SolarPACES

Thermochemical processing & storage – Part II

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Promising and well researched Thermochemical Cycles

	Steps	Maximum Temperature (° C)	LHV Efficiency (%)
Sulphur Cycles			
Hybrid Sulphur (Westinghouse, ISPRA Mark 11)	2	900 (1150 without catalyst)	43
Sulphur Iodine (General Atomics, ISPRA Mark 16)	3	900 (1150 without catalyst)	38
Volatile Metal Oxide Cycles			
Zinc/Zinc Oxide	2	1800	45
Hybrid Cadmium		1600	42
Non-volatile Metal Oxide Cycles			
Iron Oxide	2	2200	42
Cerium Oxide	2	2000	68
Ferrites	2	1100 – 1800	43
Low-Temperature Cycles			
Hybrid Copper Chlorine	4	530	39

Efficiency comparison for solar hydrogen production from water (Siegel et al., 2013)*

Process	T [°C]	Solar plant	Solar-receiver + power [MW_{th}]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	13%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%
Hybrid Sulfur-process	850	Future Solar tower	Particle 700	50%	57%	76%	22%
Hybrid Copper Chlorine-process	600	Future Solar tower	Molten Salt 700	44%	57%	83%	21%
Metaloxide two step Cycle	1800	Future Solar dish	Particle Reactor < 1	52%	77%	62%	25%

**N.P. Siegel, J.E. Miller, I. Ermanoski, R.B. Diver, E.B. Stechel, Ind. Eng.Chem. Res., 2013, 52, 3276-3286.*

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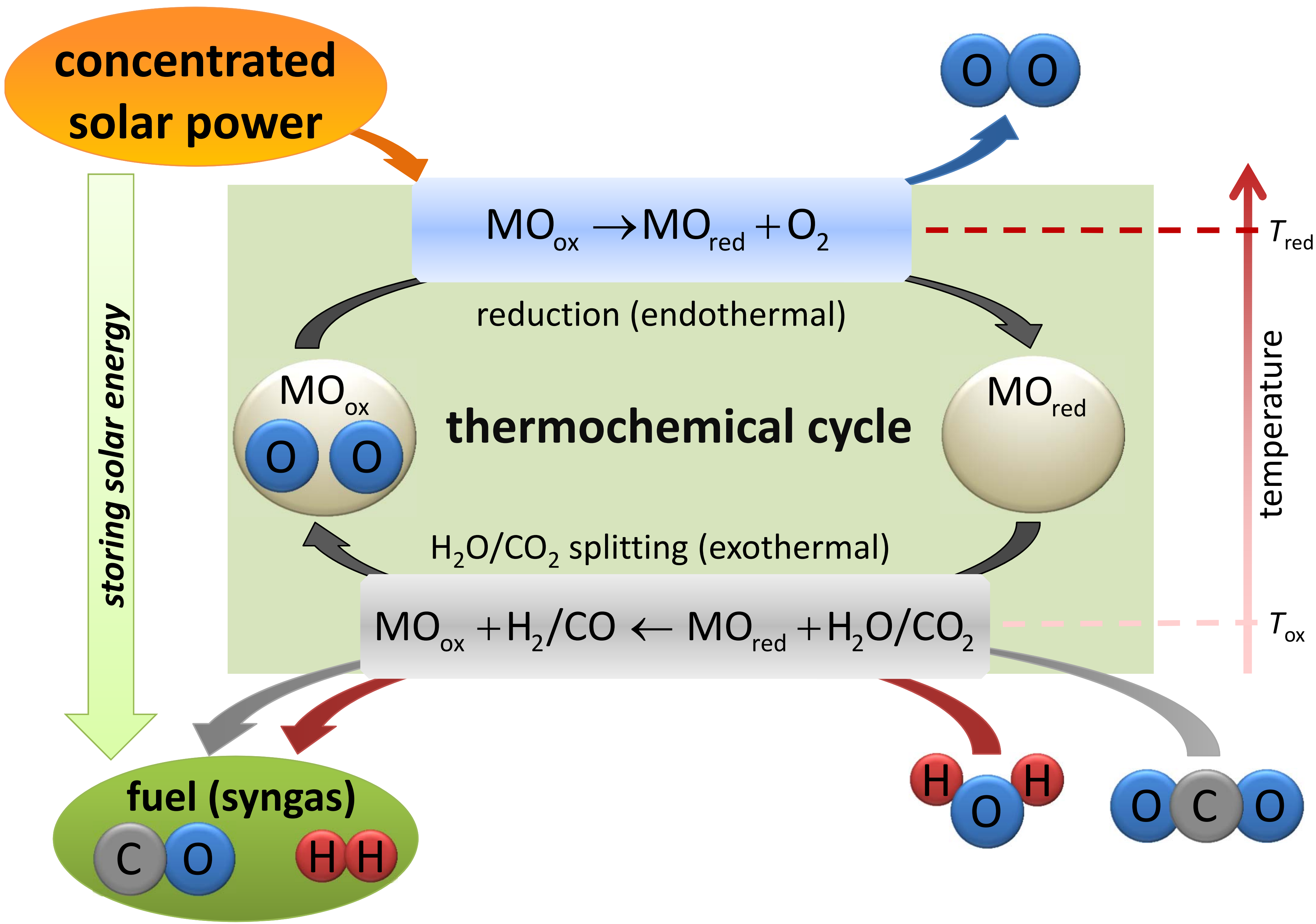
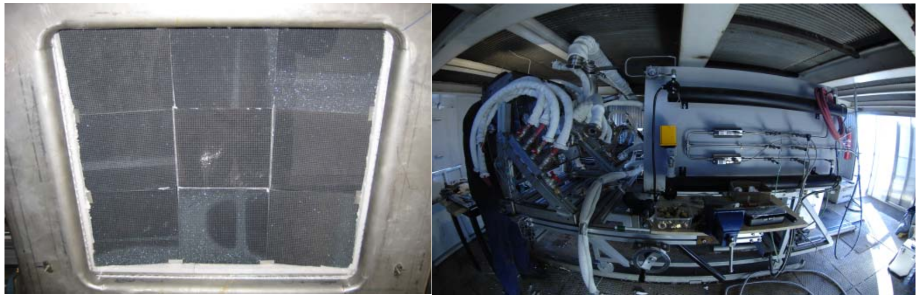
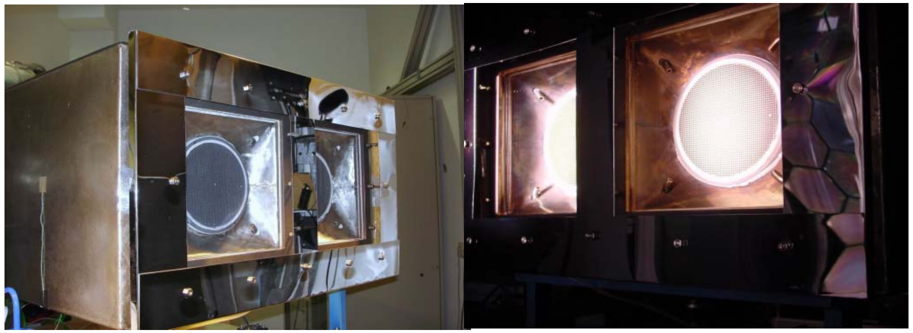

concentrated solar power
O O
$MO_{ox} \rightarrow MO_{red} + O_2$
T_{red}
reduction (endothermal)
storing solar energy
MO_{ox}
O O
thermochemical cycle
MO_{red}
temperature
H_2O/CO_2 splitting (exothermal)
$MO_{ox} + H_2/CO \leftarrow MO_{red} + H_2O/CO_2$
T_{ox}
fuel (syngas)
C O
H H
H O H
O C O

Hydrosol technology scale-up



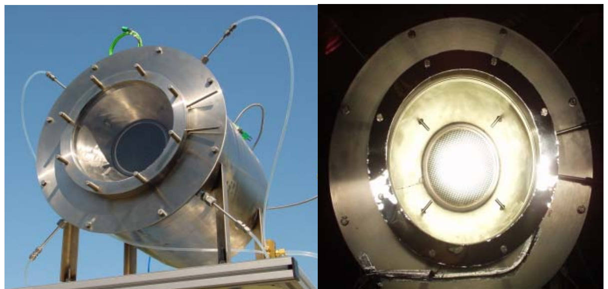
2008:

Pilot reactor (100 kW)



2005:

Continuous H_2 production



2004:

First solar thermochemical

H_2 production

PSA solar tower

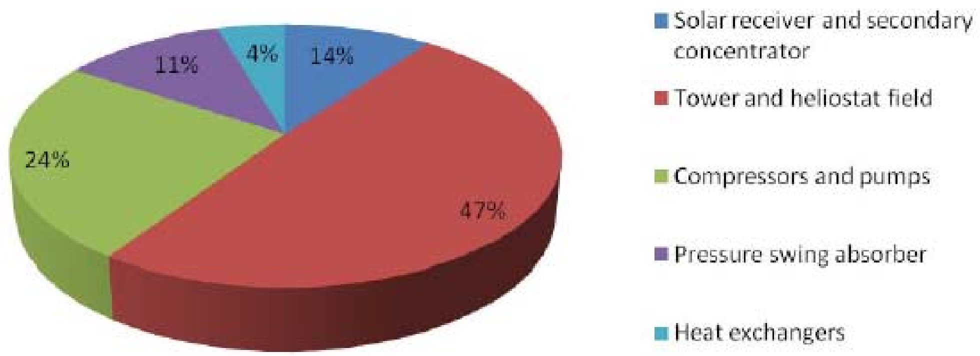
DLR solar furnace

Solar fuels from thermochemical cycles- HYDROSOL 3D project- Main results Economic analysis of the demonstration plant

- Demonstration plant thermal energy input: 1 MW
- Cost calculation of the new designed reactor was carried out.
- Cost calculation of the overall process units was performed.
- More than half of process investment results from the solar system.

