# THERMAL ENERGY STORAGE AREA

ENCUENTRO UPV/EHU CAMPUS DE ÁLAVA- CIC ENERGIGUNE

12 de mayo 2014


2014

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# SC meetings, Dec. 2009 and Sept. 2010

## Definition of interesting and potential research lines

**SHORT AND MID-TERM:** **Sensible heat**

- Research will be focused on modeling, synthesis and characterization of new fluids that remain liquid at ambient temperature and have a good thermal stability above 400 ºC. Fluids with nanoparticles should be considered

**MID-TERM:** **Phase change materials**

- The focus must be on the encapsulation of phase change materials aimed at reducing the size and cost of TES system
- The heat transfer concepts for latent heat storage must be improved, identifying, modeling and synthesizing new liquids. This could include the thermodynamic modeling of eutectic formulae to predict compositions with the ideal melting points

**LONG-TERM** **Thermochemical reactions**

- Modeling and experiments need to be combined to research limits in reaction rates and thermal power related with mass transfer
- Materials and reversible reactions for thermochemical storage also need to be investigated

***Ed. short and mid-term:*** **System Design**

- Storage through molten salt needs to be improved: it must be more profitable and reliable

# The TES Area activities and organization

| Thermal Energy Storage Area - TES Area | | Latent Heat Storage | | | Sensible Heat Storage | | Thermochemical Heat Storage | |
|---|---|---|---|---|---|---|---|---|
| 2014 People Allocation | | Metal alloys<br>StrP - Act | SAMSSA<br>EUP - Act | Nano_Salts<br>StrP - L | Sol_Pack_Bed<br>StrP - S | New<br>. . . | New<br>. . . | New<br>. . . |
| Materials & Devices Modeling | GL: BD<br>AR: JR<br>**PD: New**<br>**PD: New** | | | | | | | |
| Materials Development & Charcterization | **GL: New**<br>AR: AF<br>PD: KM<br>PhD: ER<br>PhD: IO<br>Tech: NS | | | | | | | |
| Devices Prototyping & Testing | GL: ---<br>AR: PB<br>PD: AG<br>Tech: --- | | | | | | | |

# The TES Area Researchers

### Dr. Javier Rodríguez
- Associate Researcher
- Physicist

### Dr. Pablo Blanco
- Associate Researcher
- Mechanical/Civil Engineer

### Dr. Abdessamad Faik
- Associate Researcher
- Chemist

### Dr. Antoni Gil
- Postdoctoral Researcher
- Industrial Engineer

### Dr. Karthik Mani
- Postdoctoral Researcher
- Chemist

### Naira Soguero
- Laboratory Technician
- Chemical Tech. Engineer

**Modeling**

**Materials**

**Prototyping**

### Elena Risueño
- Ph.D. Student
- Chemist

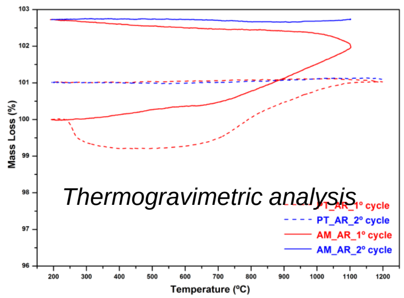
### Iñigo Ortega
- Ph.D. Student
- Chemical Engineer

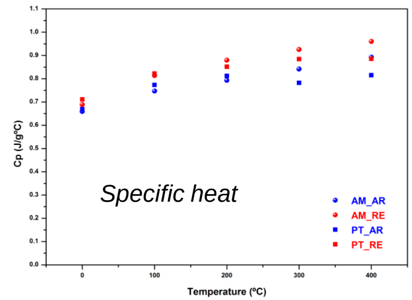
### Fernando Blanco
- Master Student
- Chemical Engineer

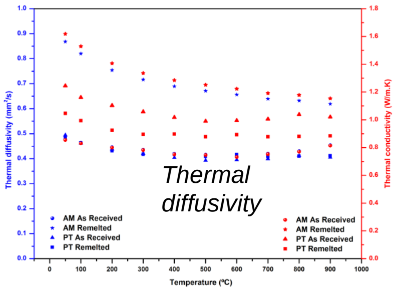
# SHORT AND MID-TERM: Sensible heat

## The thermocline system

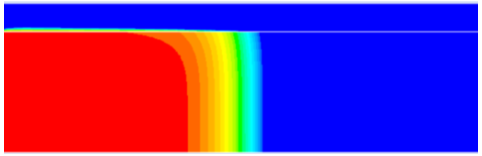
### Material preparation and characterization



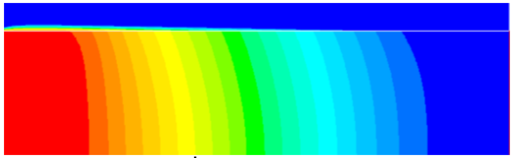




### Device modeling and design



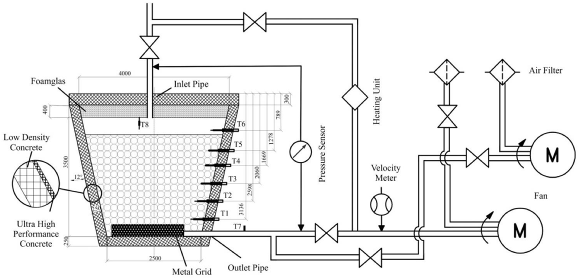
$1^{st}$ heating



$10^{th}$ heating

### Prototyping and testing (lab scale)

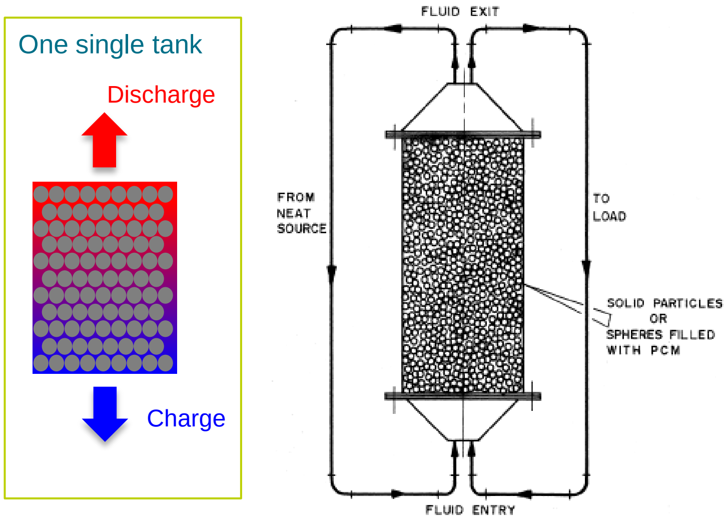
Storage system

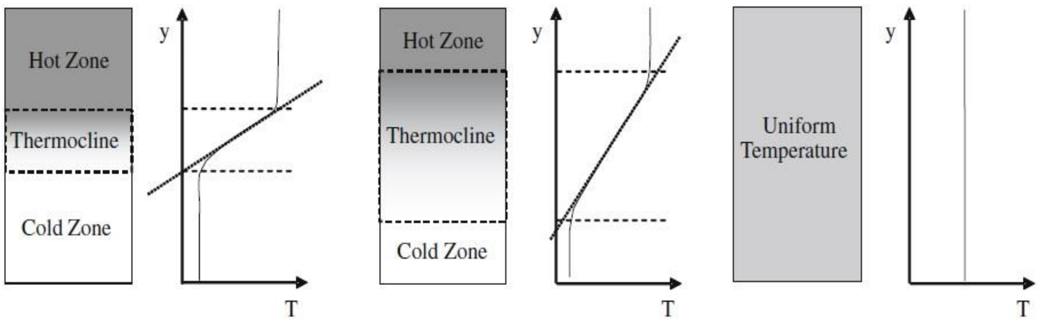



Air loop

## The thermocline system: Definition

In order to avoid the use of large amounts of liquid, or when the heat vector is a gas, the heat can be stored in solid bodies (fluid – solid heat exchange is needed).




Most of the reservoir volume (65%) is occupied by solid particles which are heated or cooled by heat exchange with the fluid

An hot – cold interface, which moves much slower than the fluid, is generated

**Such a metastable hot – cold interface is called the thermocline**

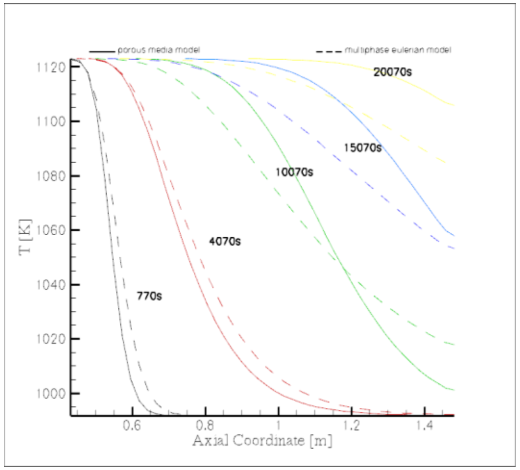
## The thermocline system: Design

The thermocline shape and behavior depend on several factors.

**Shape** - A steep thermocline (and a high storage efficiency) is generated by:

- fast heat exchange – small pebbles, highly conducting, short tank
- low heat conduction – low conduction pebbles, long tank
- low pumping power – large pebbles, short tank
- good thermal isolation – minimal surface tank

**Behavior** - The hot – cold interface widens with time, worsening the quality of stored heat




**Role of model design:**

- find the best compromise between these competing factors
- propose and investigate new ideas in order to avoid these competitions, and to reach a **high efficiency** and a **high storage capacity**

# SHORT AND MID-TERM: Sensible heat

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## The thermocline system: Slag pebbles

**The revalorization of steel slag, a by-product from metallurgic industry, through thermal energy storage**

Slags from ferrous metal production
43.5 MT

Blast furnace slag
23.5 MT

Steel slag
21.8 MT

*"Position paper on the status of ferrous slags" Euroslag and Eurofer position paper, April 2012.*

BOF slag
10.5 MT

EAF slag
8.5 MT

SMP slag
2.8 MT

1 MT

ArcelorMittal

AM-AR

Productos Tubulares, s.a.u.

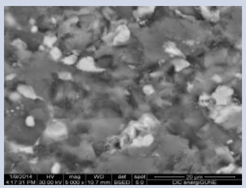
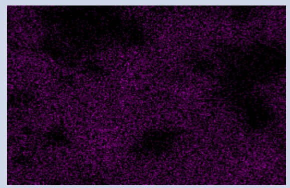
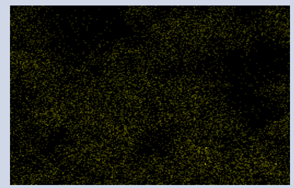
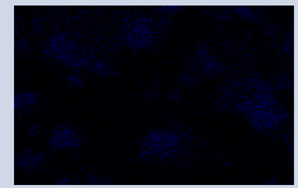
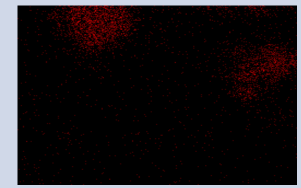
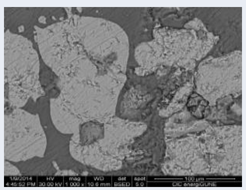
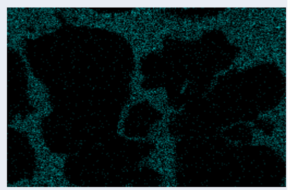
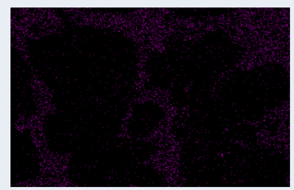
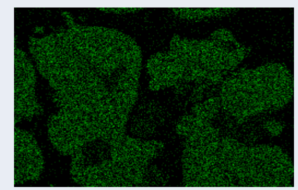
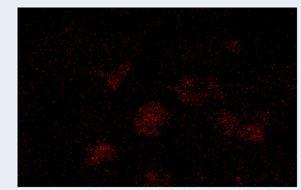
PT-AR

**Currently ≈ 75% is reused in:**
- **Construction**
- Roads
- Cement industry…

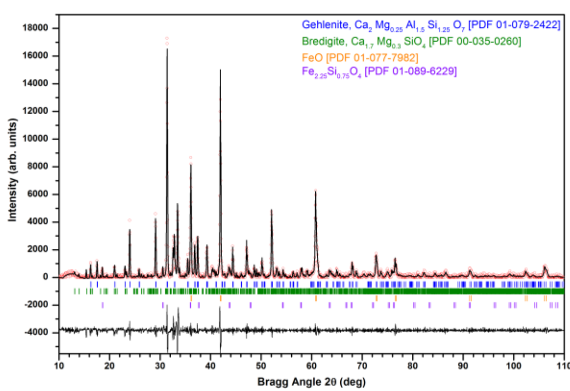
≈ 25% is landfilled and stored (around 500000 Ton/year)

