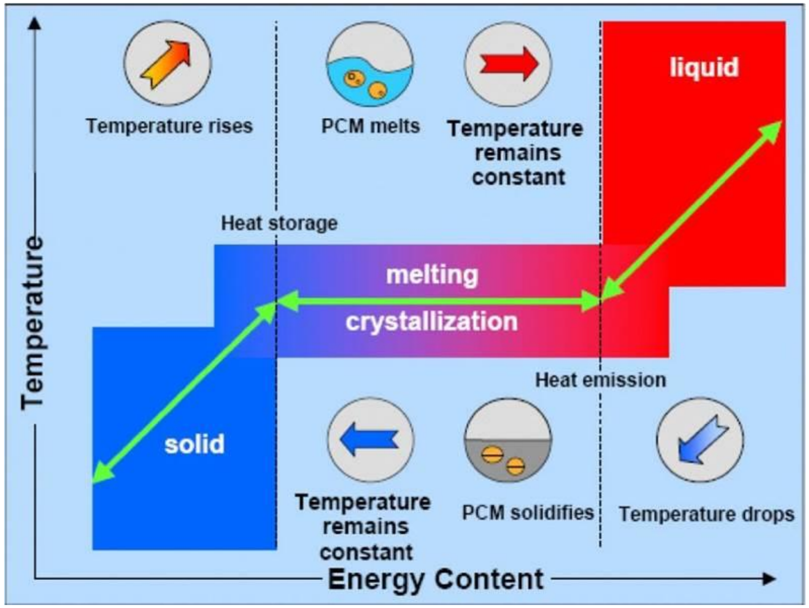
Scientific and Technological Alliance for Guaranteeing the European Excellence in Concentrating Solar Thermal Energy

Integrated Research Programme (IRP) with more than 42 partners

- WP 1 Consortium Governance and Management Issues
- WP 2 Integrating Activities to Lay the Foundations for Long-lasting Research Cooperation
- WP 3 Enhancement of STE Research Facilities Cooperation
- WP 4 Capacity Building and Training Activities
- WP 5 Relationship with Industry & Transfer of Knowledge Activities
- WP 6 International Cooperation Activities
- WP 7 Thermal Energy Storage for STE Plants (ENEA)
- WP 8 Materials for Solar Receivers and STE Components
- WP 9 Solar Fuels
- WP 10 STE plus Desalination
- WP 11 Linear Focusing STE Technologies

Advanced TES

- Use of more effective concepts and developments like latent heat storage using Phase Change Materials (PCM)
- Storage of large amounts of energy per unit volume within a very narrow temperature range of solid –liquid transtition
- Liquid metal are one of the most promising concepts of PCM due to their high thermal conductivity values and the possible use of less sophisticated heat exchangers.
- Eutectic mixture of metallic PCM can be an aggressive environment for the structural material response.

