

S^{OLAR} CRATCES





Solar Calcium looping integRAtion for Thermo-Chemical Energy Storage



Context



CSP main research lines

➤ **Cost reduction: equipment CAPEX and/or higher efficiencies**

➤ **Improving dispatchability**

- **40%** of current CSP plants with thermal storage
- CSP under development approx. **80%** with thermal storage
- At commercial scale based on Molten salts or Ruth steam accumulators

ANDASOL I: **28,500 tons of molten salt**. 60% sodium nitrate, 40% potassium nitrate. 1,010 MWh.

➤ **Environmental sustainability**



This Project has received funding from European Commission by means of Horizon 2020, the EU Framework Programme for Research & Innovation, under Grant Agreement no.727348.



Thermochemical Energy Storage Calcium-Looping (CaL)



Group	Example
Hydrogen systems $MH_n + \Delta H_r \leftrightarrow M + \left(\frac{n}{2}\right) H_2$	$MgH_2(s) + \Delta H_r \leftrightarrow Mg(s) + H_2(g)$
Carbonate systems $MCO_3(s) + \Delta H_r \leftrightarrow MO(s) + CO_2(g)$	$CaCO_3(s) + \Delta H_r \leftrightarrow CaO(s) + CO_2(g)$ $SrCO_3(s) + \Delta H_r \leftrightarrow SrO(s) + CO_2(g)$
Hydroxide systems $M(OH)_2(s) + \Delta H_r \leftrightarrow MO(s) + H_2O(g)$	$Mg(OH)_2(s) + \Delta H_r \leftrightarrow MgO(s) + H_2O(g)$ $Ca(OH)_2(s) + \Delta H_r \leftrightarrow CaO(s) + H_2O(g)$
Redox systems $M_xO_y(s) + \Delta H_r \leftrightarrow xM(s) + \left(\frac{y}{2}\right) O_2(g)$	$2BaO_2(s) + \Delta H_r \leftrightarrow 2BaO(s) + O_2(g)$ $2Co_3O_4(s) + \Delta H_r \leftrightarrow 6CoO(s) + O_2(g)$
Ammonia systems	$2NH_3(g) + \Delta H_r \leftrightarrow N_2(g) + 3H_2(g)$
Organic systems	$CH_4(g) + H_2O(l) + \Delta H_r \leftrightarrow CO(g) + 3H_2(g)$ With a side reaction: $CO(g) + H_2O(l) \leftrightarrow CO_2(g) + H_2(g) + \Delta H_r$ $CH_4(g) + CO_2(g) + \Delta H_r \leftrightarrow 2CO(g) + 2H_2(g)$ With a side reaction: $CO_2(g) + H_2(g) + \Delta H_r \leftrightarrow CO(g) + H_2O(g)$
Sulfur systems	$H_2SO_4(g) + \Delta H_r \leftrightarrow SO_2(g) + H_2O(g) + \frac{1}{2} O_2(g)$

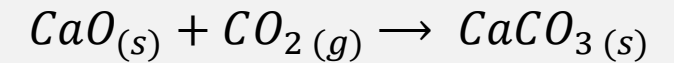
Calcium-Looping (CaL)

calcination



$\Delta H_r = +178 \text{ kJ/mol}$

carbonation



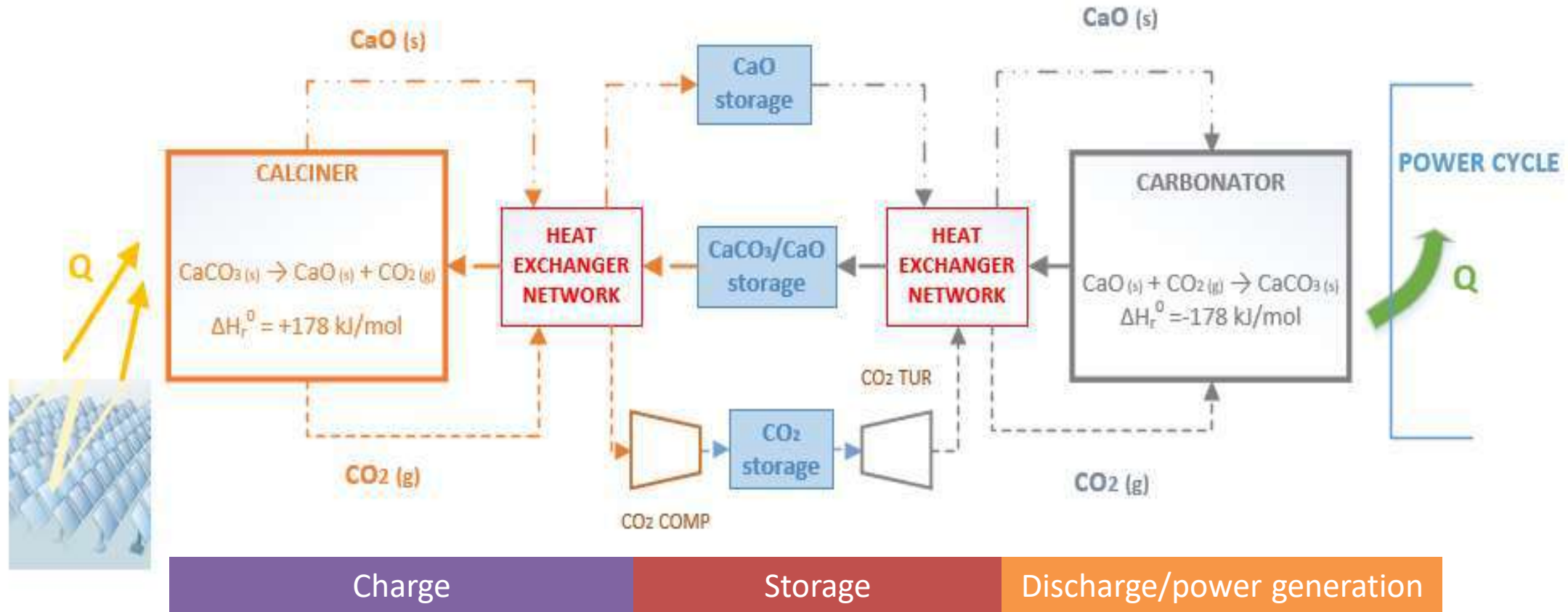
$\Delta H_r = -178 \text{ kJ/mol}$



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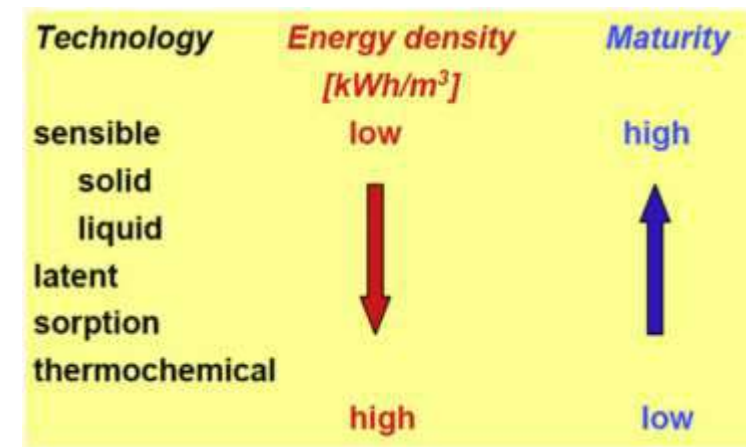
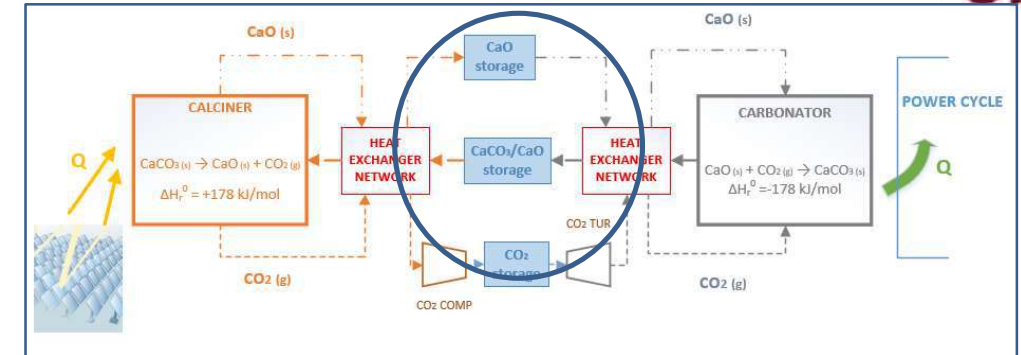
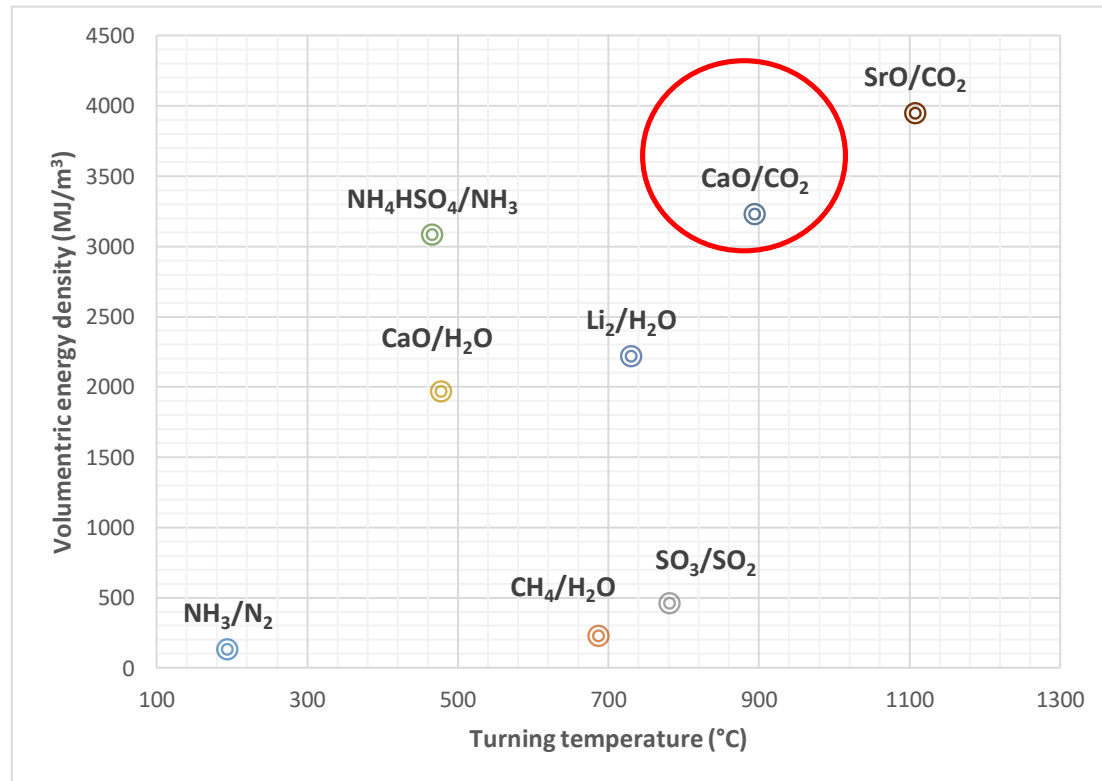
CSP-CaL Concept