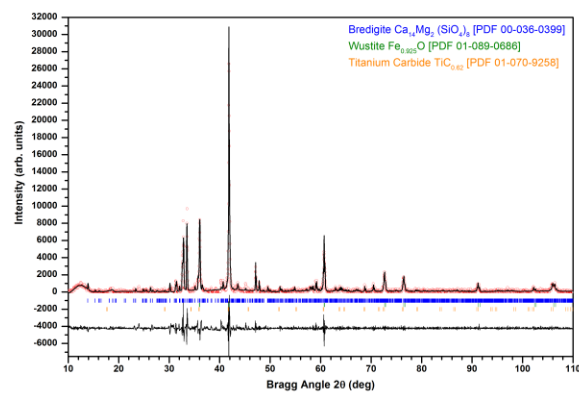
BOF: Basic Oxygen Furnace
EAF: Electric Arc Furnace
SMP: Secondary Metallurgical Process

## Slag characterization: Morphology, composition and structure

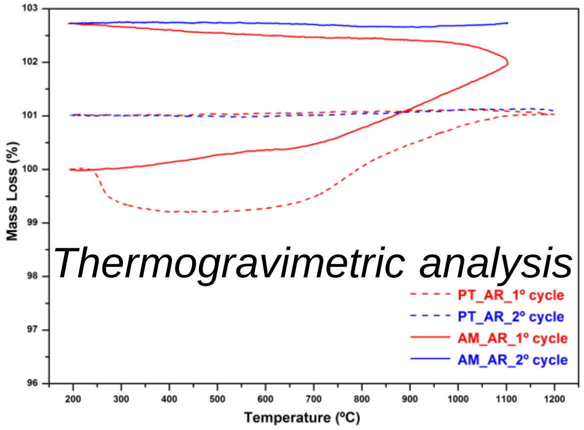
| | SEM/EDX scan | Ca | Si | Fe | Cr |
|---|---|---|---|---|---|
| AM_AR |  |  |  |  |  |
| PT_AR |  |  |  |  |  |

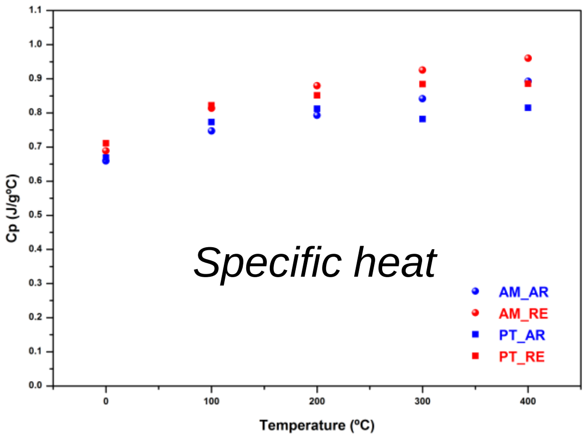
XRD analysis

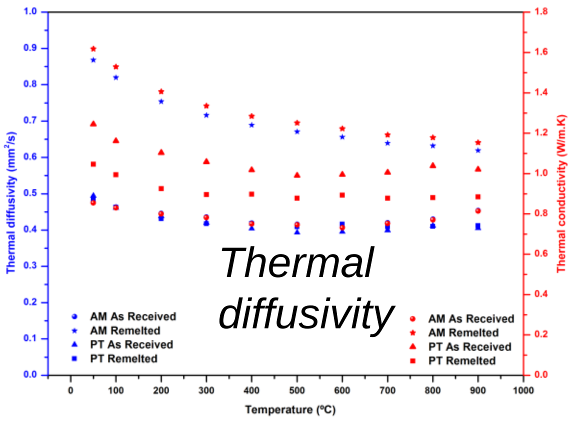


## Slag characterization: Thermophysical properties

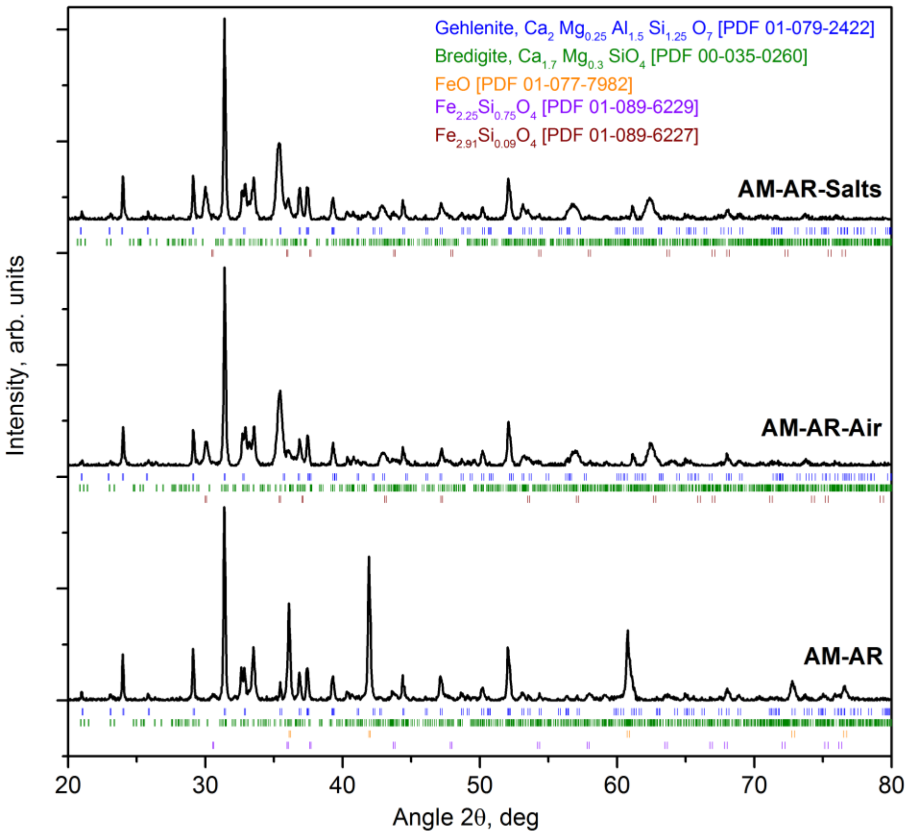


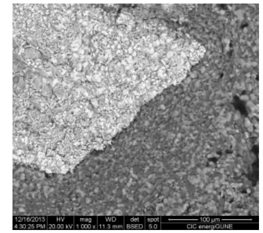
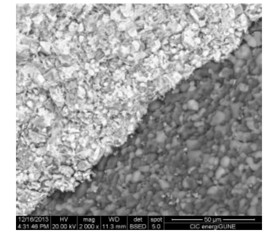



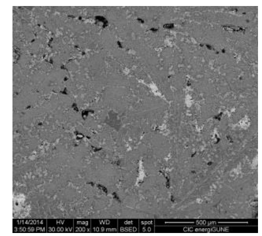
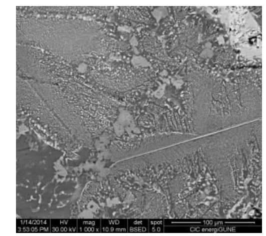
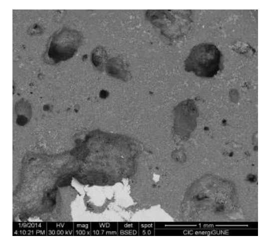
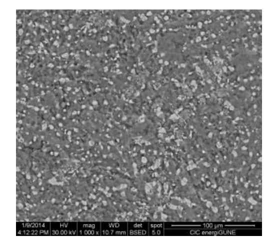




| | Arcelor Mittal | Productos Tubulares | Ceramic ($Al_2O_3$) | Concrete | Cofalit |
|---|---|---|---|---|---|
| Bulk density ($g/cm^3$) | 2.7193 | 3.7640 | 3.500 | 2.750 | 3.120 |
| Cp (J/g.K) | 0.689 | 0.711 | 0.866 | 0.916 | 0.800 |
| Thermal conductivity (W/m.K) | 1.61 | 1.24 | 1.35 | 1.00 | 1.40 |

## Slag characterization: Compatibility with air and solar salt



*XRD diffractograms at room temperature of as-received slag before and after corrosion test*

**No reaction between slag and the solar salt up to 500ºC.**

**The slag is stable in air up to 1000ºC.**

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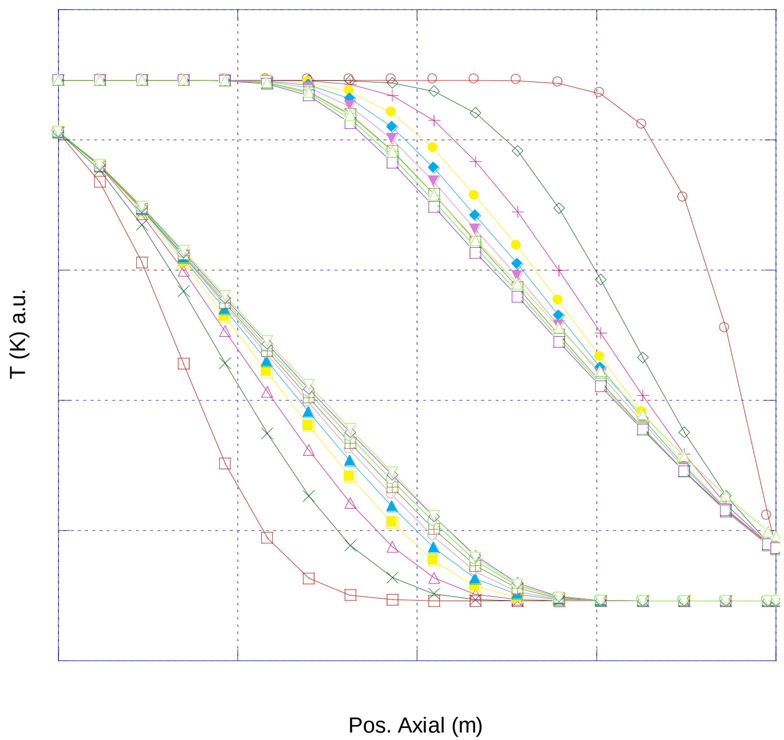
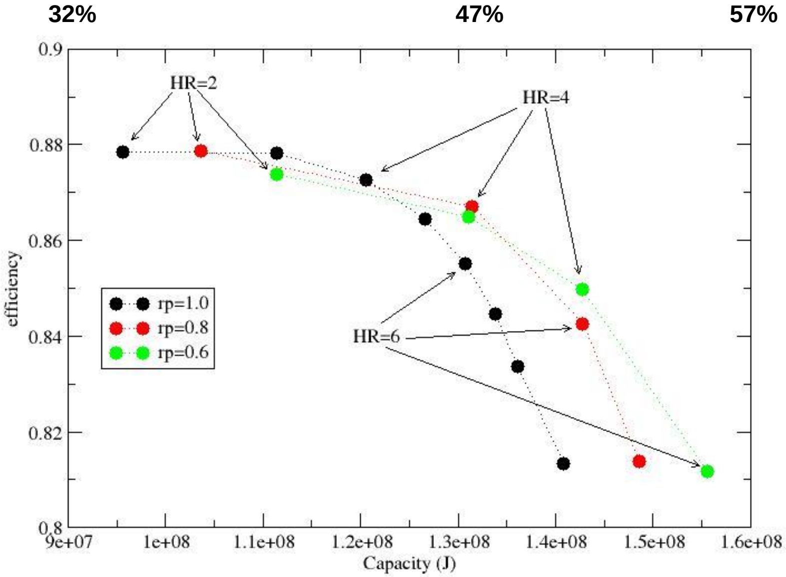
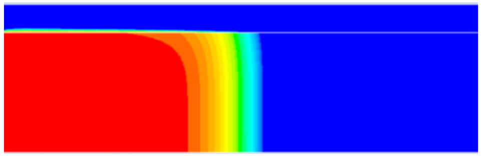
## The thermocline system: Results

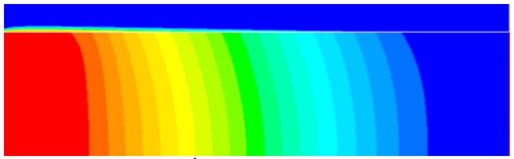
- The steady state for charge/discharge operation is reached after few cycles, typically 10
- A high storage efficiency and a high storage capacity are obtained

