Sulfur and ferrite-based thermochemical cycles for water splitting

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Outline

- Ferrite based thermochemical cycle: HYDROSOL
  - Materials
  - System Model
  - Prototypes and tests
  - Pilot plants
  - Scale-up, economics
- Sulphur based thermochemical cycle: HycycleS
  - Materials
  - Prototypes
  - Modelling
  - Scale-up
- Summary

1. Ferrite based thermochemical cycle

The HYDROSOL CONSORTIA

HYDROSOL

- APTL (GR)
- DLR (D)
- Heliotech (DK)
- Johnson Matthey (GB)

HYDROSOL-2

- APTL (GR)
- DLR (D)
- STC (DK)
- Johnson Matthey (GB)
- CIEMAT (ES)

HYDROSOL-3D

- APTL (GR)
- DLR (D)
- CIEMAT (ES)
- Total (F)
- Hygear (NL)

Thermochemical Cycle using Mixed Iron Oxides: Reaction Scheme

1. Step: Water Splitting

$H_2O + MO_{red} \rightarrow MO_{ox} + H_2$

2. Step: Regeneration

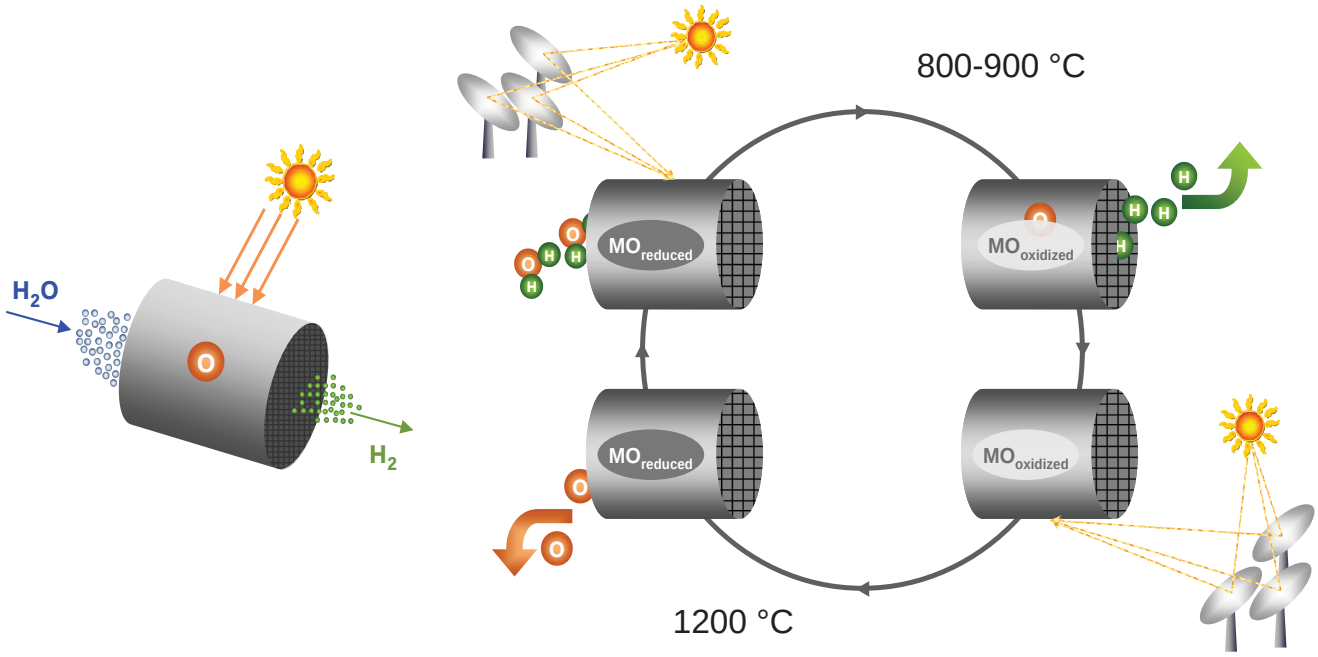
$MO_{ox} \rightarrow MO_{red} + ½\ O_2$

Net reaction: $H_2O \rightarrow H_2 + ½\ O_2$

Typical redox materials:

$ZnFe_2O_4$, $NiZnFe_2O_4$, $MnFe_2O_4$ $CoFe_2O_4$

The HYDROSOL process concept



The HYDROSOL Process

Basic Features

- Use of solar radiation absorbing ceramic honeycomb structures
- Synthesis of active water-splitting redox nanomaterials with non-conventional techniques
- Fixing/coating of the redox materials on the channels of the honeycomb

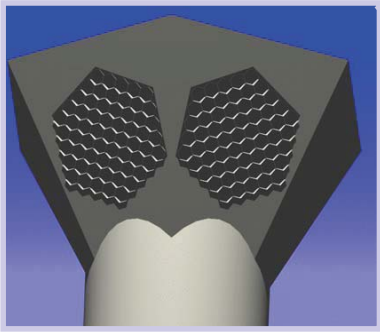
Advantages

- No circulation of (hot) solid reactants
- Product separation straightforward
- No movable components at high temperatures

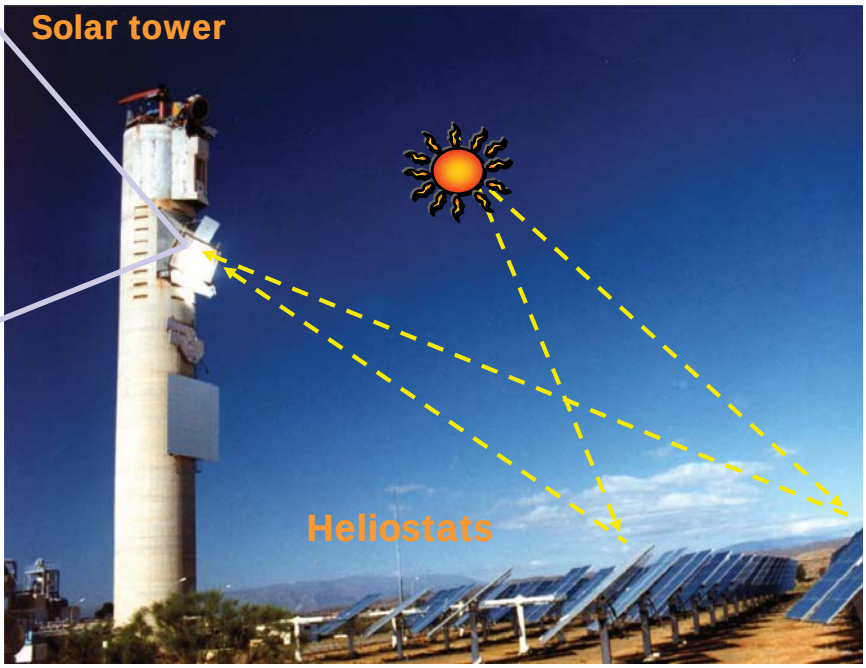
Objectives of HYDROSOL-2

- to design and build a solar Hydrogen pilot plant (100 kW_{th}) based on thermo-chemical water-splitting, carried out on monolithic ceramic honeycombs coated with active redox materials
- To set the stage for further scale-up of the HYDROSOL technology and its effective coupling with solar thermal concentration systems, in order to exploit and demonstrate all potential advantages
- To develop and identify redox materials most suitable for this cycle
- To develop and verify suitable process strategies, in particular control strategies
- To develop a fully scalable receiver-reactor to carry out the reactions involved