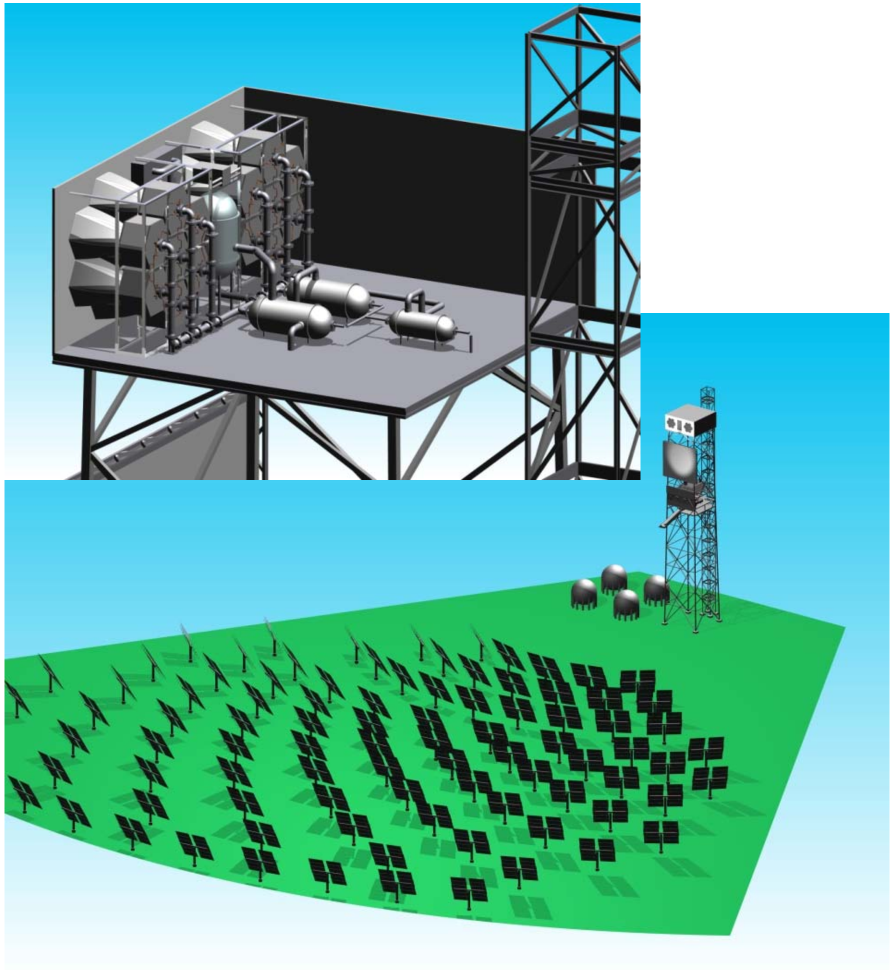
Component	Number of units	Cost per unit [€]	Total Cost [€]
Quartz plates	14	600	8400
Reactor modules	14	3000	42000
Secondary concentrator	14	12000	168000

Solar part incl. receiver-reactor[€]	1,406,847
Pressure swing absorber [€]	265,000
Compressors and pumps [€]	584,054
Heat exchangers [€]	110,493
Total cost [Mio. €]	**2.366**

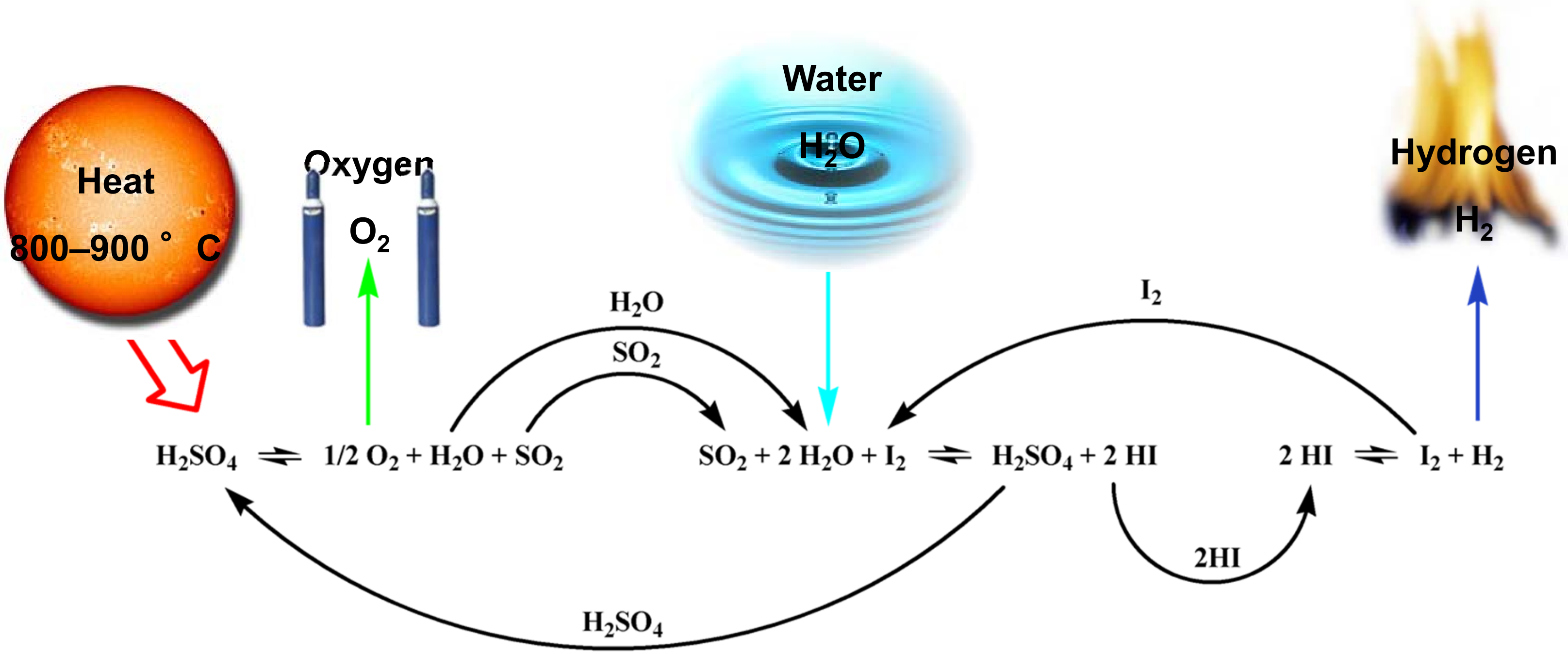


Hydrosol Plant - Design for CRS tower PSA, Spain

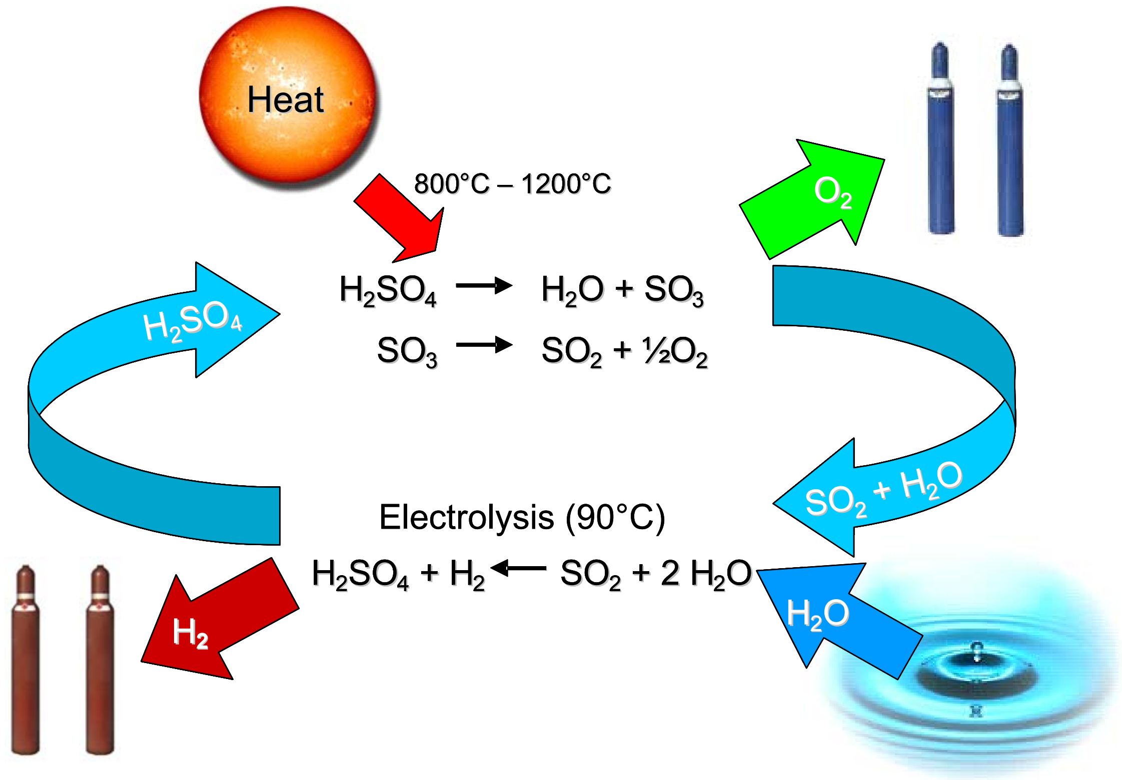
- European FCH-JU project
- Partner: APTL (GR), HELPE (GR), CIEMAT (ES), HYGEAR (NL)
- 750 kW_{th} demonstration of thermochemical water splitting
- Location: Plataforma Solar de Almería, Spain, 2015
- Use of all heliostats
- Reactor located on the CRS tower
- Storage tanks and PSA on the ground