**Air-Slag (1 cm) Thermocline 600-800 ºC**



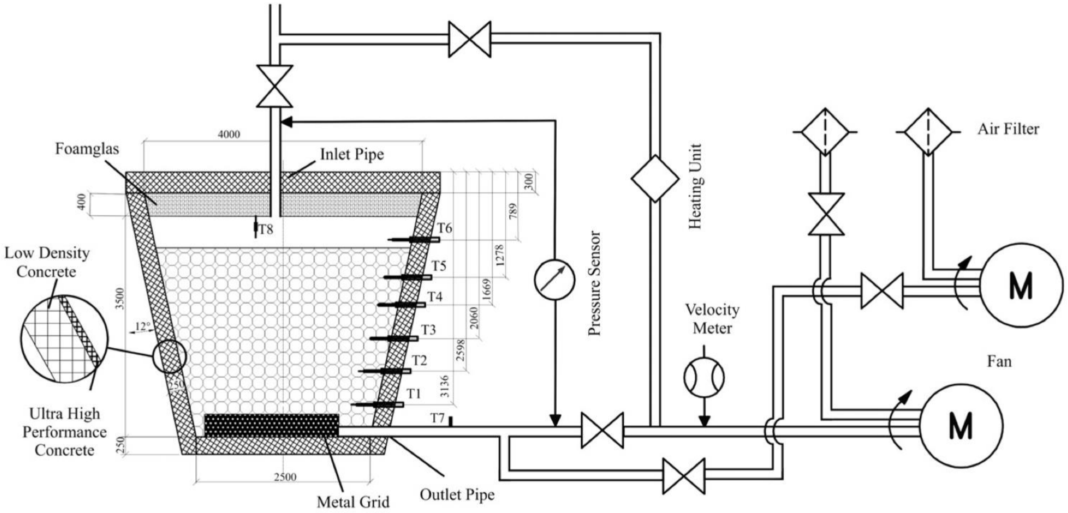





1st heating

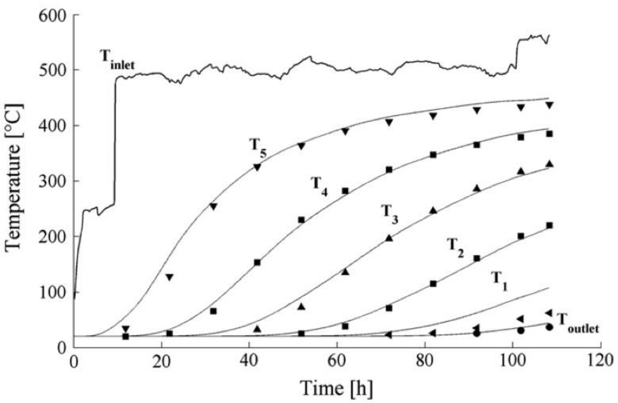

10th heating

## The thermocline system: Comparisons

G. Zanganeh et al. *Packed-bed thermal storage for concentrated solar power – Pilot-scale demonstration and industrial-scale design*, Solar Energy 86 (2012)




Scheme of the pilot-scale thermal storage configuration and experimental setup



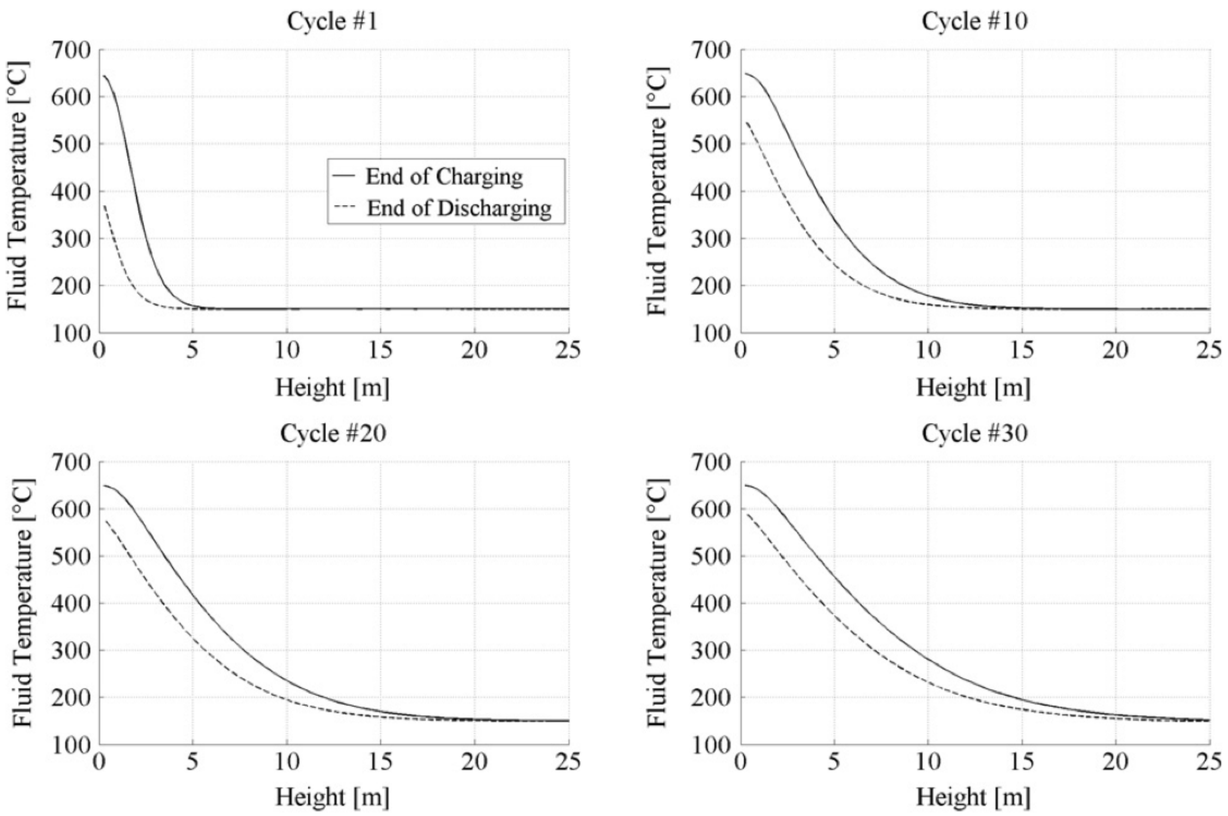

Comparison between measured data (markers) and model results (lines)

Investigated materials:

- 5 types of rocks (siliceous limestone, limestone, quartzite, calcareous sandstone, gabbro)
- 2 types of concretes (ultra-high and low density concrete)

## The thermocline system: Comparisons

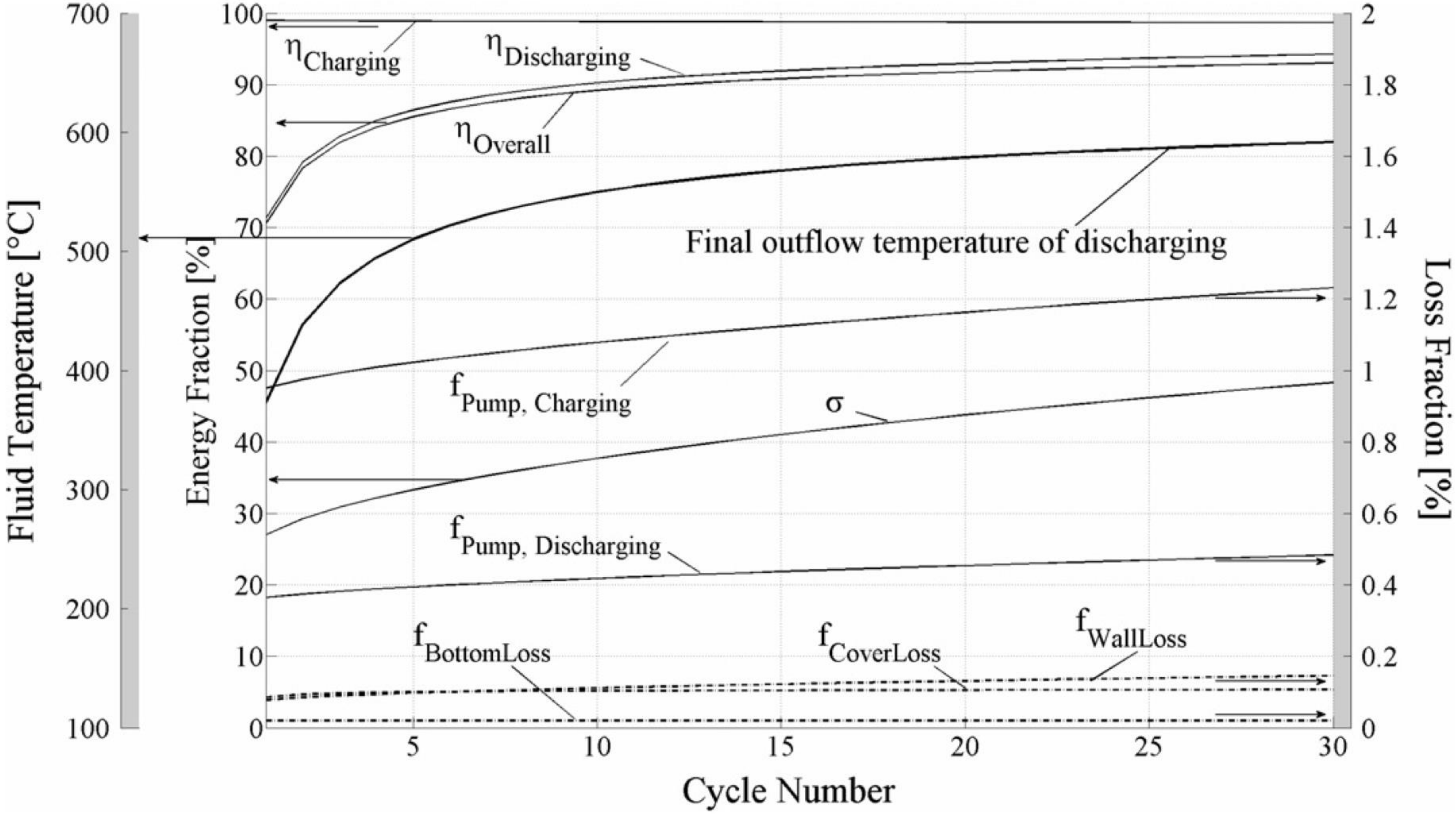
G. Zanganeh et al. *Packed-bed thermal storage for concentrated solar power – Pilot-scale demonstration and industrial-scale design*, Solar Energy 86 (2012)




Temperature profile of the packed bed at end of the charging and discharging phases for cycles 1, 10, 20 and 30.

## The thermocline system: Comparisons - The thermocline storage at Ait Baha, Morocco

G. Zanganeh et al. *Packed-bed thermal storage for concentrated solar power – Pilot-scale demonstration and industrial-scale design*, Solar Energy 86 (2012)




- Here, the storage capacity is defined as the ratio $\mathbf{E_{stored}/E_{max}}$ . In our case is defined as $\mathbf{E_{extracted}/E_{max}}$.

## The thermocline system: Coming developments

### Reminder

| | | |
|---|---|---|
| Fast heat exchange | → | small pebbles, highly conducting, short tank |
| Low heat conduction | → | low conduction pebbles, long tank |
| Low pumping power | → | large pebbles, short tank |
| Good thermal isolation | → | minimal surface tank |

### Coming modeling and simulation

High intra-particle conductivity but low inter-particle conduction can lead to both fast heat exchange and low heat conduction →

- **New storage materials**
- Storage material layering
- Storage material segmentation

Heat exchange is linear with tortuosity while momentum exchange is quadratic with it. Low tortuosity systems may provide fast heat exchange with low pumping power →

- Ordered porous storage material

Thermocline systems with liquid HTF →

- **Molten salts**
- **Nano fluids for T > 600 ºC**

## The thermocline system: Coming developments

### Coming experimental analysis

Synthesis and/or characterization of a variety of HSM ➡
- **Slag** of different compositions
- **Arraela hormigones**
- **Nano fluids** (for high T and **thermocline stabilization**

Synthesis and characterization of a variety of HSM ➡
- **Nano fluids** with enhanced thermodynamic properties

### Coming experimental set-up

Design and prototyping ➡
- **Air loop** for temperatures up to 800-1000 ºC and moderate P

Design and prototyping ➡
- **Fixed bed** for temperatures up to 800-1000 ºC and moderate P

# SHORT AND MID-TERM: Sensible heat

## The thermocline system: Cost evaluation

### Evaluation of the storage media costs

| | | | |
|---|---|---|---|
| Slags cost* | 10% salt | 1.2 | $/kWh |
| Salts cost | | 12 | $/kWh |
| Medium comp. | 64%slag+36%salt | | |
| MEDIA cost | | 5.15 | $/kWh |

| | | | |
|---|---|---|---|
| Slags cost | 10% salt | 1.2 | 1.2 |
| Enh. Salts cost | | 8.568 | 6.12 |
| Medium comp. | 64%slag+36%enh.salt | | |
| MEDIA cost | | 3.90 | 3.00 |

| | | | |
|---|---|---|---|
| Slags cost | 10% salt | 1.2 | $/kWh |
| Air cost** | | 1 | $/kWh |
| Medium comp. | 64%slag+36%air | | |
| MEDIA cost | | 1.13 | $/kWh |