Objective: Integration in a Solar Tower System

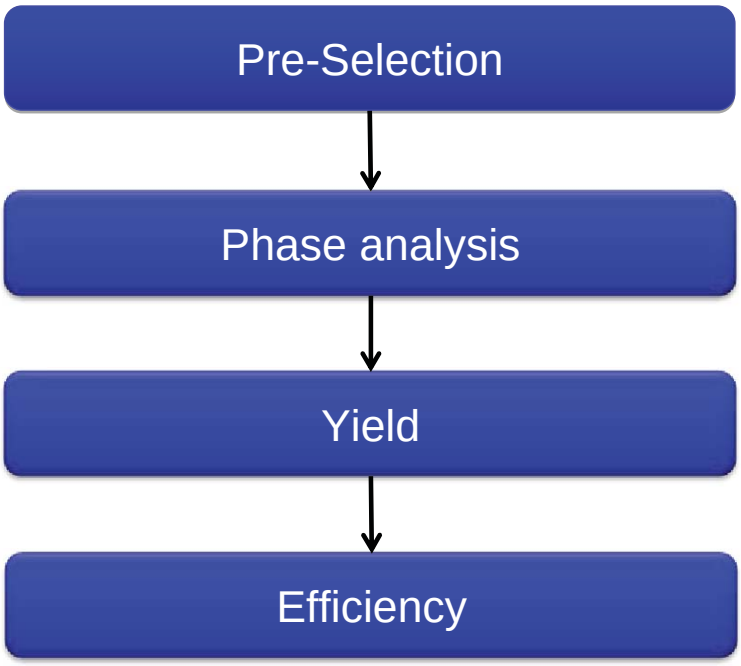


"MODULAR" DESIGN

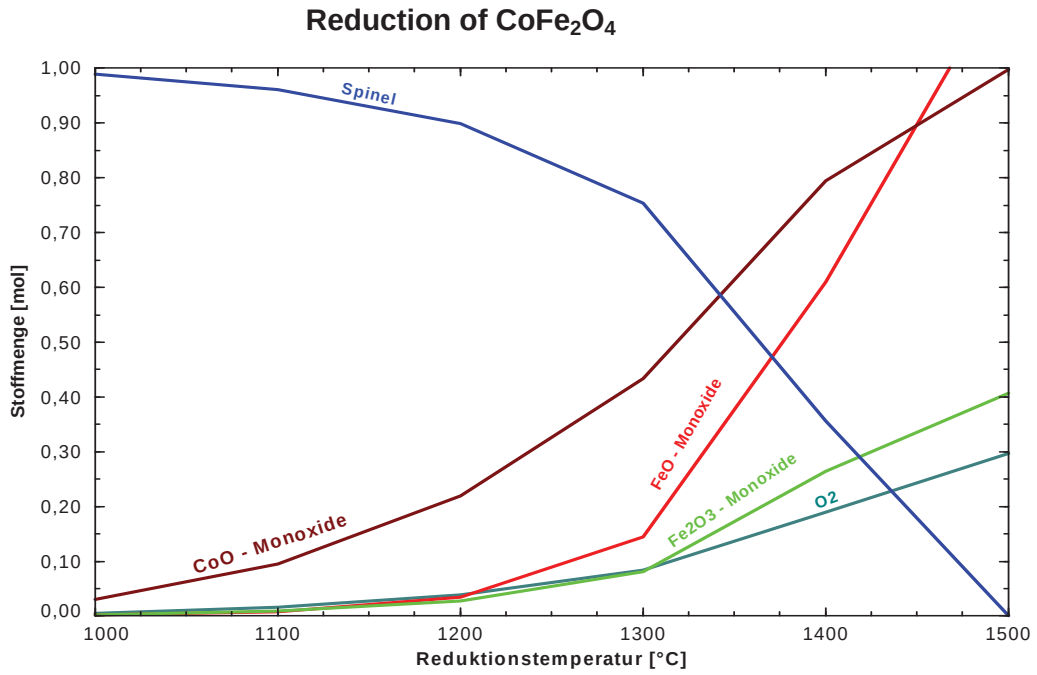


Materials development and characterisation

Consideration of Thermodynamics



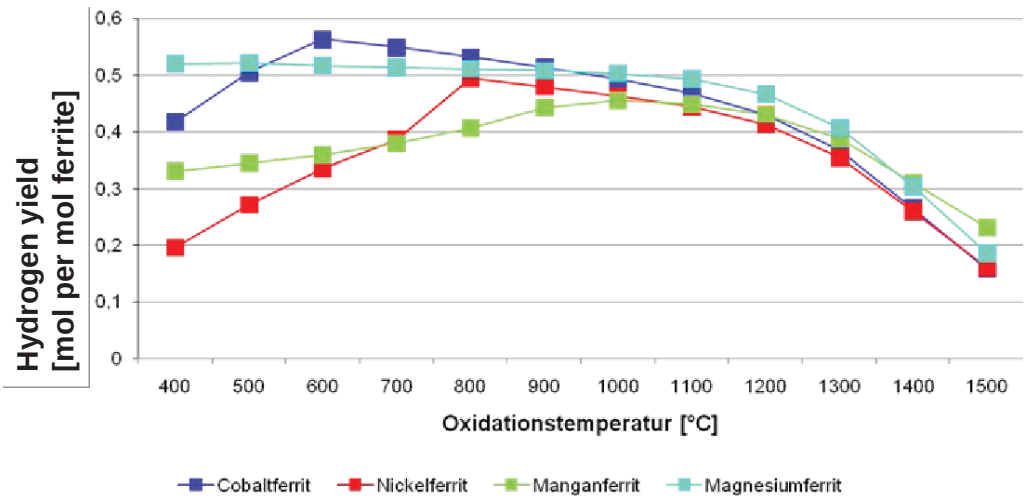
Phase analysis (calculated with FACTsage)



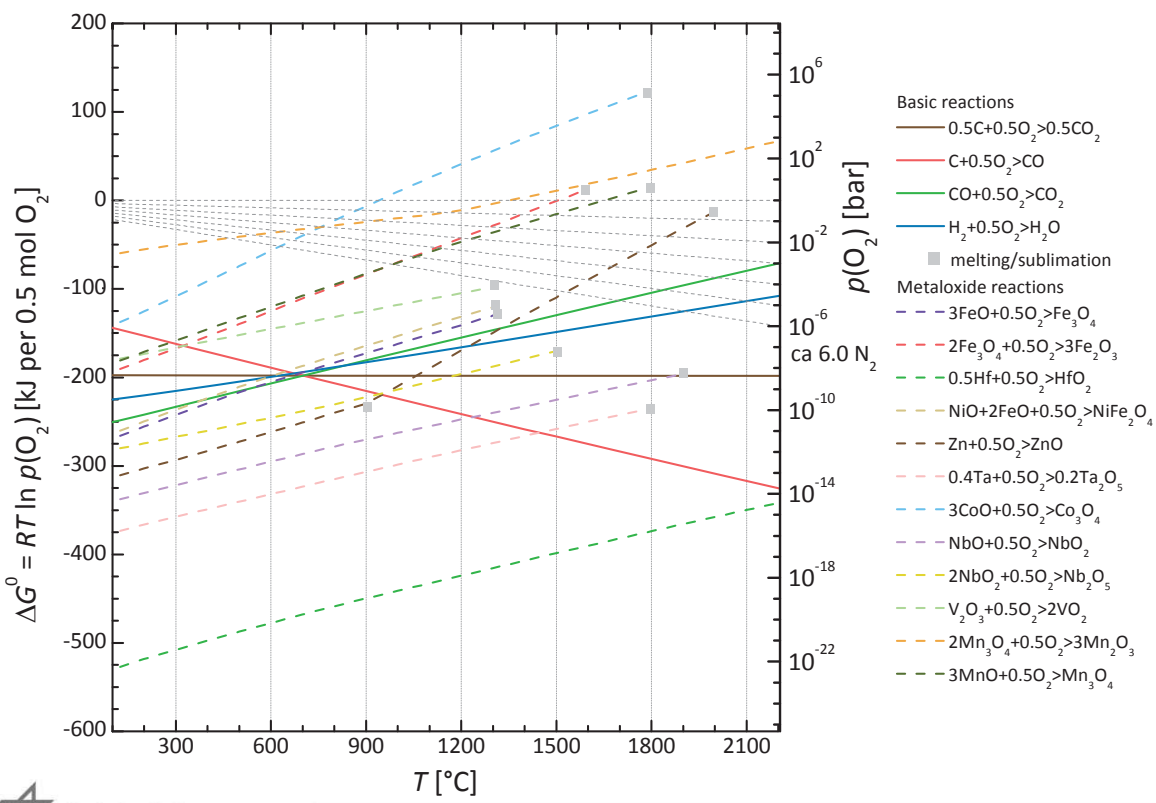
Yield (calculated)

Simulation of mixed oxides type MFe_2O_4 (M=Co, Ni, Mn, Mg)

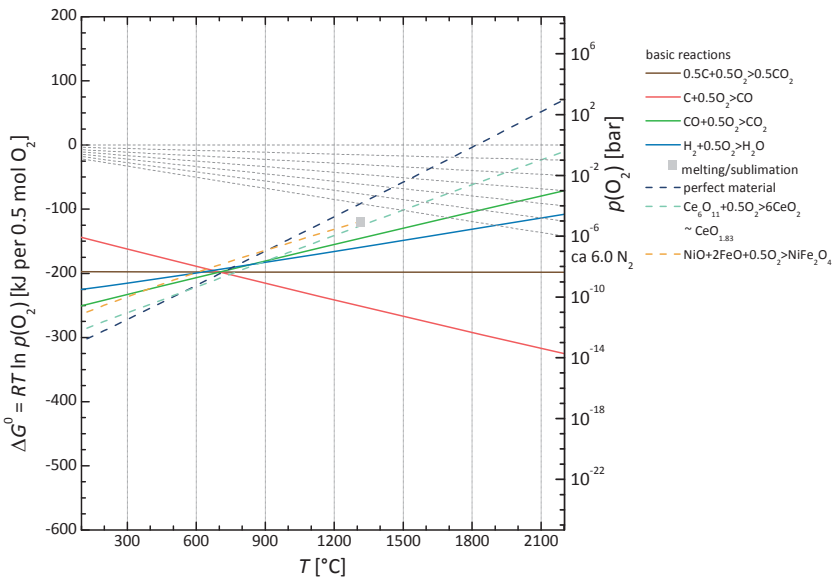
Oxidation $\rightarrow T^{reg}$ = 1500°C



Ellingham-Diagram: Transition Metals



Ellingham-Diagram: Desired Material



Reaction Schemes employed for Mixed Iron Oxides synthesis

Solid phase self-propagating high-temperature synthesis (SPSHS)

$$2k\ Fe + (1\text{-}k)\ Fe_2O_3 + x\ MnO + (1\text{-}x)\ ZnO + 1.5\ z\ O_2 \longrightarrow (Mn_xZn_{1\text{-}x})Fe_2O_4$$

Liquid phase self-propagating high-temperature synthesis (LPSHS/GC)

$$2Fe(NO_3)_3 + x\ Mn(NO_3)_2 + (1\text{-}x)\ Zn(NO_3)_2 + 3\ C_6O_7H_8 + 8\ NH_3 + 9.5\ O_2$$

$$\longrightarrow (Mn_xZn_{1\text{-}x})Fe_2O_4 + 18\ CO_2 + 8\ N_2 + 24H_2O$$

Aerosol spray pyrolysis synthesis (ASP)

$$2Fe(NO_3)_3 + x\ Mn(NO_3)_2 + (1\text{-}x)\ Zn(NO_3)_2 + (3\ C_6O_7H_8 + 8\ NH_3) + 9.5\ O_2$$

$$\longrightarrow (Mn_xZn_{1\text{-}x})Fe_2O_4 + 18\ CO_2 + 8\ N_2 + 24H_2O$$

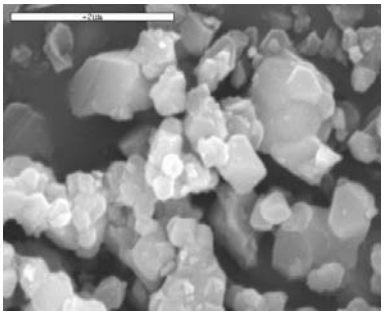
Solid state synthesis (SSS)

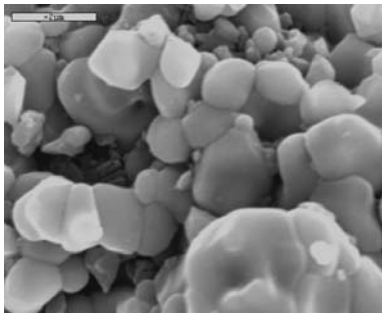
$$Fe_2O_3 + x\ MnCO_3\ (Mn_3O_4)\ (NiO) + (1\text{-}x)\ ZnO \longrightarrow (Mn_x\ (Ni)_x\ Zn_{1\text{-}x})Fe_2O_4 + x\ CO_2$$