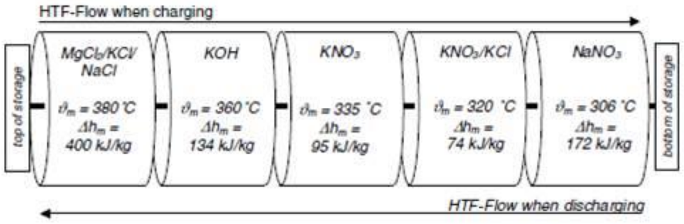


Advanced TES

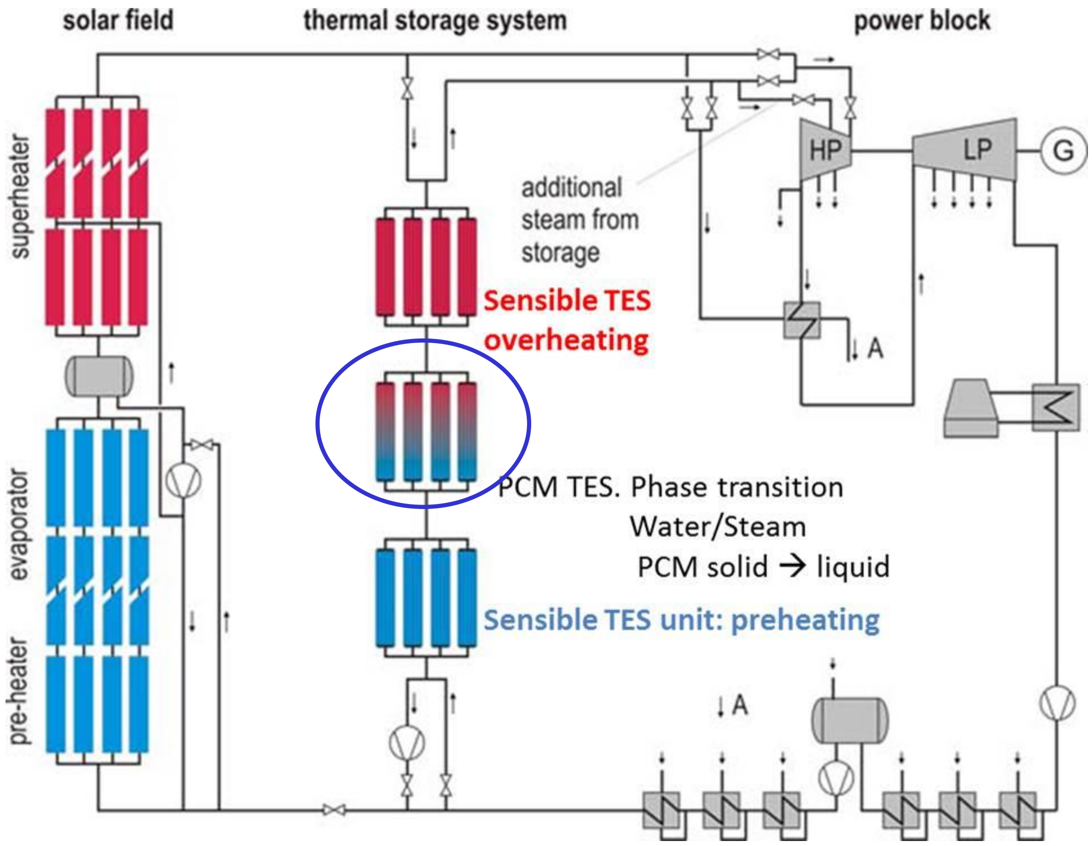
Different liquid metals and eutectic mixtures are being studied depending on the temperature regime and CSP applications

Candidates:

- AlSi
- Al Mg Zn
- Cu Si Mg
- Mg-Zn
- Mg-Zn (Ni, Cu)



Cascaded latent heat storage for parabolic trough solar power plants
Horst Michels, Robert Pitz-Paal (DLR)



Birnbaum et al. DLR, 2010

Metallic PCM

Most of liquid metals are an aggressive environment which can produce structural material degradation mechanisms like corrosion and embrittlement

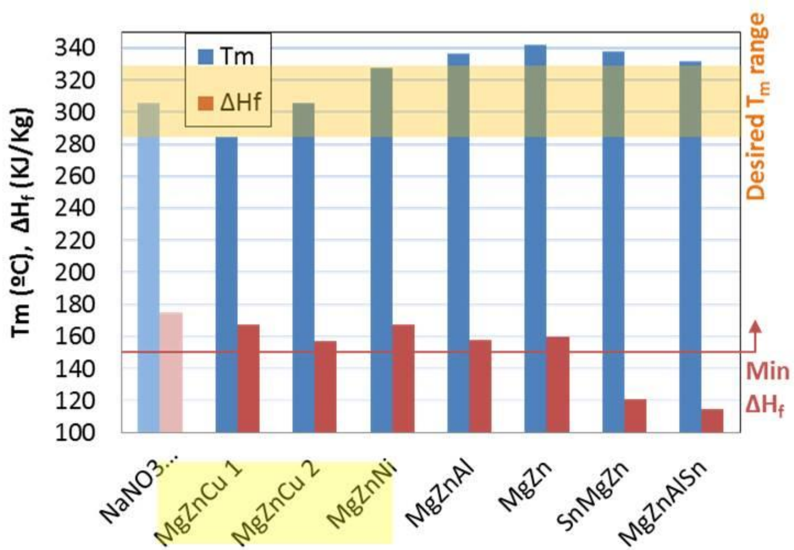
Subtask 7.3.3. TECNALIA: Designing of novel metallic PCM

Synthesis and characterization of alloys: MgZn (Cu/Ni).

Tecnalia + Ciemat: Studies on structural material degradation

Abengoa: Cost analyses

Melting temperature and Latent Heat for different alloys



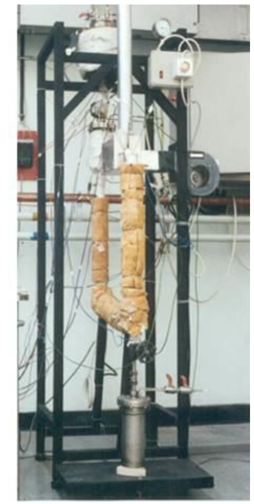
Nieto SolarPaces 2015

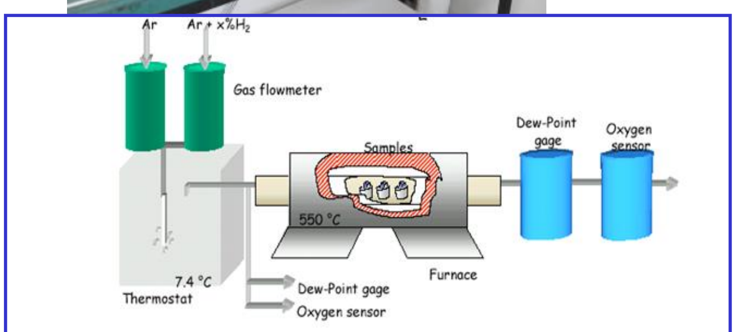
Liquid Metal facilities

Corrosion tests

- Multiprobe static autoclaves environmentally controlled
- Environment controlled furnaces
- Recirculation loops PbBi