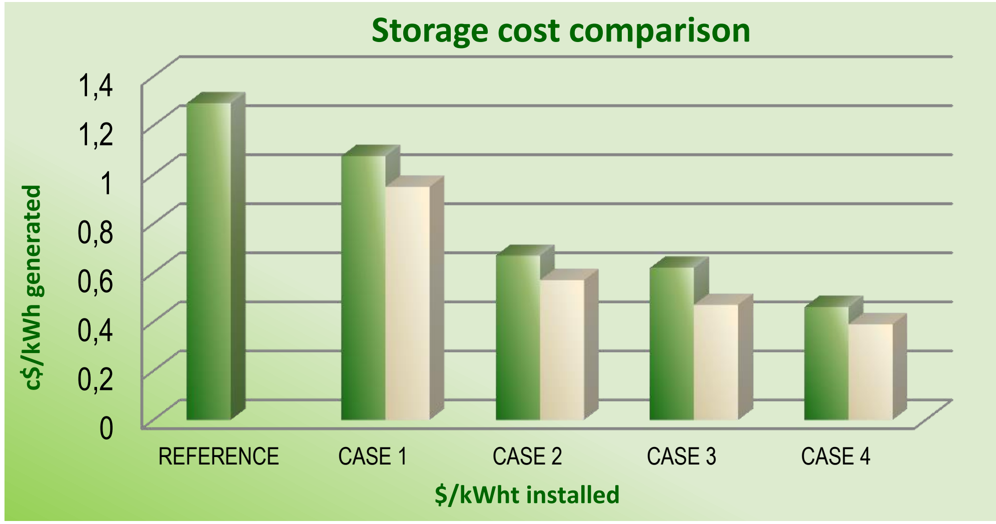
**A previous treatment of the air will be necessary
No additional cost of the heat exchanger was considered
•Price of slag was considered a 10% of the molten salts (60% NaNO3 + 40% KNO3)

### Evaluation of other storage costs (tank, foundations, piping, etc.)

Two different hypothesis are considered:

1. 35% cost reduction with respect to the baseline
2. 50% cost reduction with respect to the baseline

# The thermocline system: Cost evaluation results




| | | LCOE [c$/kWh] | % Reduction | Storage cost [c$/kWh] | % Reduction |
|---|---|---|---|---|---|
| Reference case - Baseline | 30 $/kWht | 11.40 | | 1.290 | |
| CASE 1: Two tanks with molten salts | 25 $/kWht | 11.20 | 1.75 | 1.080 | 16.28 |
| | 22 $/kWht | 11.05 | 3.07 | 0.950 | 26.36 |
| CASE 2: Packed bed with slag & salts | a 35% Red | 10.65 | 6.58 | 0.670 | 48.06 |
| | b 50% Red | 10.60 | 7.02 | 0.570 | 55.81 |
| CASE 3: Packed bed with slag & enhanced salts | a 35% Red | 10.65 | 6.58 | 0.620 | 51.94 |
| | b 50% Red | 10.50 | 7.89 | 0.460 | 64.34 |
| CASE 4: Packed bed with slag & air | a 35% Red | 10.50 | 7.89 | 0.465 | 63.95 |
| | b 50% Red | 10.40 | 8.77 | 0.390 | 69.77 |

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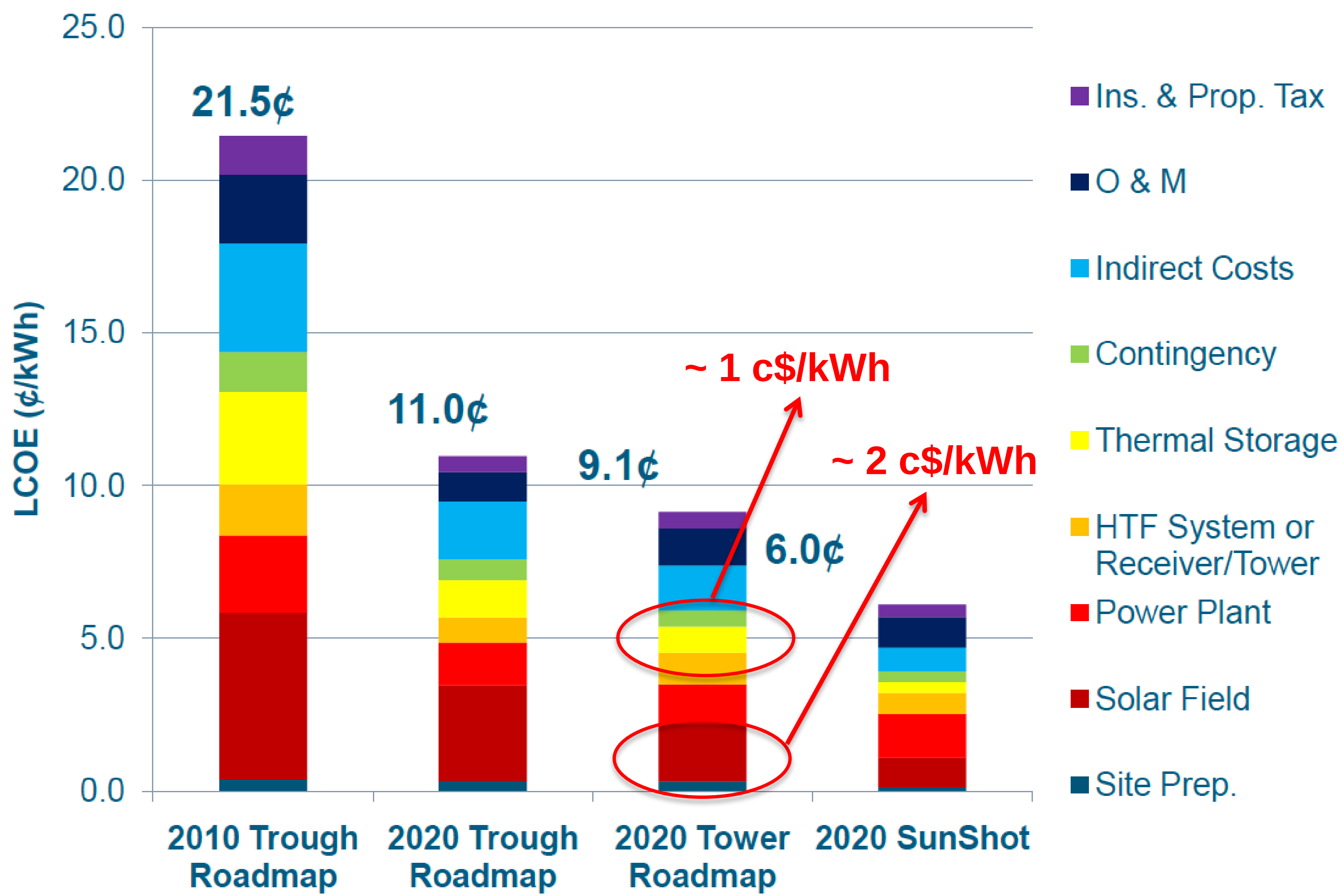
## SunShot initiative: Cost forecast



## Project preparation and submission

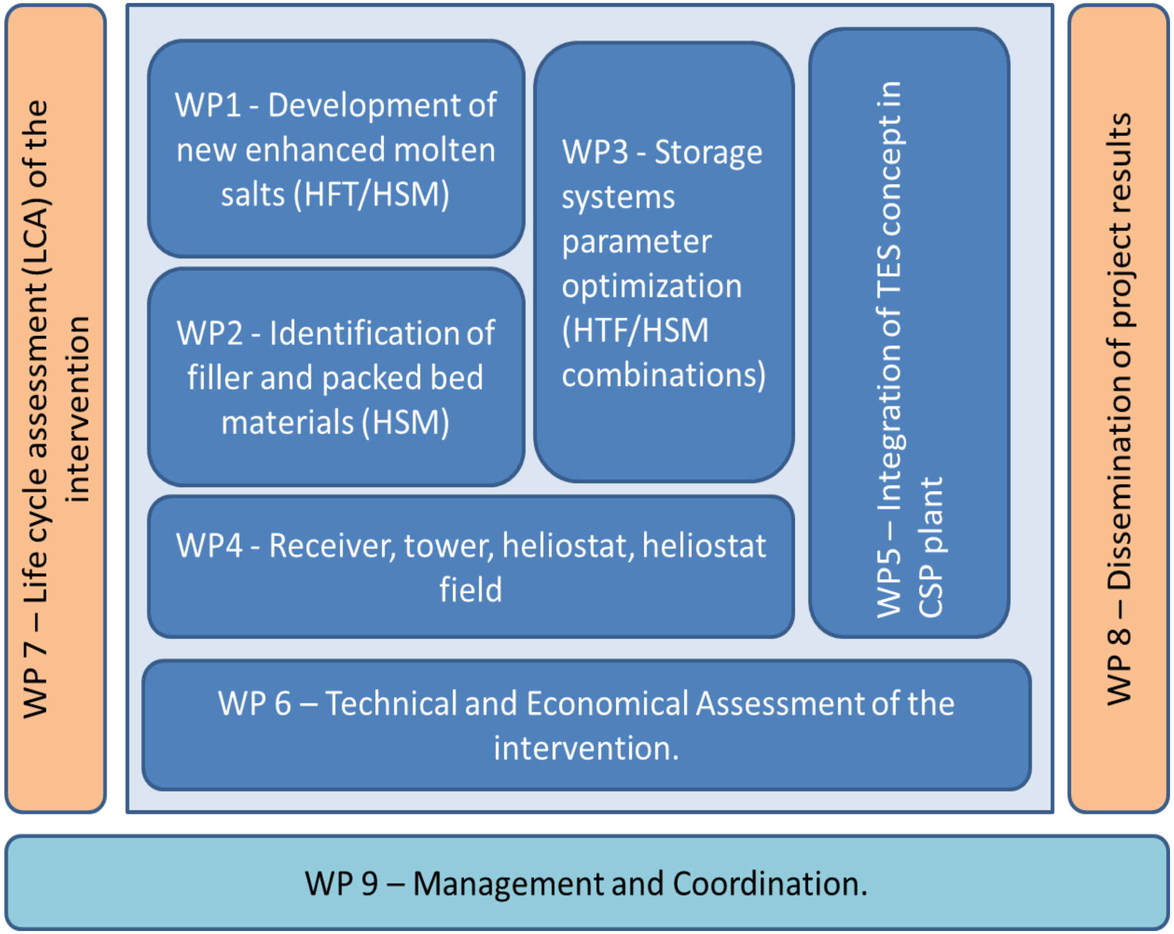
# IMPROVING CSP TOWER PLANT PERFONMANCES WITH ENHANCED COMPONENTS AND EFFECTIVE SINGLE THERMAL STORAGE TANKS

## Topic: LCE-02-2014

### RESEARCH AND INNOVATION ACTIONS – INNOVATION ACTIONS

| Nº | PARTICIPANT ORGANIZATION NAME | SHORTNAME | COUNTRY | TYPE |
|---|---|---|---|---|
| 1 | CIC ENERGIGUNE (Project Coordinator)<br>*Centro de Investigación Cooperativa de Energías Alternativas Fundación* | CICe | SPAIN | RTO |
| 2 | Plataforma Solar de Almeria-Ciemat | PSA-CIEMAT | SPAIN | RTO |
| 3 | Commissariat à l'énergie atomique et aux énergies alternatives - Institute for New Energy Technologies | CEA LITEN | FRANCE | RTO |
| 4 | Solar Tower Technologies AG | STT | GERMANY | LARGE |
| 5 | Aunergy Thermosolar S.R.L | AUNERGY | SPAIN | SME |

## Project preparation and submission




| | |
|---|---|
| Total requested amount / € | 5 800 000 |

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## Project preparation and submission

# Turning waste from steel industry into valuable low cost feedstock for energy intensive industry

Topic: WASTE-1-2014

Type of action: IA

| | PARTICIPANT ORGANIZATION NAME | SHORT NAME | PARTICIPANT ROLE | PROFILE | COUNTRY |
|---|---|---|---|---|---|
| 1 | CIC-ENERGIGUNE | CIC | Coordinator. Thermal Energy Storage systems (TES) (Pilot 2 and 3). Modeling and prototyping. Scientific coordinator: Dr. Bruno D'Aguanno. | RTO | Spain |
| 2 | ArcelorMittal | AM | Final user. Pilot 2 validations (Heat Recovery). **Waste supplier**. | LARGE | Spain |
| 3 | German Aerospace Center (DLR) | DLR | Model and simulation of heat storage design aspects. TES for Concentrated Solar Power (CSP). Cyclic materials tests (Pilot 3). | RTO | Germany |
| 4 | IK4-Azterlan | IK4 | Characterization of slags, modeling and manufacturing. | RTO | Spain |
| 5 | Productos Tubulares | PT | Final User: TES applications. Heat Recovery. **Waste supplier**.. (Pilot 2). | SME | Spain |
| 6 | Paul Scherrer Institute | PSI | Modeling of packed bed TES systems. Thermal tests of storage materials under concentrated radiation (Pilot 2 and 3). | RTO | Switzerland |
| 7 | Imperial College | IC | Characterization of final products (refractory ceramics, etc.). | RTO | United Kingdom |
| 8 | Friedrich Alexander University Erlangen-Nuremberg | FAU | Characterization of steel slags and TES systems, ceramic and glass processing. | RTO | Germany |
| 9 | Commissariat à l'énergie | CEA | Fine characterization of slags. Critical | RTO | France |