R Chacartegui, A Alovio, C Ortiz, JM Valverde, V Verda, JA Becerra, Thermochemical energy storage of concentrated solar power by integration of the calcium looping process and a CO₂ power cycle, Applied energy 173, 589-605

CSP-CaL – Advantages and opportunities

1. High energy density



Kuravi et al. (2013)



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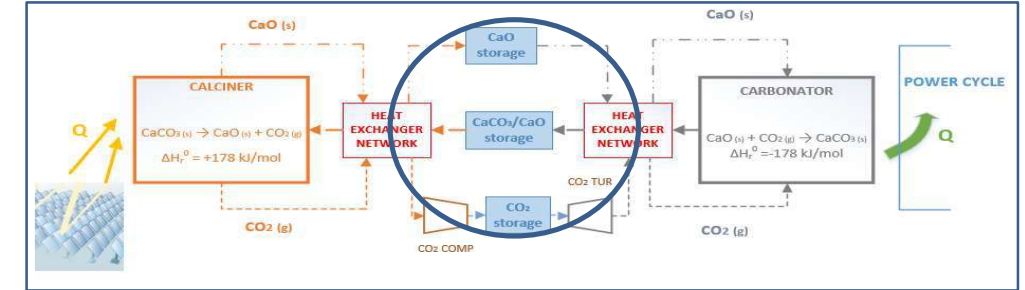
CSP-CaL – Advantages and opportunities



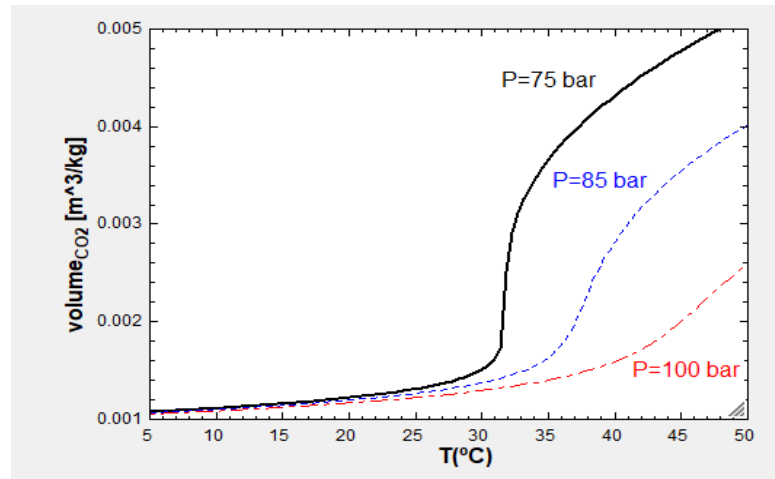
2. Low-temperature energy storage

- ✓ Minimizes thermal losses
- ✓ Reduces parasitic consumption of auxiliaries
- ✓ Capacity for seasonal storage
- ✓ Increases capacity factor

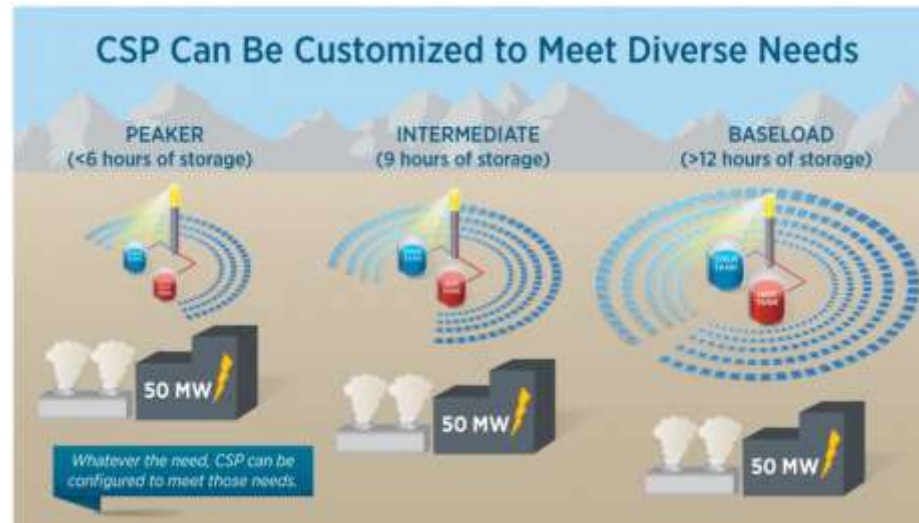
Molten salts → T min Storage ~200°C



CO₂ storage



Different solids storage strategies



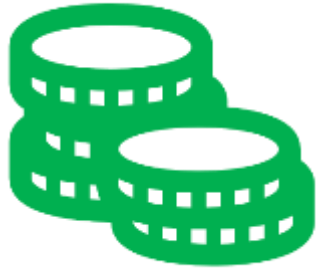
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CSP-CaL – Advantages and opportunities

3. Abundant and stable materials → limestone, dolomite, etc.

Low-price



Abundant and widely available



Non-hazardous or contaminant



**Characteristics for the large scale deployment of an
energy storage system**

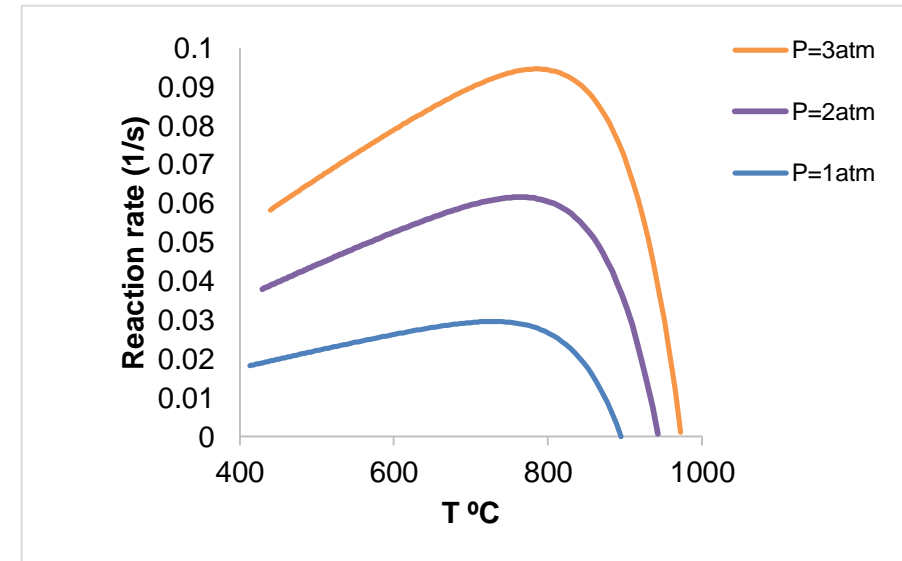
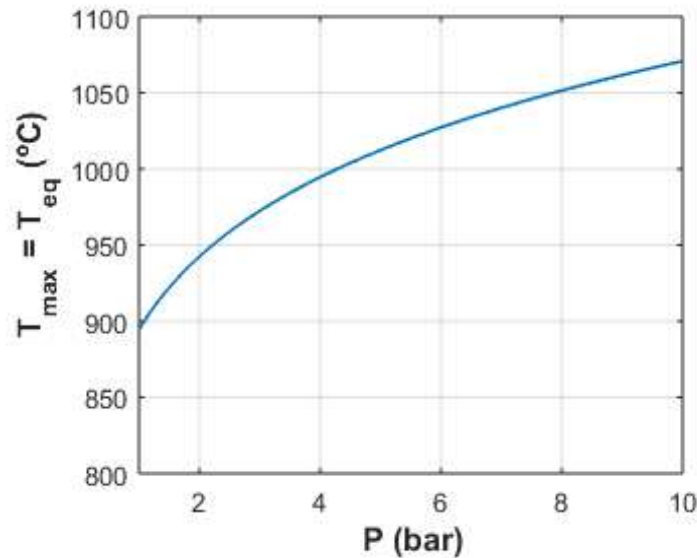
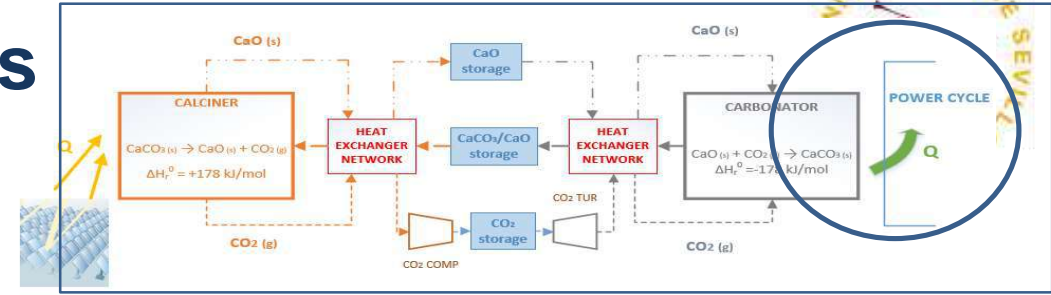


