SFERA-III

Solar Facilities for the European Research Area

1st Summer School “Thermal energy storage systems, solar fields and new cycles for future CSP plants”
WP1 Capacity building and training activities
Odeillo, France, September 9th-11th 2019

“Thermochemical thermal energy storage: challenges and issues ”

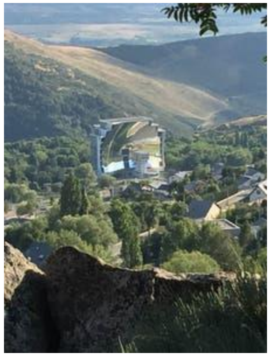
Sylvie Rougé(CEA)‘ sylvie.rouge@cea.fr

NETWORKING

THIS PROJECT HAS RECEIVED FUNDING FROM THE EUROPEAN UNION’S HORIZON 2020 RESEARCH AND INNOVATION PROGRAMME UNDER GRANT AGREEMENT NO **823802**

AGENDA

- Thermochemical heat storage fundamentals
- TCS reaction selection
- Solid / gas reactor selection
- Solid material ad-equation to the reactor and process
- Reactor modelling and upscaling: 2 application cases
- Conclusion



TCS FUNDAMENTALS (1)

Types of heat storage for CSP plants

- Sensible heat storage
- Latent heat storage
- Chemical storage
  - Decomposition Ex: ZnO, CaO production
  - Biomass conversion & XtL
  - Solar Fuels Ex: H2
  - Heat / cold storage
    - Chemical reactions
    - Sorption

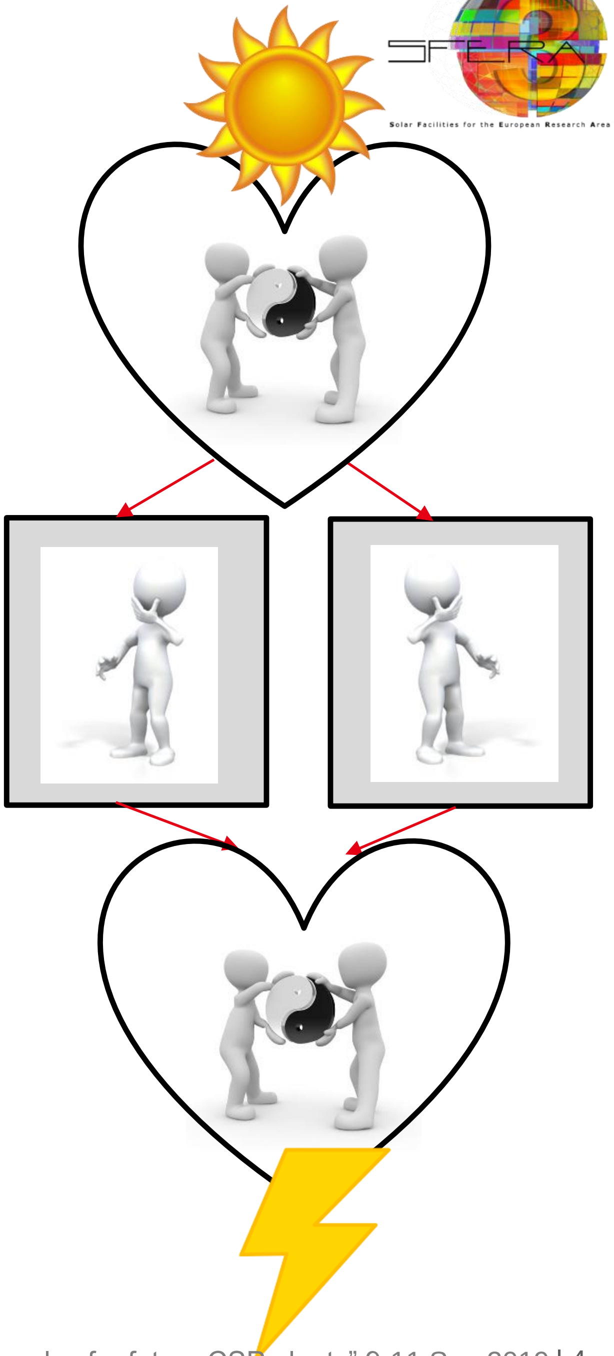
TCS FUNDAMENTALS (2)

- **Fundamentals:**

  Charge: endothermic $C + heat \rightarrow A + B$

  Discharge: exothermic $A + B \rightarrow C + heat$

- **Advantages**
  - Long-term storage: chemical potential intact
  - High storage volume density.
- **Required properties**
  - 100% reversible reaction
  - Stable for hundreds of thermal cycles
  - Products A and B must be easily separated for storage
  - Products A, B and C are easy to store
  - Products are cheap and non hazardous



TCS FUNDAMENTALS (3)

- **Organic reactions are rarely suitable (side reactions -> no 100% reversibility)**
- **Most of inorganic reactions are solid / gas reactions**
  - Advantage:
    - ✓ *Easy to separate the solid from the gas*
  - Drawback :
    - ✓ *heterogeneous gas/solid reaction -> risk of mass transfer limitations*
    - ✓ *Divided solid has a low heat transfer conductivity -> risk of heat transfer limitation*
    - ✓ *gas /solid reactor , solid handling → technology is more challenging*
    - ✓ *How to store a gas at low energetic cost?*

TCS FUNDAMENTALS (4)

- **Main questions to address:**
  - How to choose a suitable chemical reaction?
    - ✓ *Temperature criteria*
    - ✓ *Reversibility criteria*
    - ✓ *Storage density criteria*
  - How to choose the reactor technology?
    - ✓ *Heat and mass transfers: intrinsic # apparent kinetics*
    - ✓ *Integration in the whole process?*
    - ✓ *Can I discharge heat at the same temperature than charge?*
    - ✓ *Can I recover sensible heat at maximal temperature?*
    - ✓ *Do I need 2 reactors for charge and discharge*
    - ✓ *How can I upscale the reactors efficiently?*
  - Is the solid material perfectly adapted to the process and the reactor ?
    - ✓ *Some examples of improvements*

Solar Facilities for the European Research Area

TCS REACTION SELECTION:

TEMPERATURE CRITERIA

REVERSIBILITY AND CYCLABILITY

STORAGE DENSITY

REACTION SELECTION – TEMPERATURE CRITERIA (1)

- **Main types of reactions on the range 300-1100°C**

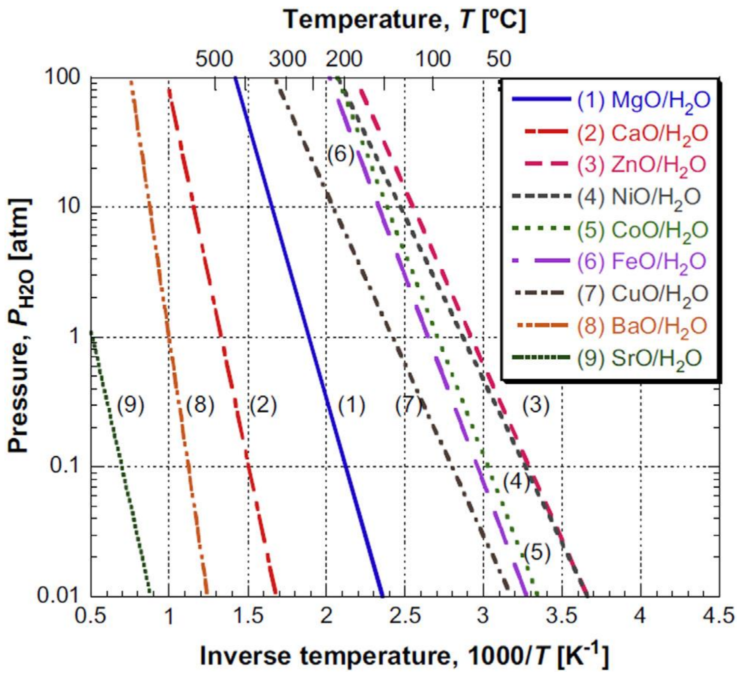
Metallic hydrides (H_2)	Carbonates (CO_2)	Hydroxides (H_2O)	Red-Ox (O_2)	Ammonia (NH_3)	Organic
Mg / MgH_2	**PbO / $PbCO_3$**	**MgO / $Mg(OH)_2$**	**CoO / Co_3O_4**	**NH_3 / N_2,H_2**	**CH_4+H_2O**
Ca / CaH_2	**CaO / $CaCO_3$**	**CaO / $Ca(OH)_2$**	**Mn_2O_3 / Mn_3O_4**	**HSO_4 / NH_4SO_4**	**$CH_4+ CO_2$**
					C_6H_{12}
					SO_3

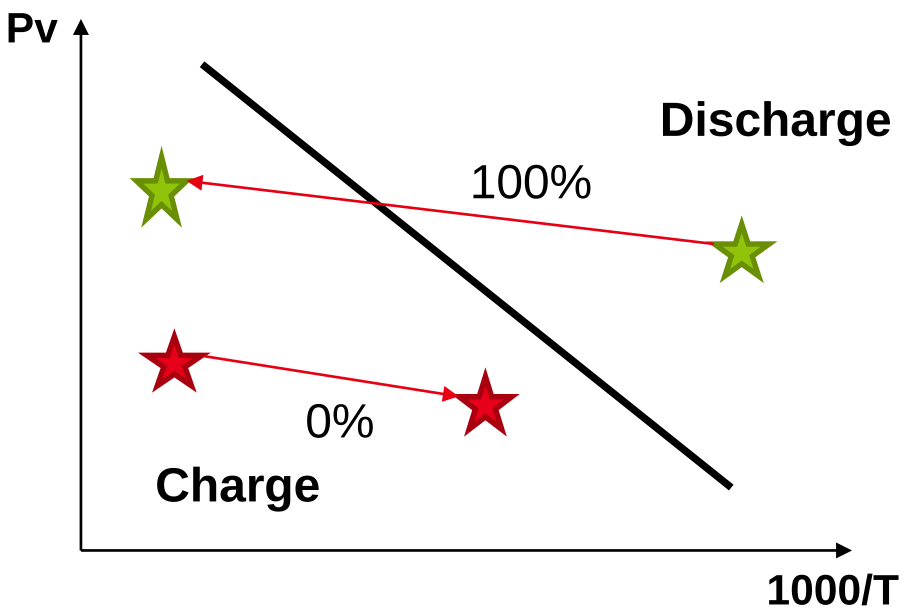
REACTION SELECTION – TEMPERATURE CRITERIA (2)

- A solid / gas reaction is generally monovariant, the equilibrium curve is derived from the Van't Hoff equation at the minimal free Gibbs energy (= no reaction):

✓ $$ln(P_{g,eq}) = -\frac{DH^o}{R.T_{eq}} + \frac{DS^o}{R}$$

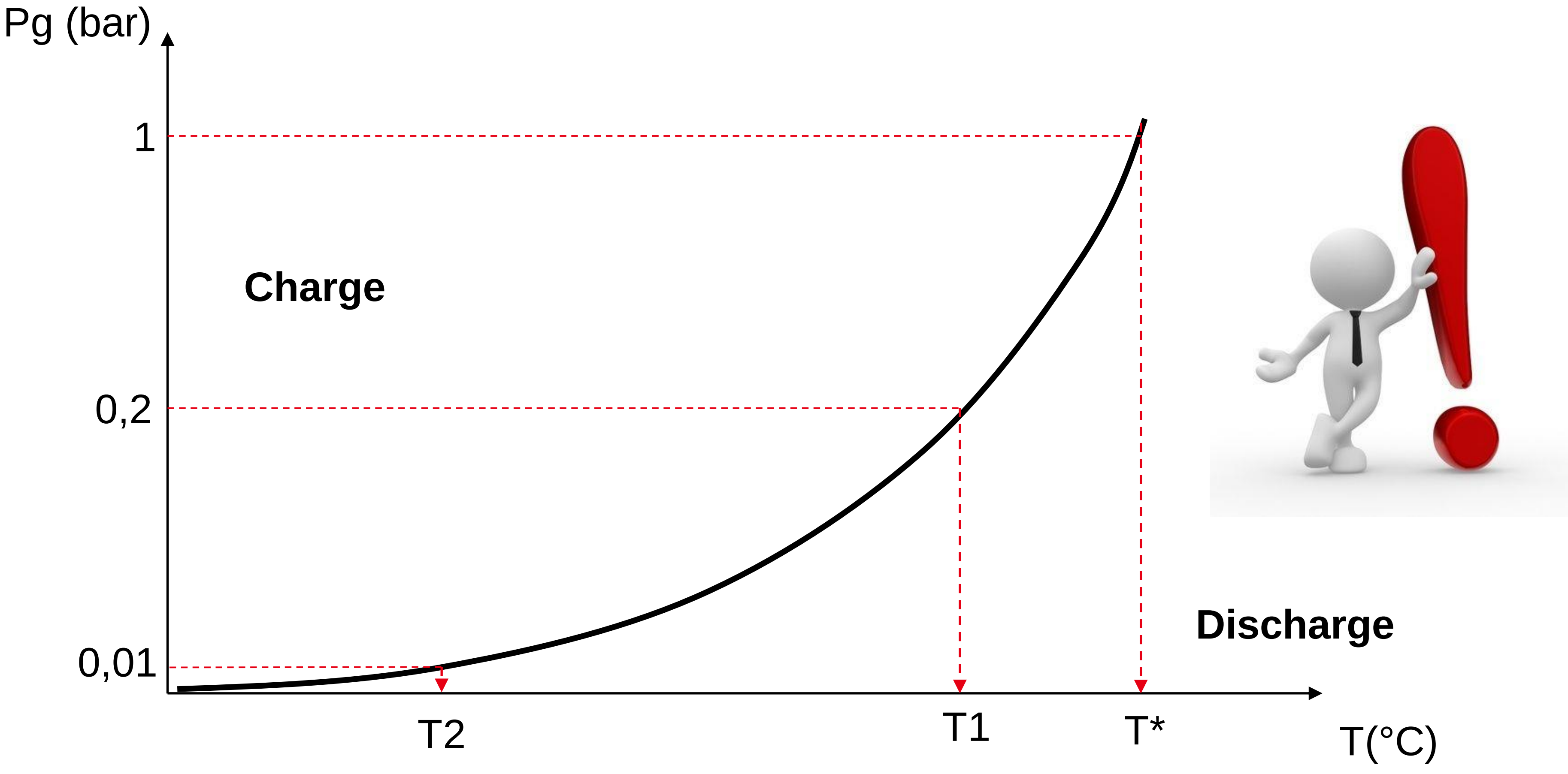
- As a consequence, the reaction conversion yield is 0% or 100% and the enthalpy of reaction is independent of the charge level