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## Project preparation and submission

| | | | | | |
|---|---|---|---|---|---|
| | atomique et aux énergies alternatives | | metals extraction from slags. Slag shaping heat recovery applications (Pilot 1, 2 and 3). | | |
| **10** | Optimum Cement | OC | Preparation and valorization of minerals extracted from slags (Pilot 1). **Intermediate product supplier**. | SME | France |
| **11** | Agenzia nazionale per le nuove tecnologie | ENEA | Concentrated Solar Powe applications (Pilot 3). | RTO | Italy |
| **12** | Technical Research Centre of Finland | VTT | Refractory Ceramic industry (Pilot 4). Innovative materials. | RTO | Finland |
| **13** | Tapojärvi company | TA | **Final user**: Refractory Ceramic industry (Pilot 4). | SME | Finland |
| **14** | Solar Tower Technologies AG | STT | **Final user**: Concentrated Solar Power industry (Pilot 3). | LARGE | Germany |
| **15** | Fraunhofer Society, Project Group for Resource Strategy and Recycling Technologies | IWKS | Energy Management, Life Cycle Analysis. | RTO | Germany |
| **16** | Life Cycle Engineering | LCE | LCA, LCC, Logistics and ICT skills. Experience in Steel sector. **Final user** | SME | Italy |

| Total requested amount / € | 9 800 000 |
|---|---|

## Project preparation and submission

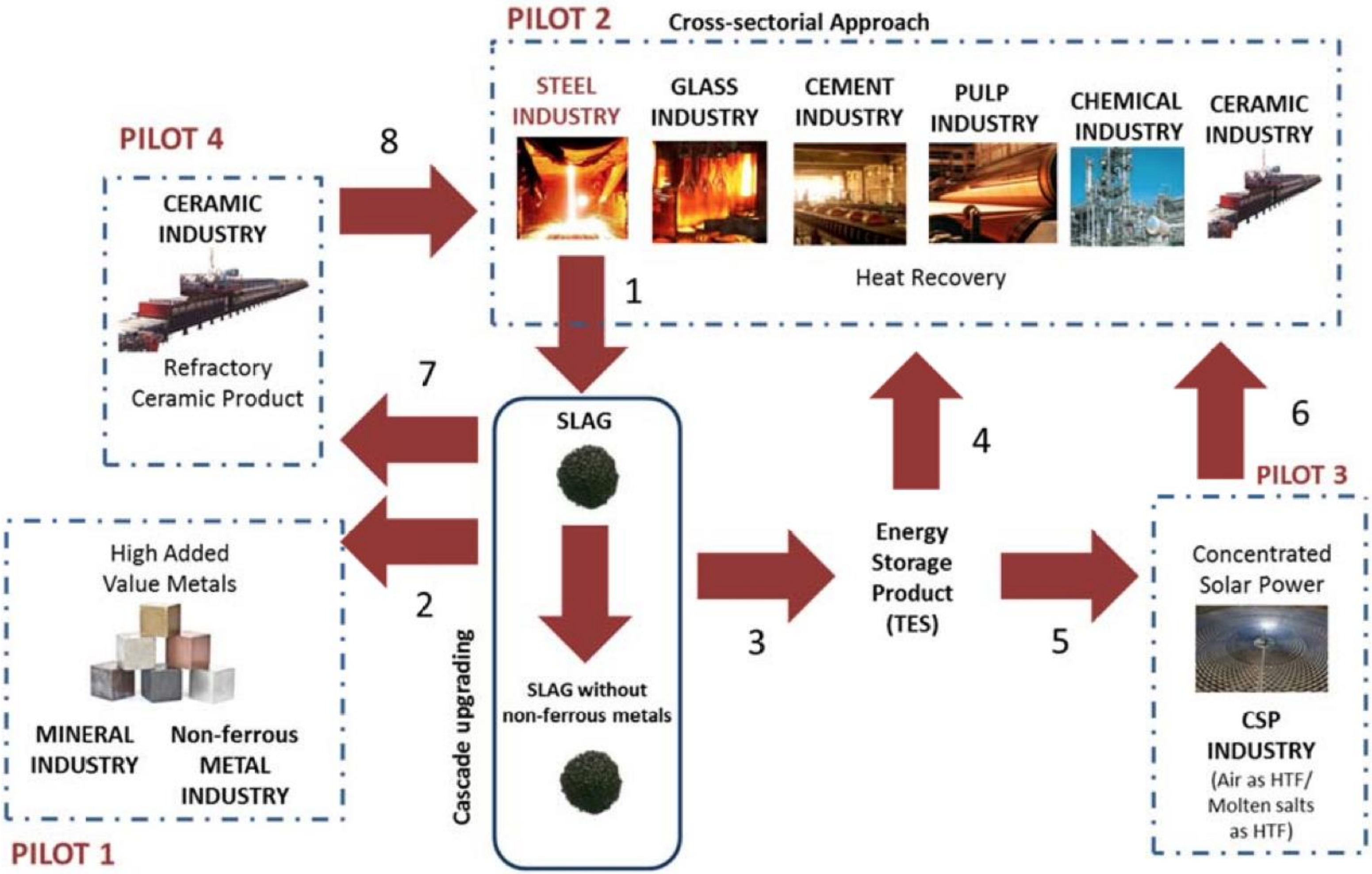



FIGURE 1: RESLAG PROJECT CONCEPT

# SHORT AND MID-TERM: Latent heat

## Metal alloys have thermal conductivity/diffusivity and high latent heat

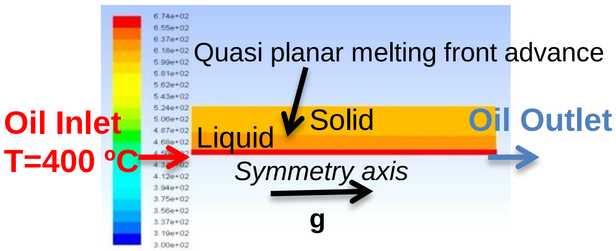
### Material preparation and characterization

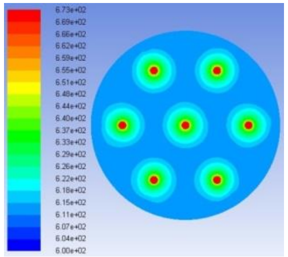
From lab scale…(g )

…trough middle term…(1 kg)

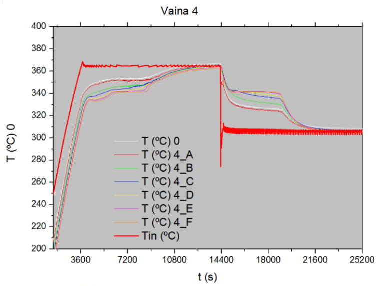
…to testing scale (100 kg)

### Device modeling and design



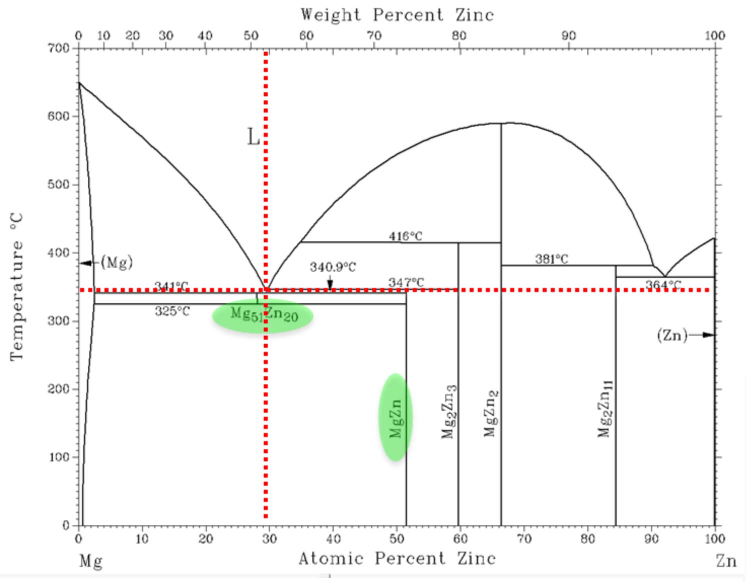
### Prototyping and testing (lab scale)



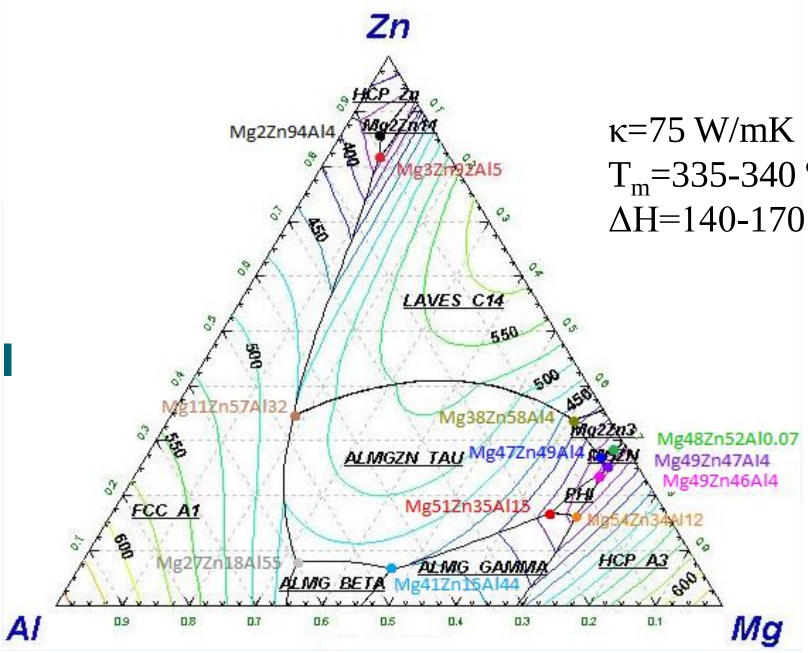

## Metal alloys have thermal conductivity/diffusivity and high latent heat

### Eutectic Mg-Zn

κ=75 W/mK
$T_m$=342 ºC
ΔH=155 J/g




### Mg-Zn-Al




κ=75 W/mK
$T_m$=335-340 ºC
ΔH=140-170 J/g

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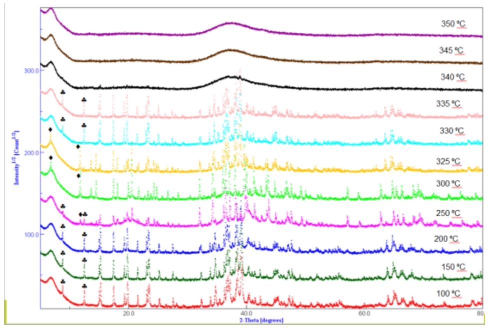
## Metal alloy preparation and characterization

From lab scale…(g)

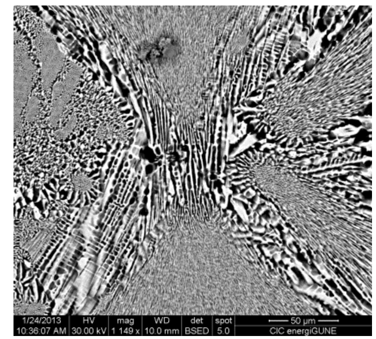
…trough middle term…(1 kg)

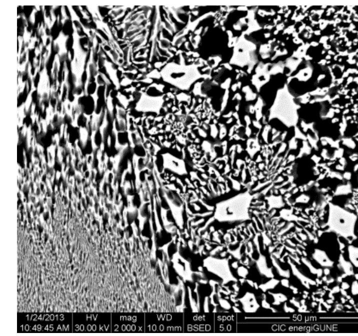
…to testing scale (100 kg)

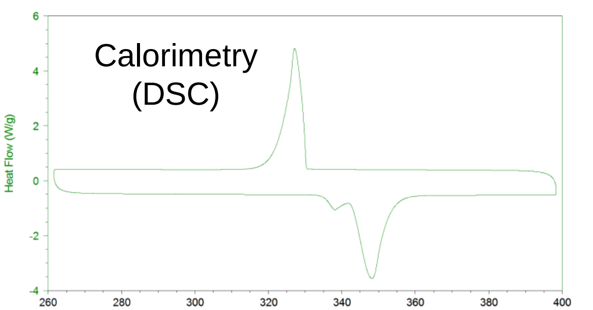
XRD (Temp.)