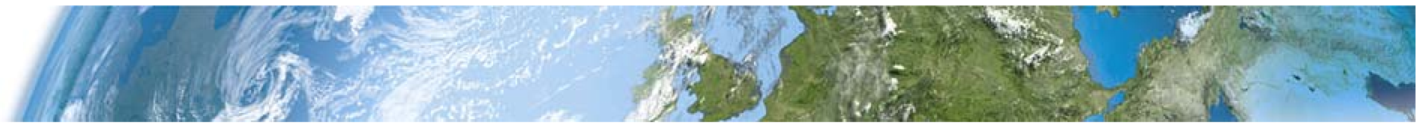


Sulphur-Iodine Process

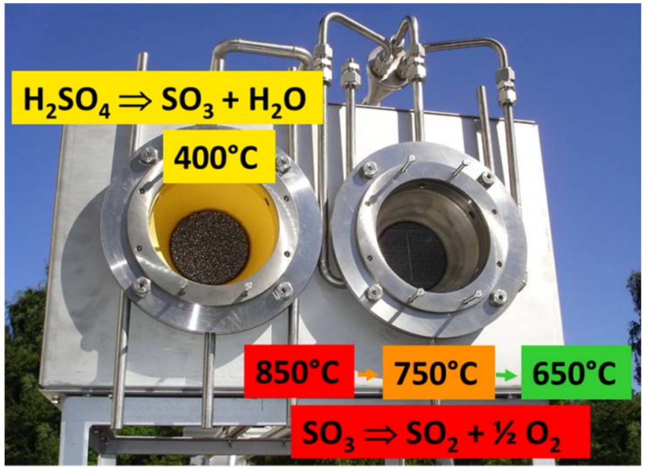


Hybrid Sulphur Cycle

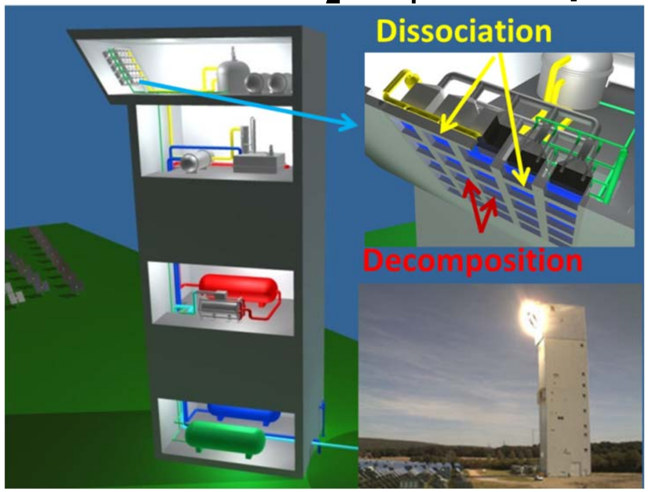




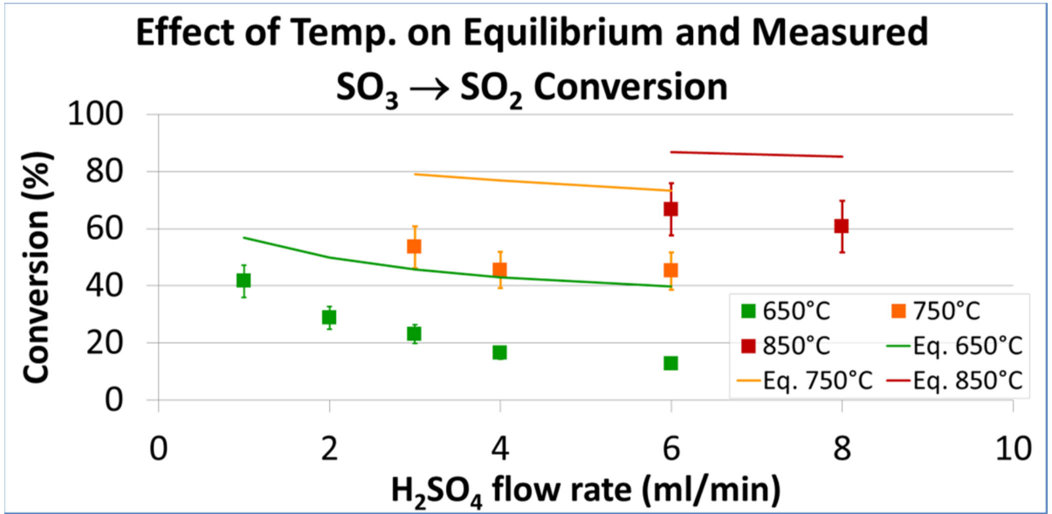
Sulfuric acid decomposition on sun using a solar furnace



A dual chamber H_2SO_4 decomposer



Conceptual scale up of a modular decomposer on a solar tower



- **Process and decomposer refinement based on test data**
- **Lower decomp. temperature to reduce solar installation cost**

D. Thomey et al., Int. Journal of Hydrogen Energy (2012)

Thermochemical Energy Storage

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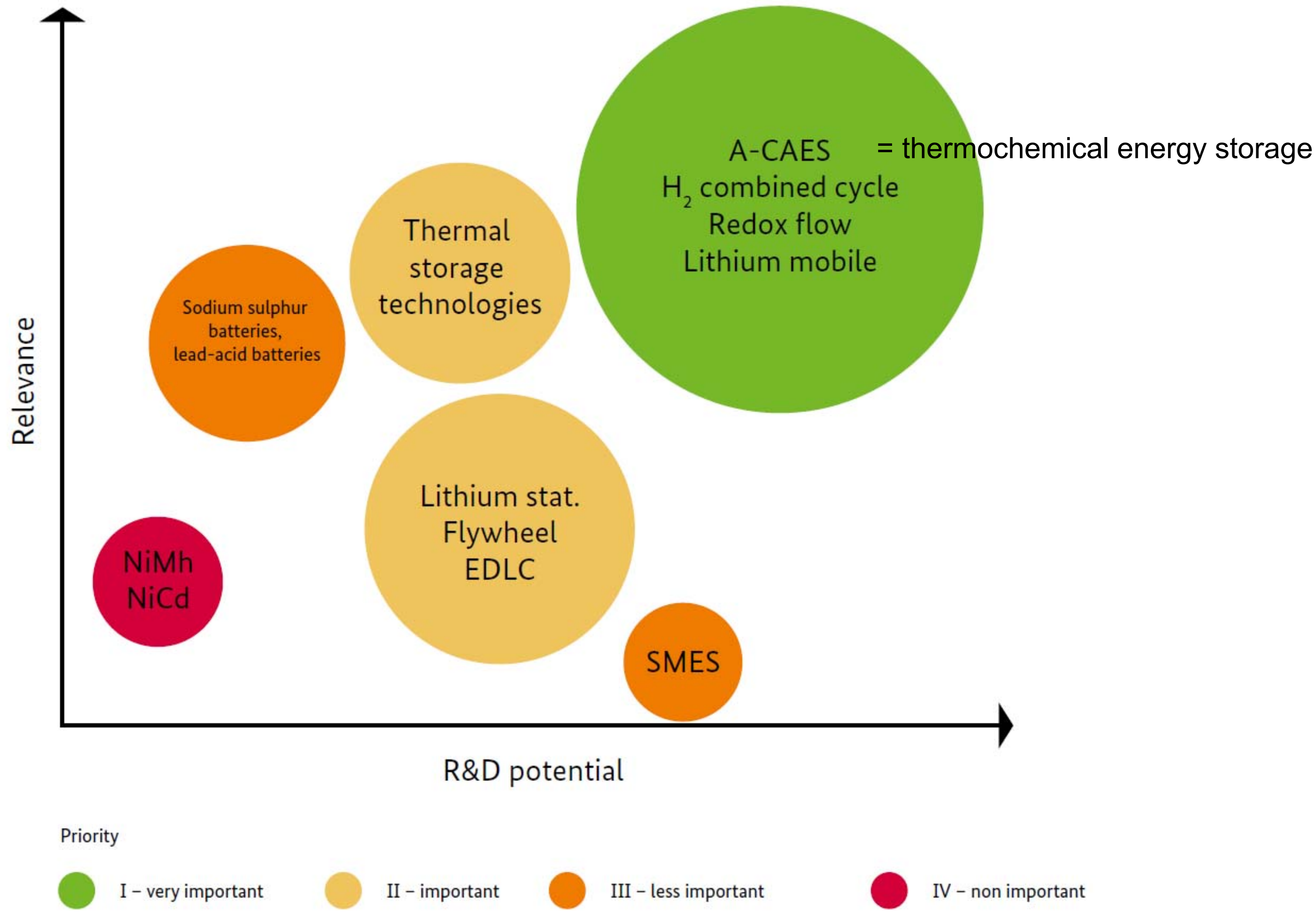
6th Energy Reserach Programme



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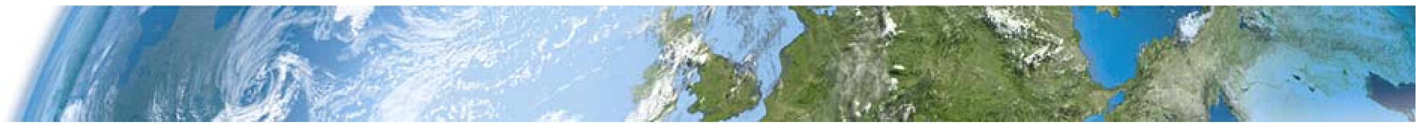
Thermochemical heat storage can provide very high energy storage densities

Technology	Energy Density (kJ/kg)
Gasoline	45000
Sulfur	12500
Cobalt Oxide	850
Molten Salt (Phase Change)	230
Molten Salt (Sensible)	155
Lithium Ion Battery	580
Elevated water Dam (100m)	1

- **High energy densities with low storage cost**
- **Ambient and long term storage**
- **Transportability**



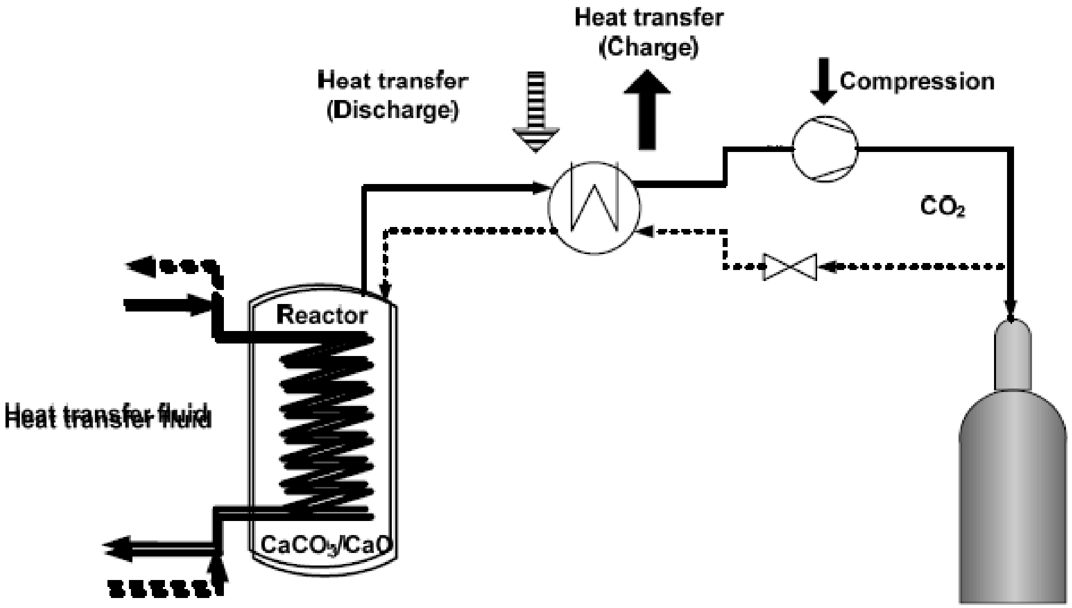
ThermoChemical Storage (TCS)

Reaction	No	ΔH (kJ/mol_{react})	T (°C)
$NH_3 + \Delta H \leftrightarrow ½ N_2 + 3/2 H_2$	(1)	49	593
$Ca(OH)_2 + \Delta H \leftrightarrow CaO + H_2O$	(2)	100	521
$CaCO_3 + \Delta H \leftrightarrow CaO + CO_2$	(3)	167	896
$2\,Co_3O_4 + \Delta H \rightarrow 6\,CoO + O_2$	**(4)**	**202**	**890**

- **HSM: NH_3, Solids: $Ca(OH)_2$, $CaCO_3$, Co_3O_4 respectively. HTF: ?**
- Among the gas-solid reactions, mentioned above "… Oxide based systems have an advantage because air is used as both the heat transfer fluid and the reactant which eliminates the requirements to either store CO_2 or to evaporate water in the other TCS alternatives…".