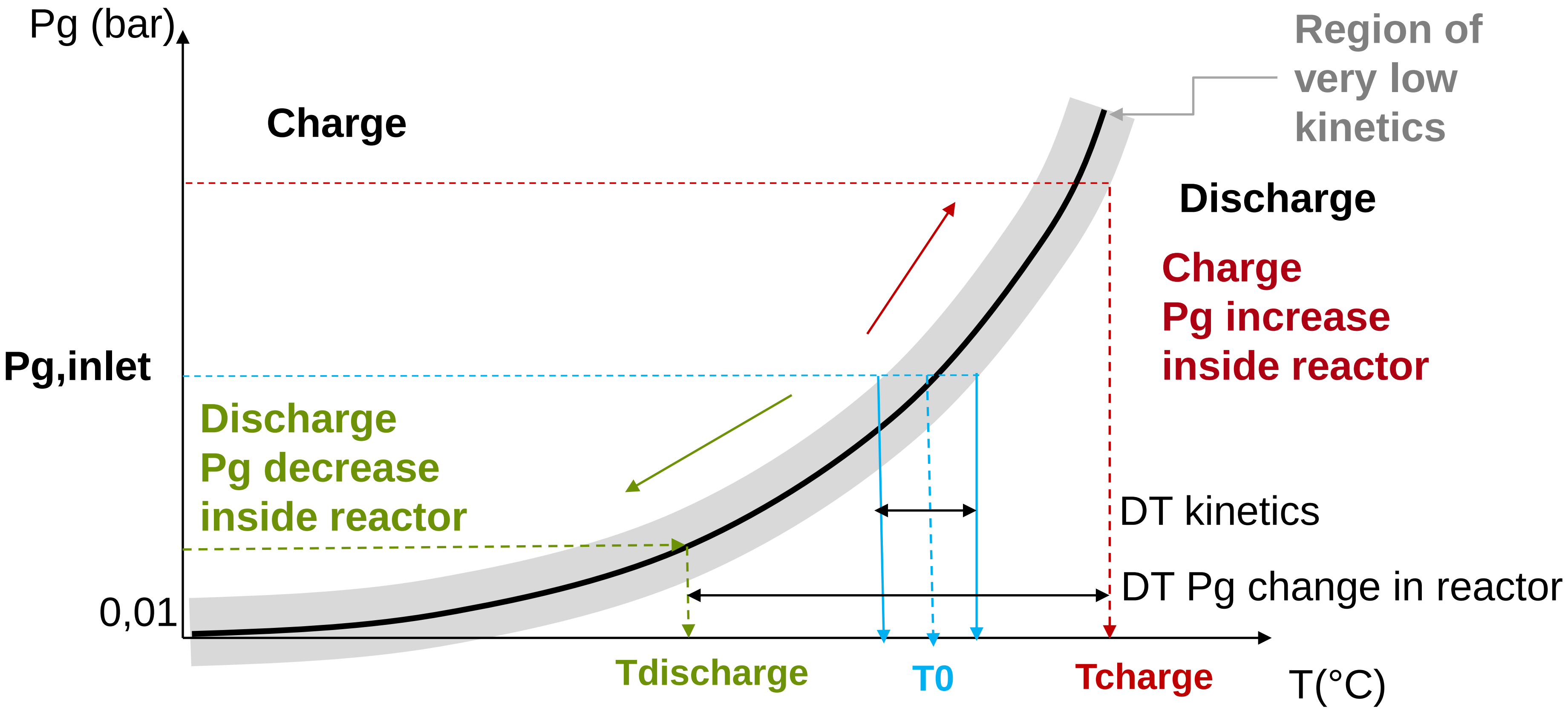
REACTION SELECTION – TEMPERATURE CRITERIA (3)

- **The tuning temperature T* (for P=1) cited in reviews is not always the one you need for your process!**



REACTION SELECTION – TEMPERATURE CRITERIA (4)

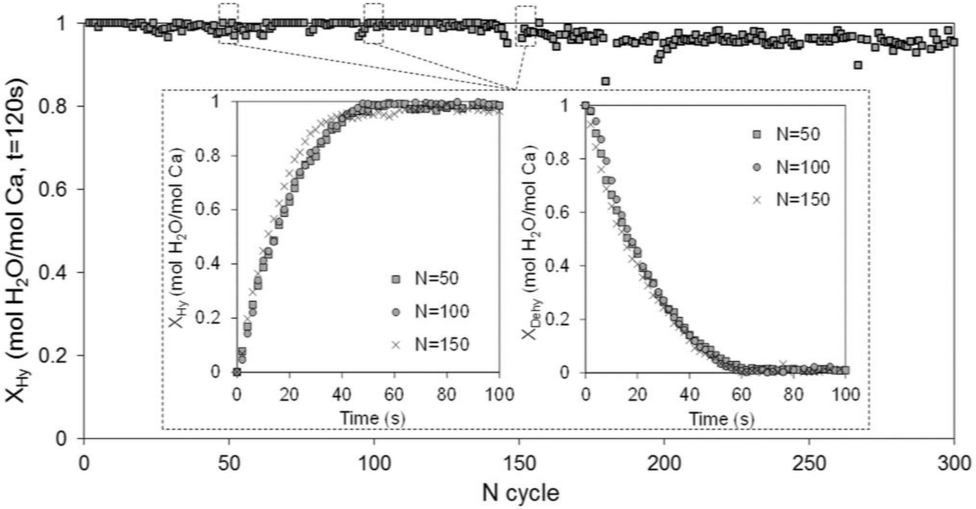
- If you operate at constant partial pressure (case of O_2/air, steam/air…), it is not possible to have the same charging and discharging temperature at large scale:



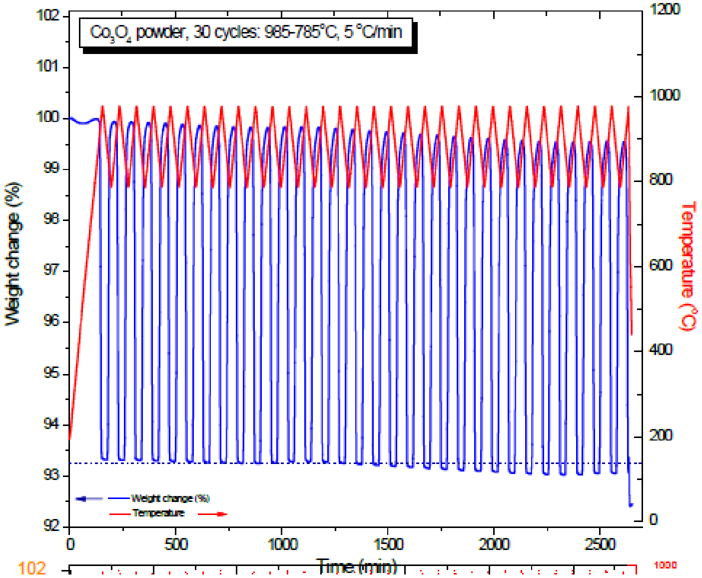
REACTION SELECTION – REVERSIBILITY CRITERIA (1)

- **The reaction must be reversible 100% under hundreds of thermal cycles**

$CaO/Ca(OH)_2$: 300 cycles under synthetic air

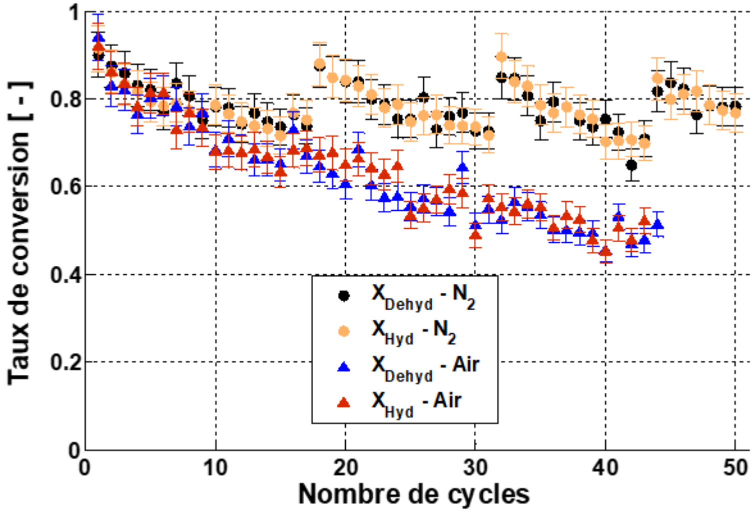


CoO / Co_3O_4 : 30 cycles



REACTION SELECTION – REVERSIBILITY CRITERIA (2)

- **Main risks**
  - Discharge can be at a much lower temperature than charge
    - ✓ *Case of MgO / $Mg(OH)_2$ (300 / 100°C), Mn_2O_3/Mn_3O_4 (1000 / 690-750°C)*
  - Charge rate can decrease after a few thermal cycles
    - ✓ *Reaction sites become ineffective: CaO/$CaCO_3$, CuO/Cu_2O (shrinkage and sintering)*
    - ✓ *Side reactions coming from ppm in gas, for instance : CaO/$Ca(OH)_2$ → $CaCO_3$ or BaO_2/BaO → $BaCO_3$*

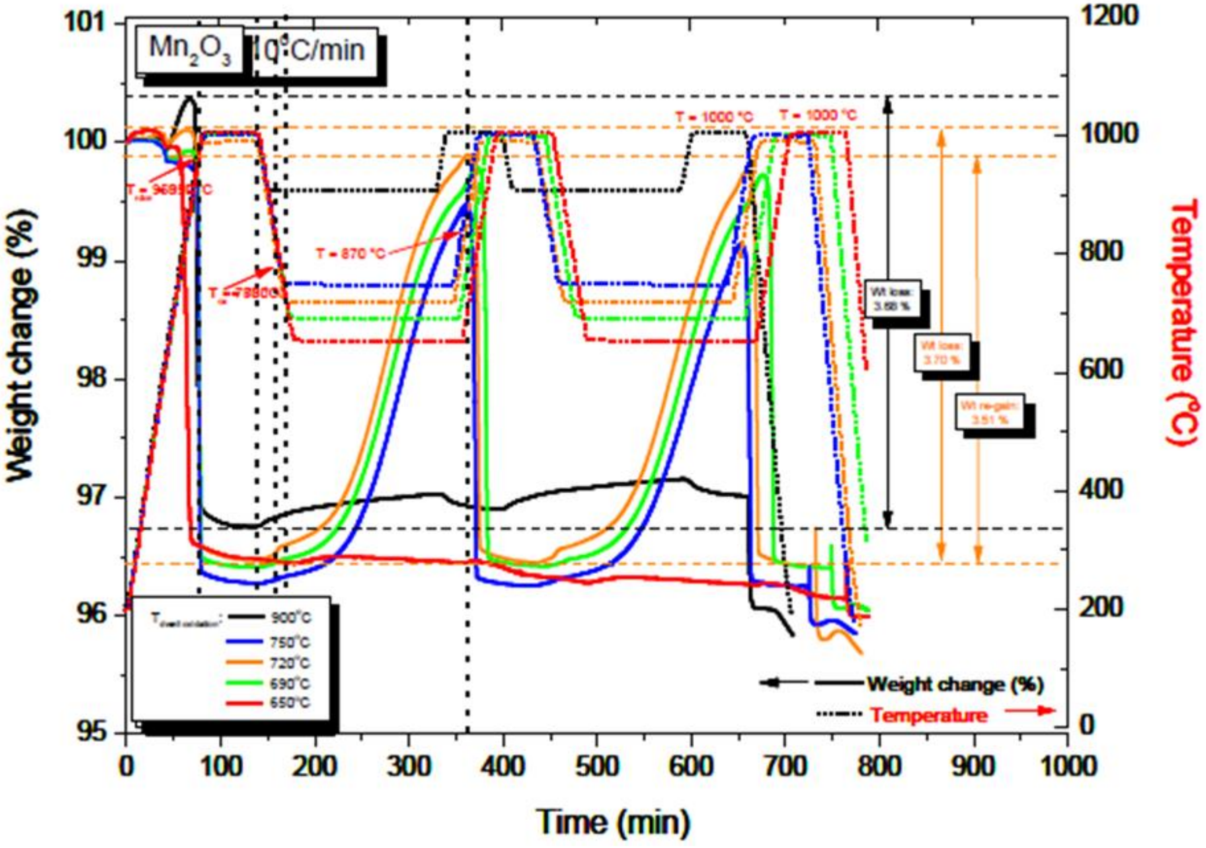


$CaO/Ca(OH)_2$: 50 cycles under air and N_2

REACTION SELECTION – REVERSIBILITY CRITERIA (3)

Mn_2O_3 / Mn_3O_4:

- ***~1000°C for reduction***
- ***narrow range of temperature 690-750°C for oxidation***



REACTION SELECTION – REVERSIBILITY CRITERIA (4)

An example of final selection for Red-Ox reactions:

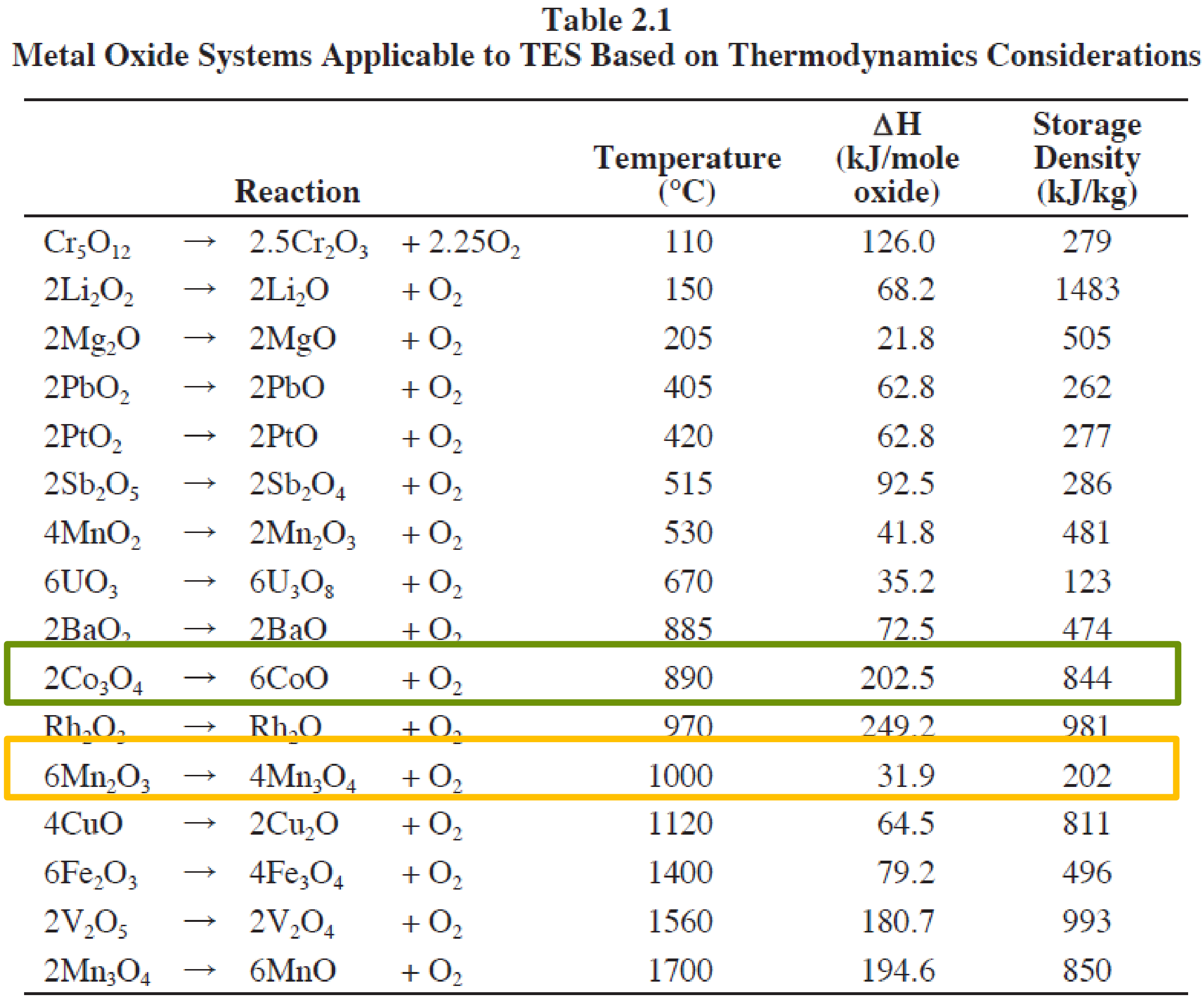


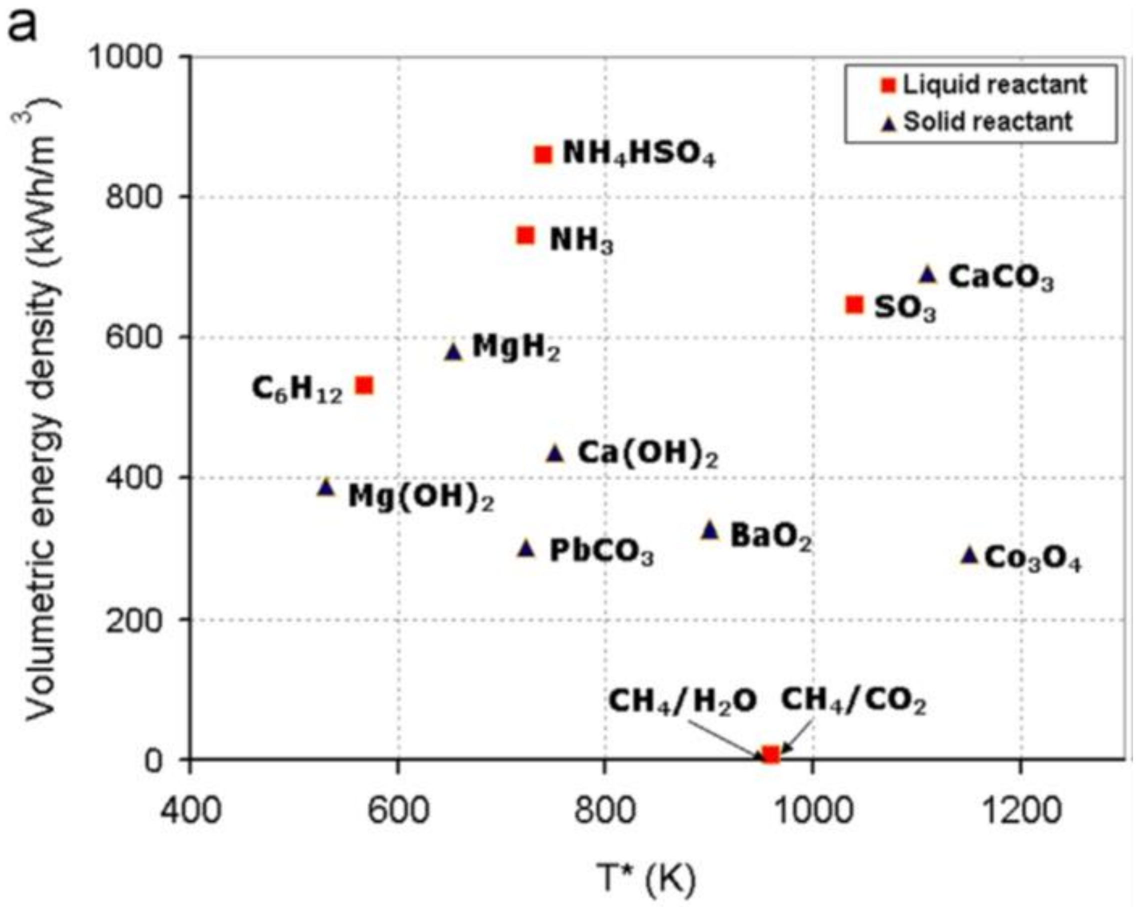
Table 2.1

Metal Oxide Systems Applicable to TES Based on Thermodynamics Considerations

Reaction	Temperature (°C)	ΔH (kJ/mole oxide)	Storage Density (kJ/kg)
$Cr_5O_{12} \rightarrow 2.5Cr_2O_3 + 2.25O_2$	110	126.0	279
$2Li_2O_2 \rightarrow 2Li_2O + O_2$	150	68.2	1483
$2Mg_2O \rightarrow 2MgO + O_2$	205	21.8	505
$2PbO_2 \rightarrow 2PbO + O_2$	405	62.8	262
$2PtO_2 \rightarrow 2PtO + O_2$	420	62.8	277
$2Sb_2O_5 \rightarrow 2Sb_2O_4 + O_2$	515	92.5	286
$4MnO_2 \rightarrow 2Mn_2O_3 + O_2$	530	41.8	481
$6UO_3 \rightarrow 6U_3O_8 + O_2$	670	35.2	123
$2BaO_2 \rightarrow 2BaO + O_2$	885	72.5	474
$2Co_3O_4 \rightarrow 6CoO + O_2$	890	202.5	844
$Rh_2O_3 \rightarrow Rh_2O + O_2$	970	249.2	981
$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$	1000	31.9	202
$4CuO \rightarrow 2Cu_2O + O_2$	1120	64.5	811
$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$	1400	79.2	496
$2V_2O_5 \rightarrow 2V_2O_4 + O_2$	1560	180.7	993
$2Mn_3O_4 \rightarrow 6MnO + O_2$	1700	194.6	850

REACTION SELECTION – STORAGE DENSITY CRITERIA (1)

Volumetric energy density (kWh/m3) of some chemical reactions, calculated on the solid material base:

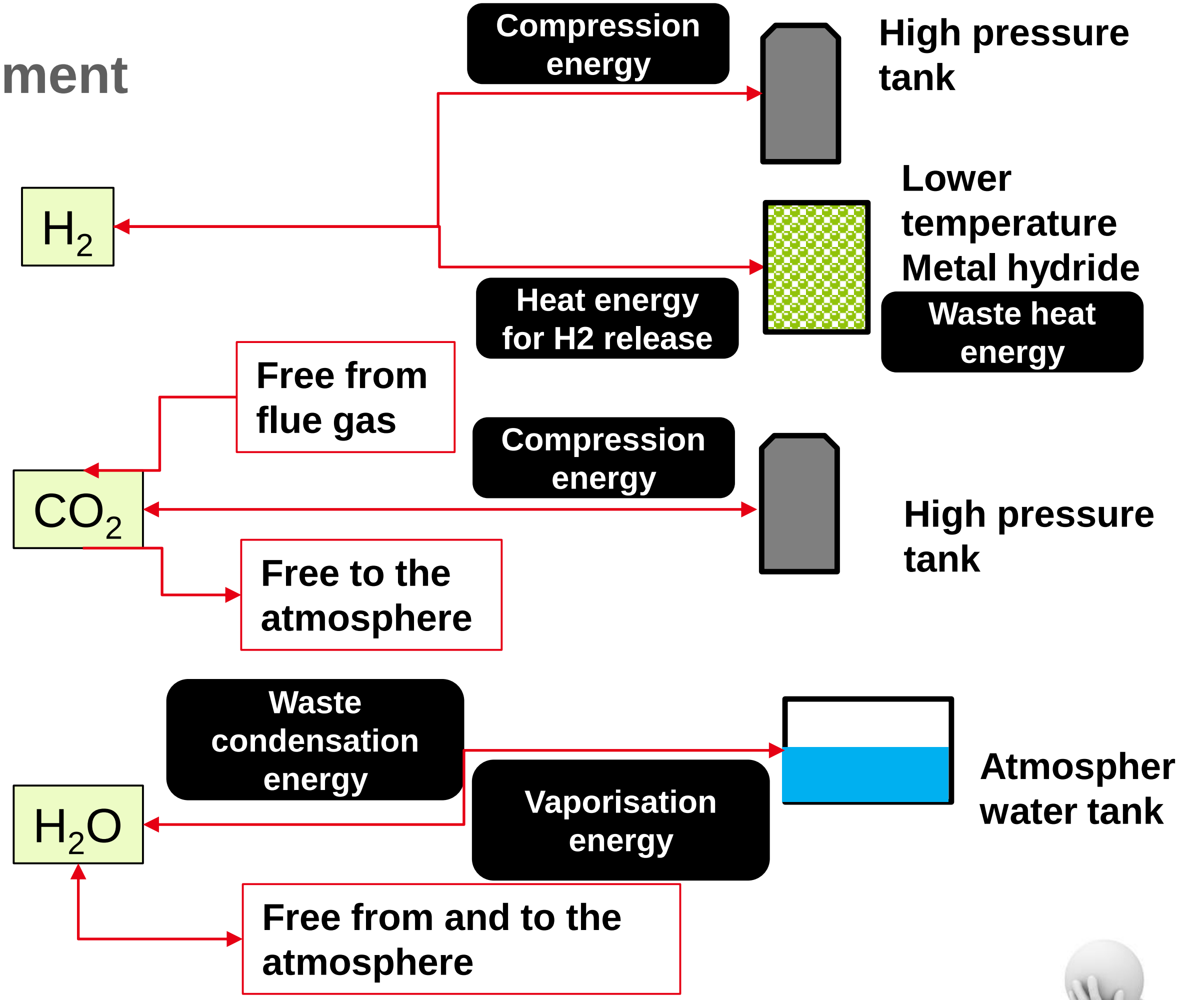


REACTION SELECTION – STORAGE DENSITY CRITERIA (2)

- **The storage density should be estimated at process level and should integrate sensible heat aspects**
  - Sensible heat stored in solids can be :
    - ✓ *An advantage :addition of sensible and chemical storage and increase of the final storage density*
    - ✓ *A drawback :waste heat for solid pre-heating*
  - Gas storage can be a main issue and a large energy sink
  - A first integration of heat and mass flows on a simplified scheme of the process allows to evaluate the **recovered heat efficiency**: $\frac{Eend-user}{Echarge+Eparasitics}$, this value can be far from 100%
  - This preliminary step allows to evaluate the approximate **nett volumetric storage density**

REACTION SELECTION – STORAGE DENSITY CRITERIA (3)

- Gas storage management
  - Di-Hydrogen
  - Carbon dioxide
  - Water steam
  - Di-Oxygen