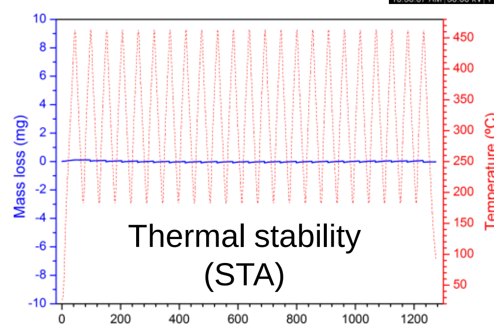


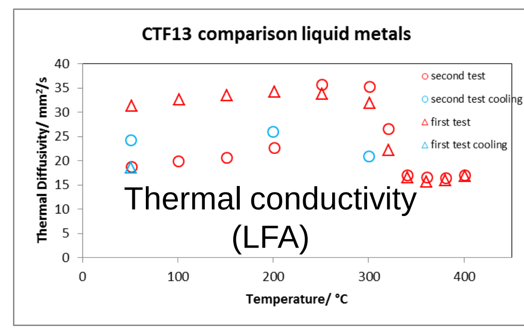

Optical and Electronic Microscopy (SEM, TEM)



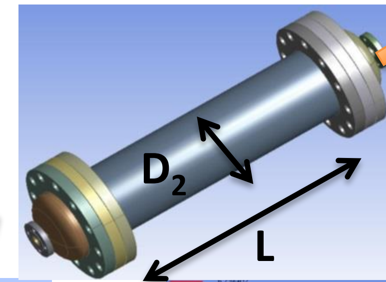



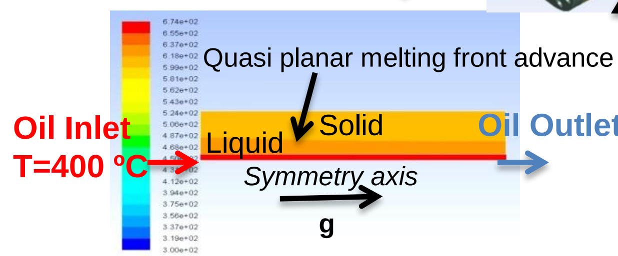



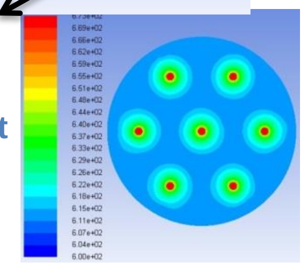

| Material | Thermal diffusivity ($m^2/s$) | Density ($kg/m^3$) | Latent heat (kJ/kg) | $kWh/m^3$ | Melting point (ºC) | Sat. vapor pressure (bar) |
|---|---|---|---|---|---|---|
| Mg-Zn | $3.5\ 10^{-5}$ | ≈2850 | 155 | 122 | 343 | 155 |
| $NaNO_3$ | $≈10^{-7}$ | 1930 | 175 | 94 | 308 | 96 |

## Modeling and design

- Theoretical calculation of relevant thermal properties: $C_p$ of alloys
- Detailed CFD analysis of the storage system
  - ✓ *Heat transfer fluid*
  - ✓ *Fluid inlet velocity*
  - ✓ *Fluid inlet temperature*
  - ✓ *Heat exchanger design*
  - ✓ *PCM amount of mass*

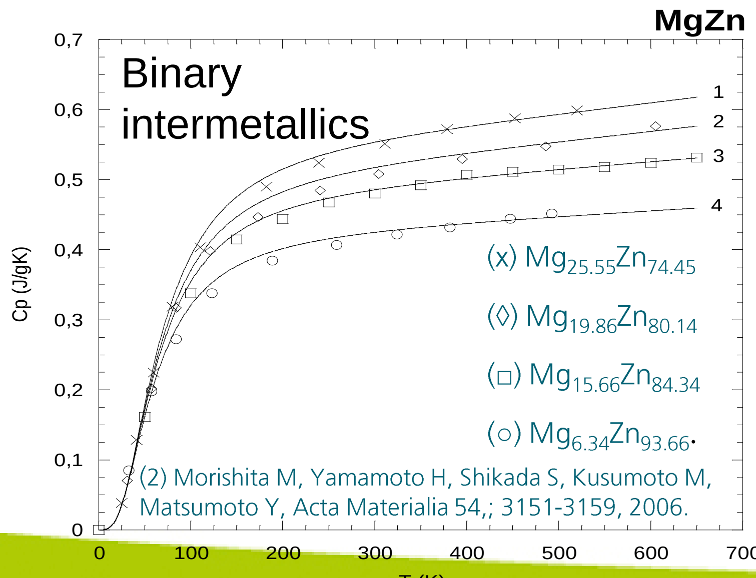


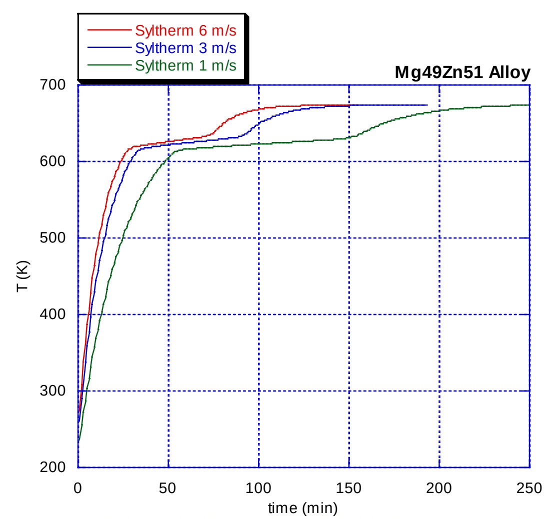



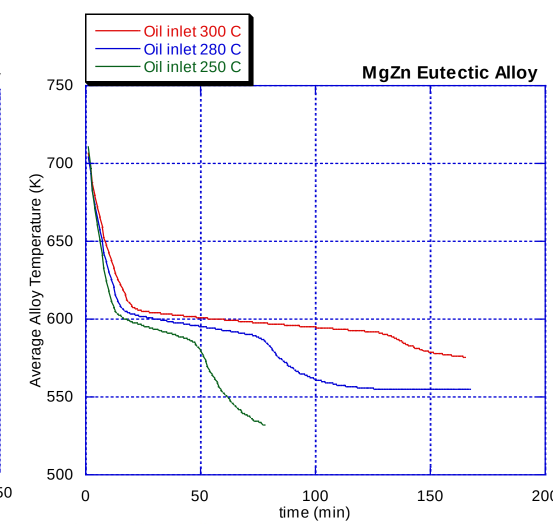



**Multi-tubular design**

High Operation Power level! ➡ Fast thermal response



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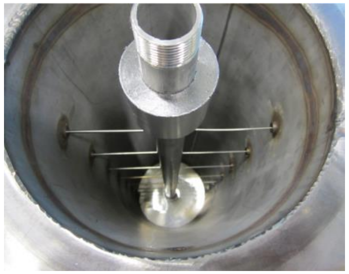
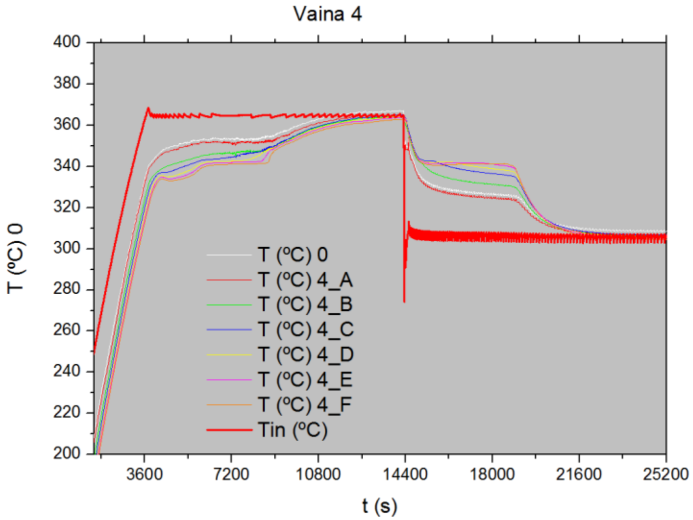
## Prototyping and testing at laboratory scale

$D_{tube}$=1”
$D_{tank}$=8”
L=50 cm



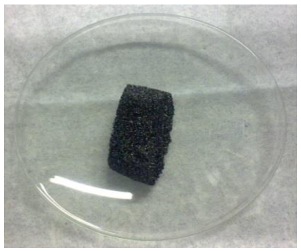
$M_{PCM}$=71,67 Kg
Stored energy = 2,86 kW*h

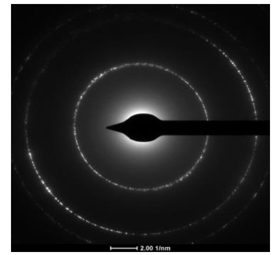


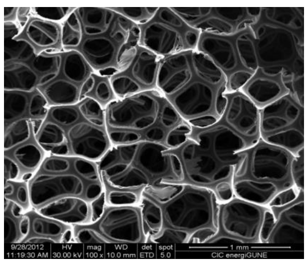

40 $kW_e$ thermal oil testing loop operating up to 400 ºC

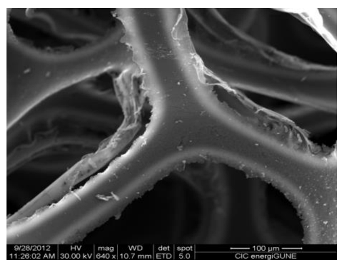
Flexible testing of materials (sensible/latent storage) under realistic working conditions

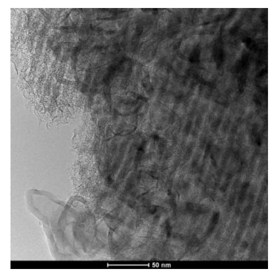
# Design and preparation of carbon foam matrices to store PCM materials (sugar alcohol) and to enhance thermal conductivity

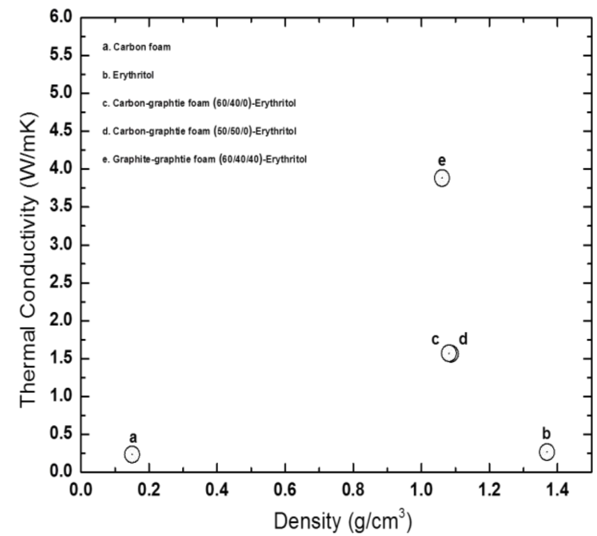




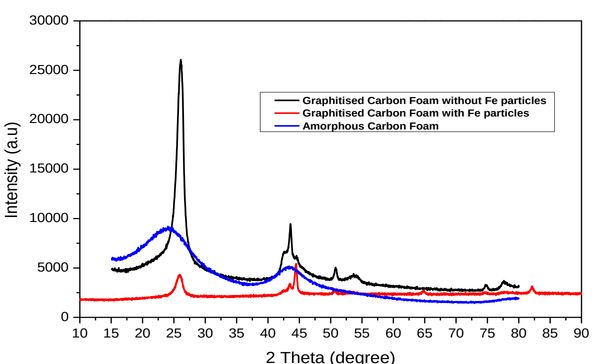


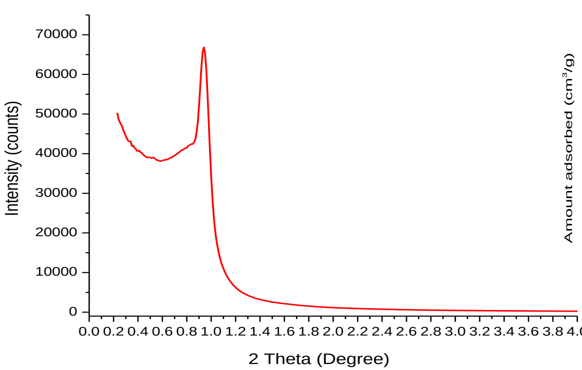


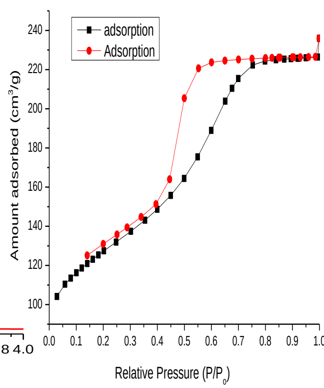


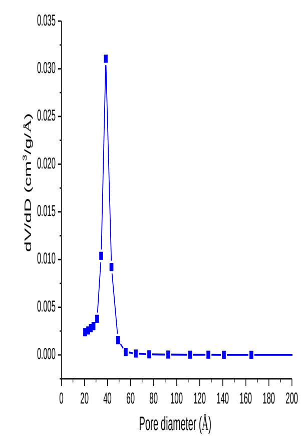



Macropore size: 50 to 600 μm; Wall thickness: 10 to 20 μm



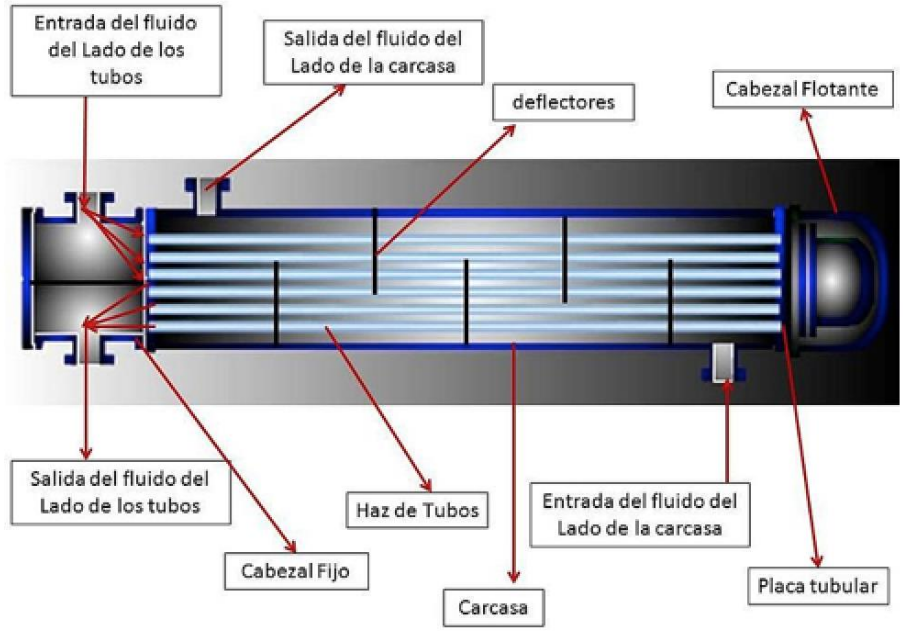



## Project preparation and submission

# Memoria del Proyecto "ACUTER"

## Acumulador de energía térmica de alta temperatura para operación de plantas termosolares




Esquema de componentes de un intercambiador.