Materials characterization: specific surface area

SSS

1-2 m^2/g



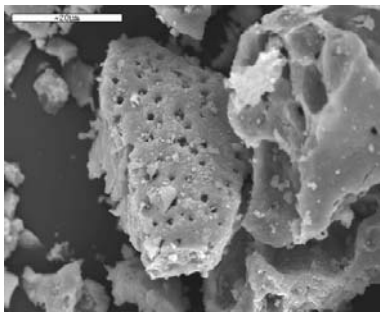


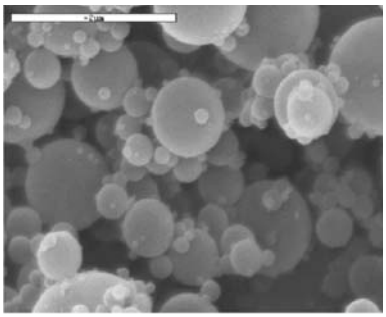
SPSHS

4-5 m^2/g

LPSHS/GC

20-40 m^2/g



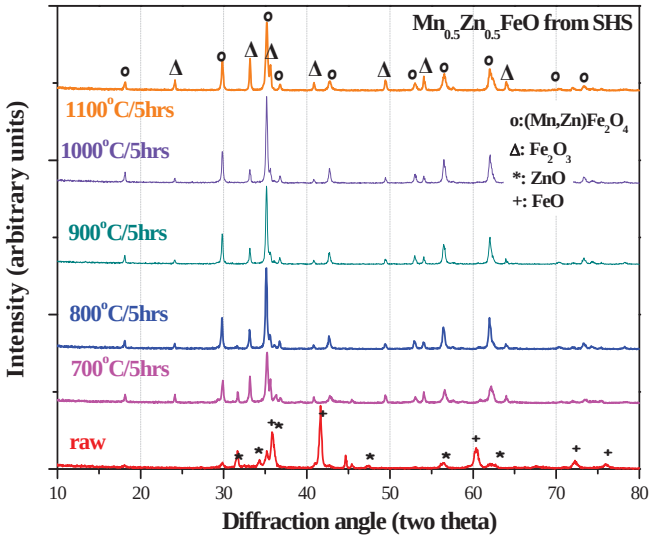


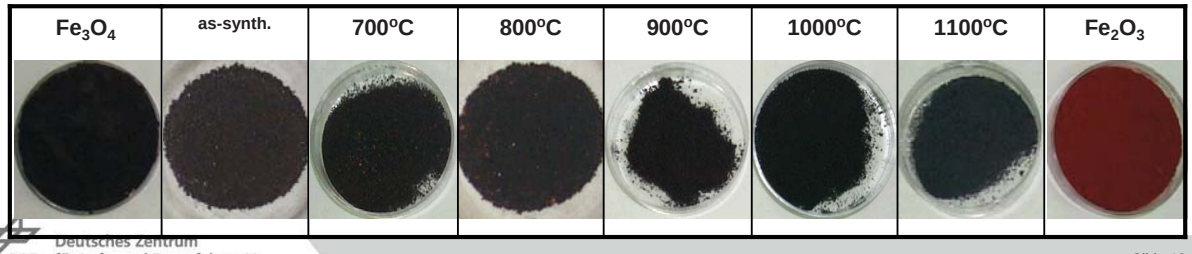
ASP

80-120 m^2/g

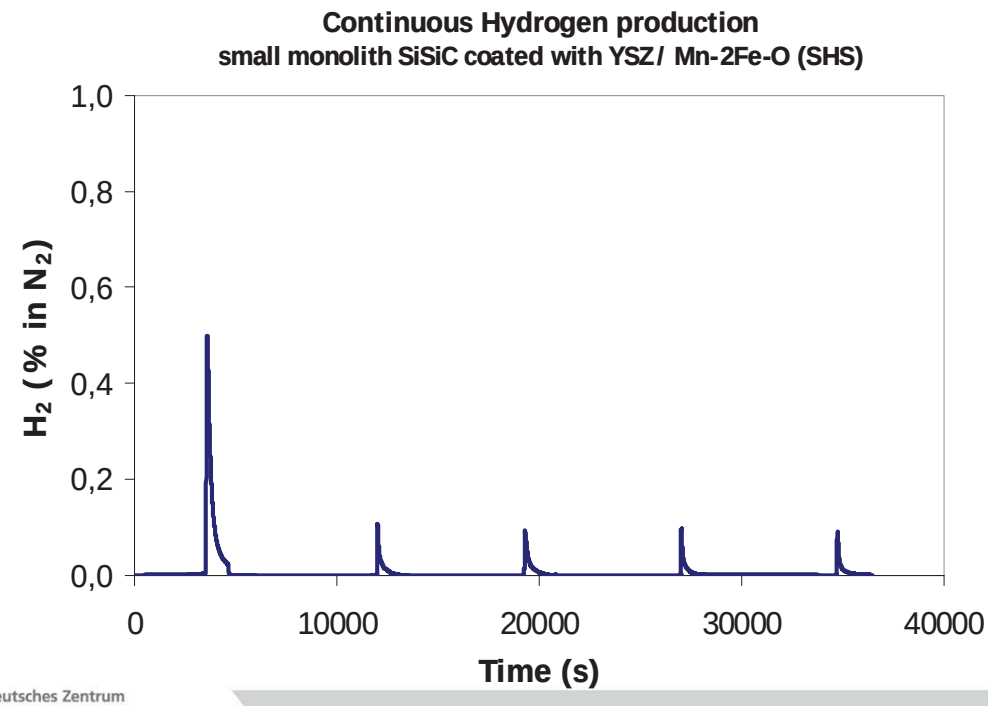
Phase and color evolution during calcination in air

$Mn_{0.5}Zn_{0.5}FeO$

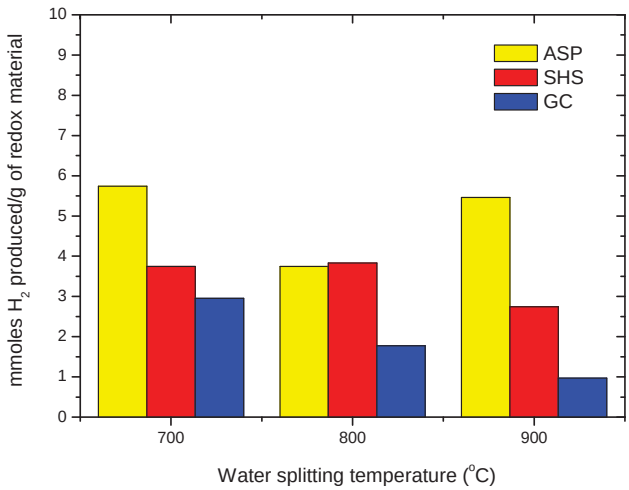




Tests with coated monoliths: Testing of Mn-Fe-O mixed oxide with respect to cyclic H_2 production (800 ^oC)



Hydrogen yield (experiment)



Stoichiometry:
Zn-Fe oxide material

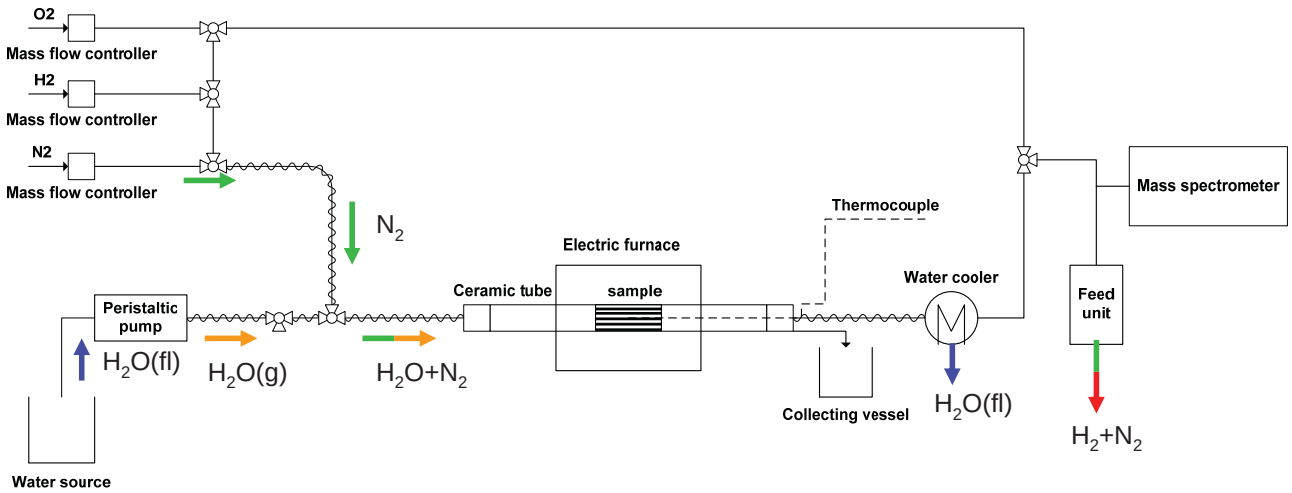
ASP-synthesized materials exhibit the highest H_2 yield, followed by the SHS- and GC-produced ones.

For a given synthesis route, there is no significant variation of the amount of H_2 produced, within 700-900^oC.