H_2

Compression energy

High pressure tank

Lower temperature Metal hydride

Heat energy for H2 release

Waste heat energy

CO_2

Free from flue gas

Compression energy

High pressure tank

Free to the atmosphere

H_2O

Waste condensation energy

Vaporisation energy

Atmospheric water tank

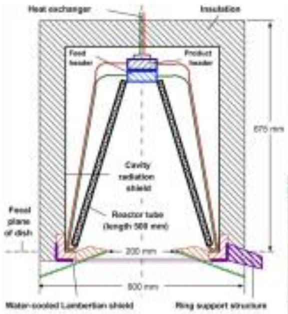
Free from and to the atmosphere

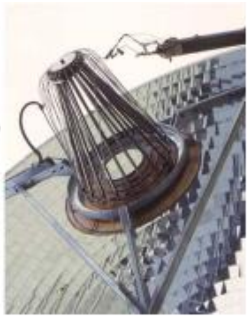
O_2

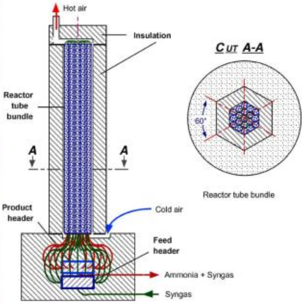
Free from and to the atmosphere

REACTION SELECTION – STORAGE DENSITY CRITERIA (4)

Ammonia dissociation: main sinks are pre-heating and compression

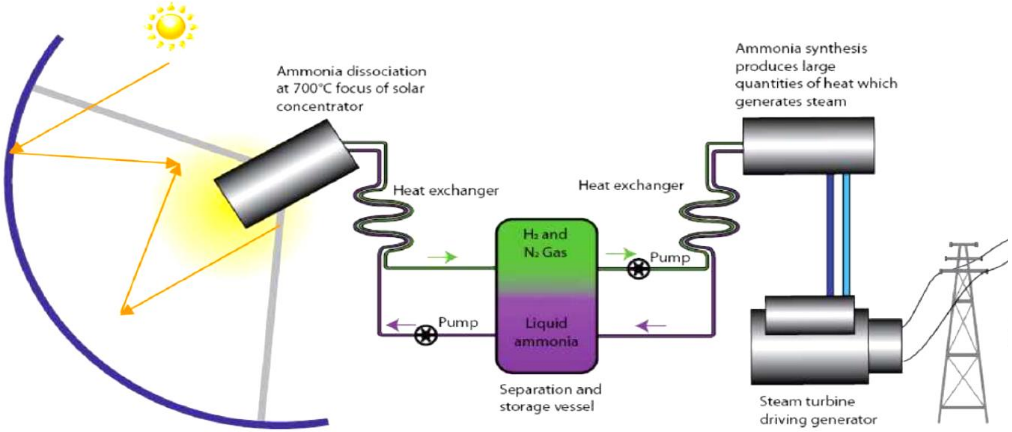




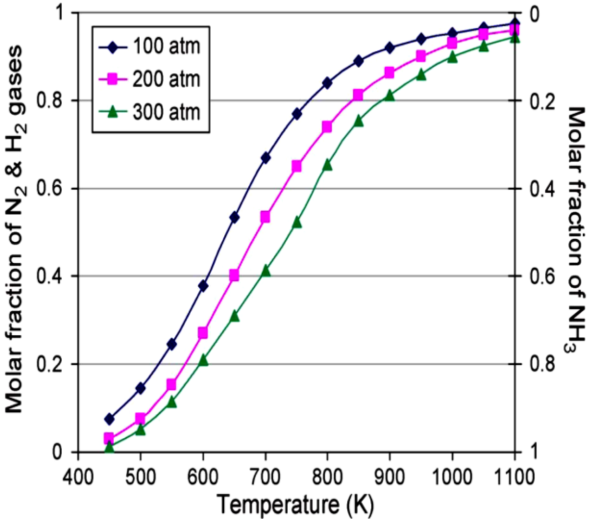


Endothermic
450°C
15 MPa

Exothermic
450°C
30 MPa



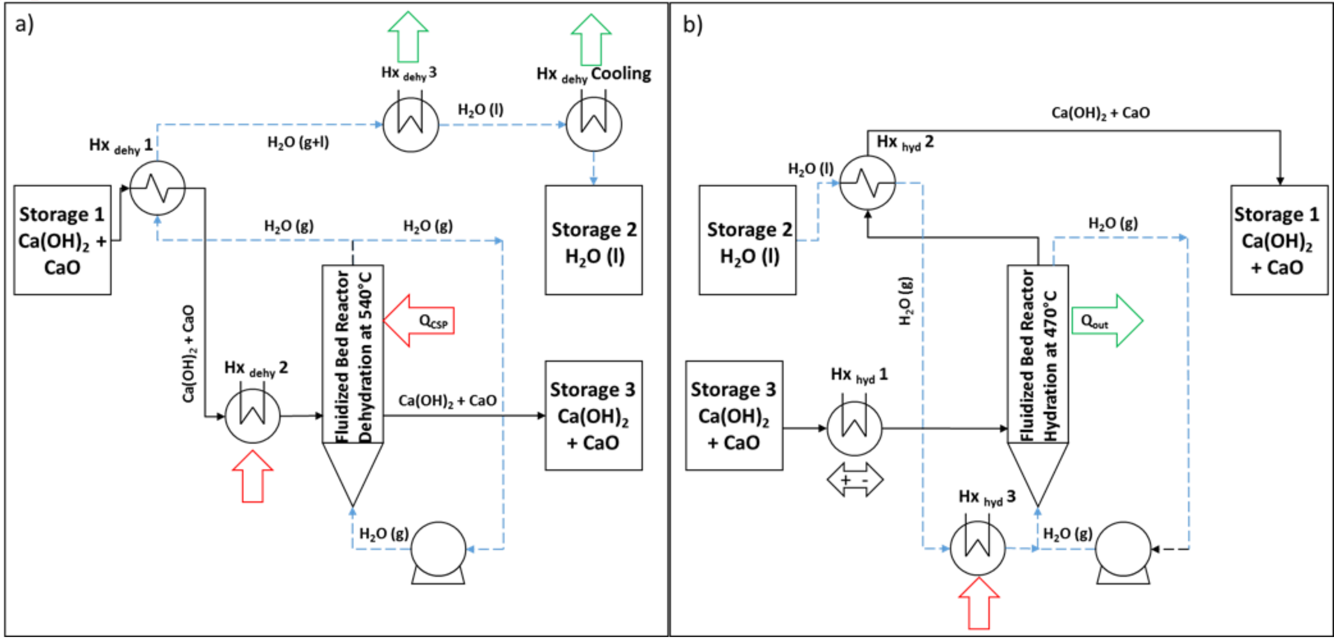
Storage tank
132°C
15 MPa

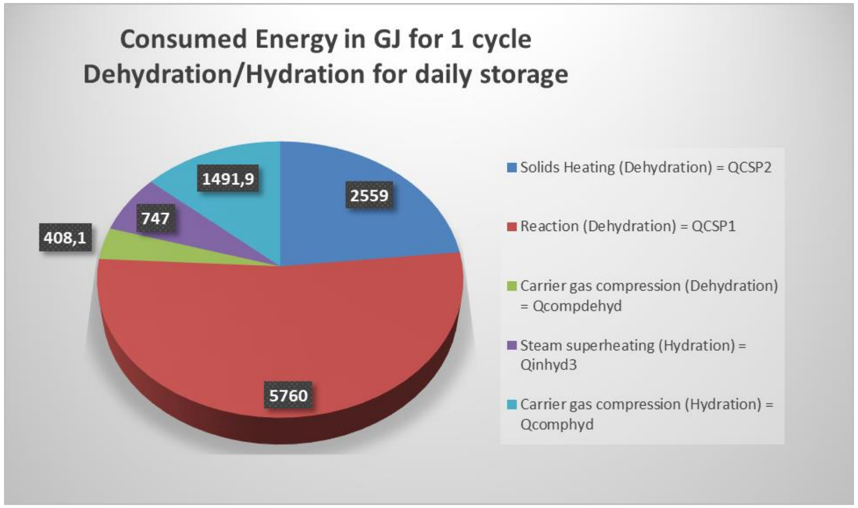


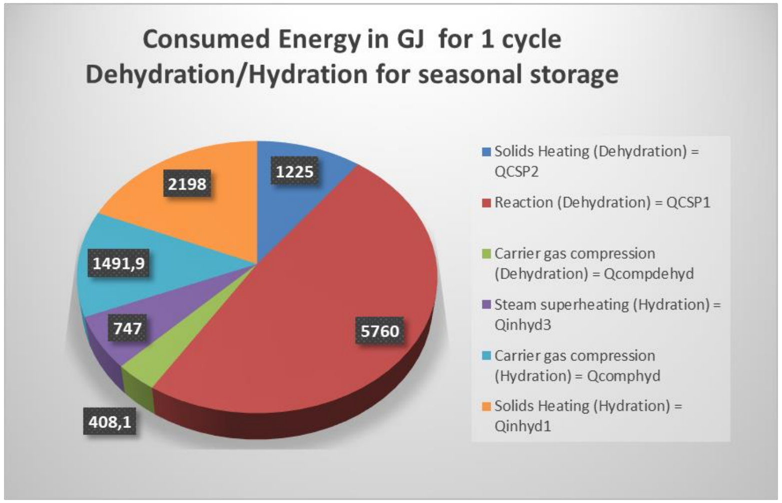
REACTION SELECTION – STORAGE DENSITY CRITERIA (4)

CaO/ Ca(OH)2: main sinks are solid pre-heating and steam vaporisation

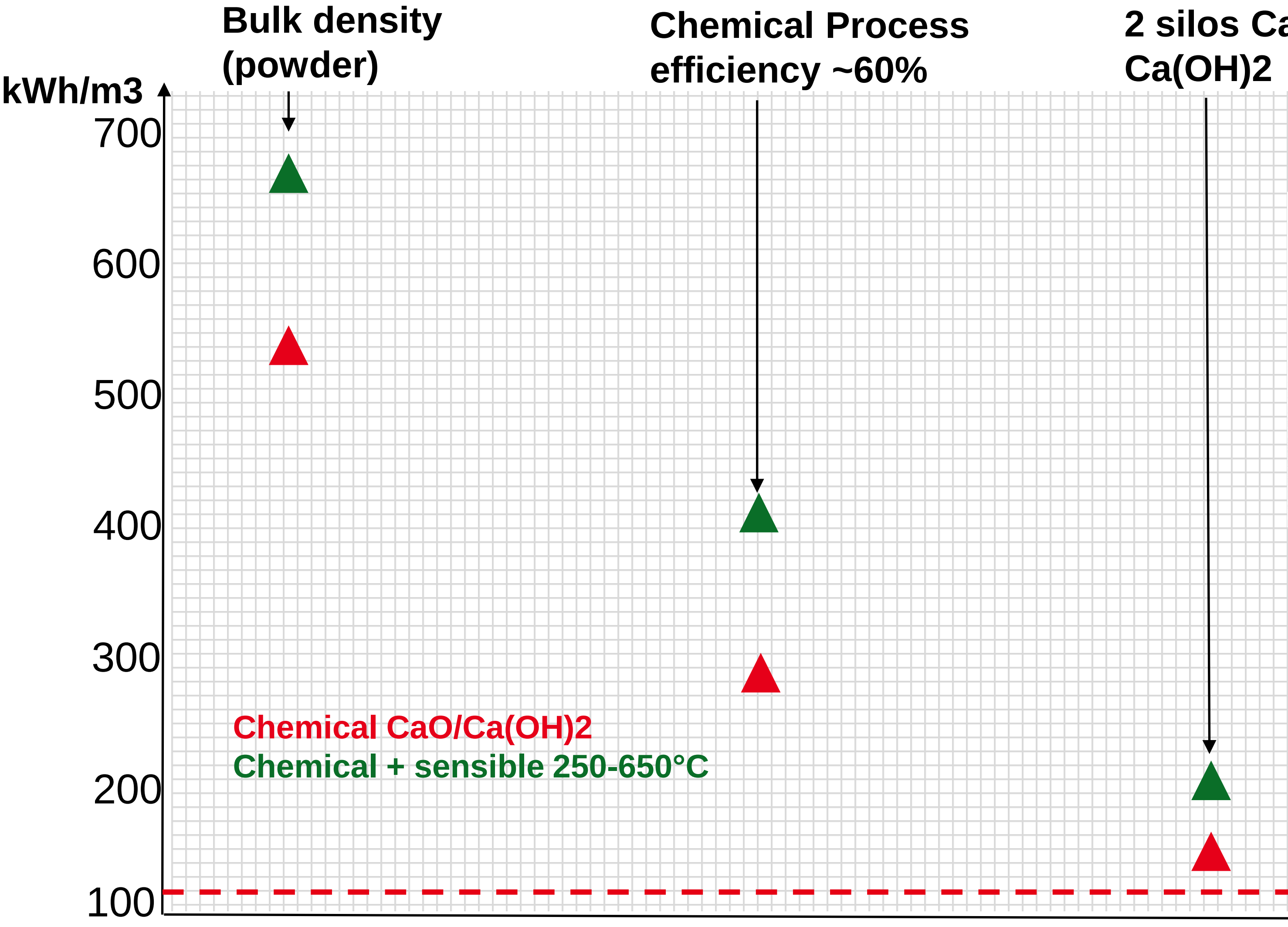
Efficiency: ~60%




Consumed Energy in GJ for 1 cycle
Dehydration/Hydration for daily storage


Consumed Energy in GJ for 1 cycle
Dehydration/Hydration for seasonal storage

REACTION SELECTION – STORAGE DENSITY CRITERIA (5)



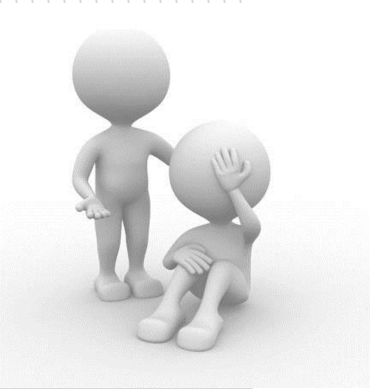
Bulk density (powder)