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CSP-CaL – Advantages and opportunities

4. High temperature exothermic reaction

- ✓ Energy delivery at high temperature 650-1000°C as a function of CO₂ partial pressure
- ✓ An advantage compared with molten salts → T_{máx} ~550-600°C due to salts degradation
- ✓ Integration of high-efficiency power cycles



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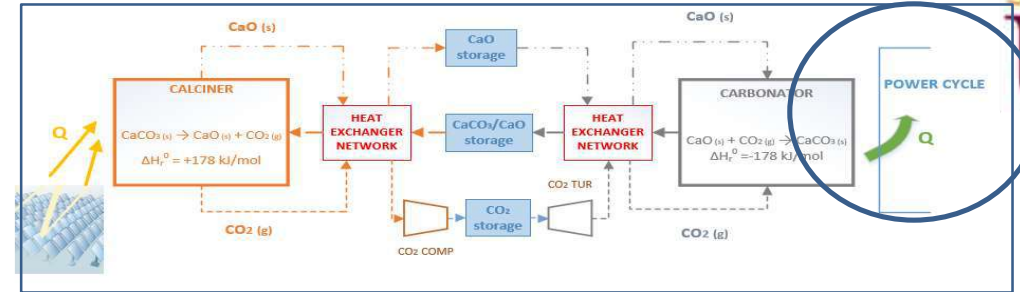


CSP-CaL – Advantages and opportunities

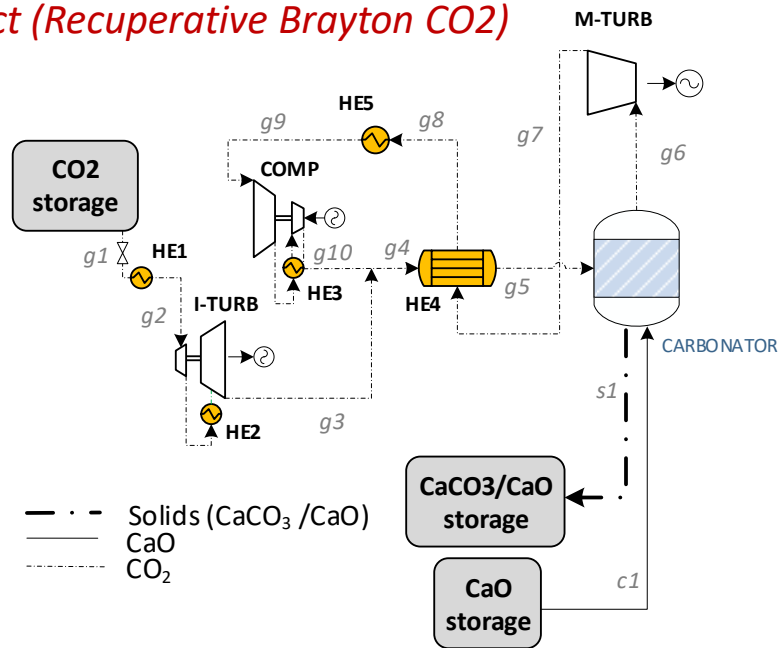


5. Direct and indirect integration of power cycles

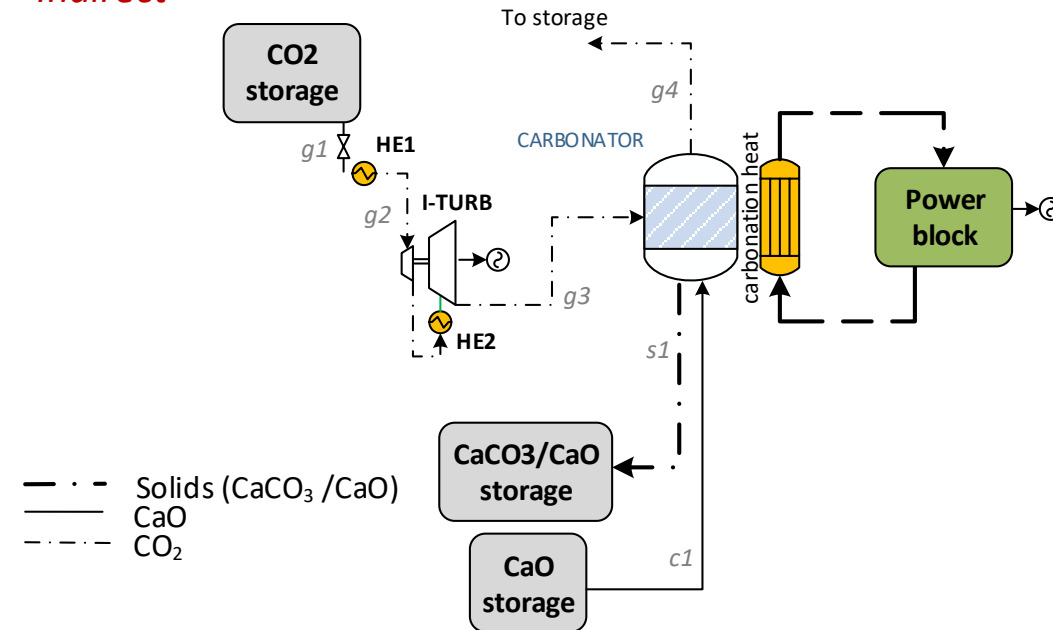
- ✓ Flexibility for design and operation
- ✓ Based on the high temperature of the reaction



Direct (Recuperative Brayton CO2)



Indirect



C Ortiz, R Chacartegui, JM Valverde, A Alovio, JA Becerra, **Power cycles integration in concentrated solar power plants with energy storage based on calcium looping**, Energy Conversion and Management 149, 815-829 2017



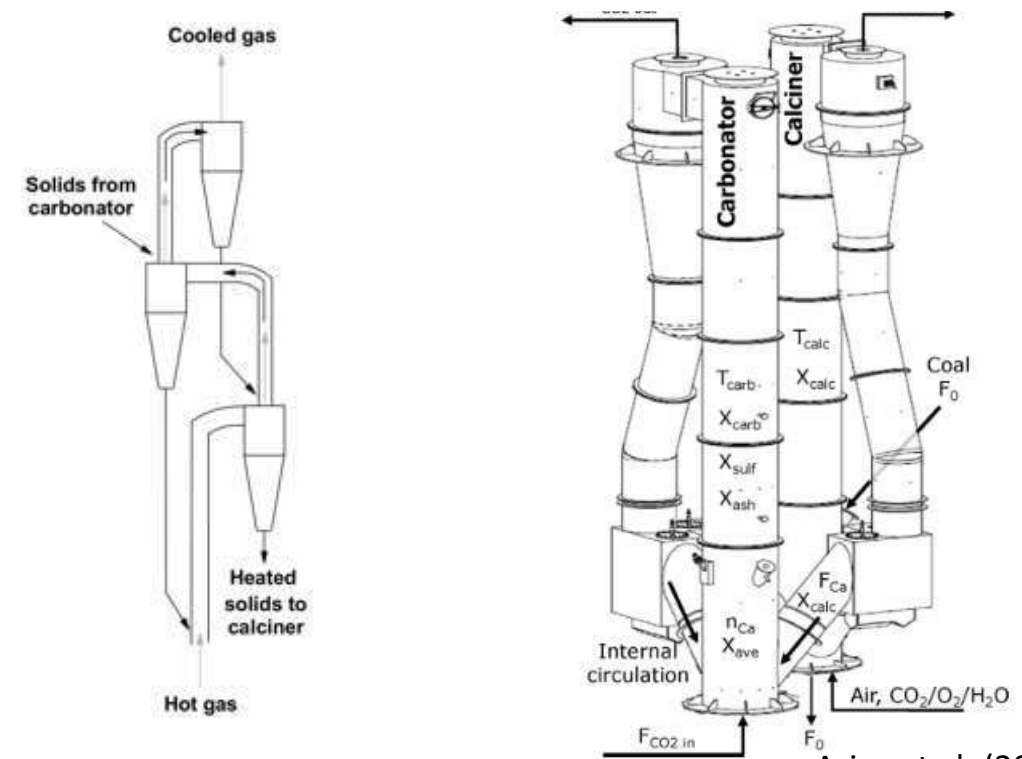
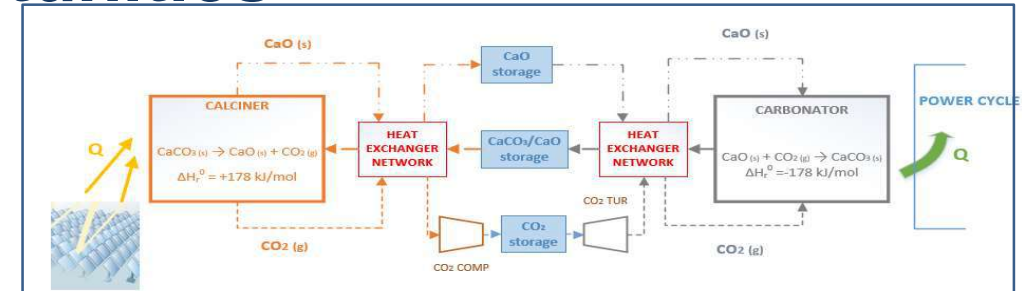
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CSP-CaL – Advantages and opportunities

6. Materials y equipment used at an industrial scale

- Proximity with cement industry
- **Calcliner (solar integration)**
- Entrained flow reactors
- Closed CO₂ Brayton cycle
- **Solids transport**
- Cyclons
- Storage tanks



Arias et al. (2013)