Kinetics of water splitting

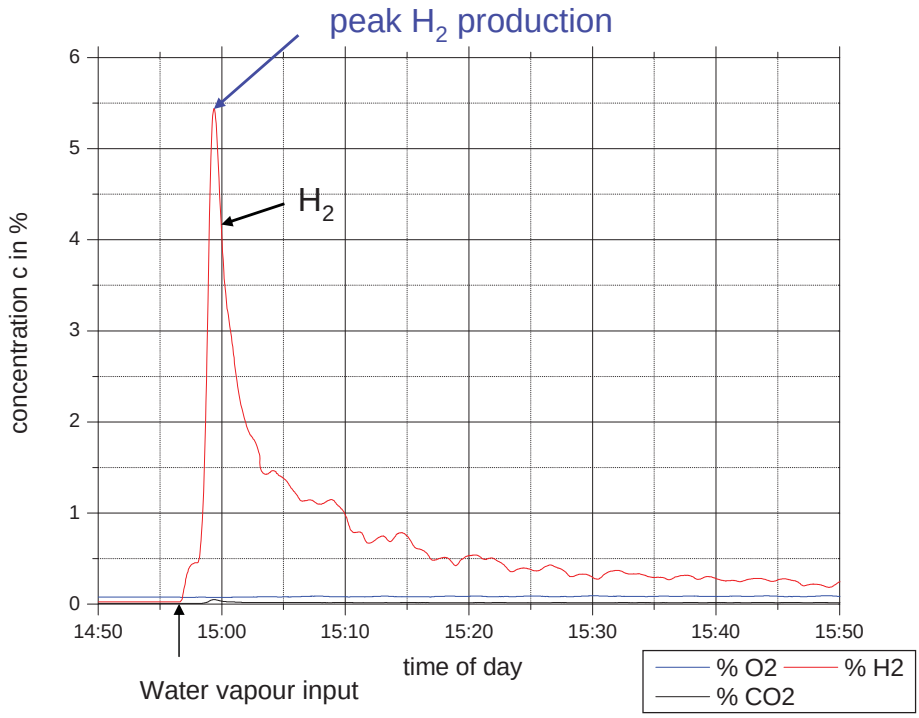
Experimental Set-Up

Water Splitting



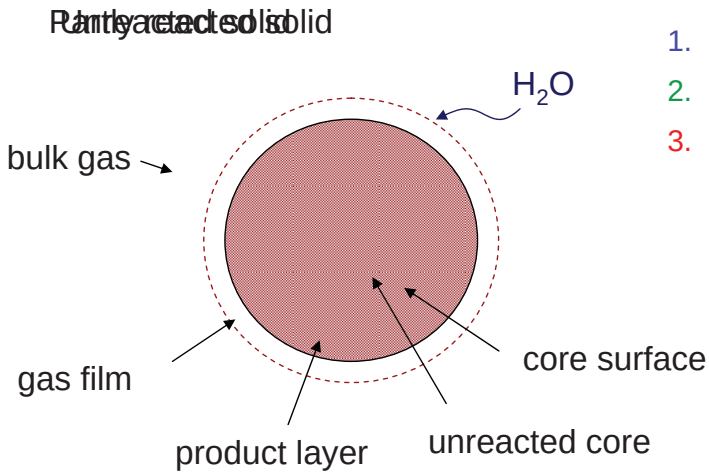
Experimental Set-Up

H_2 production curve



Reaction Model

Shrinking Core Model



Reaction Rate Controlling Steps:

1. Film diffusion
2. Internal diffusion
3. Chemical reaction

Shrinking Core Model

Shrinking Core Model derives different approaches for

X_{solid}: conversion of solid phase

$X_{solid} = f(t)$

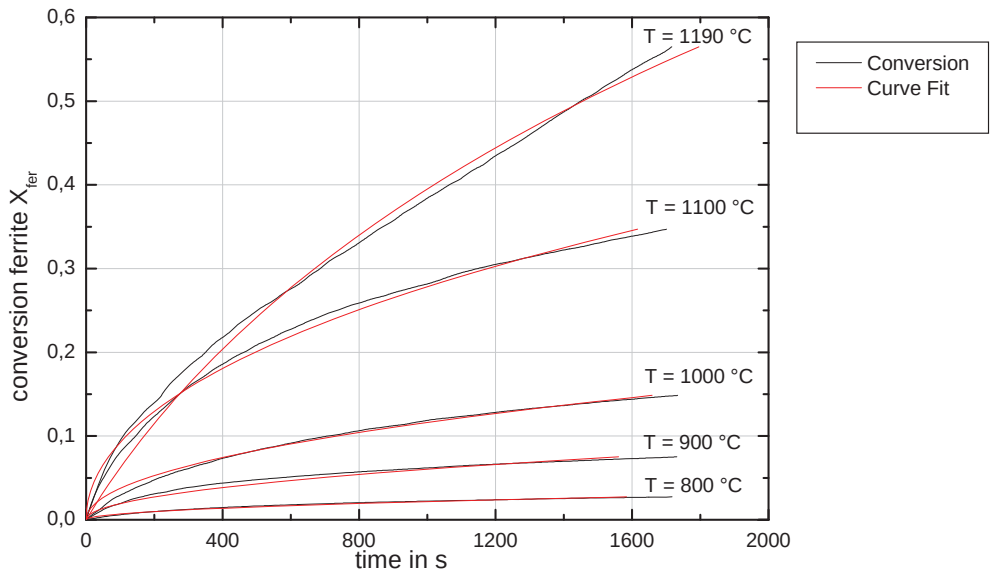
film diffusion	internal diffusion	chemical reaction
$t = k_1 \cdot X_{solid}$	$t = k_2 \cdot \left[1 - 3\left(1 - X_{solid}\right)^{2/3} + 2\left(1 - X_{solid}\right)\right]$	$t = k_3 \left[1 - \left(1 - x_{solid}\right)^{1/3}\right]$

Literature: Levenspiel, O., Chemical Reaction Engineering, 3rd. Edition, New York, Wiley, 1999

Analysis of Water Splitting Step

Conversion vs. Time

Fit function $t = k_1 \cdot X_{solid} + k_2 \cdot \left[1 - 3\left(1 - X_{solid}\right)^{2/3} + 2\left(1 - X_{solid}\right)\right] + k_3\left[1 - \left(1 - x_{solid}\right)^{1/3}\right]$



Analysis of Water Splitting Step

Results from Shrinking Core Model Curve Fit

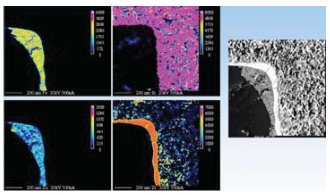
$T_{Splitting}$	k_1	k_2	k_3
800	0	6312974	0
900	0	800484	0
990	0	210547	0
1100	0	33721	0
1190	1308	7037	0

- Reaction is mainly limited by internal diffusion
- Possible film diffusion limitation at about 1200 °C

Milestones of Materials Development

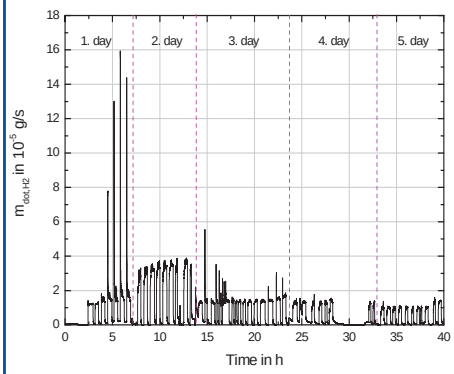
Water-splitting on redox coated honeycombs

Redox material coated SiSiC honeycombs



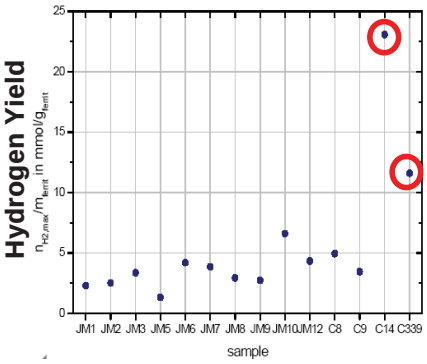
SEM analysis for the investigation of the quality of coating and the effect of solar water splitting

50-cycles of solar water-splitting



Key milestone

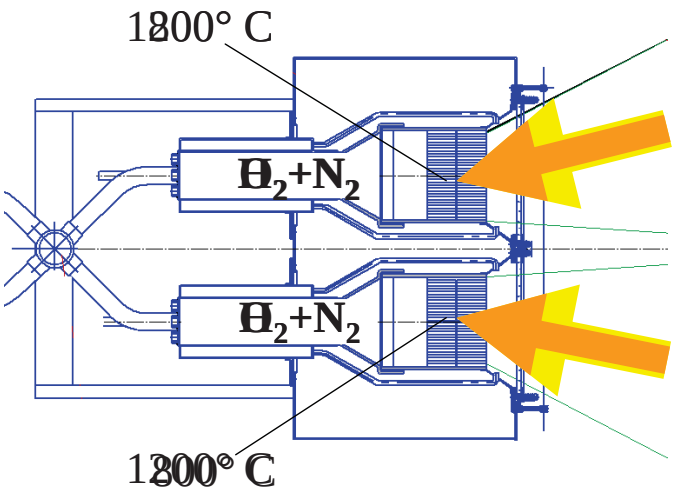
Field evaluation of coated monoliths



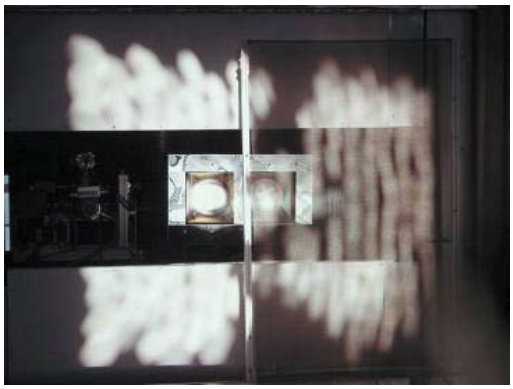
Reactor concept and reactor design

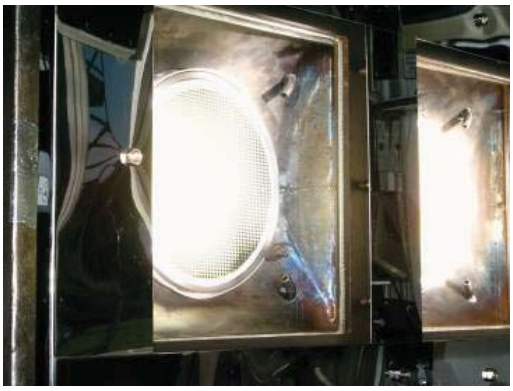
Reactor for continuous hydrogen production

- Reactor with two modules
- 10 kW two-chamber system
- Two different alternating processes:
  - Production: 800°C, water steam, nitrogen, exothermic
  - Regeneration: 1200°C, nitrogen, endothermic
- Transient steps like
  - Switching between half cycle
  - Start-up / Shutdown
- Closed system: quartz window
- Four-way-valve