Chemical Process efficiency ~60%

2 silos CaO / Ca(OH)2

Chemical CaO/Ca(OH)2

Chemical + sensible 250-650°C



Reference: 2 tanks of molten salt 250-560°C

REACTION SELECTION SUMMARY

- **To select a suitable thermochemical reaction for heat storage**
  - Identify the range of parameters (Pg, T) on the reel process
  - If the data are scarce, check the equilibrium curve
  - The temperatures of charge and discharge may be different from the tuning temperature, careful of the realistic range of partial pressure of reactant gas! Large scale reactors are not dilute systems such as thermal balances!
  - Assess the reversibility and cyclability of the reaction at particle scale
  - Perform a simplified mass and heat balance of the whole storage process to evaluate its potential interest and efficiency
  - Deduce a realistic nett volumetric storage density. It will be far away from the wonderful performances you can read in the literature, but that's life…

SOLID/GAS REACTOR SELECTION

TYPES

INTEGRATION IN PROCESS

SOLID/GAS REACTOR SELECTION – TYPES (1)

- **Main issues for heterogeneous gas / solid reactions**
  - Heat transfer
  - Mass transfer
  - Up-scale

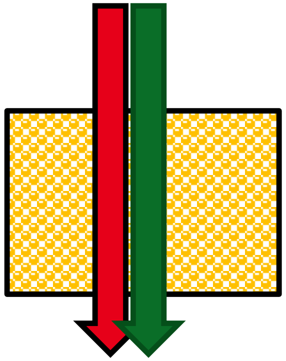
- **Existing technologies:**

Stacked bed	Fluidised beds	Entrained beds
Packed bed	Bubbling fluid. bed	Entrained flow reactor
Structured bed	Circulating fluid. bed	Cyclone
Mobile bed	Spouting fluid. bed	
Rotary kiln		
Rotary screw		

SOLID/GAS REACTOR SELECTION – TYPES (2)

- 3 methods for heat and mass transfer

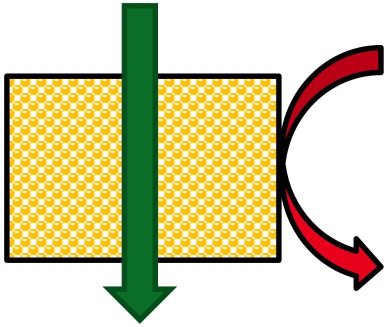
Direct:
Reactant gas part of heat transfer fluid



- Simple
- High heat transfer (large surface)
- Low flexibility
- Upscale medium

Ref: Fixed beds

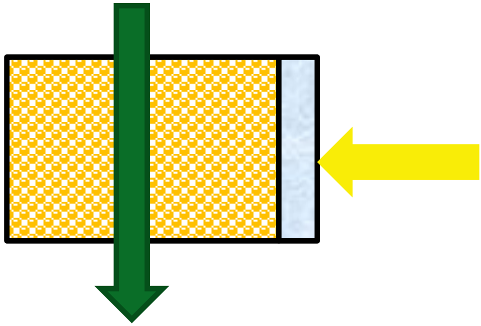
Indirect:
Reactant gas and heat transfer fluid are different



- More complex
- Indirect heat transfer: risk of low transfer
- High flexibility
- Upscale high

Ref: Fluidised beds

Direct sun:
Reactant gas
No heat transfer fluid, direct irradiation



- Very complex (specific to CSP)
- High flexibility
- Upscale low to medium

Solar particle receivers

SOLID/GAS REACTOR SELECTION – TYPES (3)

- Fixed beds are at the same time reactors and storage silos, all the other types need to transport the solid (batch or continuous)

Volume ~Energy

- High storage density (1 silo) but chemical conversion <100% (process temperature requirement)
- Simple technology: no solid movement
- Heat transfer very low: direct→ solid/HTF/reactant compatibility; or sun → low up-scale
- Low HTF velocity → large surface, fluid distribution issue
- DP: low thickness→ several beds → HTF collectors complex; or structured bed → cost?
- Larger inertia if intermittent use

Cold silo

Volume~Energy

Hot silo

Volume~Energy

Volume~Power

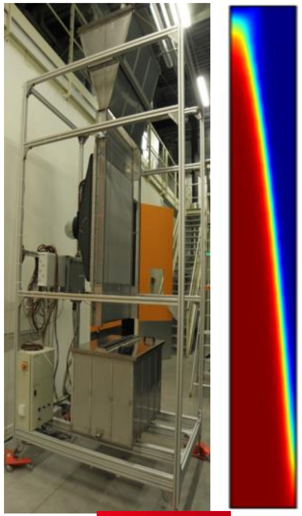
Reactor

- Chemical reaction can be 100% but 2 silos (storage density lower)
- Solid transport and feeding are complex, especially when hot
- The complex and expensive part is limited to a small reactor
- Any kind of heating: direct, indirect, sun
- Any kind of HTF if indirect: no chemical issue gas/HTF or solid/HTF
- Charging and discharging reactors can be different and optimised

SOLID/GAS REACTOR SELECTION – TYPES (4)

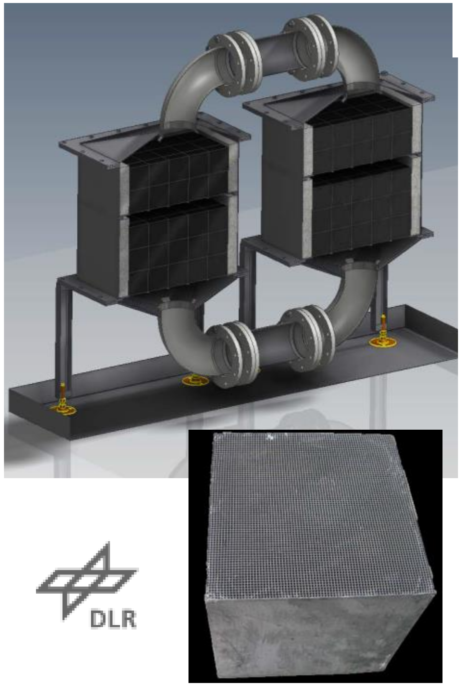
- Direct reactors examples

Packed Bed
$SrBr_2$/
$SrBr_2 . H_2O$
20-70°C

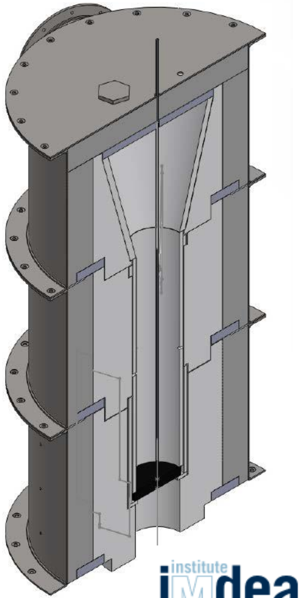


Moving Bed
$MgBr_2$/
$MgBr_2 . 6H_2O$
70-140°C

Packed bed
RD Silica gel
20-60°C



Structured bed
Co_3O_4 /CoO
800-1000°C



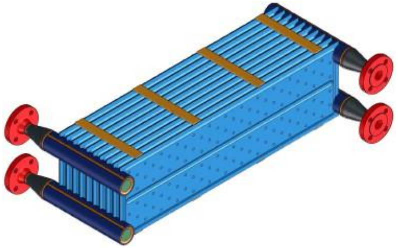
Fluidised bed
Mn_2O_3 /Mn_3O_4
650-1200°C

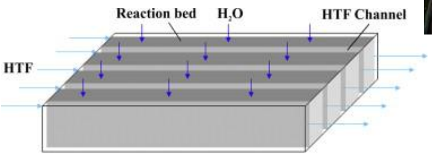
SOLID/GAS REACTOR SELECTION – TYPES (5)

- Indirect reactors examples

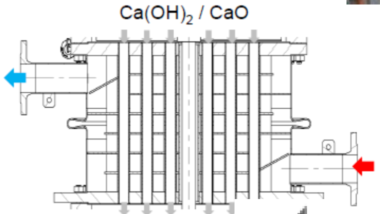
BFB batch
CaO/Ca(OH)2
300-550°C

BFB continuous
CaO/Ca(OH)2
300-600°C





Packed bed / plate heat-exchanger
CaO/Ca(OH)2
300-600°C



Moving bed
CaO/Ca(OH)2
300-600°C

BFB
CaO/Ca(OH)2
300-700°C
7 bars

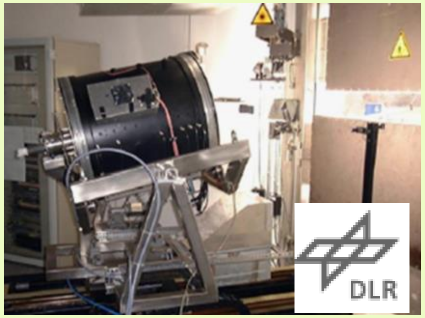
SOLID/GAS REACTOR SELECTION – TYPES (6)

- Solar particle receivers

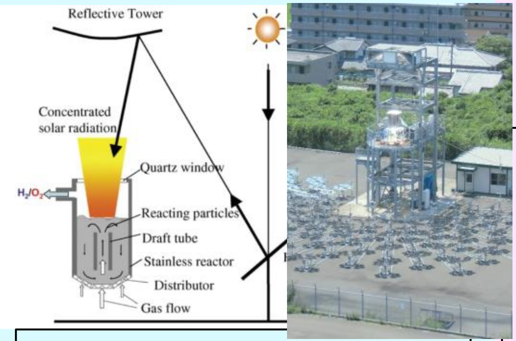
Direct irradiation

Free falling curtain (Sensible heat)

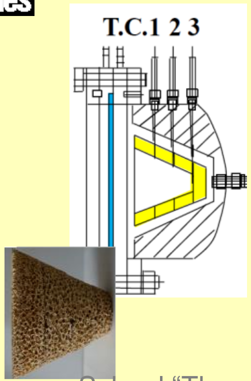
Irradiation Via quartz window

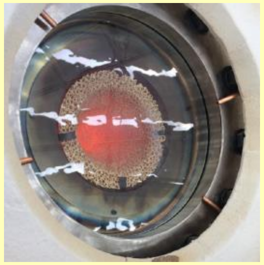


Kiln $CaCO_3$ calcination



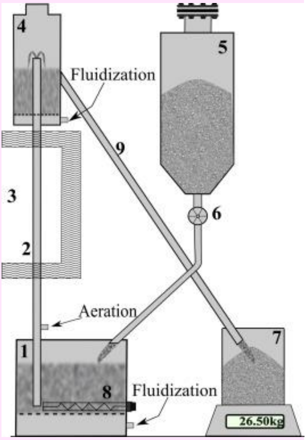
BFB $CaCO_3$ calcination



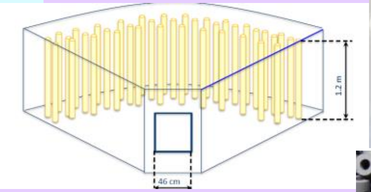


Fixed structured bed H_2 production

Heating Via walls



BFB dense in tubes (sensible heat)

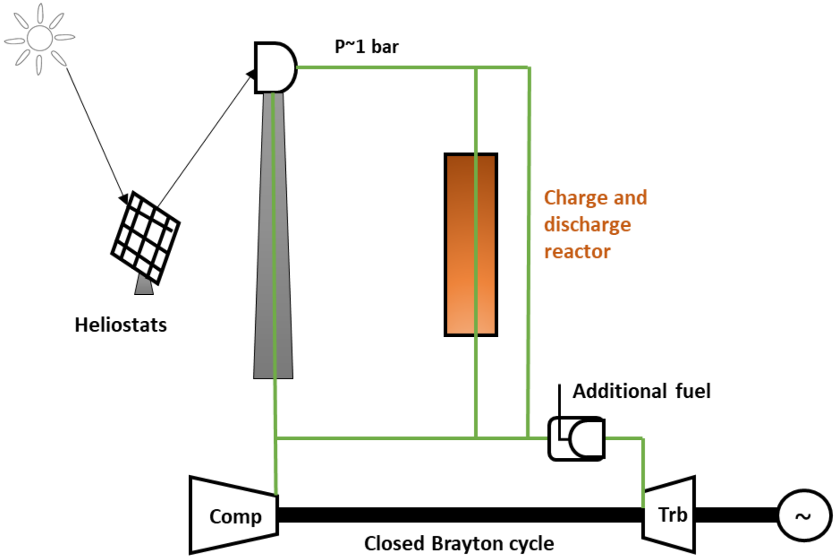


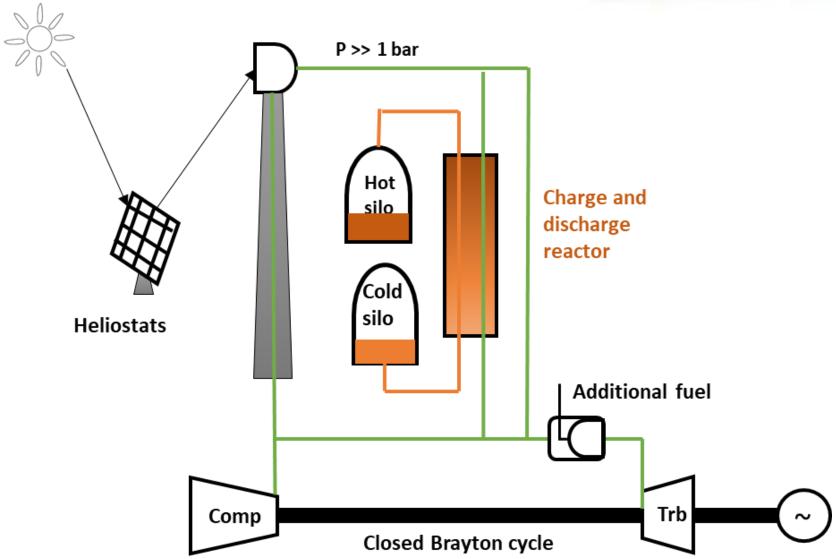
Pellets in Al tubes H_2 production

SOLID/GAS REACTOR SELECTION – INTEGRATION IN PROCESS (1)