Thermo-Chemical energy storage - system

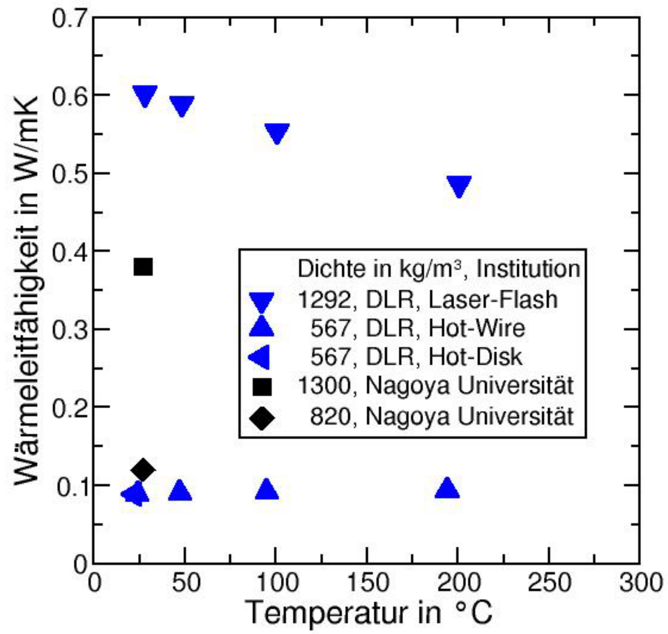
- Complex system, storage of gaseous reactant necessary
- Additional energy required (for compression)



Thermo-Chemical energy storage - material

- **Low thermal conductivity** of powder bed
- Thermal power?
- Reactor design

- **Material costs**
  - Amount of „useful“ cycles determines the amortization periode
    - Seasonal storage
    - Day / Night storage
    - Continuous operation (sorption system)



F. Schaube et al., High Temperature TC Heat Storage for CSP using Gas-Solid Reactions, Proceedings of SolarPaces 2010, Perpignan, France (2010)

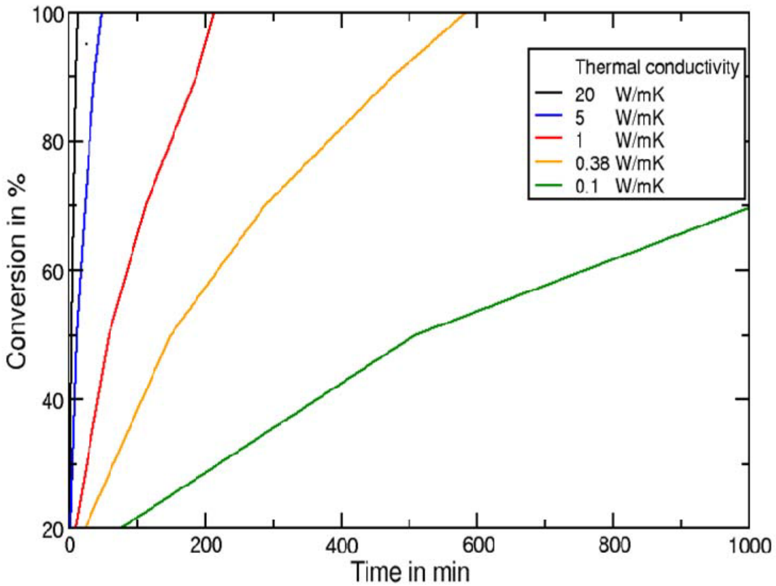
Key factors: Development of reactor systems Process integration

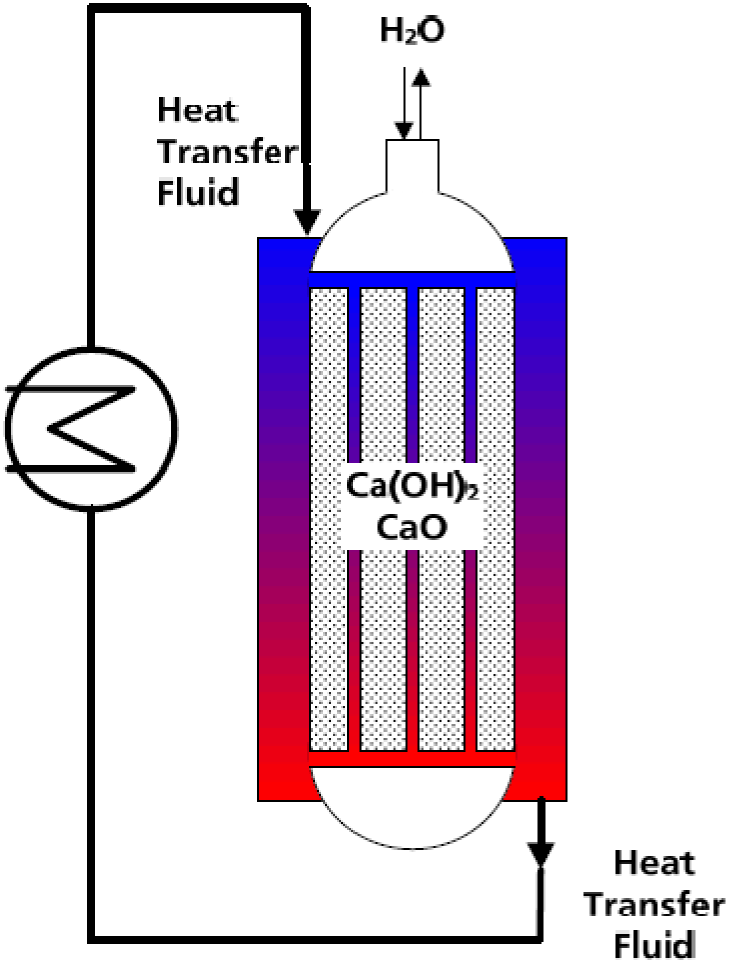
Current activites on Gas-Solid Reactions for heat applications at DLR:

- Competence Center for Ceramics and Storage in Energy Research CeraStorE
- Development of reactor systems:
    - Concept of direct heat transfer
    - $CaO/Ca(OH)_2$
    - Metaloxide Redoxcycles
    - Sulfur Cycles

CaO/Ca(OH)$_2$ system

- Temperatur range: 400 – 600 °
    - CSP plants
- Bed with **low thermal conductivity**

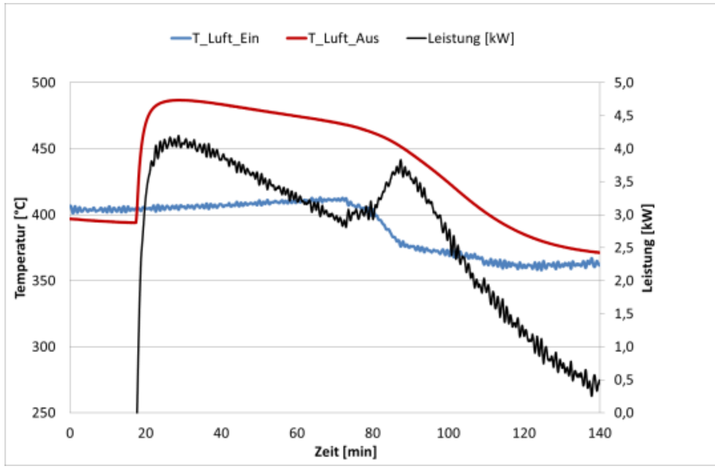


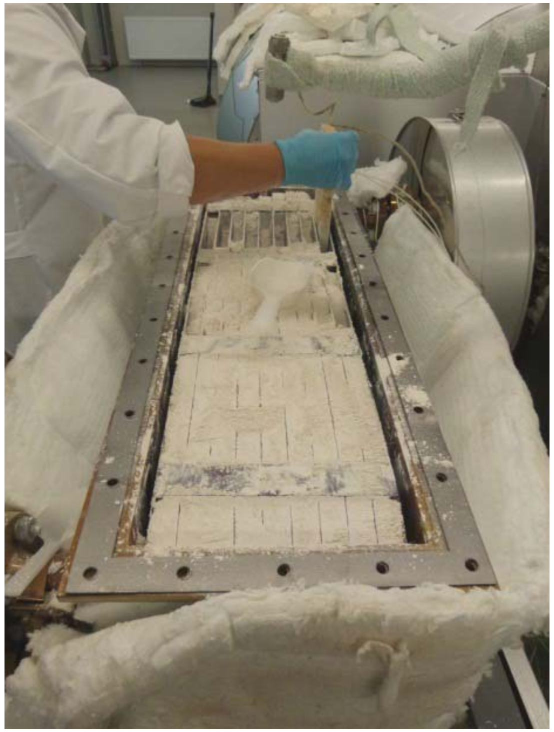


F. Schaube et al., High Temperature TC Heat Storage for CSP using Gas-Solid Reactions, Proceedings of SolarPaces 2010, Perpignan, France (2010)

$CaO/Ca(OH)_2$

- Principle successfully demonstrated in a 10 kW plant in the CeraStorE





RESTRUCTURE

- FP 7 European Project 2012 - 2016
- Redox Cycles with fixed structures: Honeycombs or foams
- Mixed-iron-oxides-based redox materials
- Demonstration of operation in the temperature range of a solar tower: 900-1500° C
- Demonstration of a solar pilot plant of 100 kW
- Identification of investment and operational cost of a 1.5MWe demo plant incorporating the particular TES system and comparison to other storage options.
- Presentation of a suitable strategy for the introduction of the technology into the market.