# SHORT AND MID-TERM: Latent heat

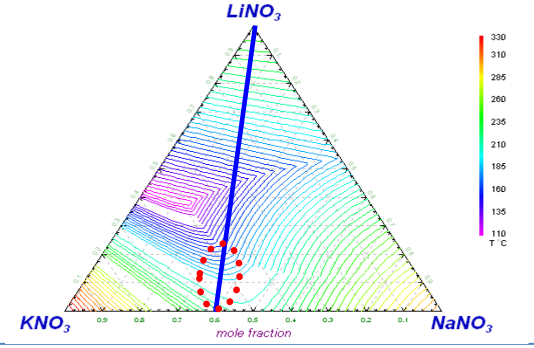
## Project preparation and submission

| Comentarios | HORAS |
|---|---|
| | F1 : Especificaciones y Selección de aleaciones |
| | T1.1. Especificaciones funcionales |
| Se va a seleccionar una aleación, comercial si es posible, que cumpla con las especificaciones establecidas en la T1.1, y se va a hacer una caracterización de sus propiedades térmicas. | T1.2. Preselección de aleaciones. Caracterización. |
| El CIC podría liderar esta fase general … | F2: Diseño Conceptual |
| El CIC puede contribuir en el diseño del sistema de almacenamiento | T2.1. Diseño escala real del equipo |
| El CIC se encargaría de la simulación de los procesos de carga y descarga del sistema de almacenamiento.<br>La simulación de la parte mecánica/estructural se haría entre ambas partes. | T2.2. Simulaciones térmica-estructural |
| | F3: Viabilidad Técnico Económica |
| El responsable de esta fase se debería encargar de las tareas de Diseño y Fabricación. La responsabilidad de estas dos tareas (T4.1 y T4.2) no se debería separar. | F4: Diseño y fabricación prototipo |
| El CIC puede contribuir con su experiencia en el diseño y construcción del prototipo. | T4.1. Diseño prototipo escala labo |
| El CIC se podría encargar de la fabricación del prototipo y montaje siguiendo los planos del diseño del prototipo ya que dispone de proveedores que podrían construirlo | T4.2. Fabricación y montaje prototipo |
| El CIC se encargaría de la puesta en marcha del prototipo (programación…) | T4.3. Puesta a punto prototipo |
| | F5: Ensayos validación |
| Dado que los ensayos se plantean realizar en las instalaciones del CIC, el CIC debería estar involucrado en la definición de los ensayos a realizar | T5.1. Definición protocolos de ensayo. Casos de prueba. |
| El CIC realizará los ensayos que se consideren oportunos | T5.2. Realización ensayos |
| Al CIC le gustaría participar en esta tarea | T5.3. Optimización Diseño Básico |
| | F6: Validación Equipo. Informe conclusiones. |

## Nano fluids for sensible and latent heat storage

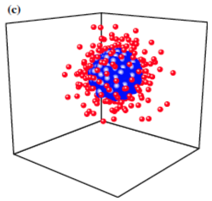
### Material preparation and characterization

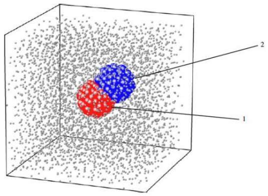
- Develop new salts mixtures derived from the commercially available solar salt,
- Experimental study of the ternary and quaternary systems.




### Material modeling and design

- Develop DF first principle simulation codes
- Develop Molecular Dynamics and Brownian Dynamics simulation codes



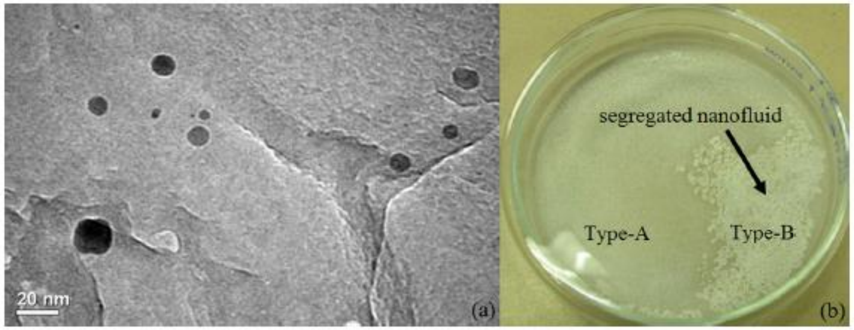
### Prototyping and testing (lab scale)

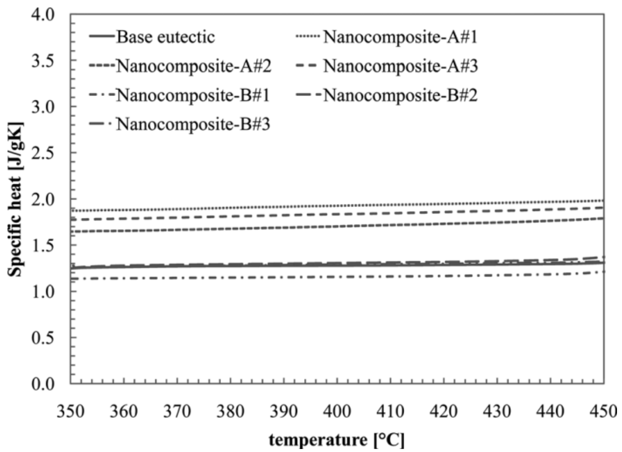
- Develop a storage unit to be coupled with the existing heating loops

**Experimental data on eutectic Li2CO3-K2CO3 (62:38 mol. ratio) with 1.5% mass fraction of dispersed silica nanopartiles (2-20 nm)**

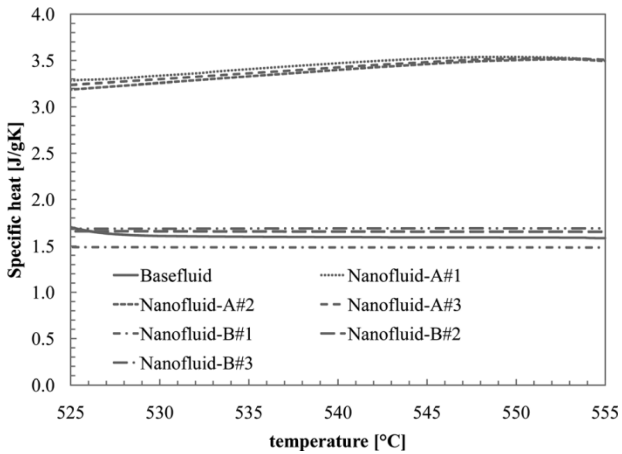
Donghyun Shin, Debjyoti Banerjee "Enhanced Specific Heat Capacity of Nanomaterials Synthesized by Dispersing Silica Nanoparticles in Eutectic Mixtures", Journal of Heat Transfer, **135** (2013).

TEM images after repeated thermocycling experiments. (a) non-agglomerated silica nanoparticles. (b) Type-A: fine amorphous powder; Type-B: coarse amorphous powder.




$C_p$ in the solid phase (350 – 500 °C). Type-A: **38-54%** enhancement.




$C_p$ in the liquid phase (525 – 555 °C). Type-A: **118-124%** enhancement.

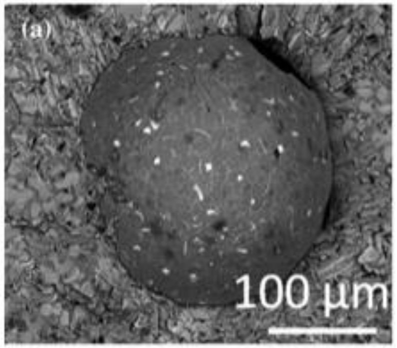
# MID-TERM: Nano fluids

## Experimental data on Al-Si/NaCl-NaF/graphite, Al/NaCl-KCl/Al/Al2O3 and Al/B2O3/graphite

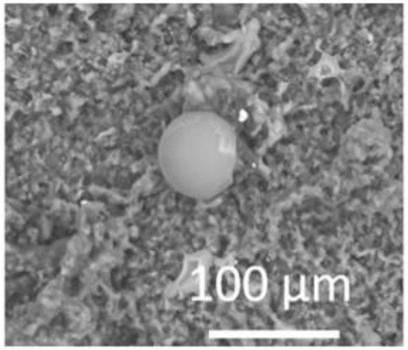
Anne K. Starace, Judith C. Gomez, and Greg C. Glatzmaier. *"Can particle-stabilized inorganic dispersions be high-temperature heat-transfer and thermal energy storage fluids?",* J. Mater. Sci., **48**:4023–4031, 2013.

- Al-Si/NaCl-NaF/graphite, Al/NaCl-KCl/Al/Al2O3 and Al/$B_2O_3$/graphite are **liquid systems stable in the 600 – 800 °C** temperature range.
    - **Dispersed phase**: Al-Si, Al; **Dispersion medium**: NaCl-NaF, NaCl-KCl, $B_2O_3$; **Stabilizer**: graphite, $Al_2O_3$
    - Dispersed phase/dispersion medium mass ratio ≃ 0.1 – 0.3

BSE ESEM micrographs of solidified Al–Si droplets (80-300 micron) embedded in NaCl–Na. Black spot: graphite




BSE ESEM micrographs of Al/B2O3/graphite system



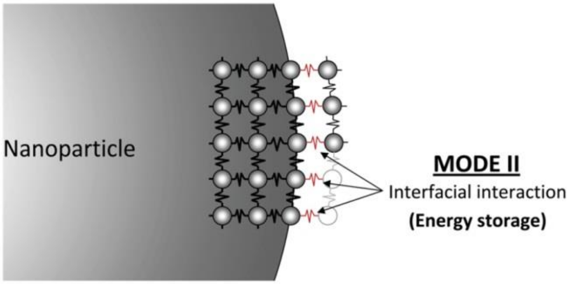

| Dispersed phase | Dispersion media | Stabilizer | Estimated stored energy (J/g) | Temperature range (°C) | J/g K |
|---|---|---|---|---|---|
| NaCl–NaF | Al–Si | C | 312 | 600–750 | 2.08 |
| Al | $B_2O_3$ | C | 346 | 600–750 | 2.31 |
| Al | NaCl–KCl | $Al_2O_3$ | 258 | 657–807 | 1.72 |

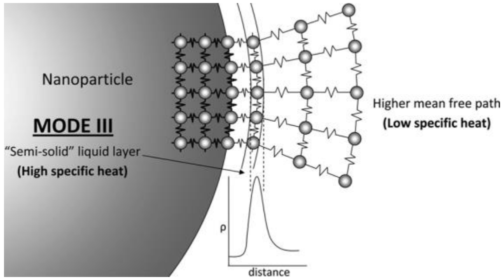
## The role of microscopic modeling in the design of nano materials with enhanced thermal properties

Four possible different mechanisms are proposed to explain the Cp and the thermal conductivity enhancements:

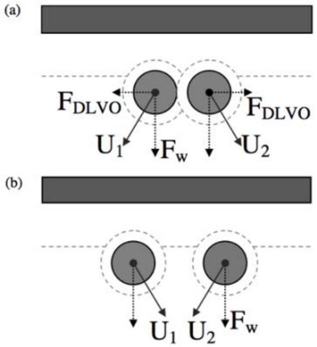
1. Transport of thermal energy by Brownian motion of nanoparticles;
2. Thermal storage in a layer formed around the nanoparticles;
3. Percolation networks formation;
4. Nanoscale convention caused by the Brownian particle motion (setup of hydrodynamic modes).