- The charge reactor may be different from the discharge reactor: it is /process / solar HTF / power block HTF/ dependant:

Example with one single reactor for charge and discharge:

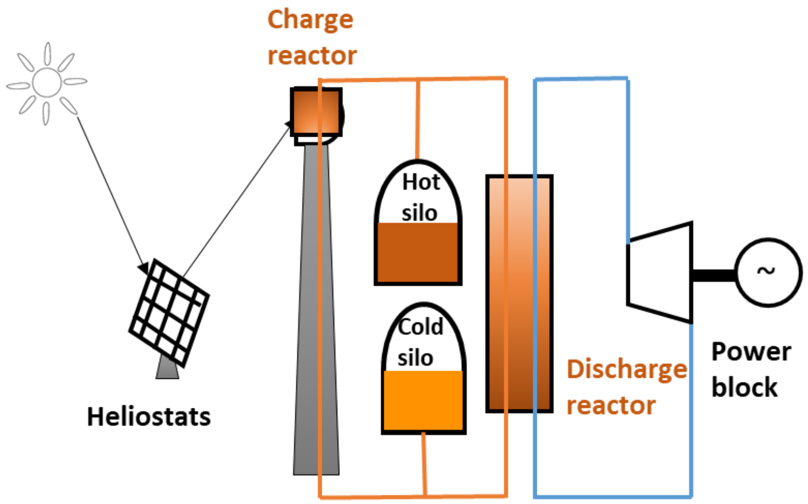




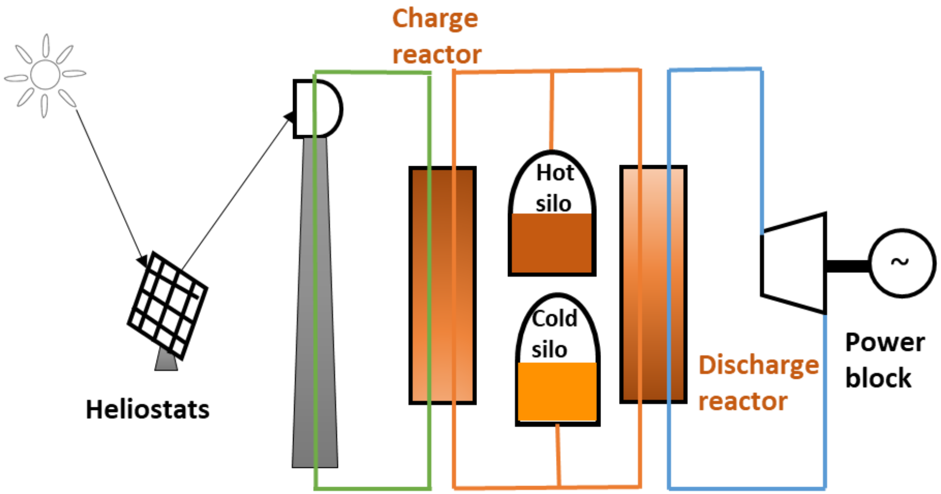
Packed or structured bed

SOLID/GAS REACTOR SELECTION – INTEGRATION IN PROCESS (2)

Example with two reactors for charge and discharge:



Solar particle receiver



SOLID/GAS REACTOR SELECTION – CONCLUSION

- **There is no ideal reactor: there is a best compromise selection that must take into account**
  - ✓ *Material properties,*
  - ✓ *Reaction kinetics,*
  - ✓ *Heat transfer fluid,*
  - ✓ *Reactant gas,*
  - ✓ *Industrial scale target: 1MWh, 10 MWh, 100 MWh or 1000 MWh*
  - ✓ *Process integration,*
  - ✓ *…*

- **The best technology is not the simpliest one!!! Look for industrial technologies, industrials look for the best techno-economic compromises. There are many BFB and CFBs in the range 50-500MW and no fixed beds for instance…**

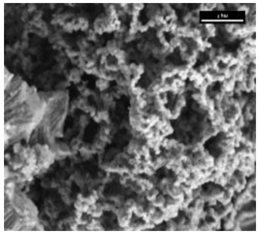
SOLID MATERIAL AD-EQUATION TO THE REACTOR TYPE AND PROCESS

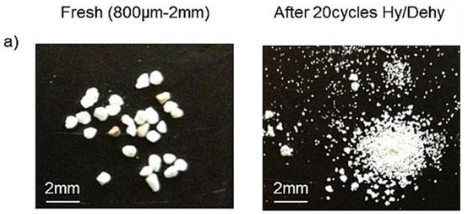
SOLID MATERIAL AD-EQUATION (1)

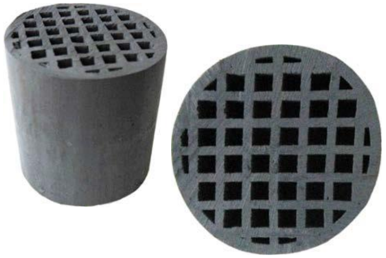
- **Solid material can:**
  - ✓ *Change volume through reaction (swelling)*
  - ✓ *Form a crust after chemical cycles (hydration in fixed bed)*
  - ✓ *Change mechanical strength through thermal of chemical cycles (break)*
  - ✓ *Sinter, agglomerate (operation T too close from softening T)*
  - ✓ *Suffer attrition (case of FB but also pneumatic transport)*
  - ✓ *Have a poor flowability / pourability (case of mobile beds)*
  - ✓ *Fluidise with difficulty (see Geldart classification)*
  - ✓ *Have chemical properties that are not optimal : for instance T discharge too low compared to T charge*
  - ✓ *…etc*
- **The material can be improved to fit better to the reactor / process specifications (careful of the final cost!)**

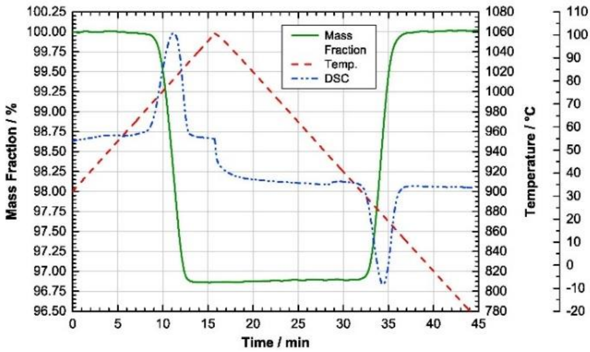
SOLID MATERIAL AD-EQUATION (2)

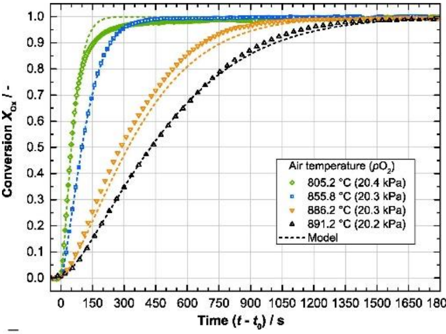
- **Some exemples**
  - Lime nano-coating (SaltX process) → improve pourability and fluidisation
  - Lime-clay composite → improve mecanical strength
  - Cobalt oxyde shaping → improve heat transfer and pressure drop
  - Mn_2O_3 doping with Fe oxide: (Fe/Mn 1:3 mol) → Red: 988°C & Ox 895°C
- **Very important to collaborate between material & reactors specialists for TCS storage**











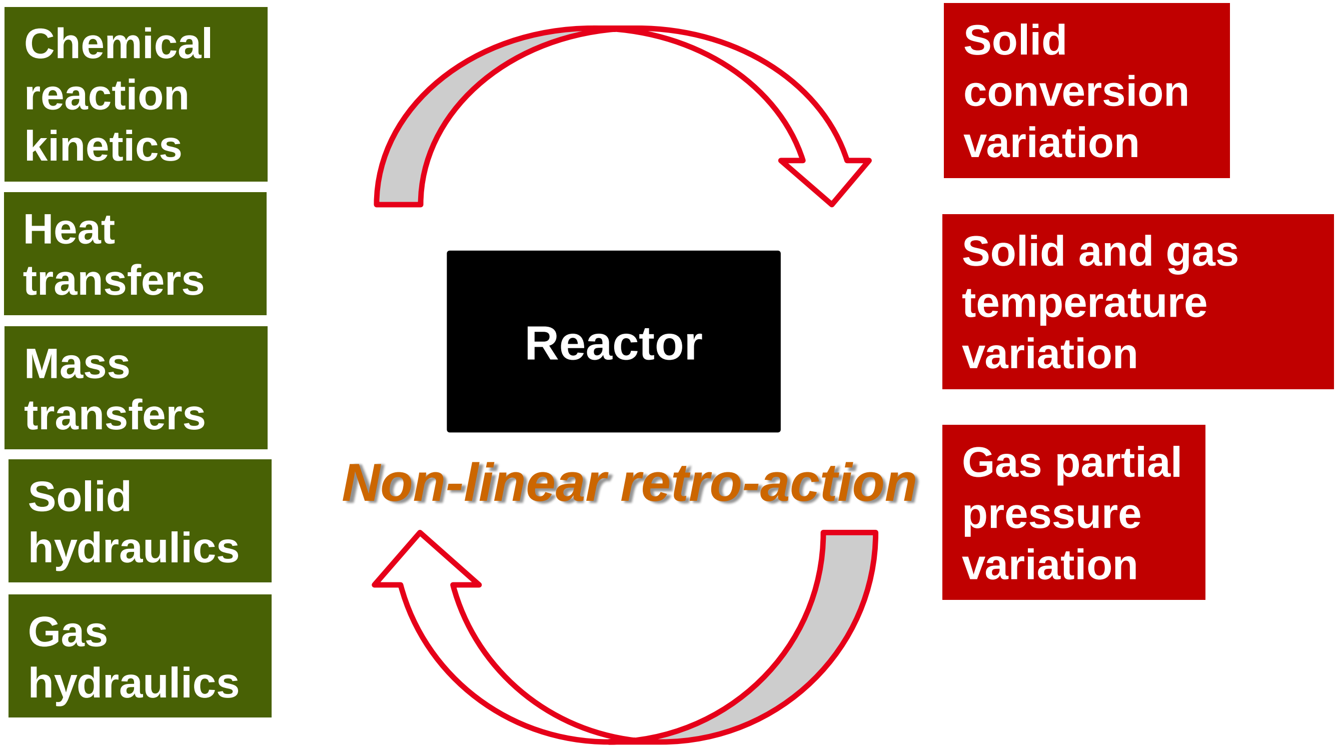
REACTOR MODELLING AND UP SCALING

CASE OF BFB AND CAO/CA(OH)2

CASE OF PACKED BED AND SORPTION

REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (1)

- **Why modelling is so important for TCS reactors?**
  - Comprehension of experimental data at pilot scale is complex
  - Transposition from pilot to industrial scale is not straight
  - Need of upscaling tool



Chemical reaction kinetics

Heat transfers

Mass transfers

Solid hydraulics

Gas hydraulics

Reactor

Non-linear retro-action

Solid conversion variation

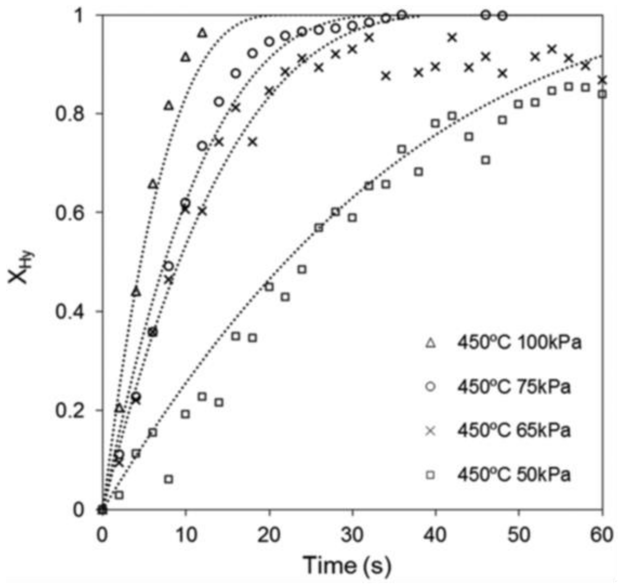
Solid and gas temperature variation

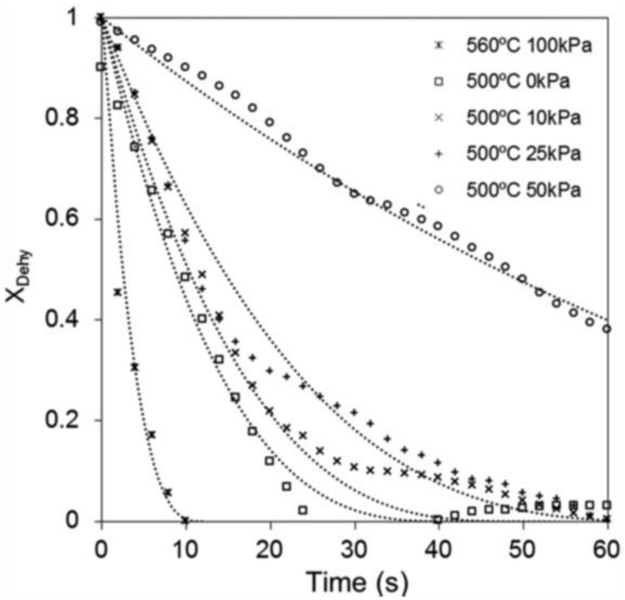
Gas partial pressure variation

REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (2)

- 1st example: CaO/ Ca(OH)$_2$
- **The reaction is fast and allows to select a FB reactor**
  - General industrial criteria for FB: 500 to 1000 kW/m^2 → low parasitics
  - The intrinsic kinetics of the reaction has a standard form:

✓ $$\frac{dX}{dt} = k_o * exp\left(\frac{-Ea}{R*T}\right) * \left(P_v - P_{v,eq}\right)^n * (1-X)^m$$