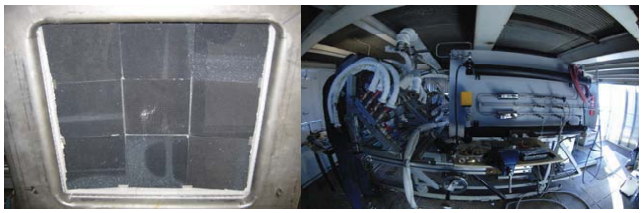


HYDROSOL: Continously operating reactor during exposure to sunlight



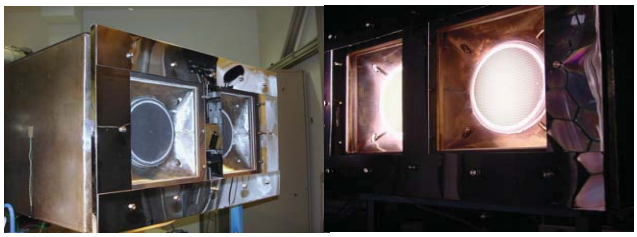


Hydrosol technology scale-up

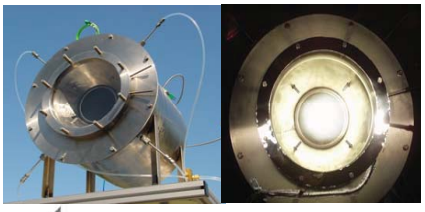


2008:
Pilot reactor (100 kW)

PSA solar tower



2005:
Continuous STC H_2 production



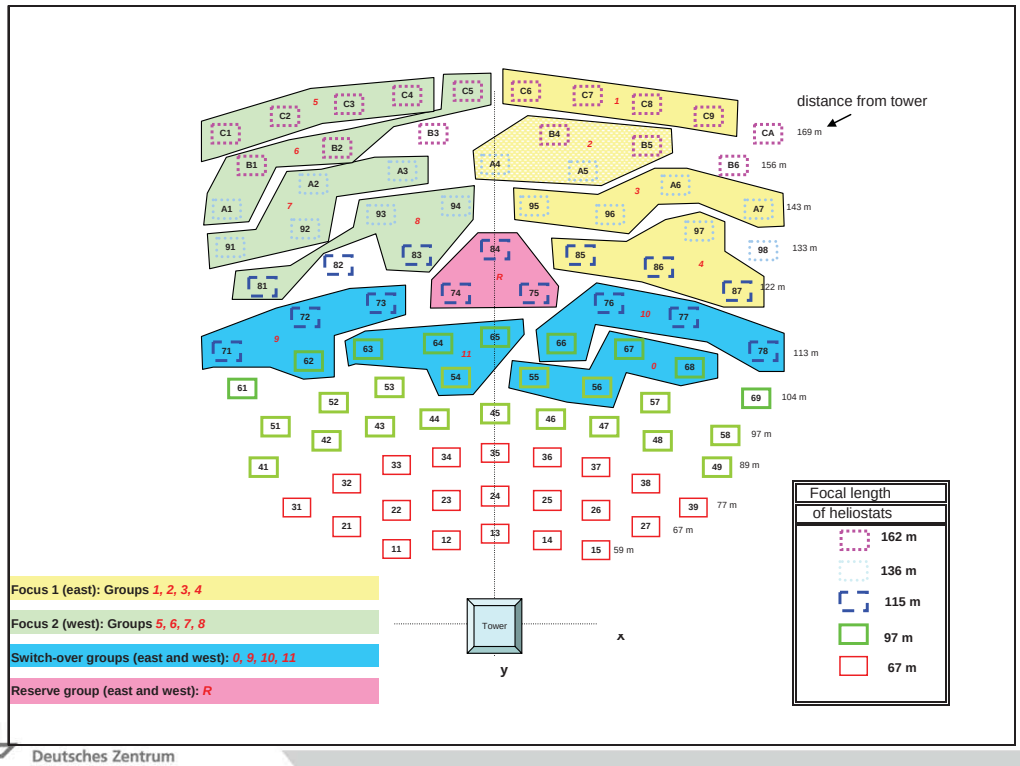
2004:
First solar thermochemical
H_2 production

DLR solar furnace

Pilot plant installation and testing

Scale-up: 100kW-pilot-plant

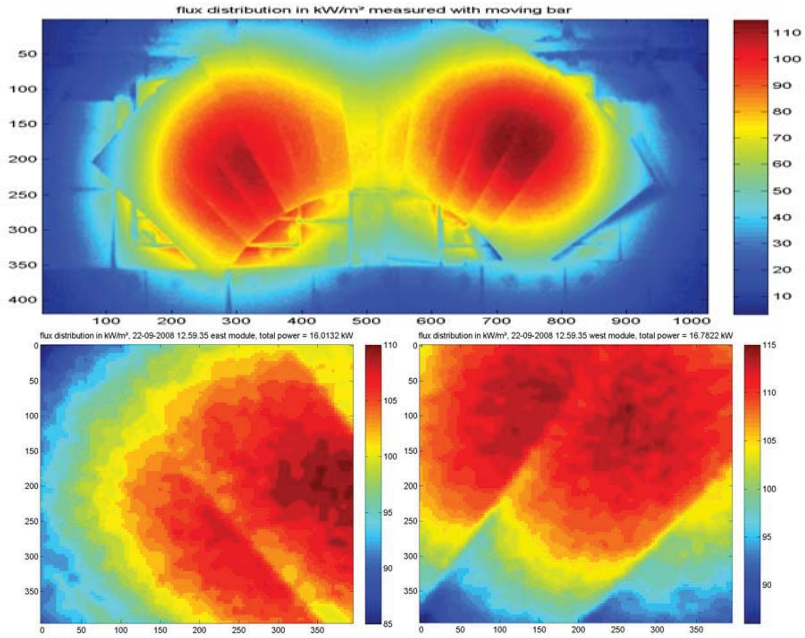
Process strategy for thermal cycling



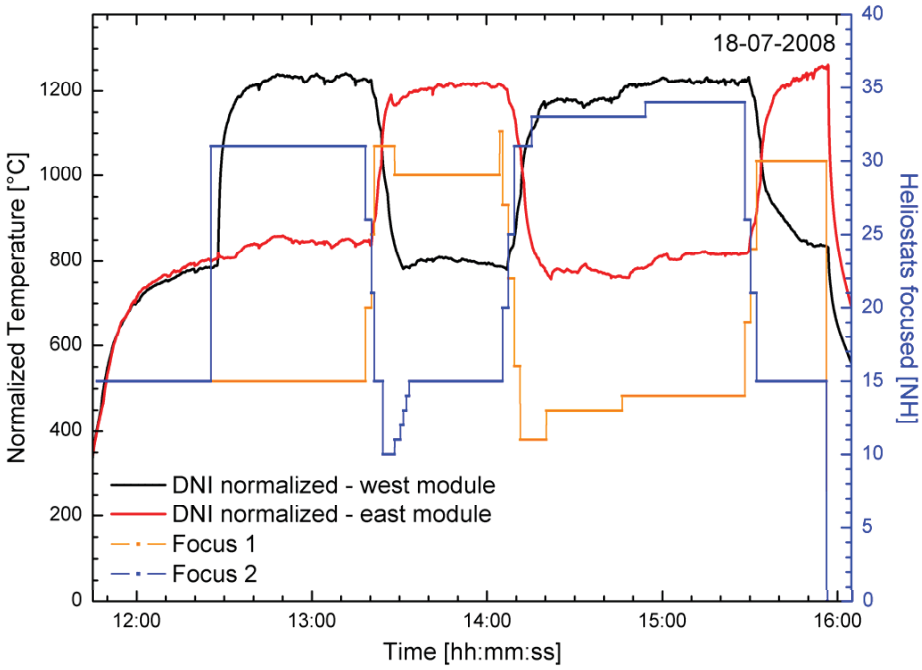
Experiments – Solar Flux

Flux Measurement at test operation

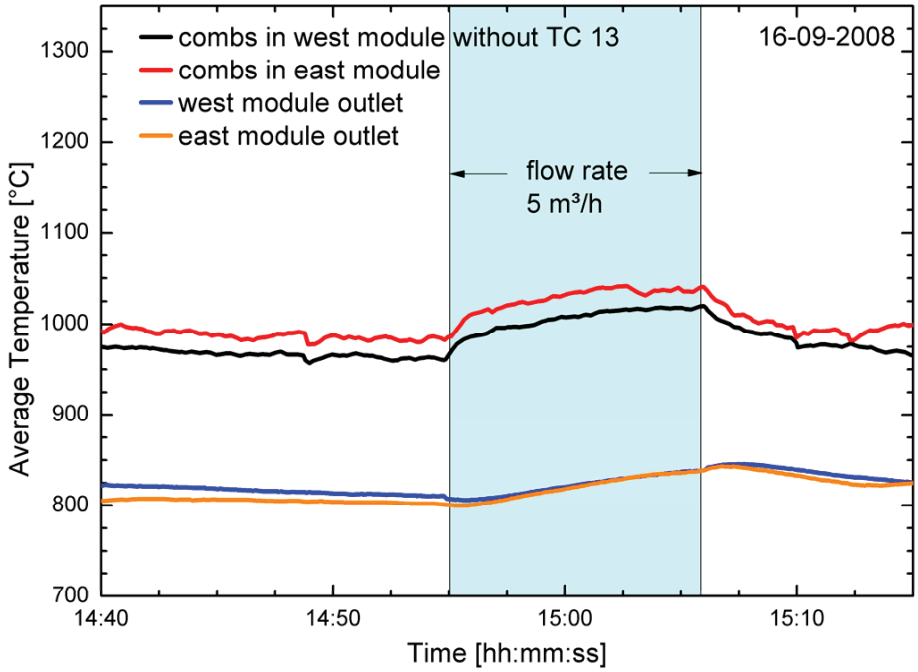
$Flux_{Max_{both\ Modules}} = 115 kW/m^2$