BAT for cement industry (2013)



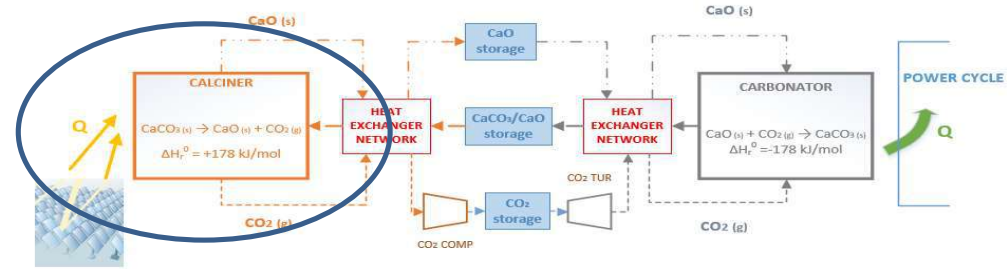
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Main Challenges

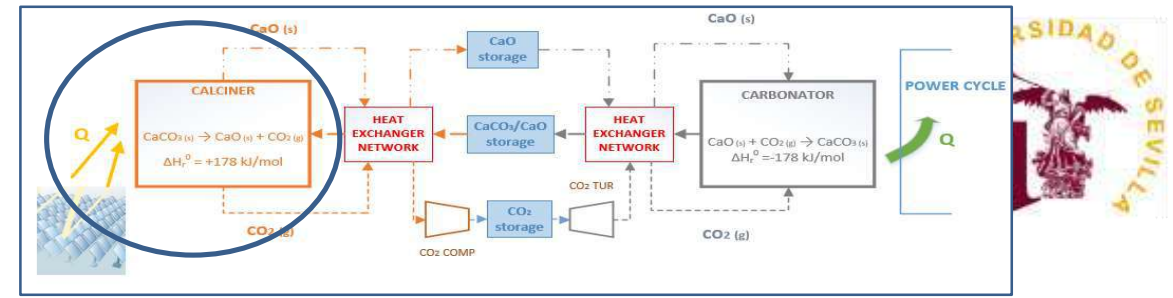
1. Solar calciner. High-temperature receivers

- i) Particles residence time
- ii) Particles circulation within the system
- iii) Closed CO₂ loop operation
- iv) Thermal gradients control
- v) Continuous operation for scaling up



Particles solar receivers **High-temperature**

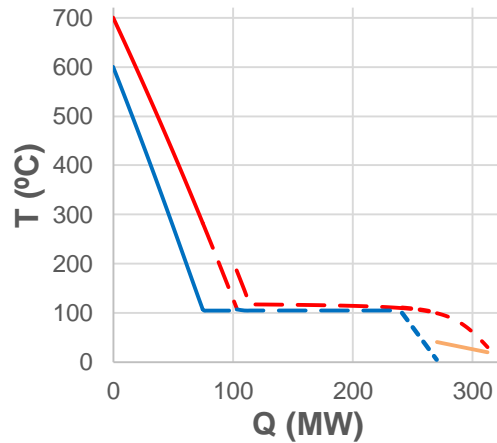
Main Challenges



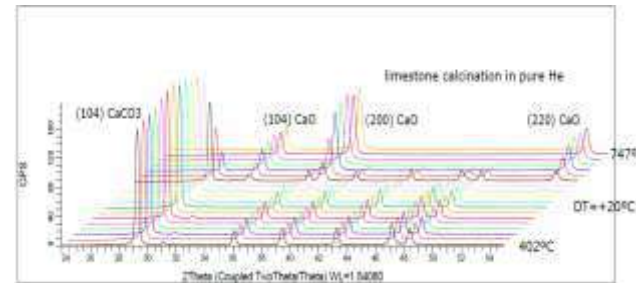
Alternatives for reducing the calcination temperature

Steam calcination

- Commercial availability
- Closeness to CSP tower
- Separation condensing
- **Effects on particles structure**

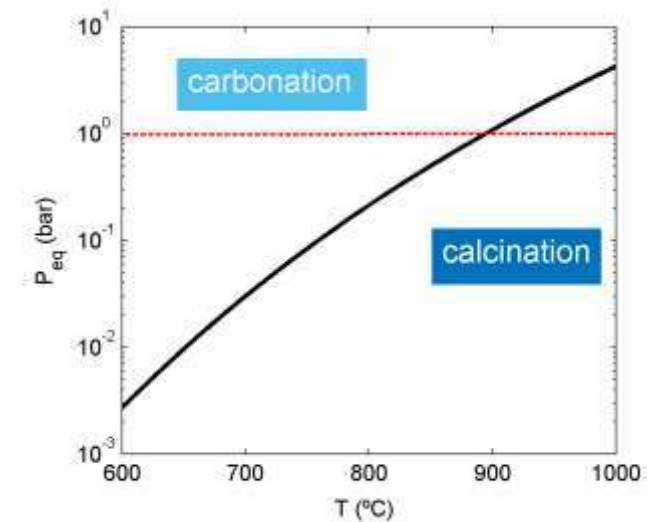


Helium calcination



- Reduced loss of activity with cycles
- **Membranes separation**

Vacuum calcination

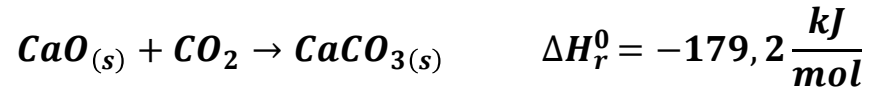


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Main Challenges

2. Multicyclic CaO conversion



Deactivation with the number of cycles

It affects to plant performance

$$X = \frac{\text{mol CaO reacted}}{\text{mol CaO in}} = \frac{\text{mol CaCO}_3 \text{ produced}}{\text{mol CaO in}}$$

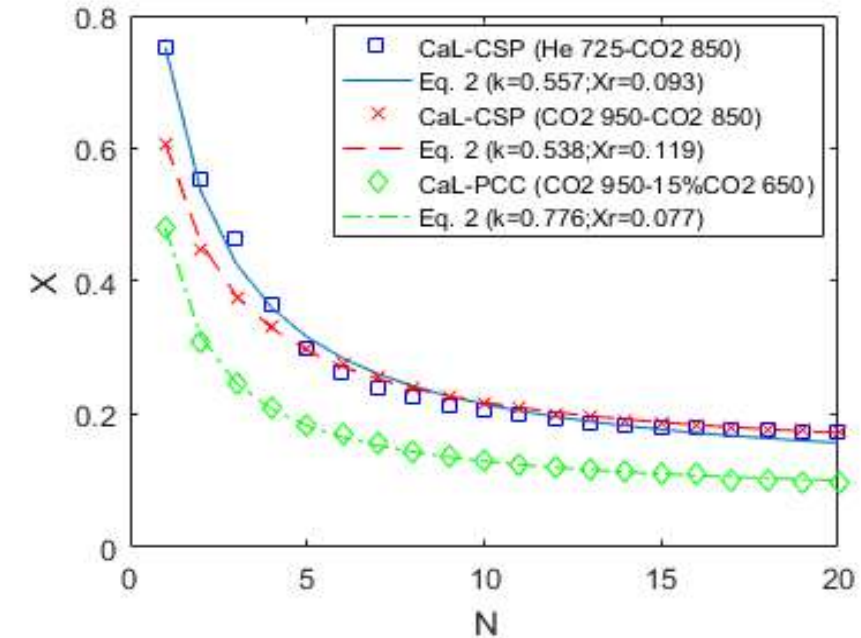
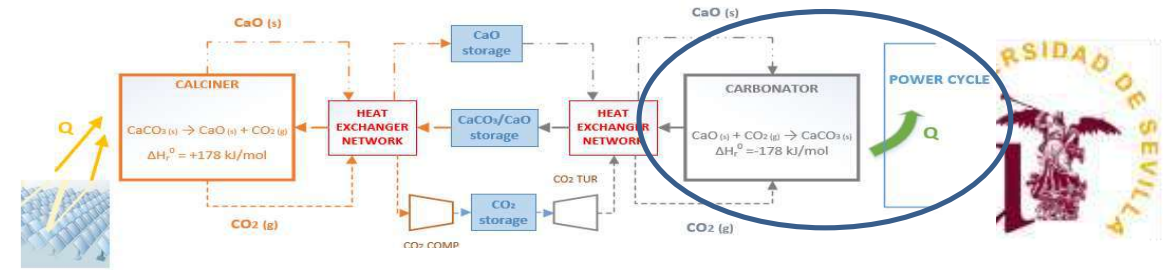
$$\text{CO}_2 \text{ captured} = \text{CaCO}_3 \text{ formed} = \text{CaO} \cdot X$$

$$(1 - X) = \text{solids inerts} \longrightarrow \text{Efficiency penalty}$$

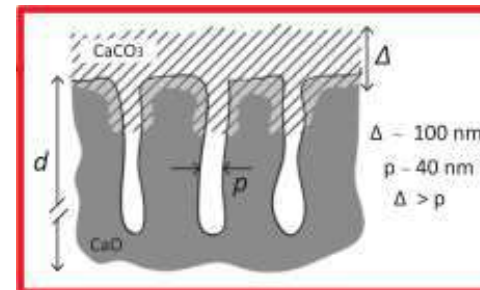
Deactivation is highly dependent on the design conditions of reactors, **material and processes**



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B Sarrión, A Perejón, PE Sánchez-Jiménez, N Amghar, R Chacartegui, ..., Calcination under low CO2 pressure enhances the calcium Looping performance of limestone for thermochemical energy storage, Chemical Engineering Journal, 127922,2020



Summary of main benefits of CaL Storage concept (SOCRATCES)



1 CaO precursors:



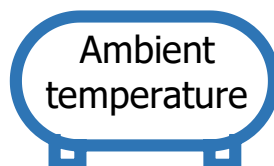
- ✓ Low price
- ✓ wide availability
- ✓ harmlessness