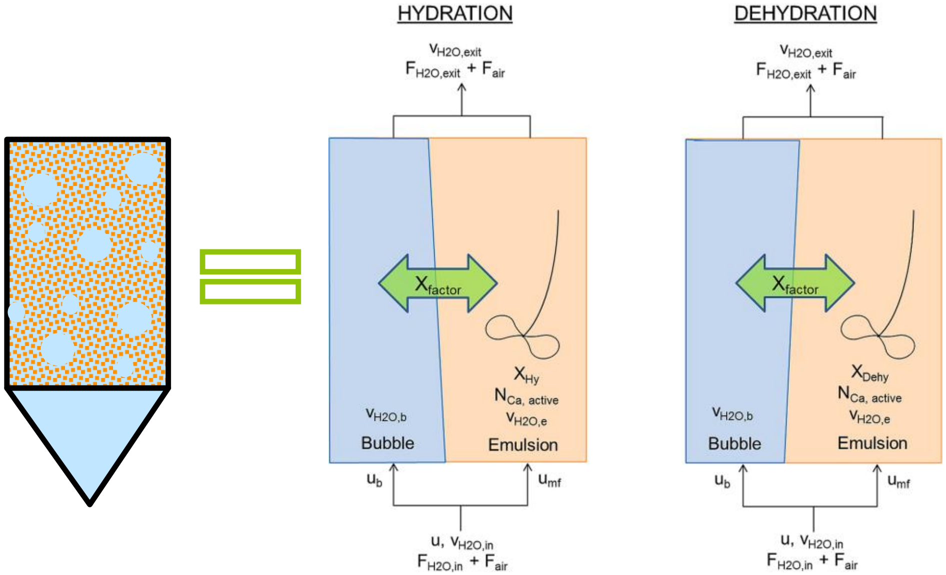


REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (3)

- **At pilot scale, the reactor is a perfectly mixed reactor:**
  - Same temperatures everywhere in the bed
  - Variation of gas pressure along the height of the bed → conversion varies
  - Far away from the minimum velocity of fluidisation, 2 phases of bubble and emulsion → mass transfer limitations between the gas phases are possible

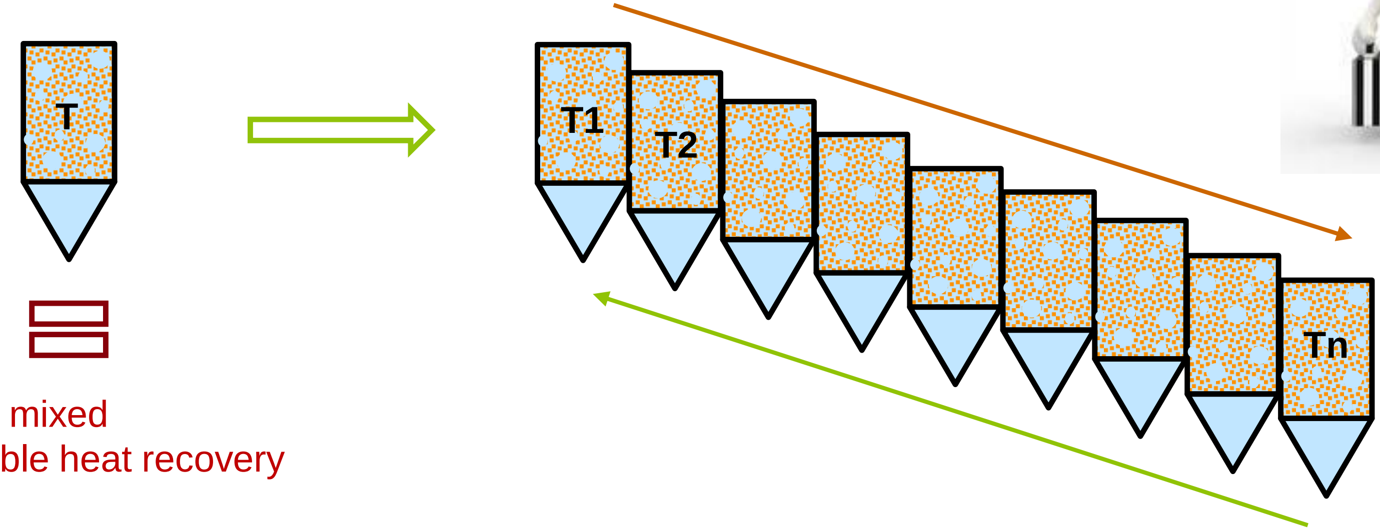
CEA batch and continuous BFB reactors

Experimental tests in batch and continuous BFB validate this limitation when kinetics is fast -> Xfactor ~5



REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (4)

- **At industrial scale the objective is to recover both sensible heat and chemical heat**
  - Sensible heat can cover 20 to 30% of the stored energy

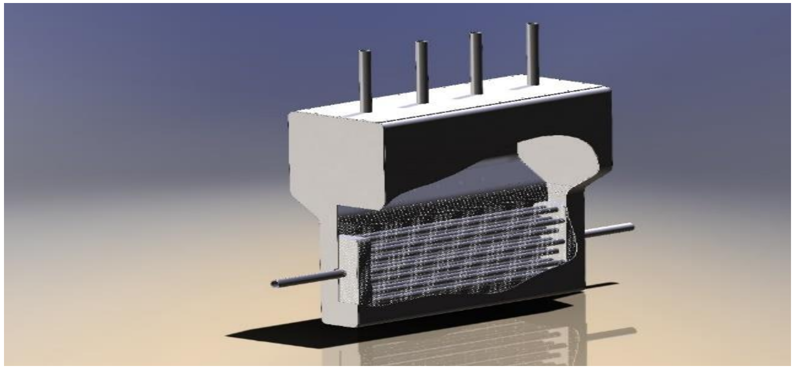


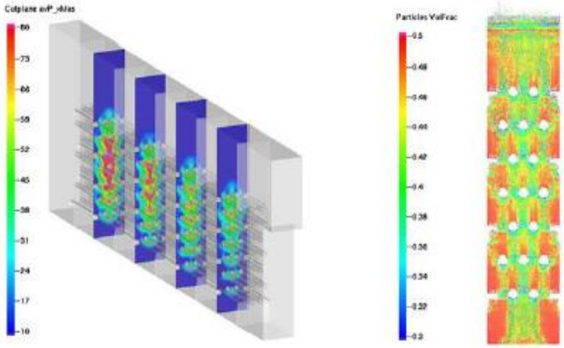
Perfectly mixed
No sensible heat recovery

REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (5)

- **The industrial concept is:**
  - A tube-calander heat exchanger BFB reactor with indirect exchange between the tubes (HTF) and the calander (gas-solid emulsion)
  - The emulsion is flowing from one end to the other

- **The model is simplified :**
  - 1D model along the length of reactor
  - Pure steam (no vertical profile in each section)
  - Perfect mixing in each section in the tube bundle (CFD validation, many data)
  - Plug-flow of emulsion along the length





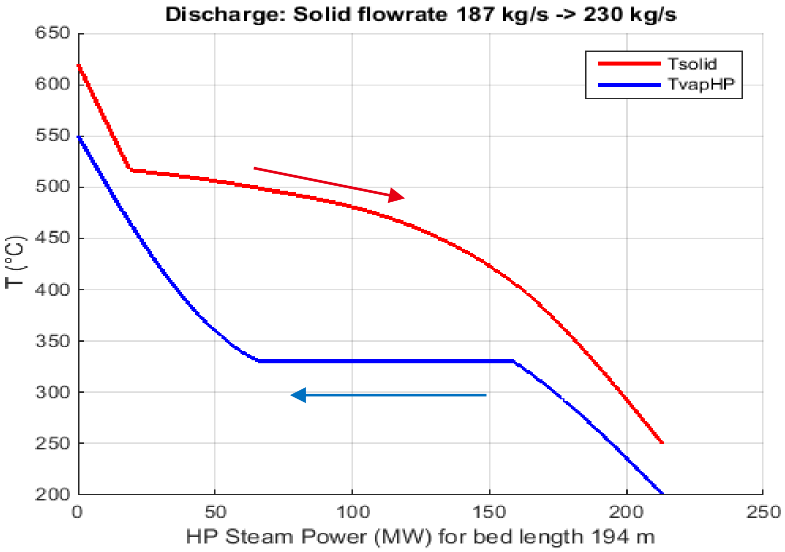
REACTOR MODELLING AND UP SCALING – CAO/CA(OH)$_2$ (6)

Example for hydration reactor:

- 210 MWth
- HTF: HP water 110 bar, 200→550°C
- Inlet solid: Pure CaO, 600→250°C

Result:

- 187 kg/s CaO + inert (25%)
- 100% conversion at the end
- Length: 194 m
- Section: 1,15 x 1,20 (700 tubes)

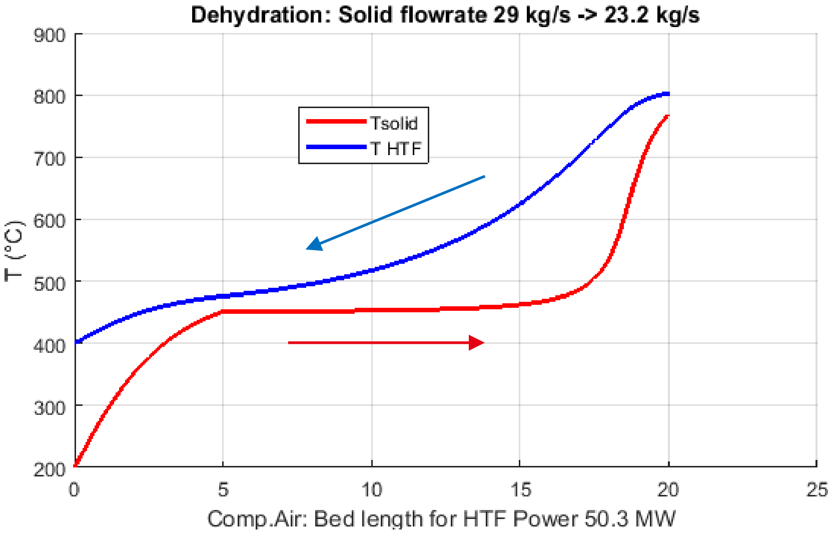


Example for dehydration reactor:

- 50 MWth
- HTF: air 20 bar, 800→400°C
- Inlet solid: Pure Ca(OH)$_2$, 200→780°C

Result:

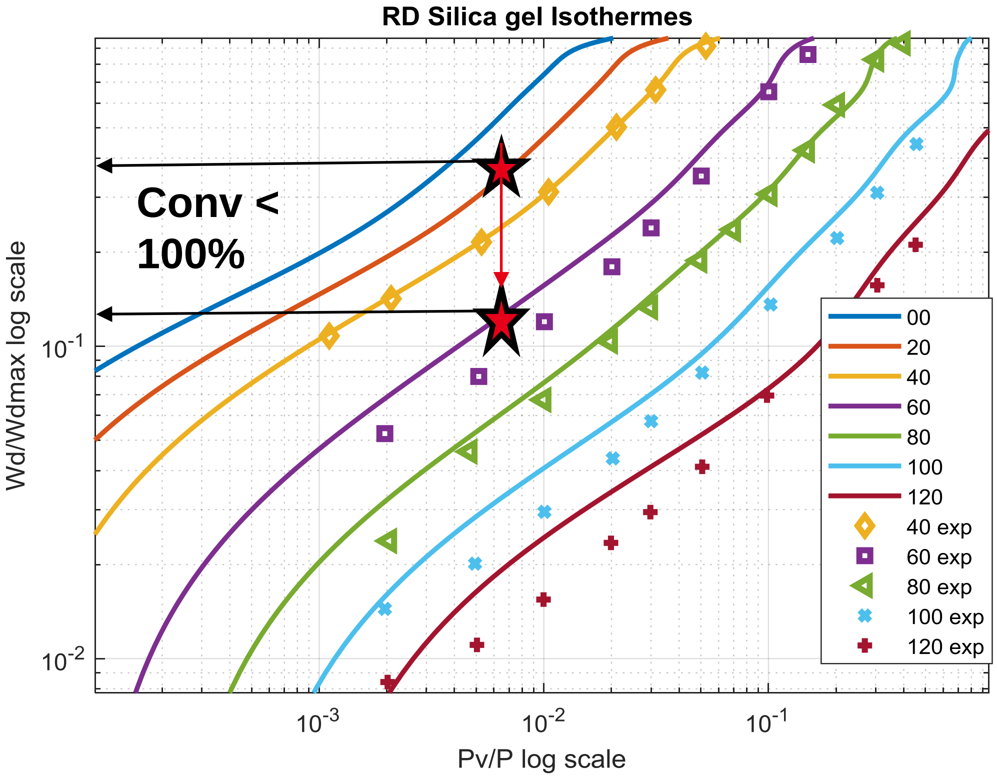
- 29 kg/s Ca(OH)$_2$ + inert (25%)
- 100% conversion at the end
- Length: 20 m
- Section: 1,8 x 2 m (945 tubes)



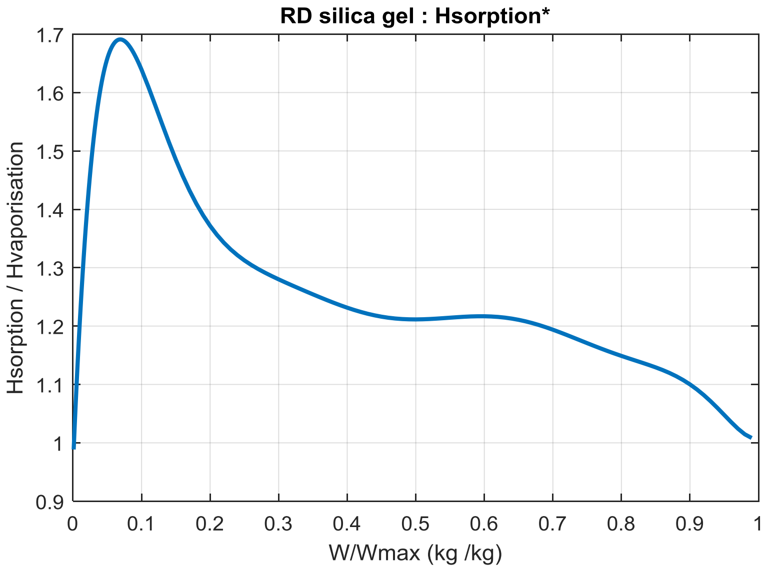
REACTOR MODELLING AND UP SCALING – SORPTION (1)