From TES with sensible heat to TCS with redox oxides

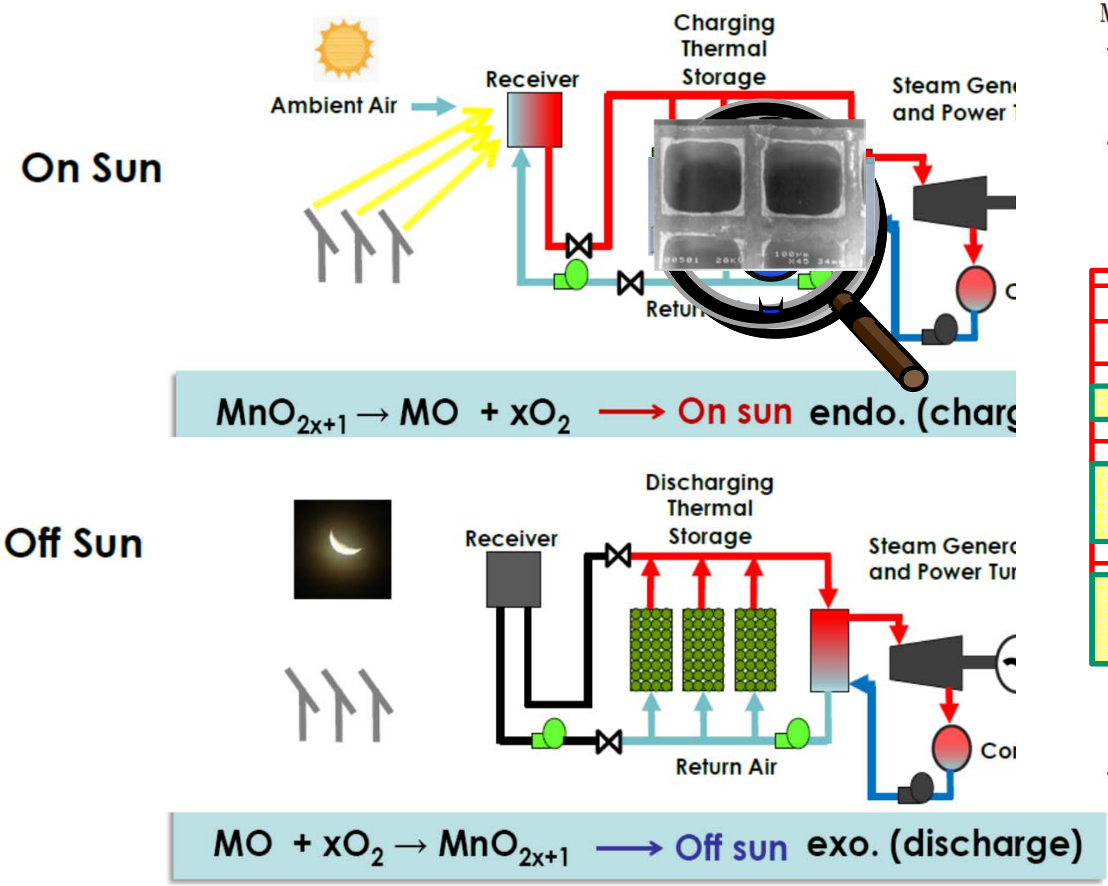


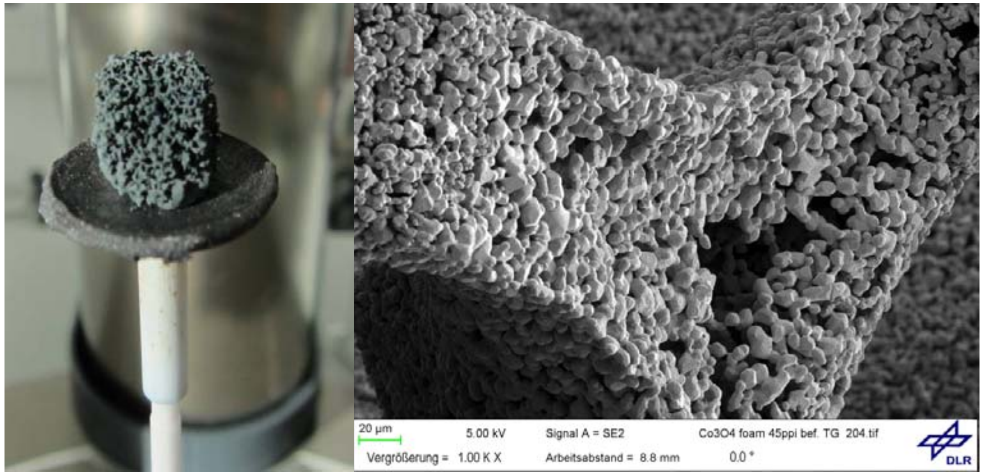
Table 2.1
Metal Oxide Systems Applicable to TES Based on Thermodynamics Considerations

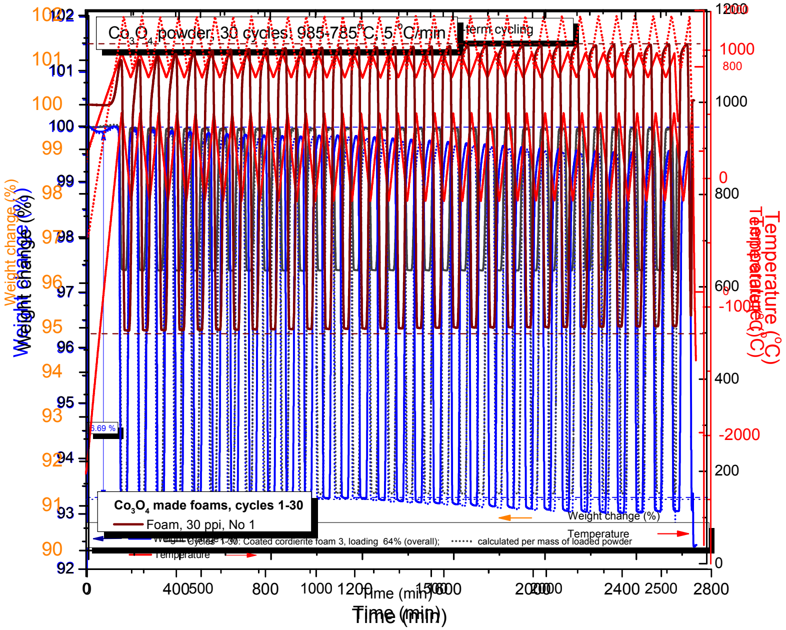
Reaction				Temperature (°C)	ΔH (kJ/mole oxide)	Storage Density (kJ/kg)
Cr_5O_{12}	→	$2.5Cr_2O_3$	$+ 2.25O_2$	110	126.0	279
$2Li_2O_2$	→	$2Li_2O$	$+ O_2$	150	68.2	1483
$2Mg_2O$	→	$2MgO$	$+ O_2$	205	21.8	505
$2PbO_2$	→	$2PbO$	$+ O_2$	405	62.8	262
$2PtO_2$	→	$2PtO$	$+ O_2$	420	62.8	277
$2Sb_2O_5$	→	$2Sb_2O_4$	$+ O_2$	515	92.5	286
$4MnO_2$	→	$2Mn_2O_3$	$+ O_2$	530	41.8	481
$6UO_3$	→	$6U_3O_8$	$+ O_2$	670	35.2	123
$2BaO_2$	→	$2BaO$	$+ O_2$	885	72.5	474
$2Co_3O_4$	→	$6CoO$	$+ O_2$	890	202.5	844
Rh_2O_3	→	Rh_2O	$+ O_2$	970	249.2	981
$6Mn_2O_3$	→	$4Mn_3O_4$	$+ O_2$	1000	31.9	202
$4CuO$	→	$2Cu_2O$	$+ O_2$	1120	64.5	811
$6Fe_2O_3$	→	$4Fe_3O_4$	$+ O_2$	1400	79.2	496
$2V_2O_5$	→	$2V_2O_4$	$+ O_2$	1560	180.7	993
$2Mn_3O_4$	→	$6MnO$	$+ O_2$	1700	194.0	830

-General Atomics: GA–C27137: THERMOCHEMICAL HEAT STORAGE FOR CONCENTRATED SOLAR POWER THERMOCHEMICAL SYSTEM REACTOR DESIGN FOR THERMAL ENERGY STORAGE ; Phase II Final Report, 2011

Co_3O_4 /CoO: TGA

- Co_3O_4 can operate in a quantitative, cyclic and fully reversible reduction/ oxidation mode within 800-1000^oC (950^oC).
- As powder, coated on honeycombs/ foams or shaped in foams.

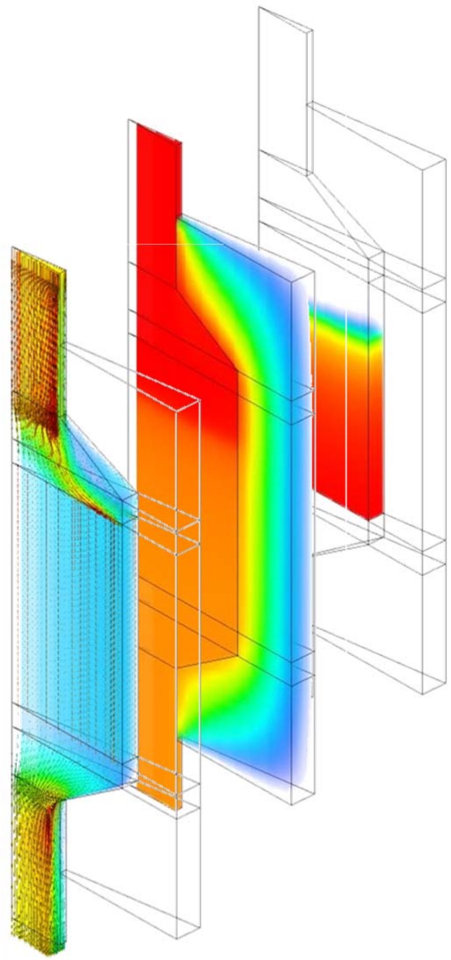




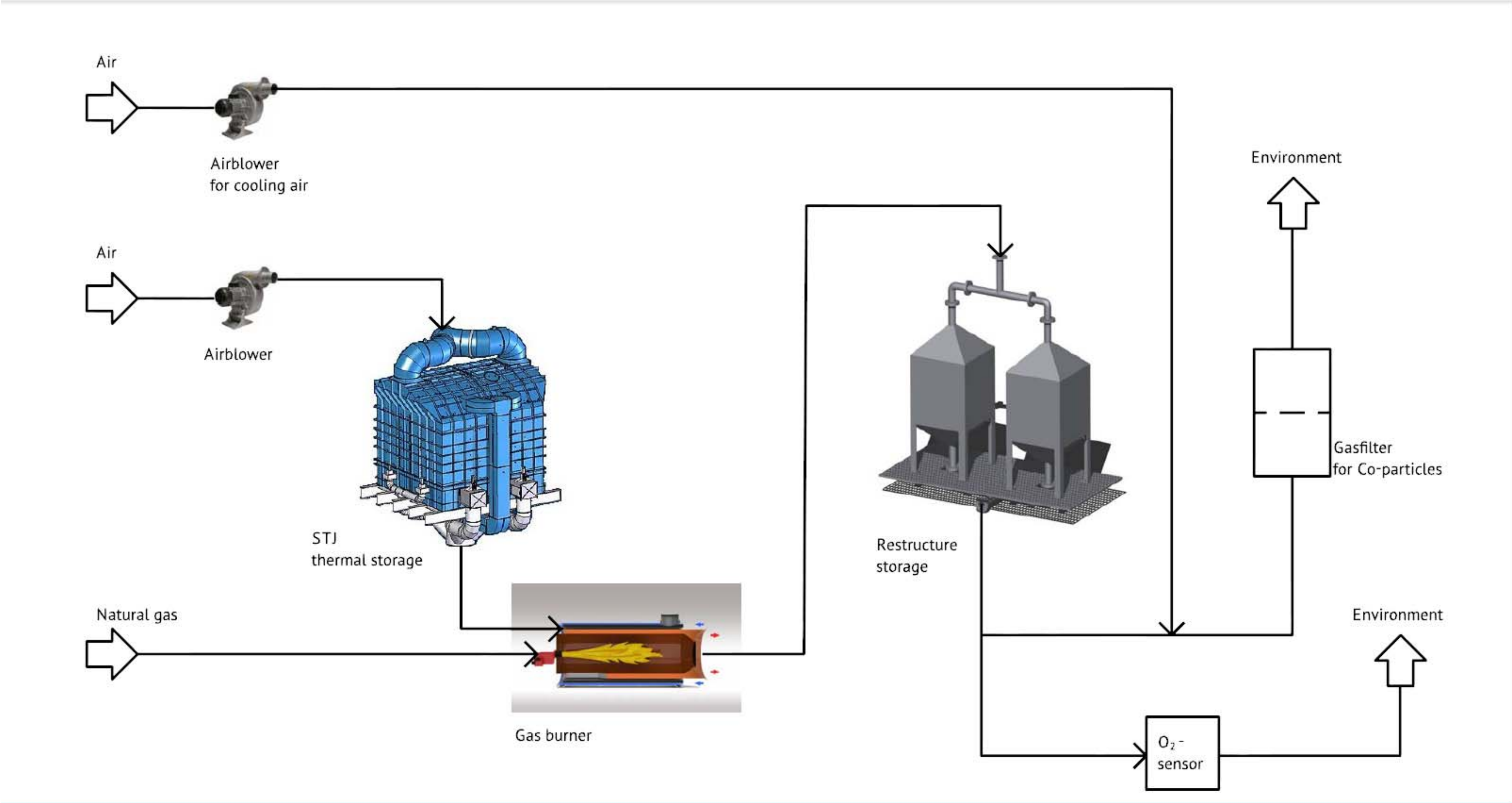
-Agrafiotis, Roeb, Schmücker, Sattler, Solar Energy, (2014), (2015).