2 Carbonation for generating heat $\sim 650-1000^{\circ}\text{C}$



- ✓ High efficient generation of electricity

3 Reactants and products can be stored at ambient temperature

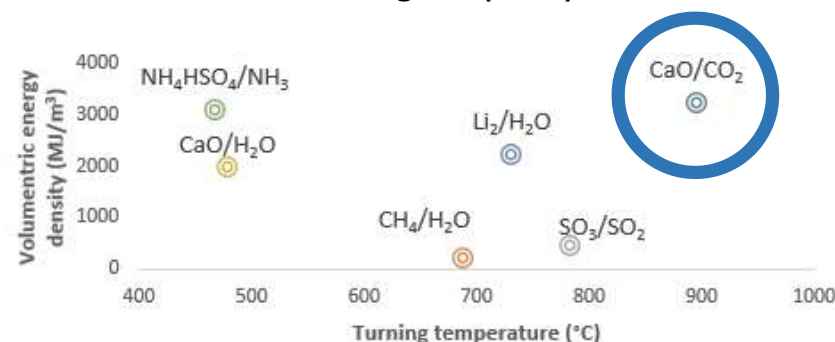


5 Materials and process equipment



- ✓ Well-known in the cement industry

4 High energy density to maximize storage capacity



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SOCRATCES operation conditions

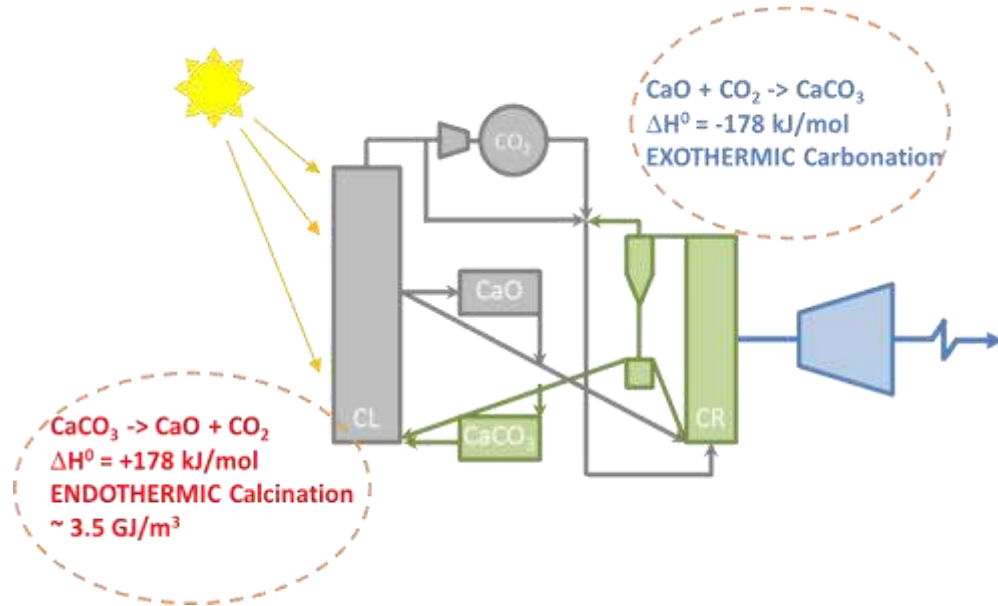


Figure 1: Schematic representation of SOCRATCES.

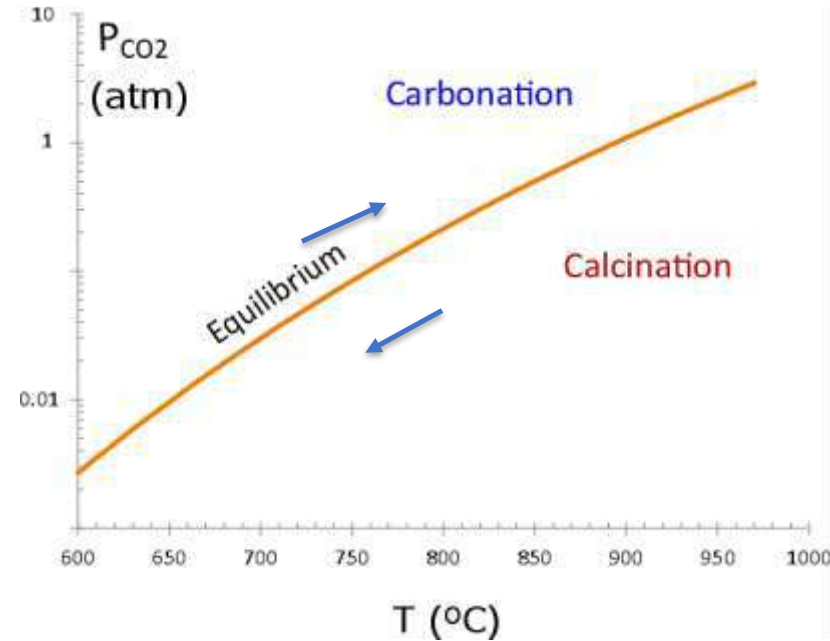
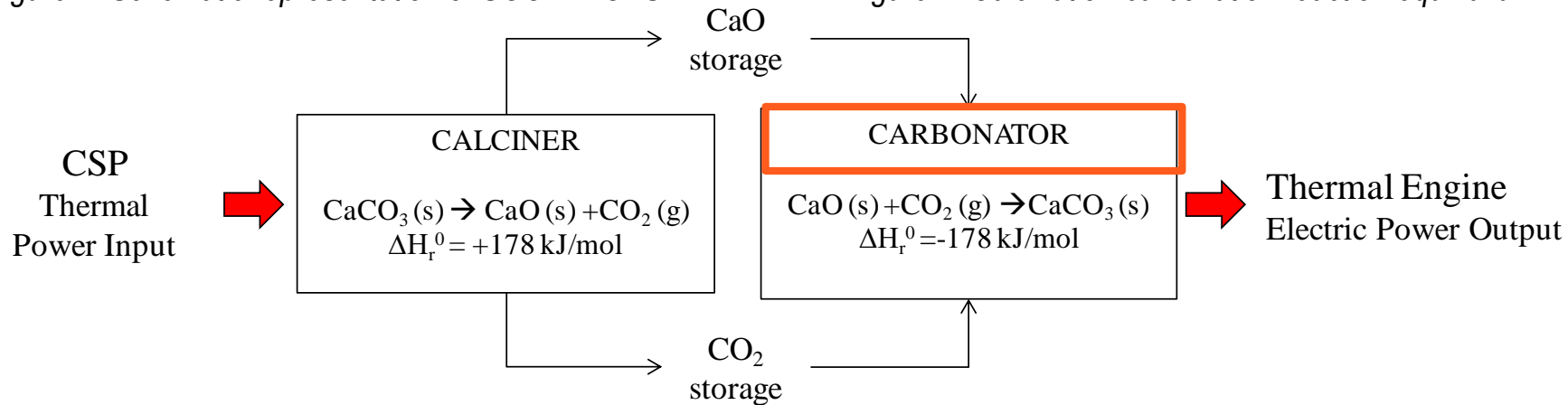


Figure 2: Calcination-carbonation reaction equilibrium



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Material behaviour under SOCRATCES operation conditions

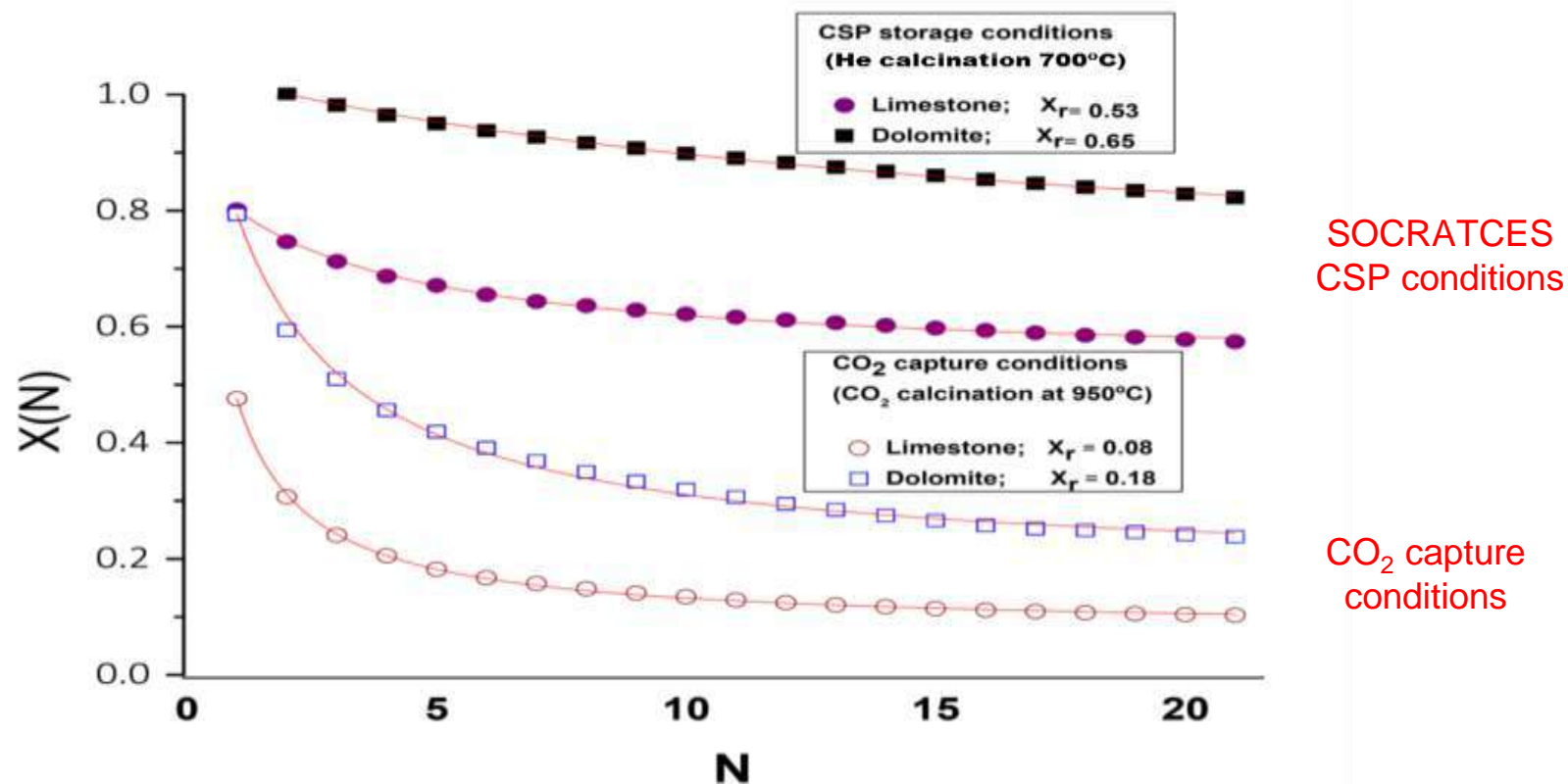


Figure 1: The humble limestone and dolomite show high residual conversion (X_r) at SOCRATCES conditions

Objectives.