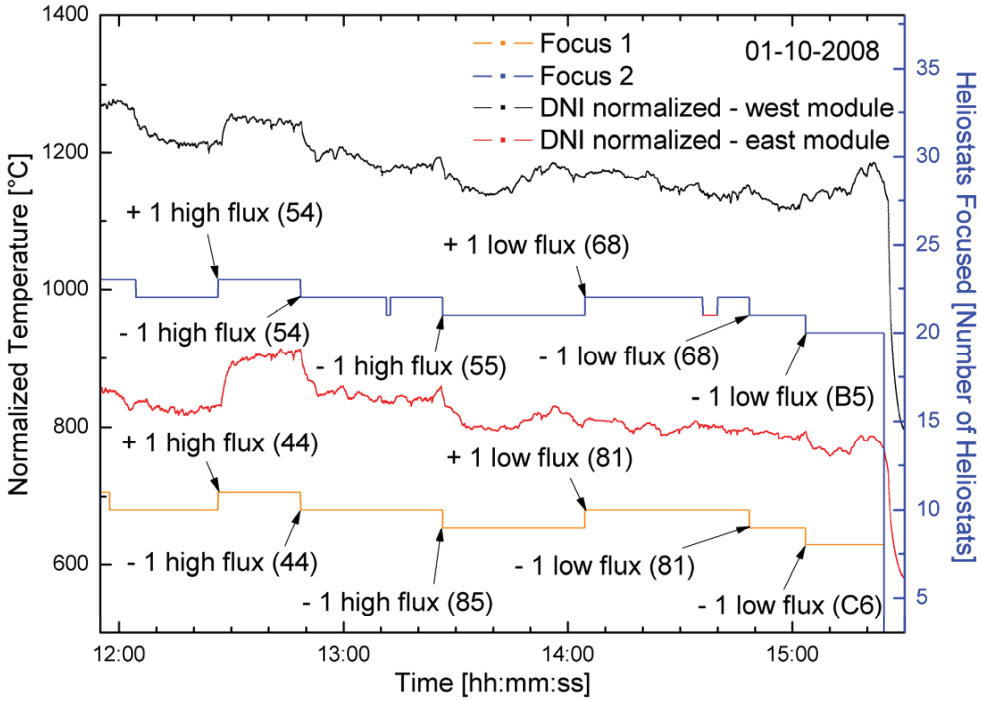
Experiments: Thermal cycling



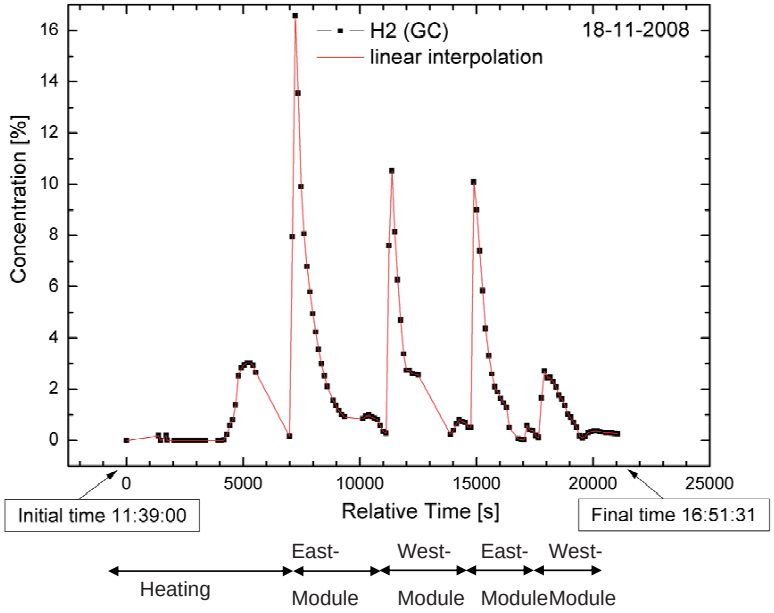
Parametric study – mass flow



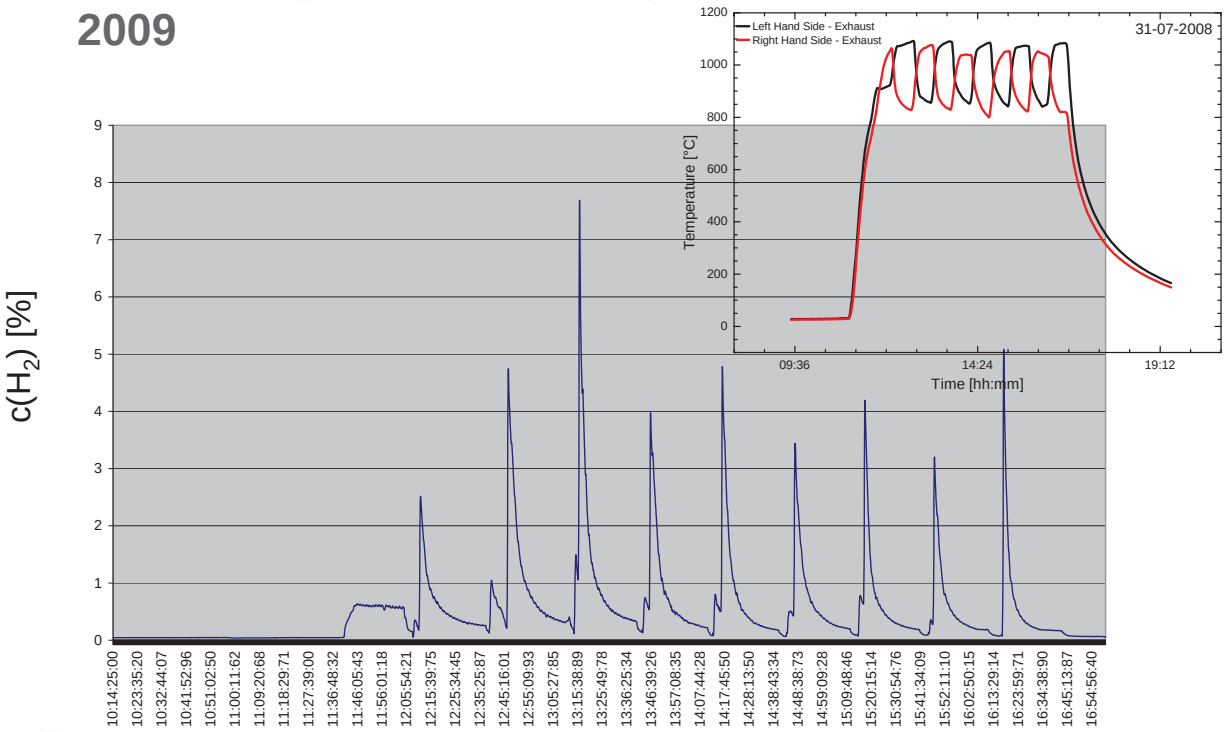
Parametric study – heliostats



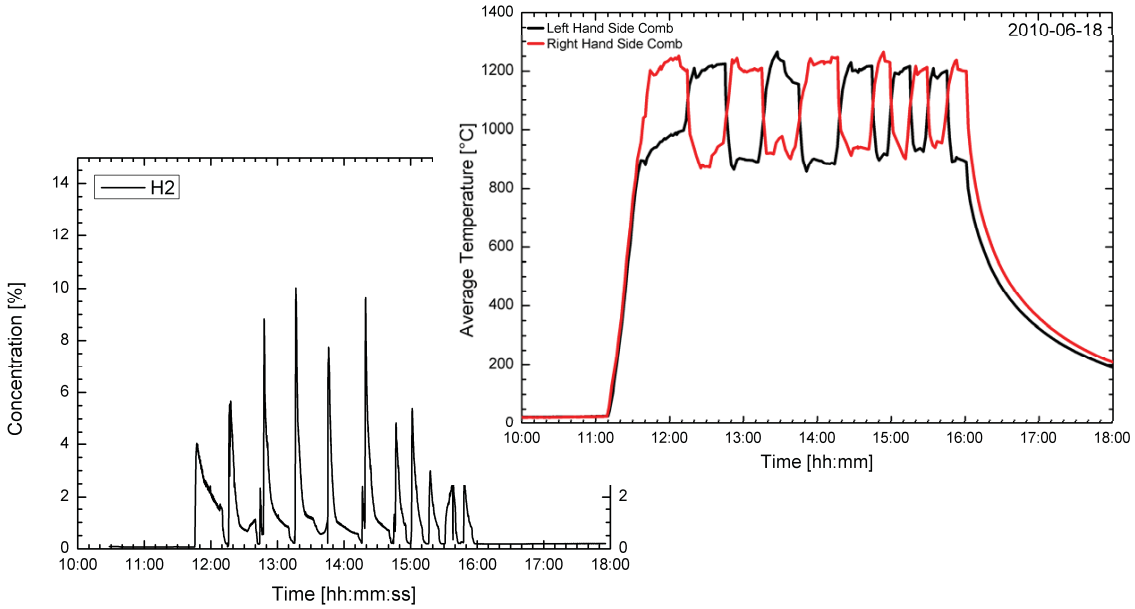
First Hydrogen Production



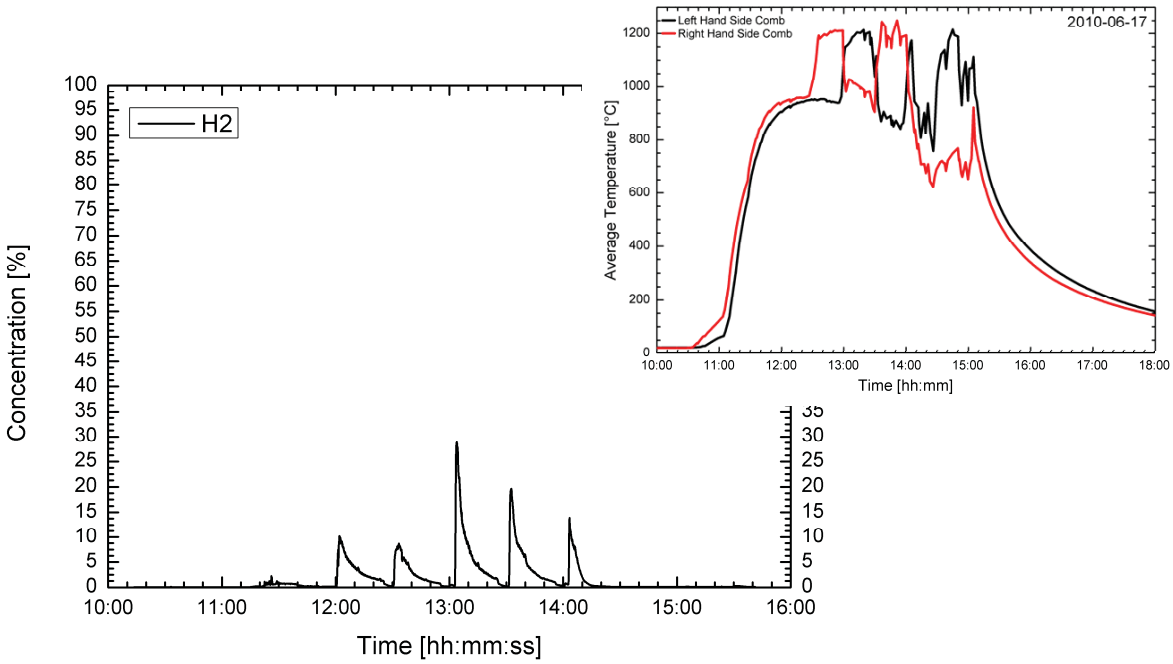
Hydrogen production in experimental series in July 2009