- **2nd case : sorption for cold storage**
  - Adsorption is exothermic and desorption is endothermic
  - Sorption is a surface reaction. The gas molecule must leave the surface site to have it active again → the sorption kinetics is very fast but controlled by the diffusion inside the sorbant grains (Knudsen and Surface diffusion) which is slow
  - The reaction is bi-variant : 3 parameters are relied: partial pressure of gas, temperature and level of sorbant charge X (kg reactant/kg sorbant)
  - The adsorption and desorption are not complete
  - The enthalpy of sorption is close to the enthalpy of vaporisation for water sorption → steam must be 'free' for steam sorption (atmospheric moisture)
  - The enthalpy of sorption varies with the level of charge of the solid sorbant

REACTOR MODELLING AND UP SCALING – SORPTION (2)



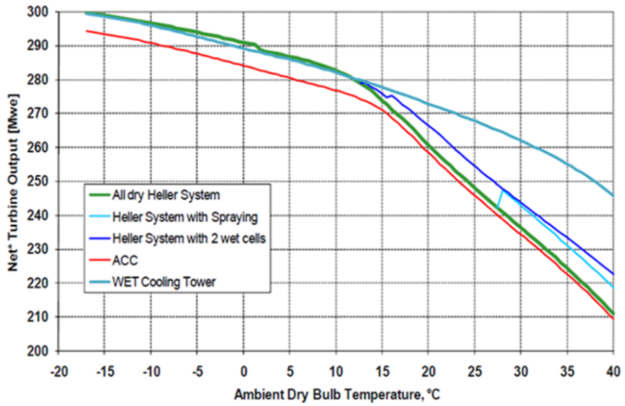
RD silica gel properties

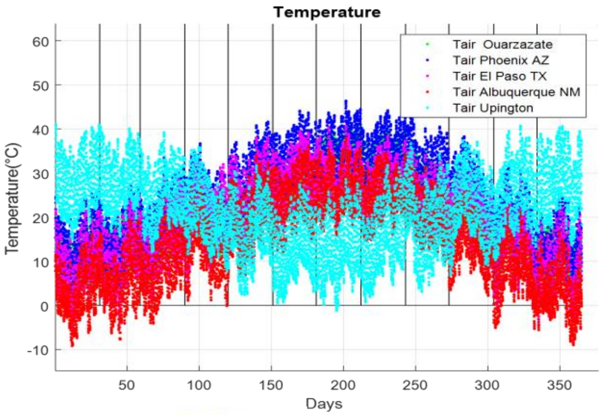


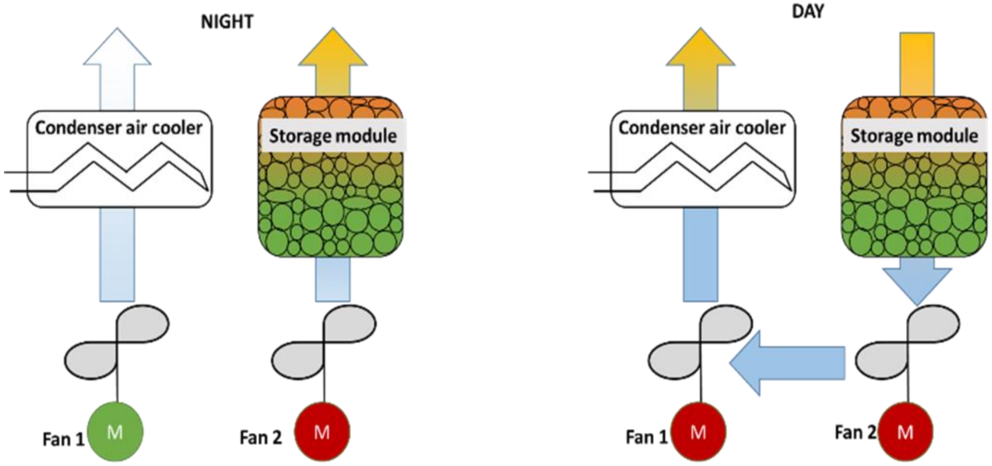
REACTOR MODELLING AND UP SCALING – SORPTION (3)

What is the use for CSP plants?

- Thermodynamic power plants waste 1 to 4 m^3/MWh of water, 90% for the condenser cooling.
- A solution for arid regions is air cooling.
- Steam Turbine Output decreases fast when ambient air is hotter than 15°C whereas Ambiant air can reach 40-45°C during hot periods in arid regions
- The idea is to store cold and moisture of ambiant air during nights (adsorption) and cool hot air during days (desorption)

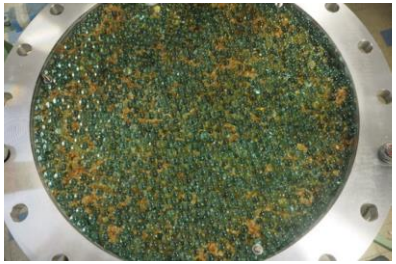


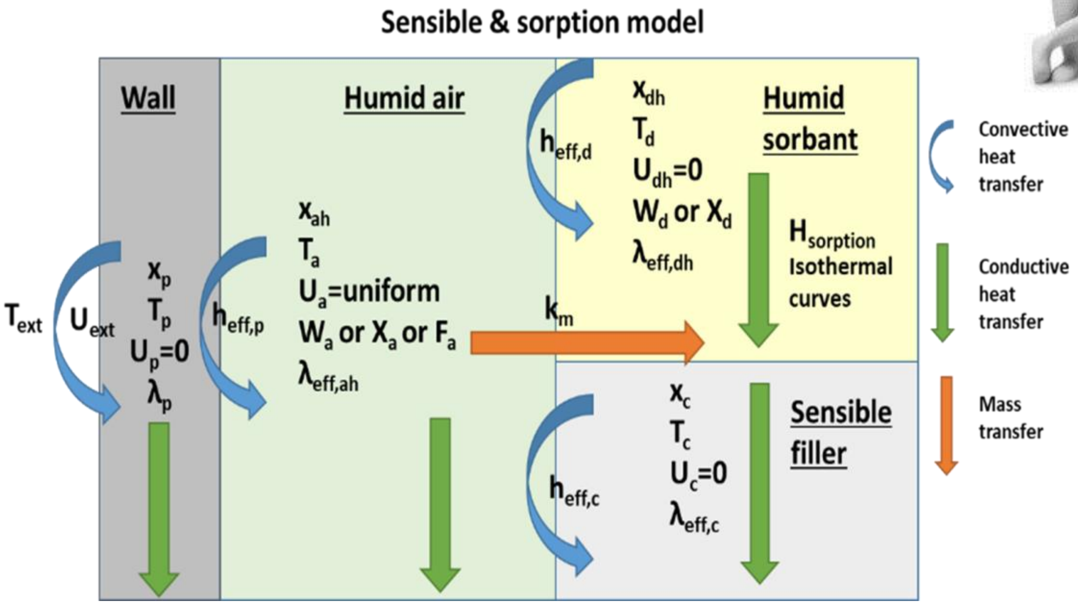




REACTOR MODELLING AND UP SCALING – SORPTION (4)

- Sorption selection: desorption <50°C → RD silica gel or zeolite Z01, 02 or 05
- Low DP + sensible storage : sensible material (lass beads at pilot scale)
- Reactor: slow kinetics + ambiant air → packed bed of sorbant and sensible material
- Model of packed bed: 6 phases, 4 temperatures

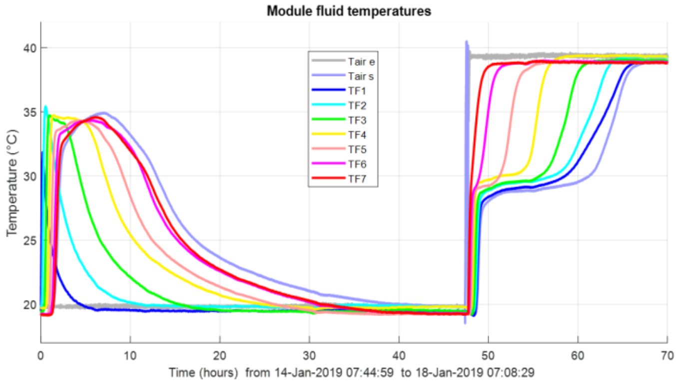


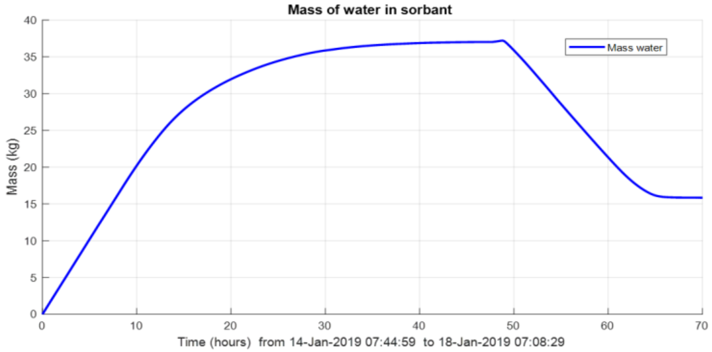


Sensible & sorption model

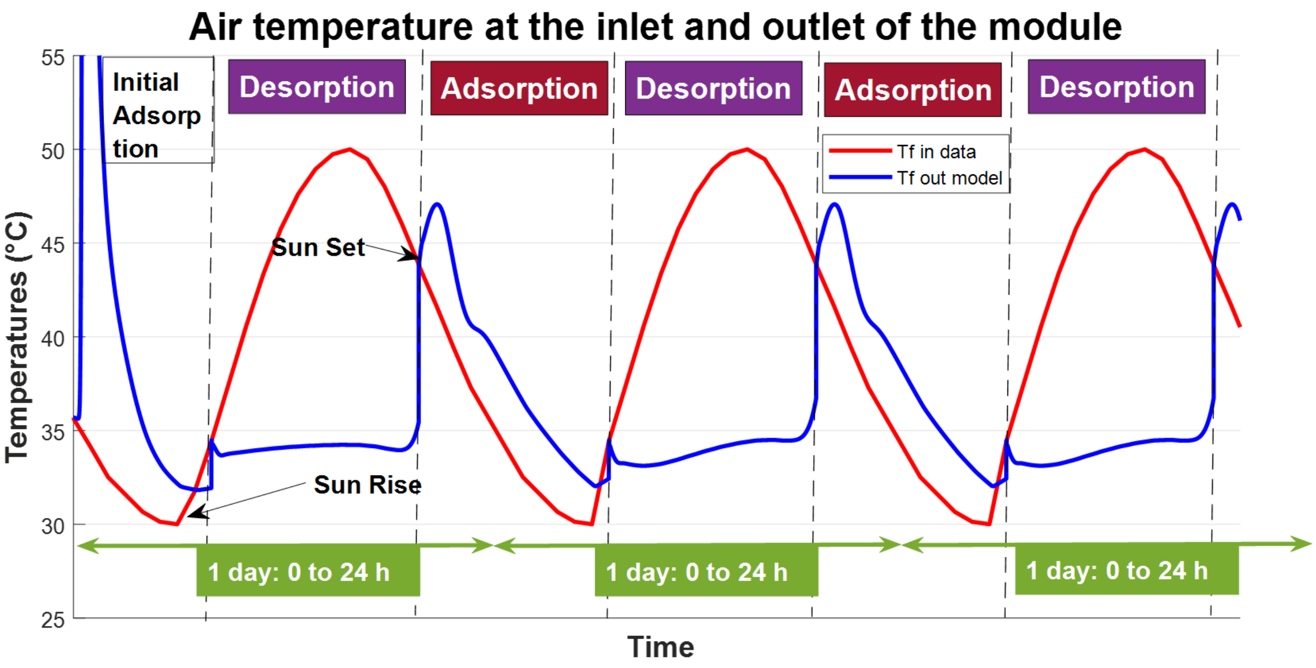
REACTOR MODELLING AND UP SCALING – SORPTION (5)

Exp results of a sorption at Pv/P=0,007, Tad=20°C Tdes=40°C





Model prediction
Air 30→ 50°C
Pv/P~cte



Solar Facilities for the European Research Area

CONCLUSION

THERMOCHEMICAL HEAT STORAGE CONCLUSION (1)

- **Developing a TCS concept for CSP is a challenging and iterative process that must identify and characterise:**
  - A chemical reaction
  - The range of realistic operations
  - The integration in the whole CSP process, the links with solar HTF, power block HTF, solid storage, gas storage, minimize heat wastes….
  - One or 2 reactors technologies
  - The ad-equation of the solid properties with the whole process
  - A model coupling chemical reaction, heat and mass transfers and hydraulics: very needed for understanding and upscaling
  - Evaluate the storage process at economic and environmental level: what is the final advantage?
- **This is very important to have close relationship between material, reactors and process experts.**

THERMOCHEMICAL HEAT STORAGE CONCLUSION (2)

- **When applying TCS to a process, never forget the main advantages:**
  - Long-term chemical storage (a few weeks to a few month)
  - Sensible heat stored longer in a solid (low conductivity, no convection)
  - Sensible heat temperature can be high (~800°C for lime, >1000°C for RedOx)
  - Heat easy to transport = transport of a solid → many transverse applications are possible (ex: industry → District heating)
  - Higher storage density → useful when space is limited

Thank you for your attention!