- SOCRATCES global objective is to **advance in the knowledge of the Calcium Looping (CaL) for thermochemical energy storage (TCES)**.
- The project **develops prototypes of the different components and implements their integration in order to reduce the core risks of scaling up** TCES-CaL technology, to identify and to solve challenges; to advance in the understanding of the processes and to optimize the performance of components and global systems with the longer-term goal of enabling highly competitive and sustainable TCES-CSP plants integrating the TCES-CaL technology.
- SOCRATCES is oriented to **generate new knowledge** about the whole CaL process: equipment, materials, reactions, transport, etc. in order **to identify and solve the challenges** for the development of the TCES-CaL system at a commercial scale of MWs.



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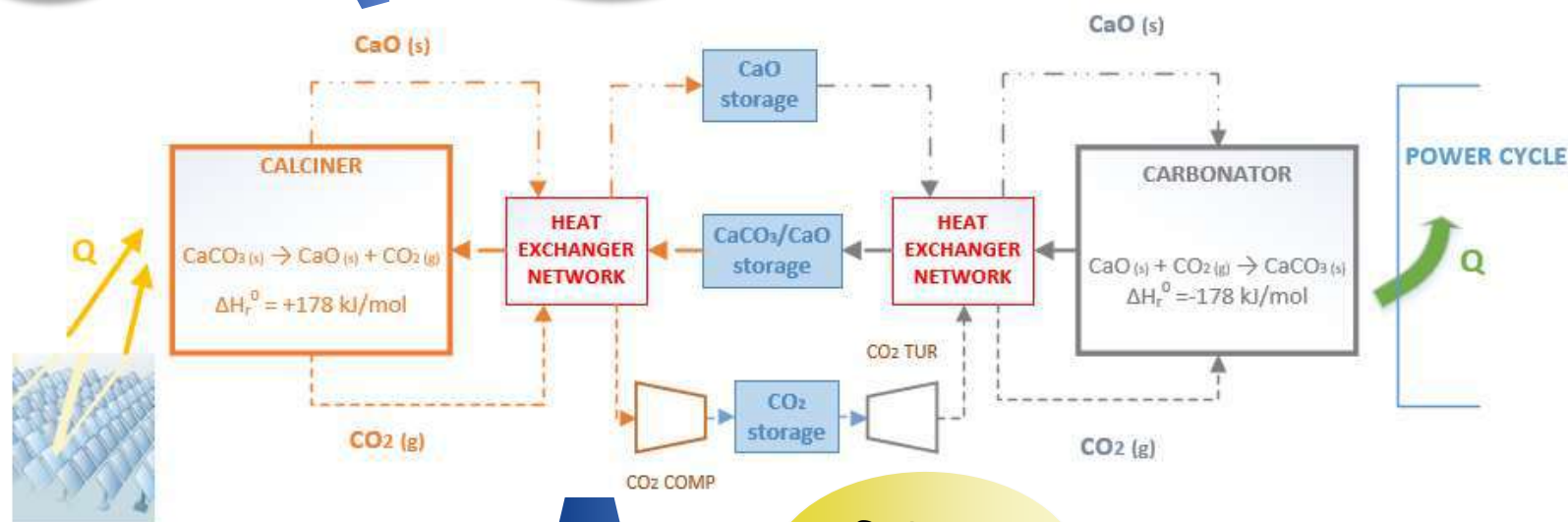
S²CRATCES

New materials

R & D

Reactions
(Ch/Ph)

Scaling-Up
Assessment



Systems
integration
& control

Engineering
Construction

Systems
development

Power
Systems
technologies



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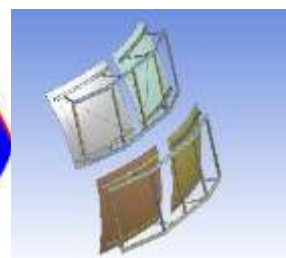
SOCRATCES Prototypes. First of their kinds



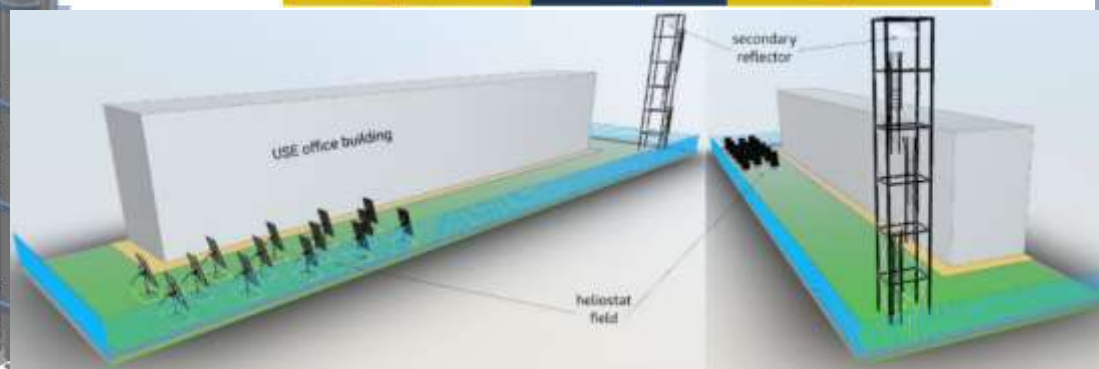
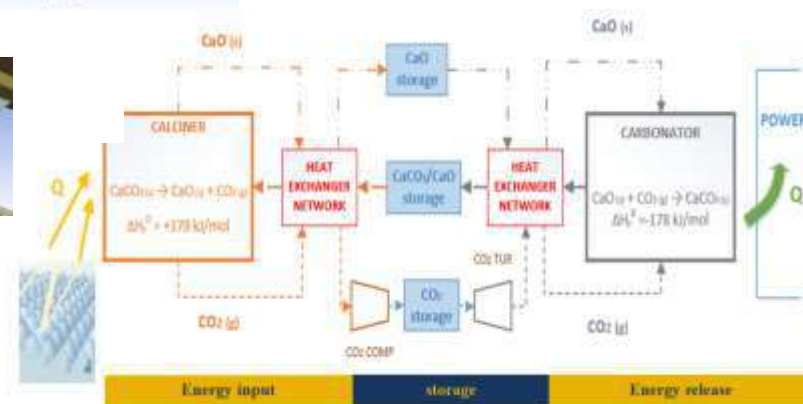
Solar cyclone calciner



Downer gravity closed loop calciner



Secondary reflector/reactor



Downer carbonator reactor

$\text{CO}_2 + \text{CaO}$ particles
(800°C)

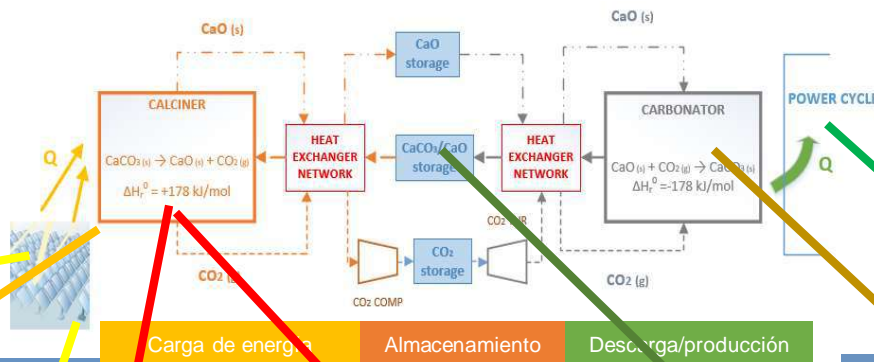
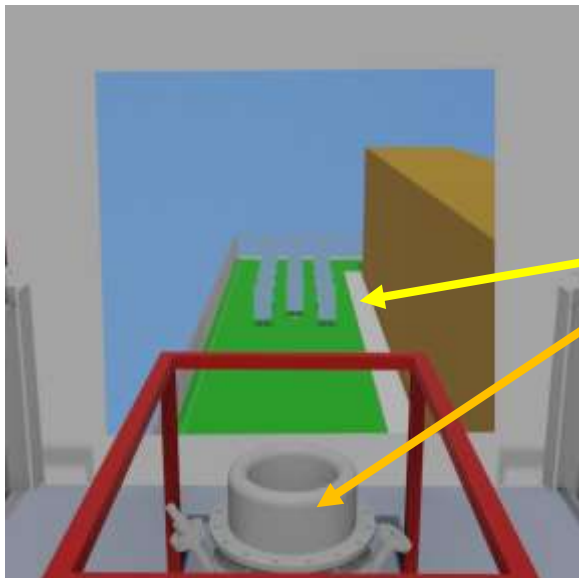
CO_2 preheating