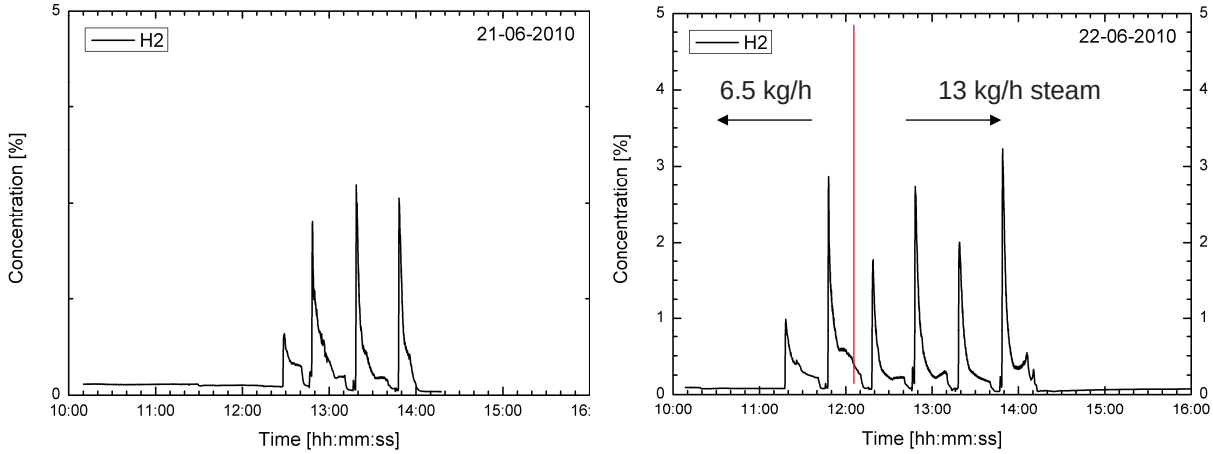
Hydrogen production on June 18th 2010



Hydrogen production on June 17th 2010



Hydrogen production on June 21st/22nd 2010

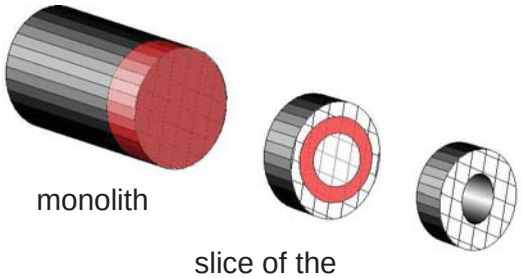


Modelling of reactor and process

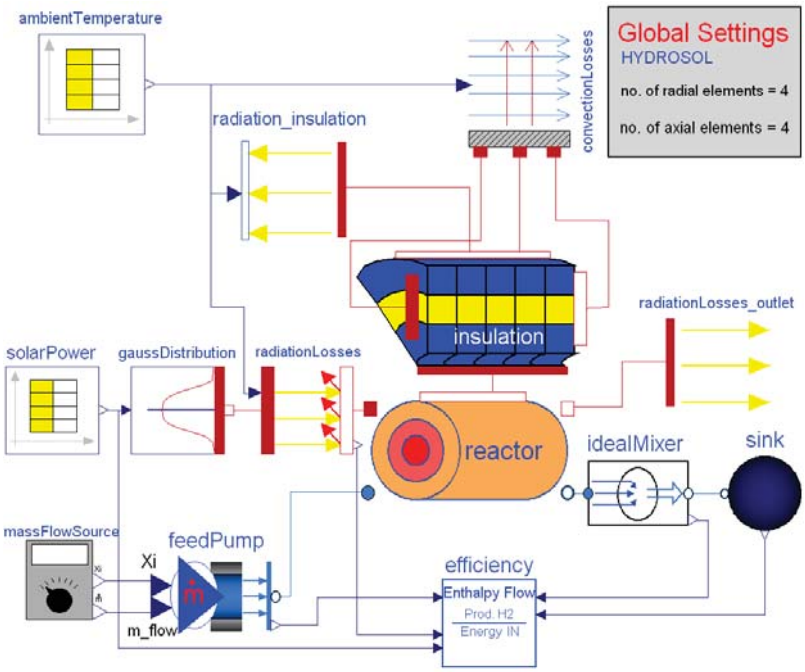
Model of Solar Furnace Reactor

Monolith

Absorber model



Overall Model of Solar Furnace Reactor



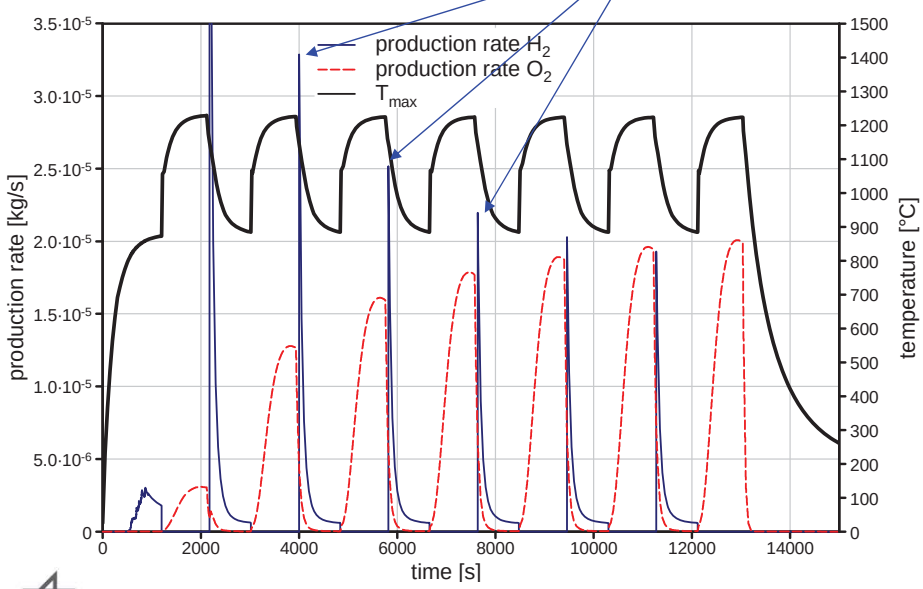
Model incluces:

- Irradiation and conduction among the individual absorber elements
- Intrusion of solar irradiation into the absorber channels
- Solar power input: gaussian distribution
- Irradiation losses through the reactor front window
- Thermal losses through the housing