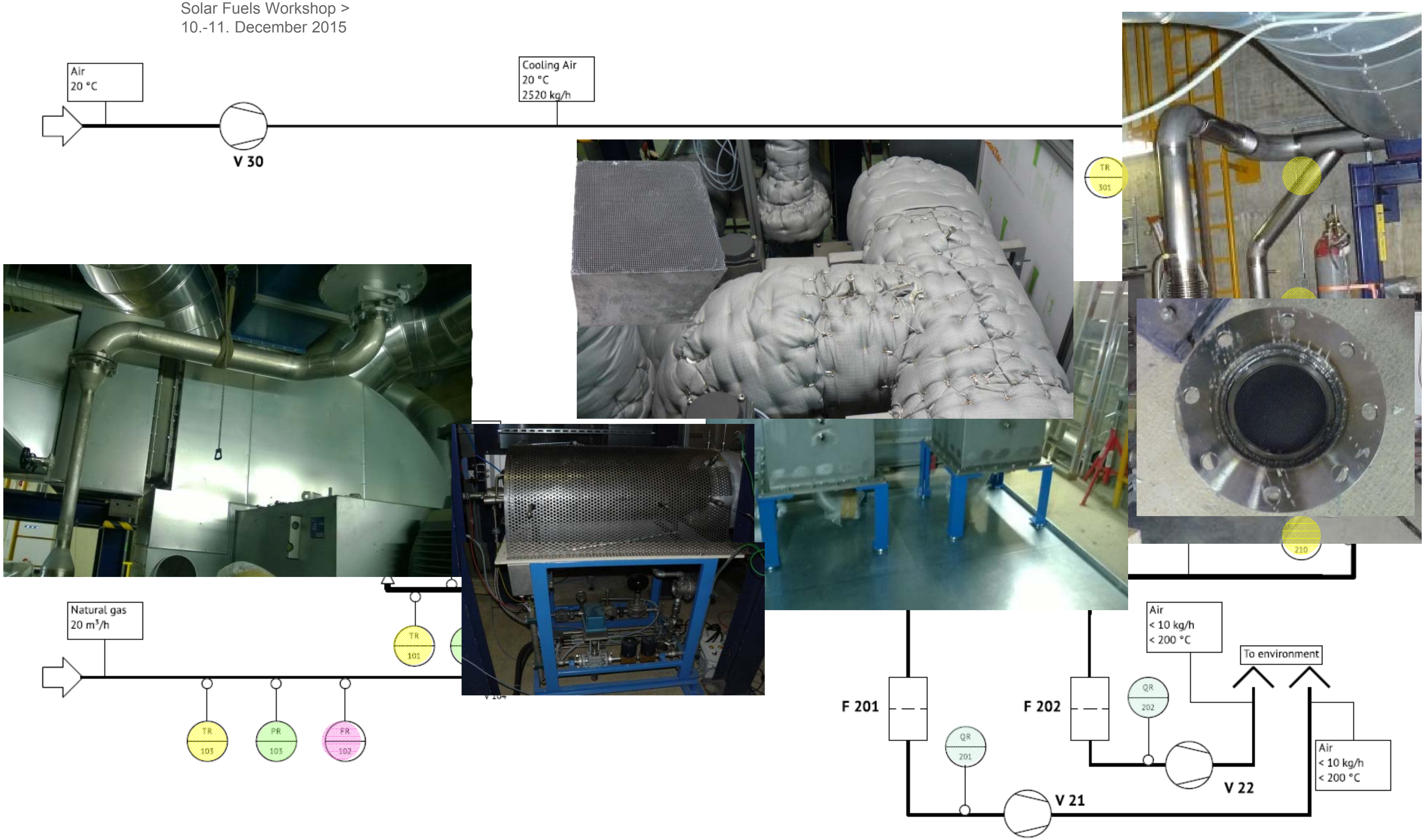
Numerical modelling of the reactor

- gas flow – heat transfer – chemical reaction were modeled
- kinetics model from experimental data was implemented
- predict a cycle
- define the optimal reactor geometry



Implementation in an existing solar facility




Air
20 °C
V 30
Cooling Air
20 °C
2520 kg/h
TR 301
210
Natural gas
20 m³/h
TR 101
TR 103
PR 103
FR 102
Air
< 10 kg/h
< 200 °C
To environment
F 201
F 202
QR 202
QR 201
V 22
V 21
Air
< 10 kg/h
< 200 °C

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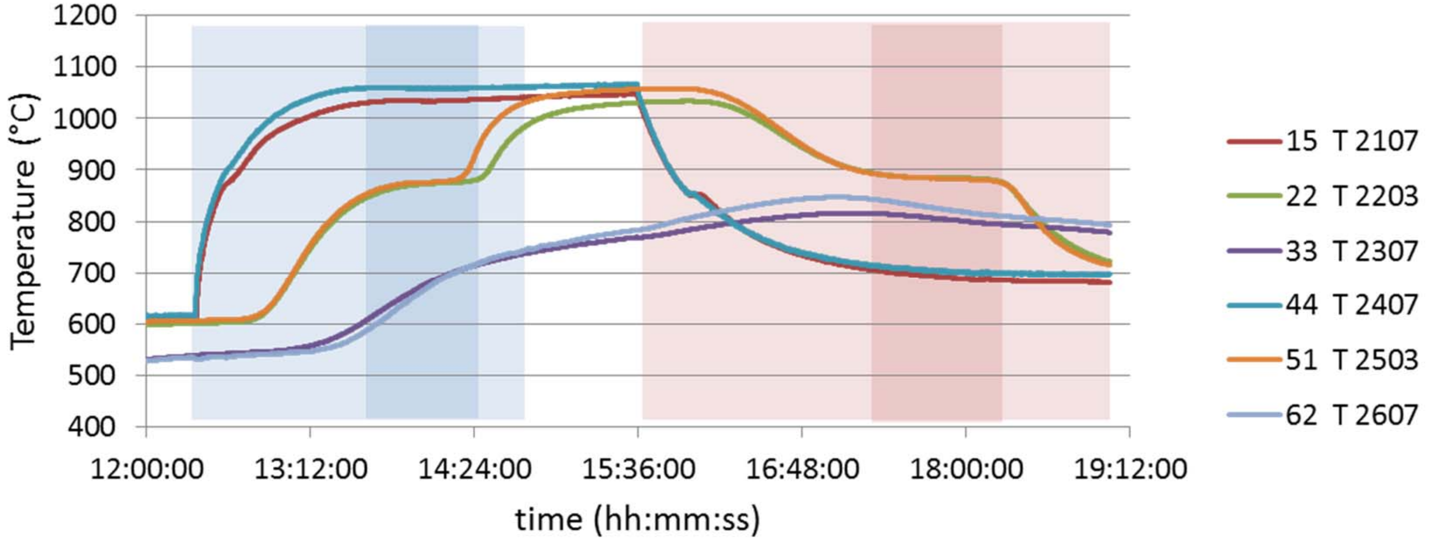
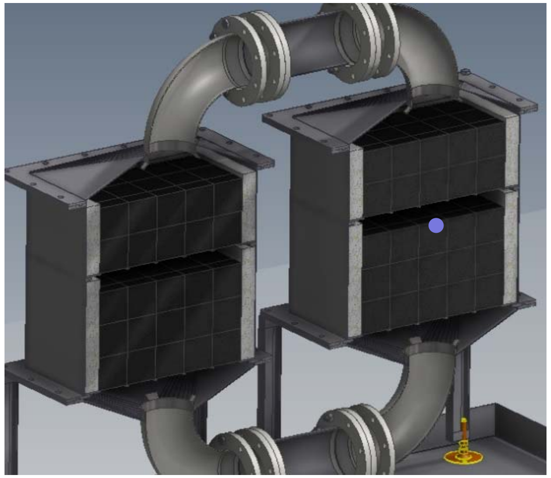
Chemical Tests

-considering half of one chamber (≈25kg cobalt)

	Energy stored (kWh)	Average Power (kW)	time	at constant temperature
Charge	38	11.2	3.5 h	1 h
Discharge	32	9.6	3.25 h	1 h

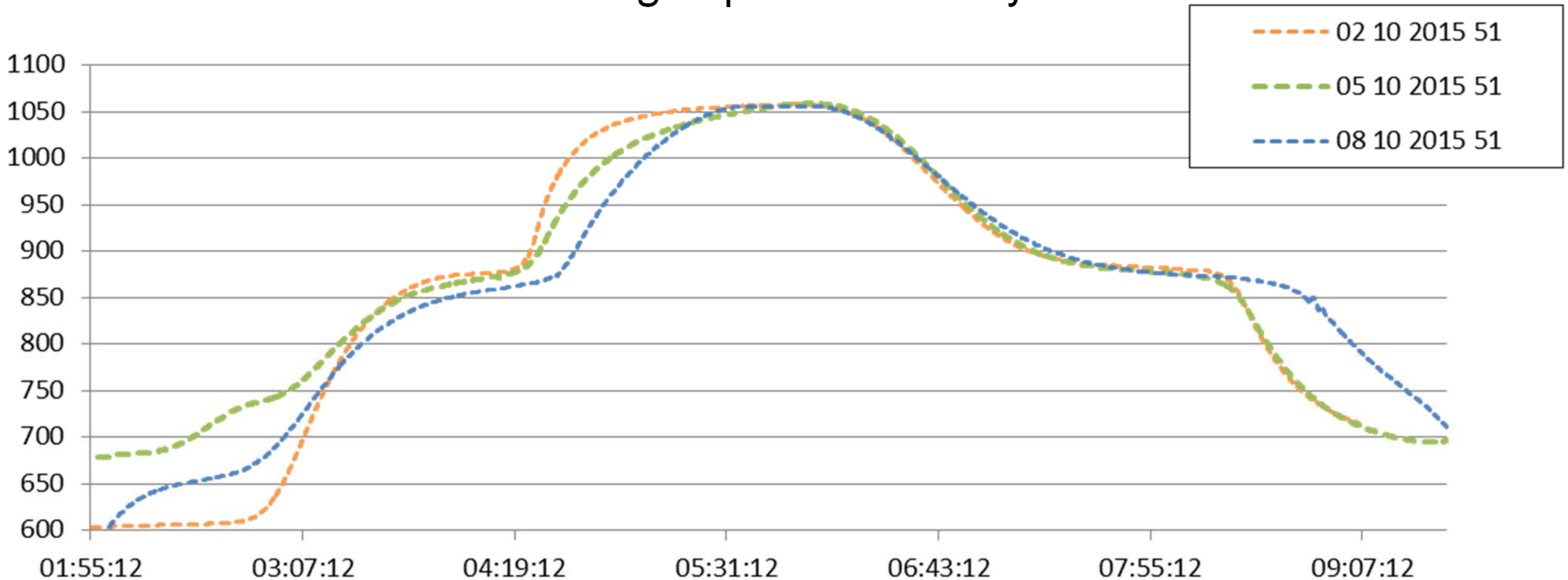


Chemical Tests



-3 complete cycles:

- reproducible results
- material doesn't loose storing capacities in 3 cycles



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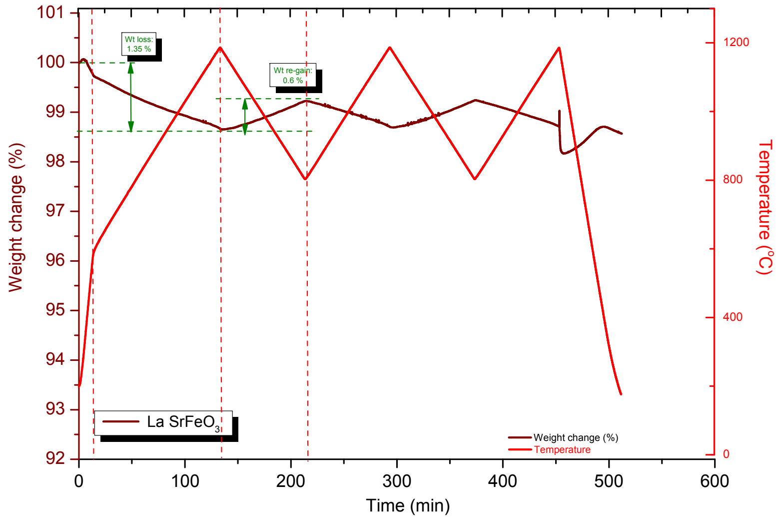
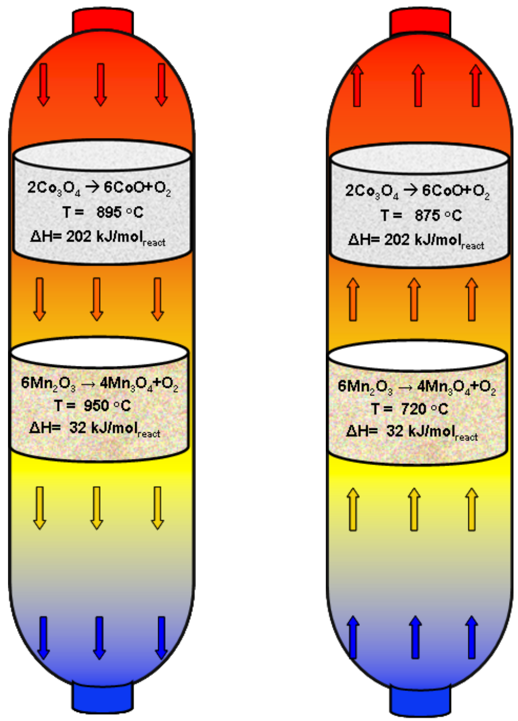
Cascaded ThermoChemical Storage (CTCS)

- CuO/Cu_2O: reduction temperature very close to m.p. of Cu_2O (shrinkage and sintering).
- BaO_2/BaO: BaO reacts with CO_2 present in air to $BaCO_3$
- Perovskites: loose/gain (little) weight continuously with temperature:

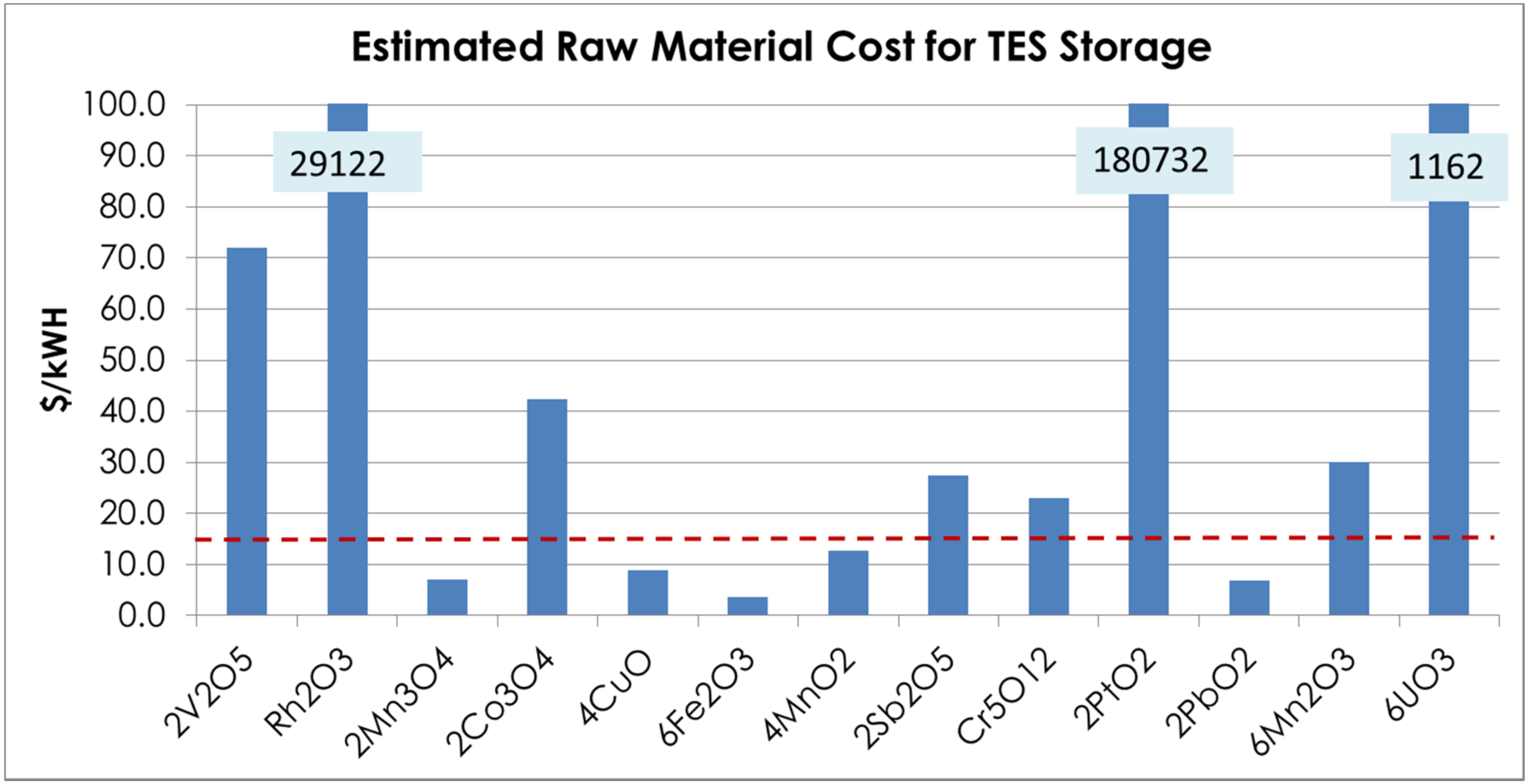


Reaction	ΔH (kJ/mol)	T_{red} (°C)	T_{ox} (°C)
$2\ Co_3O_4 + \Delta H \rightarrow 6\ CoO + O_2$	202.5	895	875
$6\ Mn_2O_3 + \Delta H \rightarrow 4\ Mn_3O_4 + O_2$	31.9	950	720



Preliminary economics can be estimated through energy related costs

- **Energy related costs include raw materials, storage and process cost etc.**



DOE target

- **Low raw material cost required for large scale use**

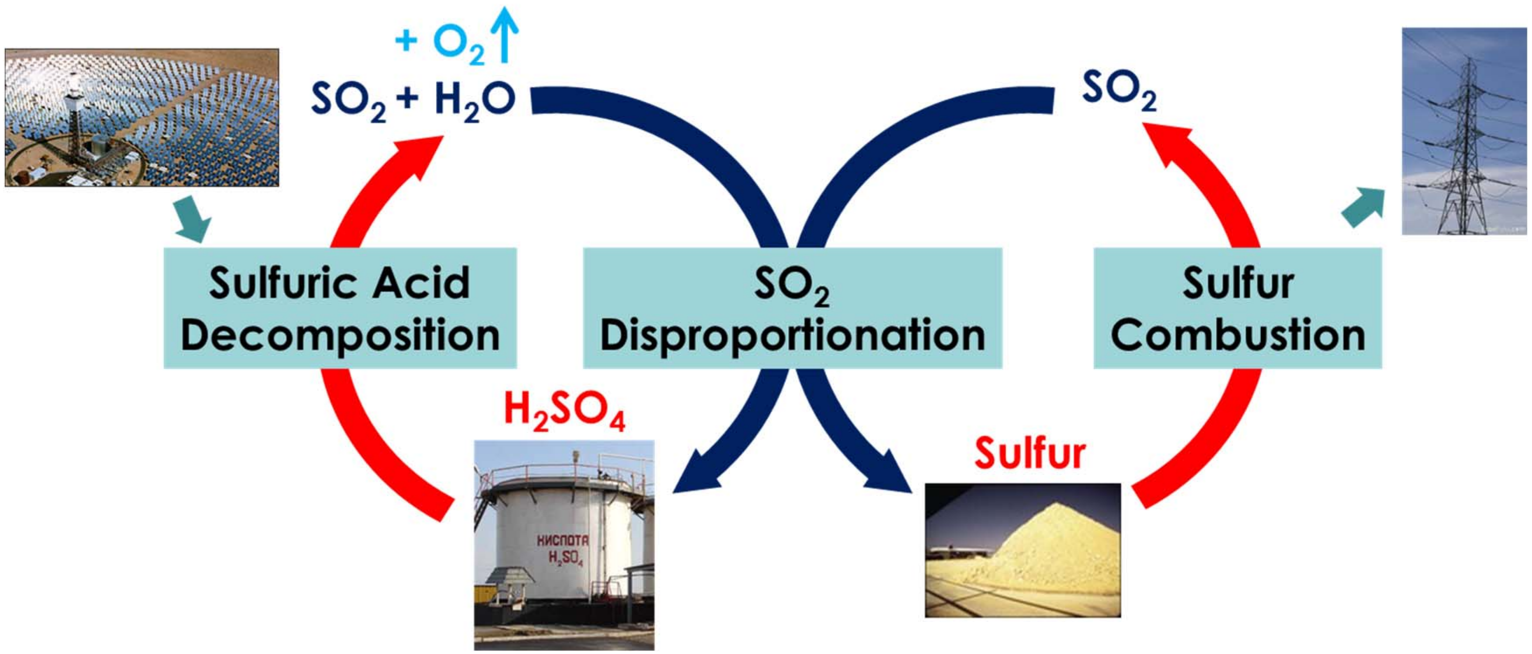
REDOX of solid oxide is applicable to thermochemical energy storage for CSP

- Mixed oxides greatly improves REDOX kinetics and cycle repeatability
- Materials cost is the main driver of TES economics
- A moving bed reactor is required to minimize parasitic cost

DOE Metric	Unit	2015	Mn-Fe	Co-Al
Storage Cost	$/kWh	15	15-35	50-100
LCOE	$/kWh	0.06	0.09-0.11*	0.13-0.17*
Efficiency	%	93	>93	>93