HTF to thermal engine

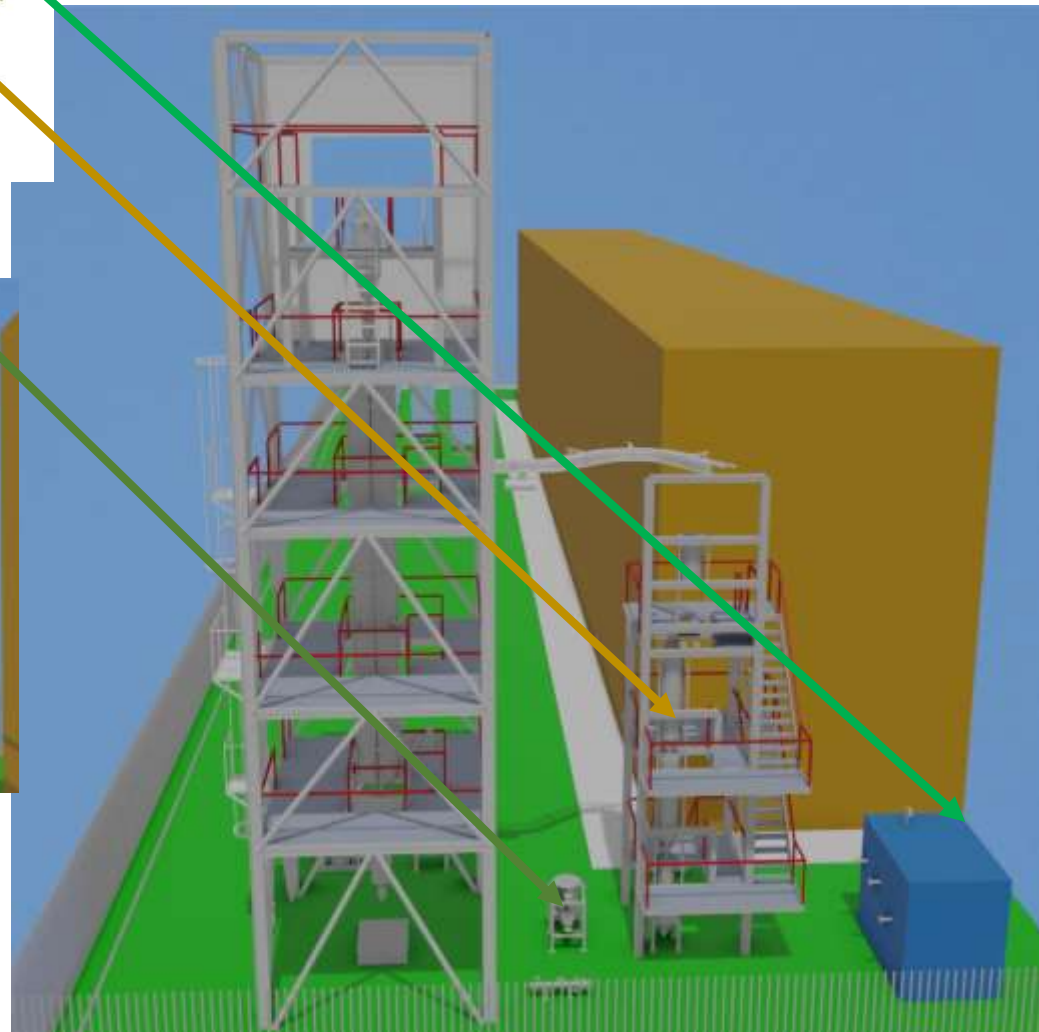
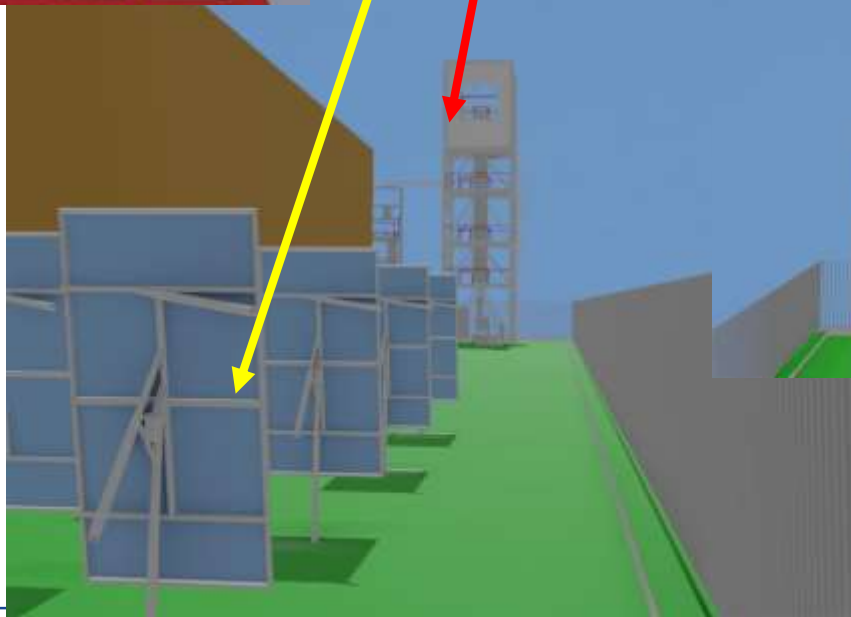
HTF from thermal engine

Downer closed loop carbonator



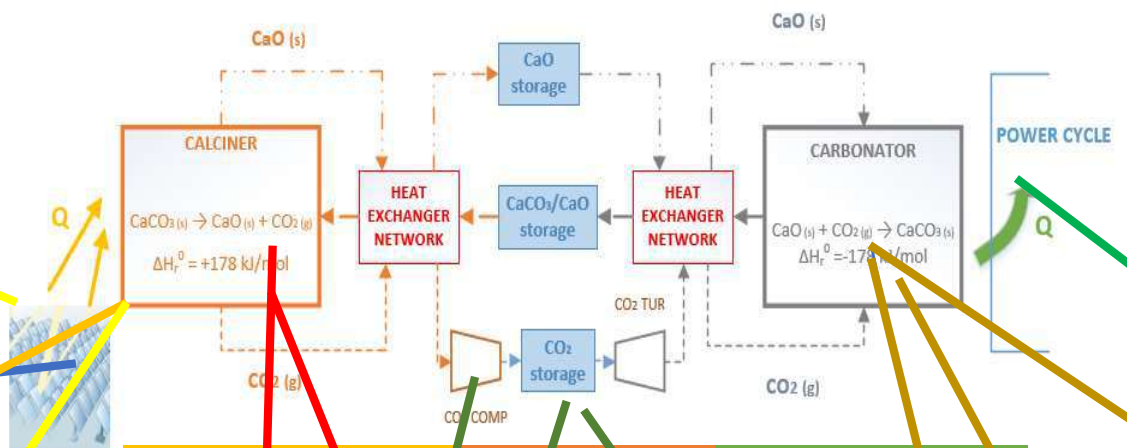


SO CRATCES



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SO CRATCES



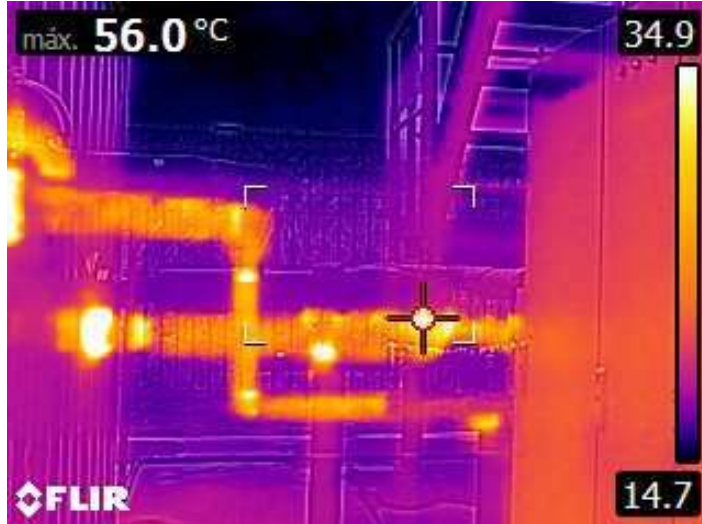
Carga de energía Almacenamiento Descarga/producción



This Project has received funding by means of Horizon 2020 Research & Innovation

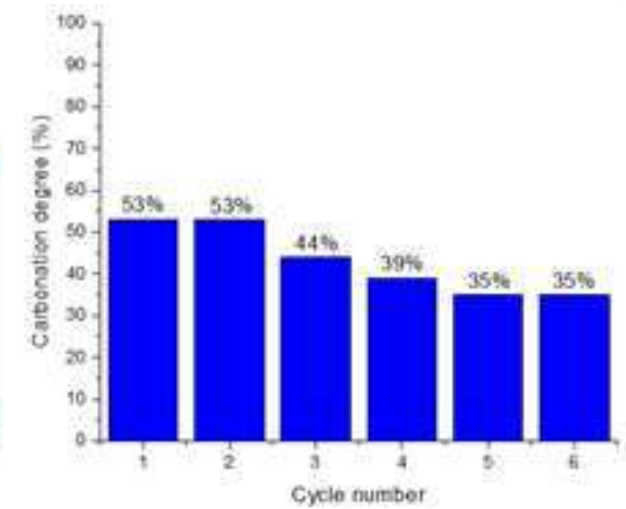
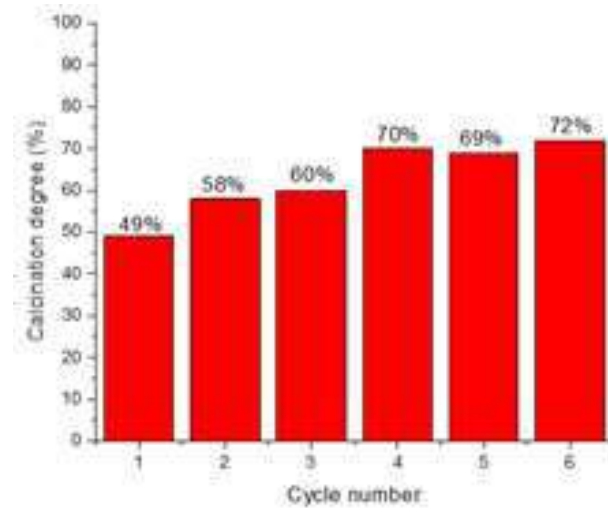
S-CRATCES

And the pilot plant operates



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And it provides results...