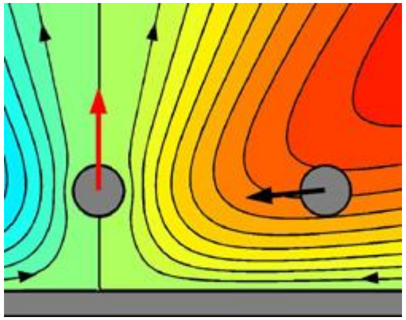
**Thermal storage** in a layer formed around the nanoparticles

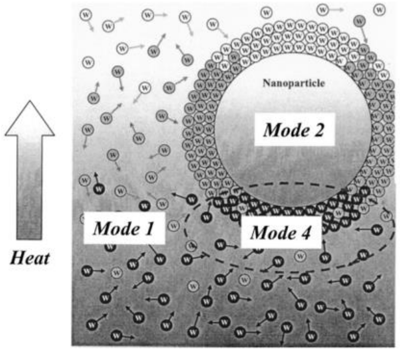



**Thermal conductivity** due to nanoscale convention caused by the Brownian particle motion (setup of hydrodynamic modes)






**Mode 1:** coll. In base fluid
**Mode 2**: therm. diff. nanoparticle
**Mode 3**: coll. Nanoparticles
**Mode 4**: interfase interactions

# MID-TERM: Nano fluids

## The role of microscopic modeling in the design of nano materials with enhanced thermal properties

Ling Li, Yuwen Zhang, Hongbin Ma, Mo Yang *"Molecular dynamics simulation of effect of liquid layering around the nanoparticle on the enhanced thermal conductivity of nanofluids",* Journal of Nanoparticle Research, **12** (2010).

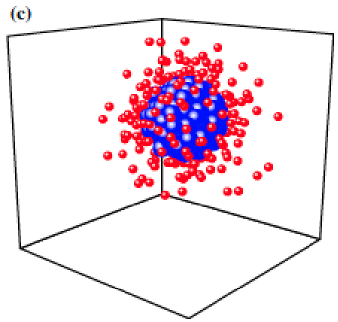
Specific heat and thermal conductivity can be obtained from Molecular Dynamics simulations.

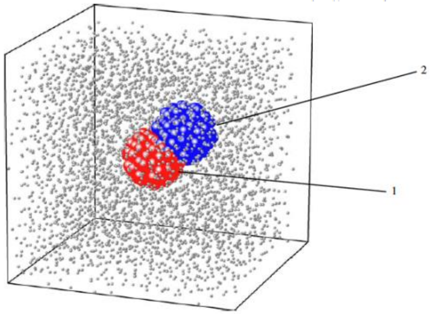
Example: the thermal conductivity from the Green-Kubo relation

$$k = \frac{1}{3Vk_B T^2}\int_0^{\infty} \langle \mathbf{J}_q(0)\mathbf{J}_q(t)\rangle \mathrm{d}t$$

where $\mathbf{J_q}$ is the instantaneous microscopic heat current vector

$$\mathbf{J}_q = \sum_{k=\alpha}^{\beta}\sum_{i=1}^{N_k}\frac{1}{2}m_i^k\left(v_i^k\right)^2\mathbf{v}_i^k - \frac{1}{2}\sum_{k=\alpha}^{\beta}\sum_{l=\alpha}^{\beta}\sum_{i=1}^{N_k}\sum_{j=1}^{N_l}\left[\mathbf{r}_{ij}^{kl}\frac{\partial\Phi_{ij}^{kl}}{\partial\mathbf{r}_{ij}^{kl}} - \Phi_{ij}^{kl}\mathbf{I}\right]\cdot\mathbf{v}_i^k - \sum_{k=\alpha}^{\beta}h_k\sum_{i=1}^{N_k}\mathbf{v}_i^k$$




First outcome from MD simulations:

- as compared to the larger particles, smaller nanoparticles contribute more to the mass fraction of the layered compressed phase;
- more work is needed to understand the quantities controlling the thickness of the compressed layer, its stiffness, and the role hydrodynamics mode.

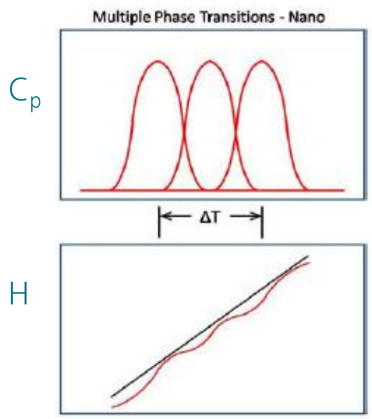
## The role of microscopic modeling in the design of nano materials with enhanced thermal properties

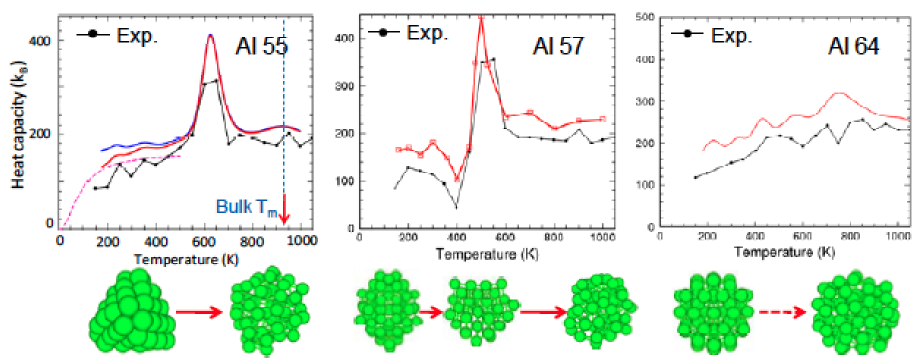
Glatzmaier, G. C.; Pradhan, S.; Kang, J.; Curtis, C.; Blake, D. *"Encapsulated Nanoparticle Synthesis and Characterization for Improved Storage Fluids",* SolarPACES 2010.

Improved materials can also be obtained by encapsulating metals or metal alloys nanocluster with silica coating.

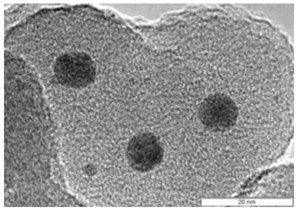
Advantages:

- The melting point of nanoclusters varies as a function of the number of atom within the nanocluster
- The melting transition occurs over a temperature range




Comparison between exp. data and MD results on Al nanoclusters



TEM: silica-coated silver nanoclusters

These advantages allow the phase-change enthalpy of the nanocluster to contribute uniformly to the sensible enthalpy of the fluid.

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## Target properties of Nano Fluids for sensible heat storage

Projected storage fluid properties to reach unsubsidized cost parity with fossil fuel-generated electricity.

Table from: *US Department of Energy (2012) Multidisciplinary university research initiative: high operating temperature fluids funding opportunity announcement*

| | Therminol VP-1[4] | Solar Salt (60% $NaNO_3$/40% $KNO_3$)[5] | MURI: HOT Fluids Specifications |
|---|---|---|---|
| Thermal Stability (as a liquid) | 400°C | ~600-650°C | **Target:** ≥ 800°C<br>**Stretch Target:** ≥ 1300°C |
| Melting Point | 12°C | 228°C | **Target:** ≤ 250°C<br>**Stretch Target:** ≤ 0°C |
| Heat Capacity | 2.33J/g·K@ 300°C<br>2.62J/g·K@ 400°C | 1.5J/g·K | **Target:** ≥ 1.5 J/g·K<br>**Stretch Target:** ≥ 3.75 J/g·K |
| Vapor Pressure | 2.55atm@ 300°C<br>10.6atm@ 400°C | ≤ 1 atm | **Target:** ≤ 1 atm |
| Viscosity | 0.000217 Pa-s @ 300°C<br>0.000147 Pa-s @ 300°C | 0.003 Pa-s @ 300°C<br>0.001 Pa-s @ 600°C | **Target:** ≤ 0.012 Pa-s @ 300°C<br>**Target:** ≤ 0.004 Pa-s @ 600°C |
| Density | 812kg/m$^3$@300°C<br>696kg/m$^3$@400°C | 2,084 kg/m$^3$@ 300°C<br>1,867 kg/m$^3$@ 600°C | **Target:** ≤6,000 kg/m$^3$@ 300°C<br>**Target:** ≤5,400 kg/m$^3$@ 600°C |
| Thermal Conductivity | 0.0956 W/m·K@300°C<br>0.0759 W/m·K@400°C | ≥0.51 W/m·K @300°C<br>≥0.58 W/m·K @600°C | **Target:** ≥0.51 W/m·K @300°C<br>**Target:** ≥0.58 W/m·K @600°C |

# List of research projects

| Project | Program | Dates | Partners | Description |
| --- | --- | --- | --- | --- |
| ***Finished.*** | | | | |
| **Latent heat for seasonal thermal storage** | **ETORTEK2011 (Basque Government)** | 01/01/2011 31/12/2013 | CIC Energigune, UPV/EHU | Use of metallic PCM as storage media around 340 ºC. Mg-Zn // Mg-Zn-Al |
| **Characterization of steel slags for validation in thermal storage systems** | **Alava Innova 2013. (Regional)** | 01/01/2013 31/12/2013 | CIC Energigune | Different steel slag characterization and modeling of TES alternatives in various applications |
| ***On going…*** | | | | |
| **New formulations of salts at high temperature for solar thermal plants** | **ETORTEK2012 (Basque Government)** | 01/01/2012 31/12/2014 | CIC Energigune, UPV/EHU | New salt composition with extended operation and improved thermal properties |
| **New materials for sensible heat: steel slags integration in TES systems** | **ETORTEK2013 (Basque Government)** | 01/01/2013 31/12/2014 | CIC Energigune, UPV/EHU, Tekniker | Revalorization of steel slag for thermal energy storage |
| **Materials for Advanced compact storage systems (SAM.SSA)** | **FP7-ENERGY-2011-2. (EU)** | 01/04/2012 31/03/2015 | CNRS, RHODIA, FhG, IMNR, TUE, CICe, AIDICO, PPL, EURICE | Sugar alcohol/impregnated conductive matrix composites for seasonal storage |

# List of research projects

## *Accepted (1st ranked!!)*

| | | | | |
|---|---|---|---|---|
| **Low-cost Sustainable Thermal Energy Storage Systems Made of Recycled Steel Industry Waste (SLAGSTOCK)** | **SOLAR-ERA.NET Transnational Calls 2013:PV1 and CSP1. (EU)** | December 2013 (Accepted) | CICe, PSI, IK4-Azterlan, SENER, Prod. Tubulares, ArcelorMittal, FAU, Tellus Ceram, Promes CNRS | Revalorization of steel slag for thermal storage in CSP. Thermocline design. |

## *Resolution pending…*

| | | | | |
|---|---|---|---|---|
| **Thermal Energy Storage based on slags for energetic efficiency improvement in steel production processes (TESLAG)** | **RFCS (EU)** | ---- | ArcelorMittal, Productos Tubulares, IK4 Azterlan, Tellus Ceram, CICe, DLR | Revalorization of steel slag in Industrial heat recovery applications |
| **Metal alloys for latent heat thermal energy storage (MALTES)** | **National Plan "retos" (National)** | ---- | CIC Energigune | Metallic alloys as PCM in the 100-1000 ºC temperature range. Mg-Zn // Mg-Zn-Al// Al-Si … |
| **"Acumulador de energía térmica de alta temperatura para operación de plantas termosolares" (ACUTER)** | **Gaitek (Basque Government)** | ---- | CIC Energigune, … | Metal alloy based storage technology implemented in CSP environment |

# List of research projects

### *Resolution pending…*

| | | | | |
|---|---|---|---|---|
| **Turning waste from steel industry into a valuable low cost feedstock for energy intensive industry (RESLAG)** | **H2020-WASTE-2014-two-stage (EU)** | --- | CICe, ArcelorMittal, DLR, IK4-Azterlan, Prod. Tubulares, PSI, Imp. College, FAU, CEA, Opt. Cement, ENEA, VTT, Tapojarvi, STT, Fraunhofer, LCE, | Revalorization of steel slag for various thermal energy storage solutions, covering valuable metal recovery, industrial heat recovery and CSP heat storage applications. |
| **Improving CSP tower plant performances with enhanced components and effective single thermal storage tanks (CSP-ONE_ST)** | **H2020-LCE 2-2014-1 (EU)** | --- | CICe, PSA-CIEMAT, CEA, STT, Aunergy | Increase CSP competitivity and efficiency by means of a multi-component improvement approach. Storage, Receiver, Tower, Solar Field, Heliostats optimization and enhancement. |
| **Hot disk TPS 2500S** | **Scientific Equipment – Basque Government** | **Submitted 24/01/2014** | CIC Energigune | Thermal Constant Analyzer, TPS 2500S. Thermal conductivity, thermal diffusivity, Cp from room T to 1000 ºC |


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# Final divertissement

Our research work concerns HEAT.

About HEAT, modern physics states:

**… HEAT IS A KIND OF MOTION***

… **HEAT** AND WORK **DO NOT EXIST**: **THERE IS NOT ONE THING THAT IS THE HEAT** AND ONE THING THAT IS THE WORK!**

*** S.G. Brush *"The kind of motion we call heat - A history of the kinetic theory of gases in the 19th century - Book 1*" in Studies in *Statistical Mechanics*, Vol. VI, E.W. Montroll, J.L. Lebowitz, 1986**

** **Peter Atkins, "*Galileo's Finger: The Ten Great Ideas of Science*" (Oxford University Press, 2004)**