*SAM (NREL) using 2010 costs

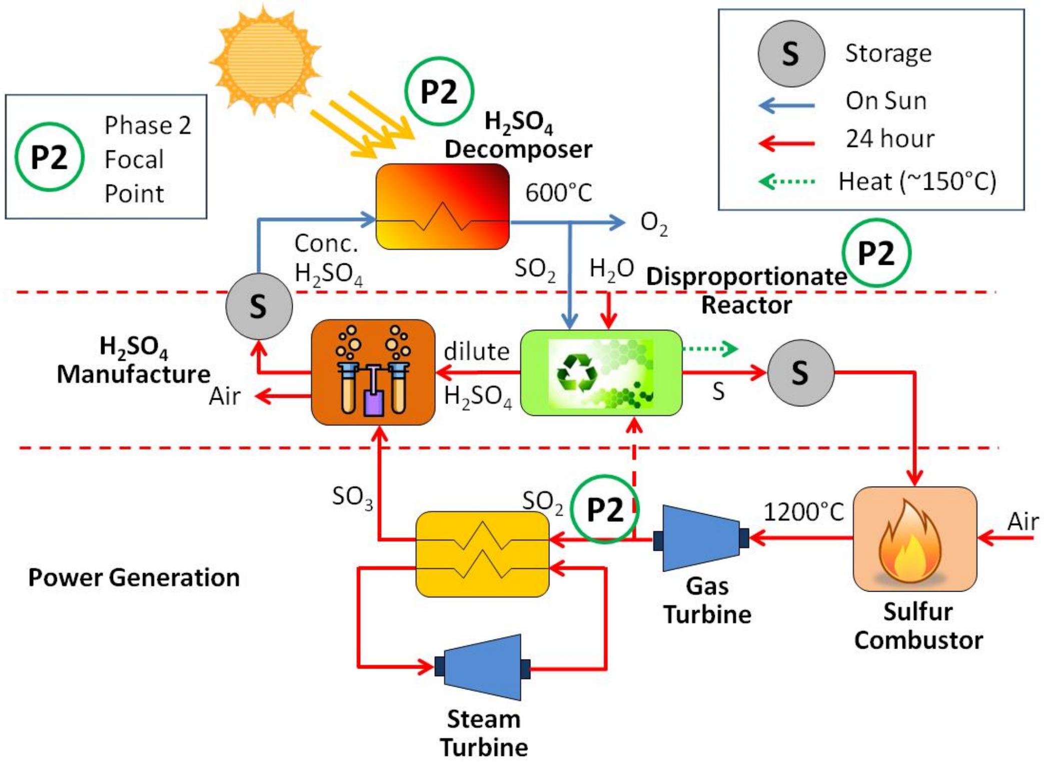
Sulfur based



	Reaction	Temp (° C)
H_2SO_4 Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + O_2(g) + 2SO_2(g)$	800
SO_2 Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(l)$	150
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	1200

An improved flowsheet was established based on modeling and experimental data from Phase I

- **Plant design incorporated established processes from sulfuric acid manufacturing plant**



DOE Metric	LCOE (¢/kWh$_e$)
DOE Target	6.5
CSP w/Sulfur Storage	8.1*

***SAM (NREL) using 2012 costs**

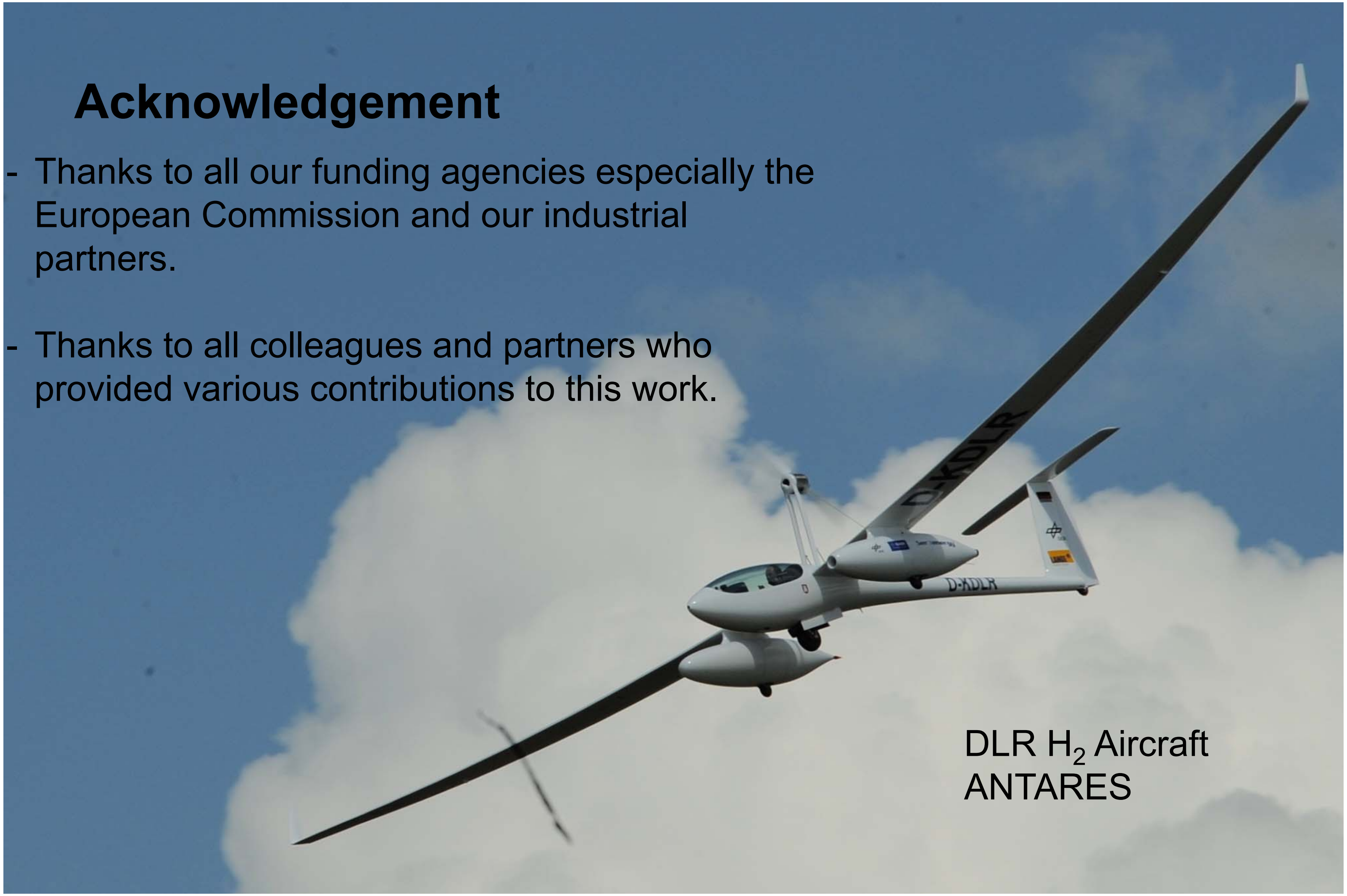
- **Storage cost is < $2/kWh**
- **LCOE is ~6¢/kWh$_e$ based on proposed Sunshot targets**

Summary and Outlook

- **Thermo-Chemical Energy** storage
  - Has a high potential for the future energy economy as well for Germany as stated in the 6th ERP as for the EU which just implements it in the HORIZON 2020 framework
  - DLR will contribute to these efforts

  - **Technically it offers several advantages** like
    - potentially high storage density,
    - lossless long-term storage

  - **the crucial points are**
    - adapted reactor systems and
    - process integration

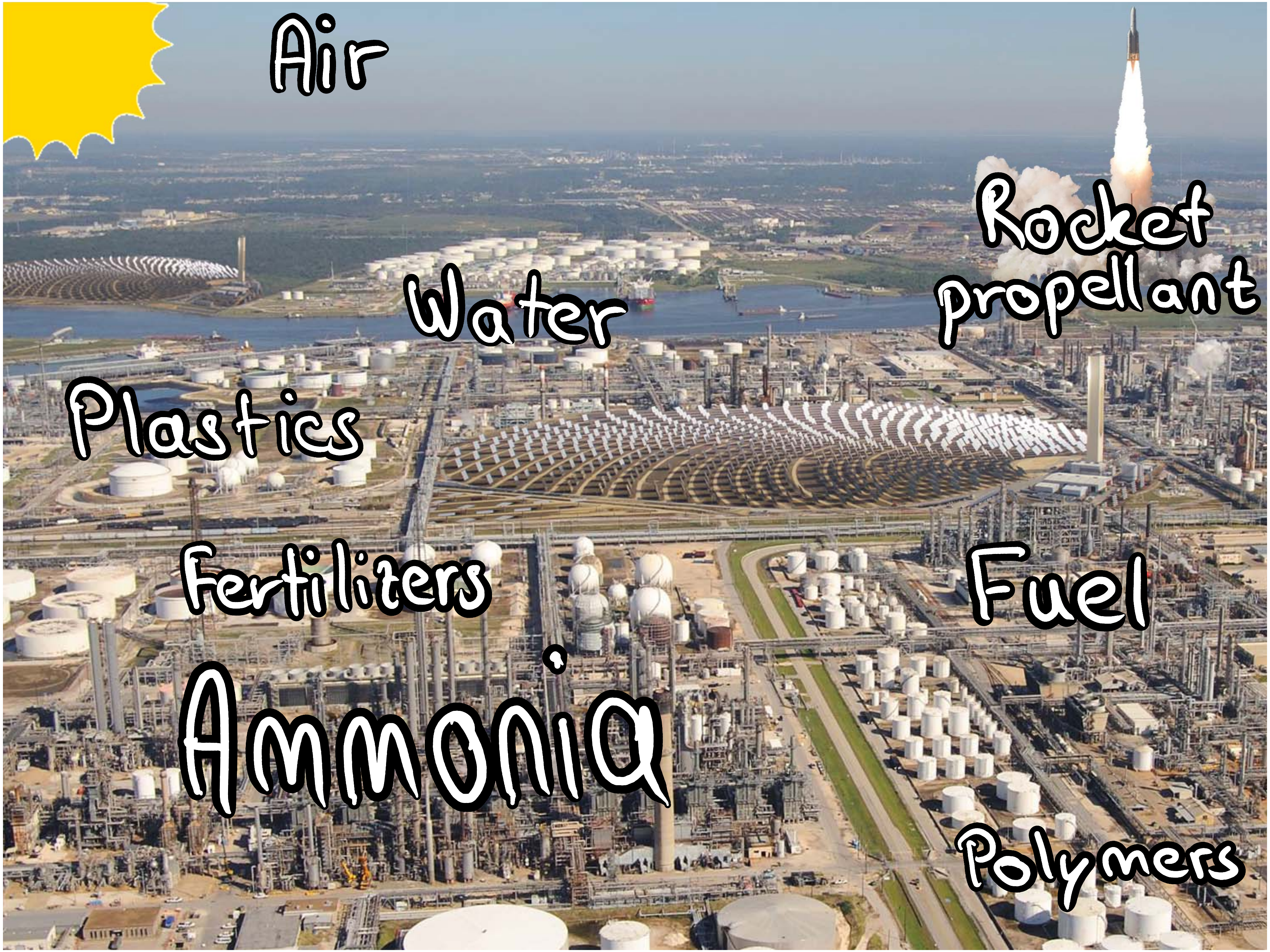


Acknowledgement

- Thanks to all our funding agencies especially the European Commission and our industrial partners.

- Thanks to all colleagues and partners who provided various contributions to this work.

DLR H_2 Aircraft
ANTARES


Air
Rocket propellant
Water
Plastics
Fertiliters
Fuel
Ammonia
Polymers

Thank you very much for your attention!

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