That combined with models, they predict a good performance at other scales



Source: IRENA Renewable Cost Database and IRENA Auction and PPA Database.

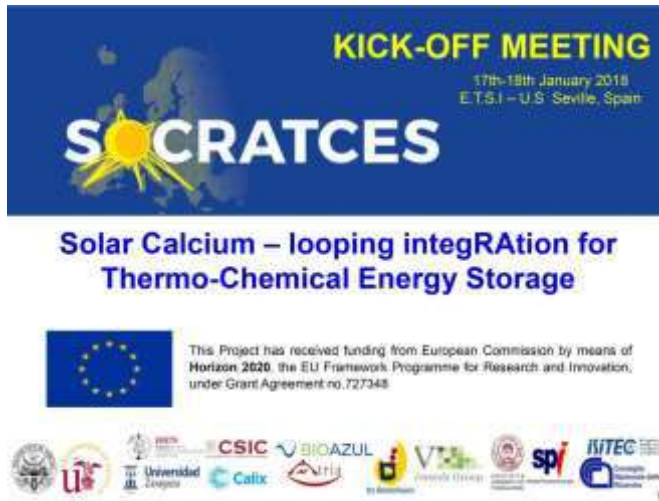
Figure 15: Levelised cost of electricity and auction price trends for CSP, 2010-2021[23].
Socratces technology positioning.



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SOCRATCES a 4 years journey

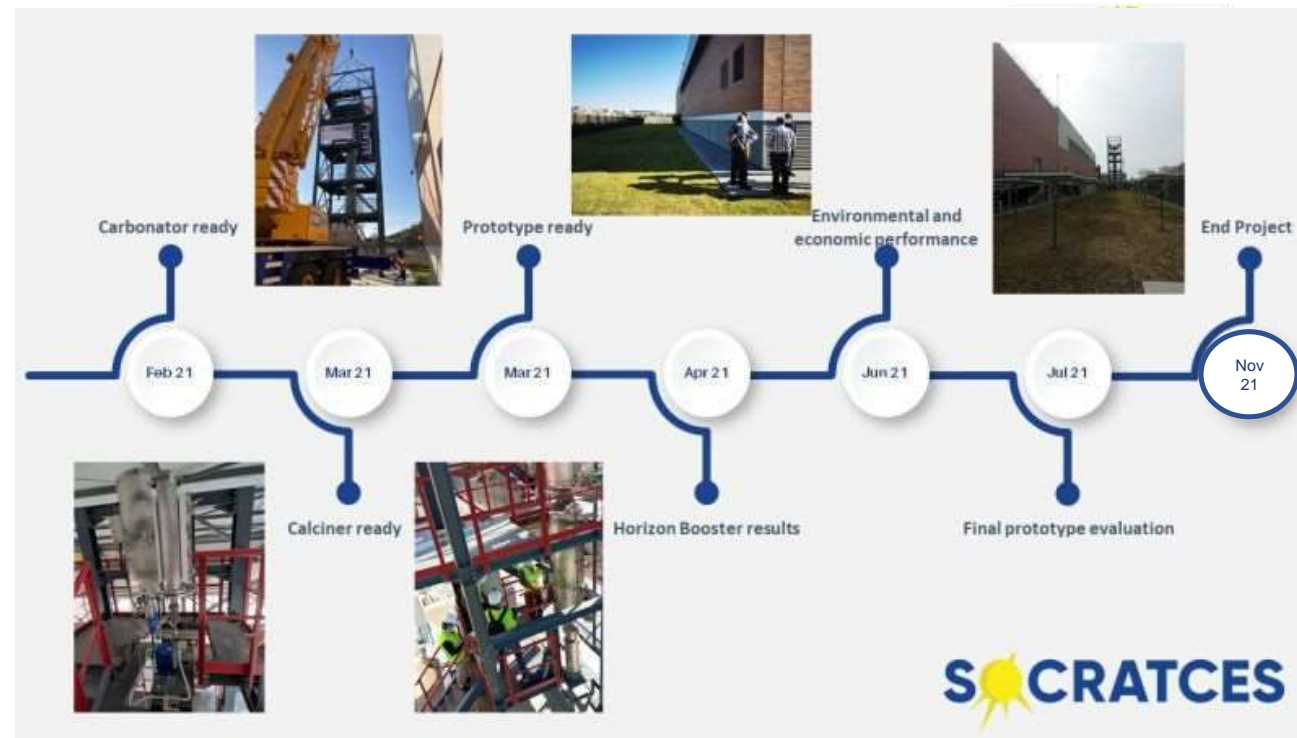


6th GENERAL ASSEMBLY

7th July 2020



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<https://socratces.eu/>

Nov 21

<https://www.linkedin.com/company/socratces/>



Published results, analysis, data (a non complete sample)



Integrations and processes

- R Chacartegui, A Alovio, C Ortiz, JM Valverde, V Verda, JA Becerra, **Thermochemical energy storage of concentrated solar power by integration of the calcium looping process and a CO₂ power cycle**, Applied energy 173, 589-605 **First publication**
- A Alovio, R Chacartegui, C Ortiz, JM Valverde, V Verda, **Optimizing the CSP-calcium looping integration for thermochemical energy storage**, Energy Conversion and Management 136, 85-98 2017 **Seasonal storage**
- C Ortiz, MC Romano, JM Valverde, M Binotti, R Chacartegui, **Process integration of Calcium-Looping thermochemical energy storage system in concentrating solar power plants**, Energy 155, 535-551 2018 **Hot storage**
- C Ortiz, R Chacartegui, JM Valverde, A Alovio, JA Becerra, **Power cycles integration in concentrated solar power plants with energy storage based on calcium looping**, Energy Conversion and Management 149, 815-829 2017 **Power cycles analysis**
- C Ortiz, M Binotti, MC Romano, JM Valverde, R Chacartegui, **Off-design model of concentrating solar power plant with thermochemical energy storage based on calcium-looping**, AIP Conference Proceedings 2126 (1), 210006 2019 **Off design**

Materials

- C Ortiz, JM Valverde, R Chacartegui, LA Perez-Maqueda, **Carbonation of limestone derived CaO for thermochemical energy storage: from kinetics to process integration in concentrating solar plants**, ACS Sustainable Chemistry & Engineering 6 (5), 6404-6417 2018 **Scales impact**
- C Ortiz, JM Valverde, R Chacartegui, **Energy Consumption for CO₂ Capture by means of the Calcium Looping Process: A Comparative Analysis using Limestone, Dolomite, and Steel Slag**, Energy Technology 4 (10), 1317-1327 **Effect of different materials**
Biomaterialized materials
- J Arcenegui-Troya, PE Sánchez-Jiménez, A Perejón, JM Valverde, ...**Calcium-Looping Performance of Biomaterialized CaCO₃ for CO₂ Capture and Thermochemical Energy Storage**, Industrial & Engineering Chemistry Research 59 (29), 12924-12933, 2020 **Biomaterials**
- B Sarrión, A Perejón, PE Sánchez-Jiménez, N Amghar, R Chacartegui, ..., **Calcination under low CO₂ pressure enhances the calcium Looping performance of limestone for thermochemical energy storage**, Chemical Engineering Journal, 127922,2020 **Low-Pressure Calcination**



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Published results, analysis, data (a non complete sample)

Components

- B Sarrión, A Perejón, PE Sánchez-Jiménez, N Amghar, R Chacartegui, ..., **Calcination under low CO₂ pressure enhances the calcium Looping performance of limestone for thermochemical energy storage**, Chemical Engineering Journal, 127922,2020
Calcliner Effect of Low pressure calcination
- U Tesio, E Guelpa, C Ortiz, R Chacartegui, V Verda, **Optimized synthesis/design of the carbonator side for direct integration of thermochemical energy storage in small size Concentrated Solar Power**, Energy Conversion and Management: X 4, 100025, 2019
Carbonator

CaL Perspectives and challenges

- C Ortiz, JM Valverde, R Chacartegui, LA Pérez-Maqueda, ..., **Scaling-up the Calcium-Looping Process for CO₂ Capture and Energy Storage**, KONA Powder and Particle Journal 38, 189-208, 2021
Reviews
- C Ortiz, JM Valverde, R Chacartegui, LA Perez-Maqueda, P Giménez, **The calcium-looping (CaCO₃/CaO) process for thermochemical energy storage in concentrating solar power plants**, Renewable and Sustainable Energy Reviews 113, 109252 2019

Hybrid CaL CSP/PV

- R Bravo, C Ortiz, R Chacartegui, D Friedrich, **Multi-objective optimisation and guidelines for the design of dispatchable hybrid solar power plants with thermochemical energy storage**, Applied Energy 282, 116257, 2021
Data clustering
- R Bravo, C Ortiz, R Chacartegui, D Friedrich, **Hybrid solar power plant with thermochemical energy storage: A multi-objective operational optimization**, Energy Conversion and Management 205, 112421, 2020
Optimization operation
- R Fernández, C Ortiz, R Chacartegui, JM Valverde, JA Becerra, **Dispatchability of solar photovoltaics from thermochemical energy storage**, Energy Conversion and Management 191, 237-246 2019
Concept

CaL Combined Cycle

- C Ortiz, R Chacartegui, JM Valverde, A Carro, C Tejada, J Valverde, **Increasing the solar share in combined cycles through thermochemical energy storage**, Energy Conversion and Management 229, 113730, 2021



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Novel Concept. More recent approach. An alternative pathway?





**Solar Calcium looping integRAtion
for Thermo-Chemical Energy Storage**

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Thanks for your attention



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