Creep in HLM





Conclusions

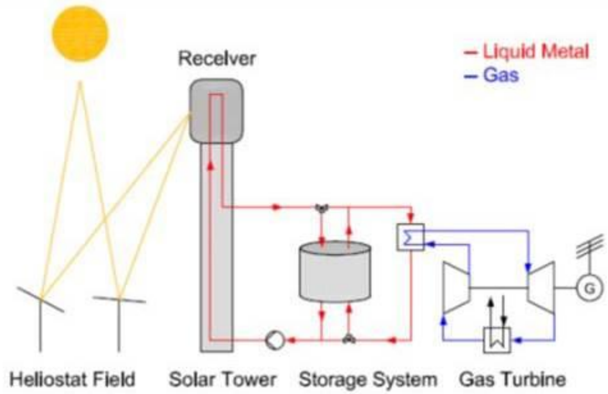
- Structural material compatibility with molten nitrate salts plays an important role on construction and operation of CSP plants
- Material corrosion depends on the formation of protective oxide layers and several factors must be taken into account like: material type, molten salt composition or operating conditions
- New technologies are being developed with other MS and higher working temperatures.
  - Ternary or quaternary mixtures of nitrate molten salts
  - Other molten salt types like mixtures of chloride, carbonate
- Metallic PCM´s are one of the most promising concepts for using on advanced TES system
- Structural material compatibility with new HTF and HSM will be a key parameter in these new technologies

Thank you for your attention

m.navas@ciemat.es

Liquid Metal

Liquid Metal: Temperature range as HTF and Heat transfer coefficient (tubes 12mm n=1m/s)



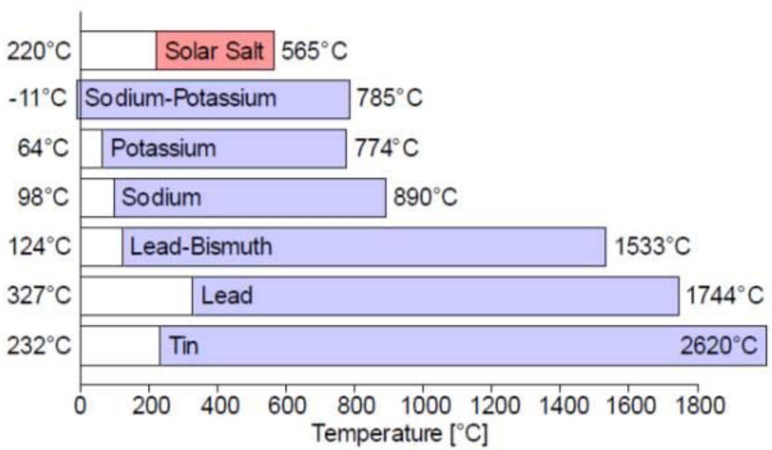
Gas turbine (Brayton cycle)

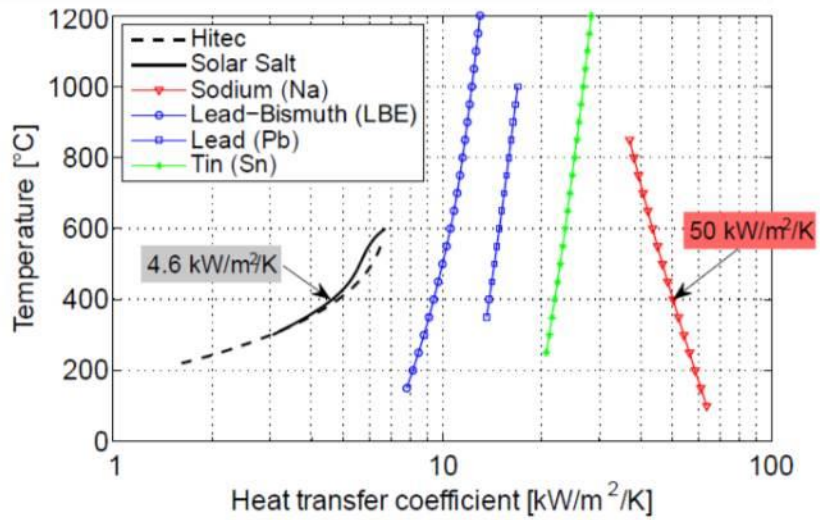
Open or closed cycle

DCHX possible for closed cycle

Liquid metal candidates:

Up to 850 °C:	Na, Pb, Pb-Bi, Sn
Above 900 °C:	Pb, Pb-Bi, Sn





Fristch et al Energy Procedia 2015