Hydrogen Production

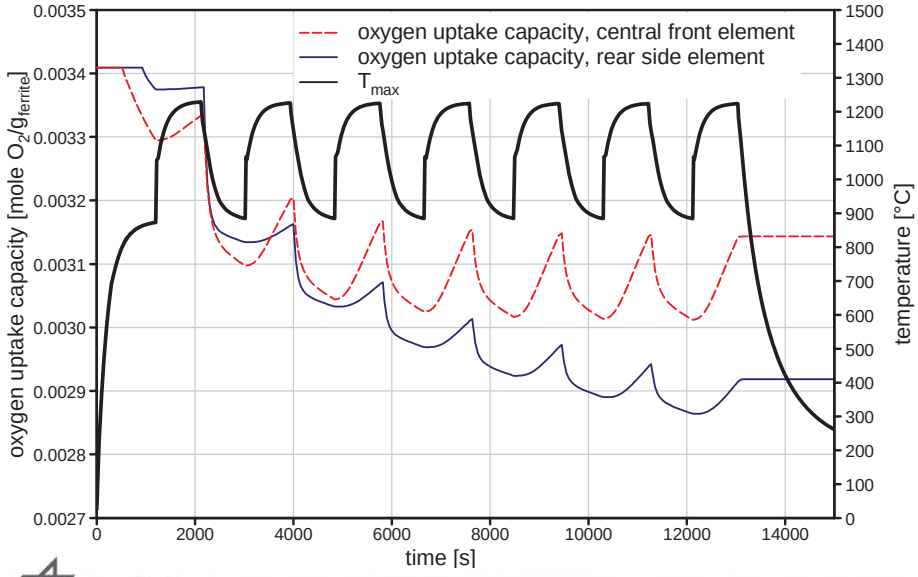
H_2 and O_2 production

Peak hydrogen production decreases



Ferrite Composition

Oxygen uptake capacity of ferrite

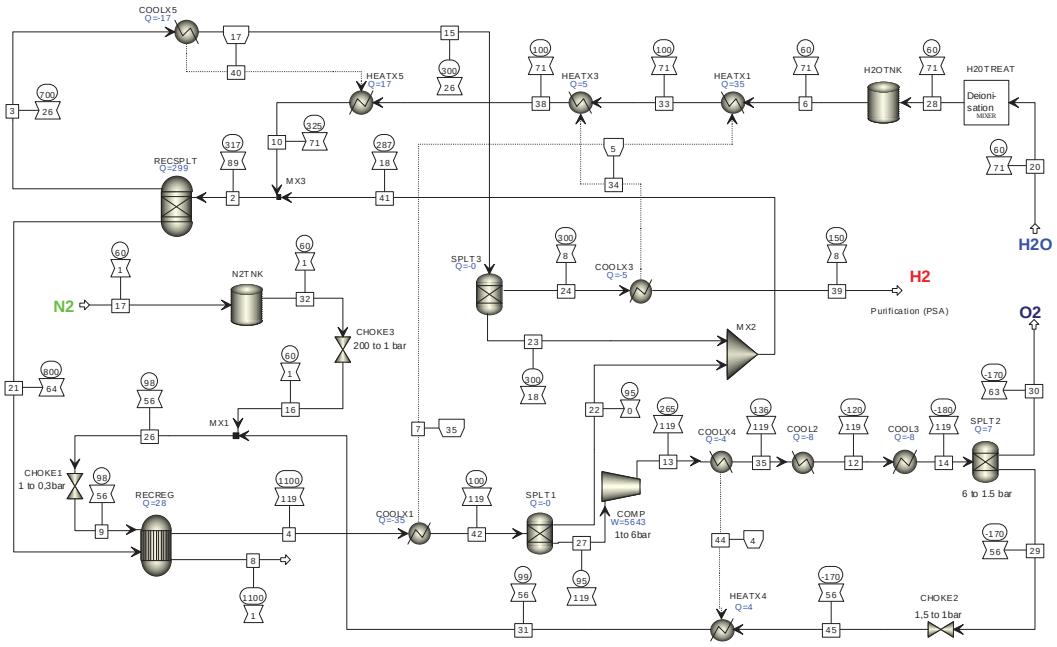


Low temperatures at the absorber rear side

→ poor regeneration

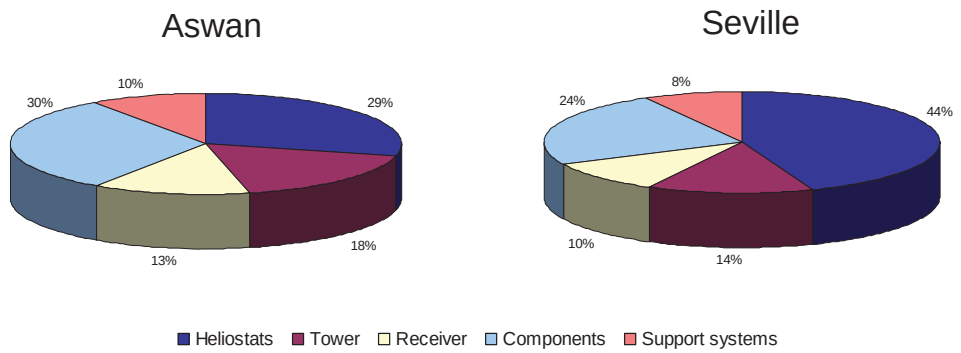
Scale-up

Flow sheet of HYDROSOL process



Economics

	Hydrosol 1 MW*)	Hydrosol 50 MW	Hybrid-Sulphur Cycle	Water Electrolysis	
Total investment	1.46	1.07	2.03	0.18	€/kg_{H2}
Operational costs	13.02	5.73	2.64	6.32	€/kg_{H2}/year
By-product credits	23,277	3,484,955	3,140,705	2,069,475	€/a
Hydrogen production costs	15.38	6.75	5.35	5.80	€/kg_{H2}



Hydrosol 3D

- **The principal objective of HYDROSOL-3D is the in-detail preparation of a plant for solar thermo-chemical hydrogen production from water via the HYDROSOL technology, in a 1 MW scale on a solar tower.**
- **HYDROSOL-3D focuses on the next step towards commercialization and involves all activities necessary to prepare the erection of a HYDROSOL-technology-based 1 MW solar demonstration plant.**
- **In this respect HYDROSOL-3D is concerned with the complete pre-design and design of the whole plant including the solar hydrogen reactor and all necessary upstream and downstream units needed to feed in the reactants and separate the products and the calculation of the necessary plant erection and hydrogen supply costs.**

Process variation: synfuels

CO_2 reduction using metal oxides

2-step synthesis of CO using multi-valent metal oxides

1. Step: Reduction

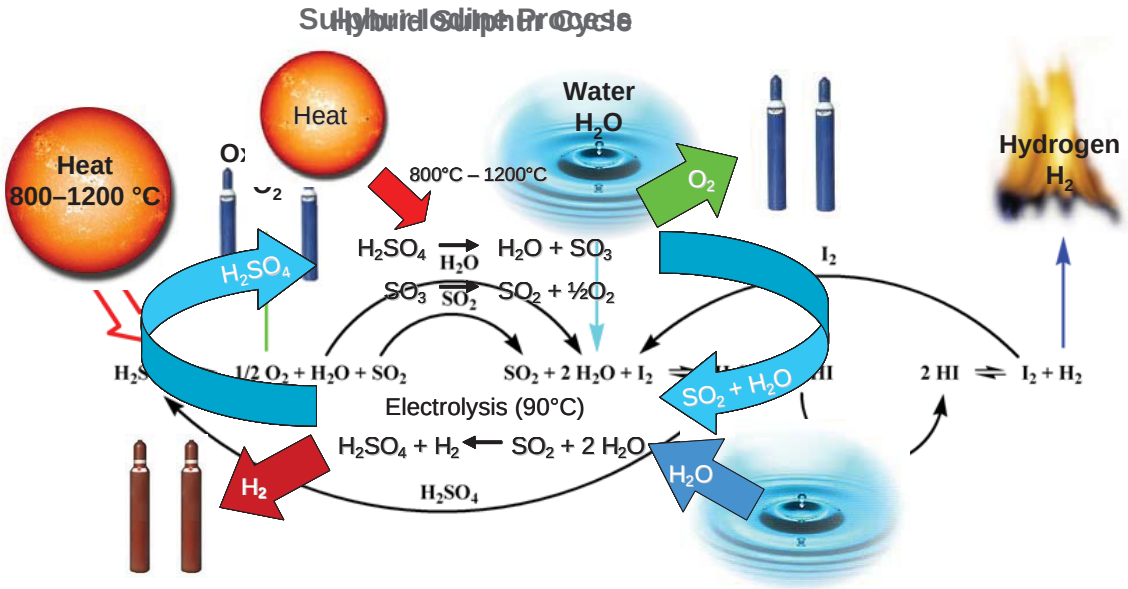
   $MO_{oxidiert} \leftrightarrow MO_{reduziert} + ½\ O_2$

2. Step: Oxidation oder CO_2 splitting

   $MO_{reduziert} + CO_2 \leftrightarrow MO_{oxidiert} + CO$

2. Sulphur Based Thermochemical Cycles

Examples of Sulphur based thermochemical cycles



Project Overview: HycycleS

The Consortium

Deutsches Zentrum für Luft- und Raumfahrt e.V. / DLR

EC - Joint Research Center

The University of Sheffield

Commissariat à l'Energie Atomique

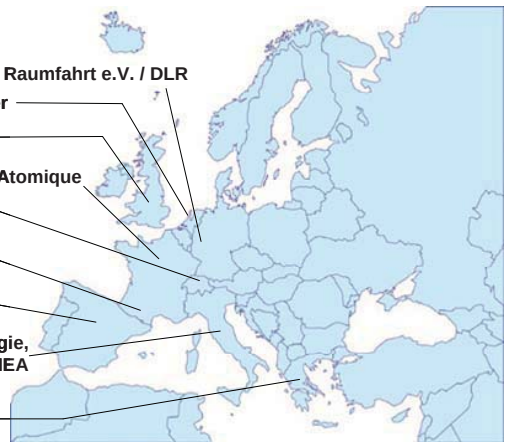
ETH Zürich

Boostec Industries

Empresarios Agrupados

Ente per le Nuove tecnologie, l'Energia e l'Ambiente / ENEA

Aerosol and Particle Technology Laboratory / CERTH-CPERI



HycycleS - Materials and components for **Hy**drogen production by sulphur based thermochemical **cycles**

EU FP7 - ENERGY

Duration: January 2008 – March 2011

Main topics:
Suitability of construction and catalyst materials for H_2SO_4 decomposition section

Material and design of H_2SO_4 decomposer (as heat exchanger)

Material and design of H_2SO_4 decomposer (as solar receiver-reactor)

Materials and design of SO_2/O_2 separator (membranes for enhancing the performance of SO_3 decomposition)

Solar reactor development, testing and simulation

Objective

- Development of a solar receiver-reactor (multi-chamber concept)
  - Evaporation and decomposition of sulphuric acid
  - Volumetric receiver-reactor concept
- Testing in DLR solar furnace
  - Variation of operating conditions and configuration
  - Analysis of different catalyst systems

HYTHEC receiver-reactor

DLR solar furnace

H_2SO_4 decomposition in 2 steps

Absorbers:

1. Evaporation of liquid sulphuric acid (400°C)

$$H_2SO_{4\,(aq)} \rightarrow H_2SO_{4\,(g)} + H_2O_{\,(g)}$$

$$H_2SO_4 \rightleftharpoons SO_3 + H_2O$$

SiSiC foam

2. Decomposition (reduction) of sulphur trioxide (850°C)

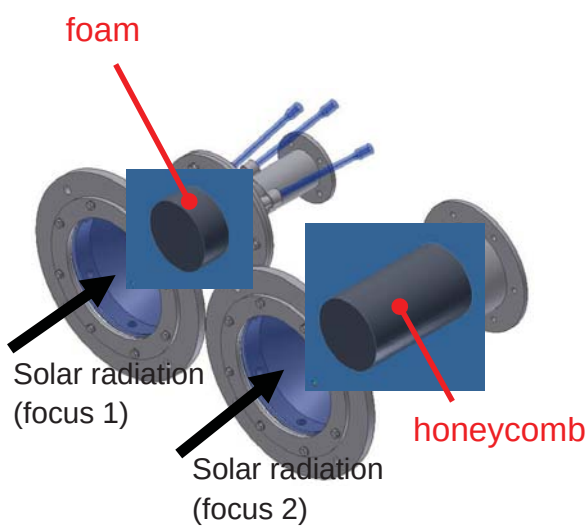
$$SO_3 + H_2O \rightleftharpoons SO_2 + \tfrac{1}{2}\,O_2 + H_2O$$

SiSiC honeycomb

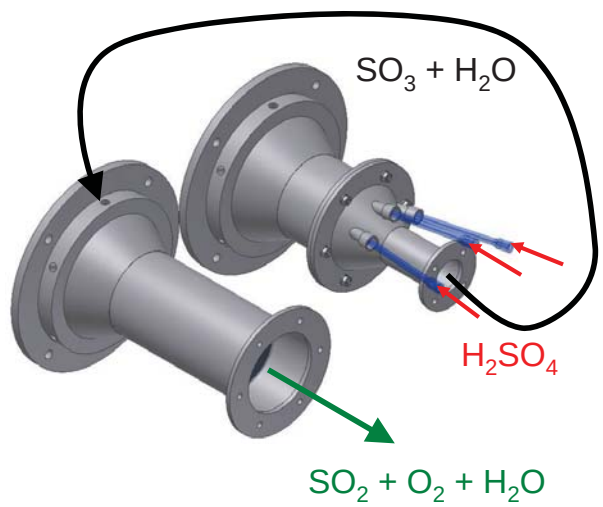
Procedure of technology development

1. Preliminary design of a multi-chamber concept
2. numerical analysis: FEM, Dymola, CT and continuum model
3. Finalization of the design
4. Construction and assembling of the reactor
5. Initial operation followed by first testing series
6. Optimisation of the set-up followed by second testing series
7. Further optimisation and testing (if necessary)

Design of multi-chamber solar reactor

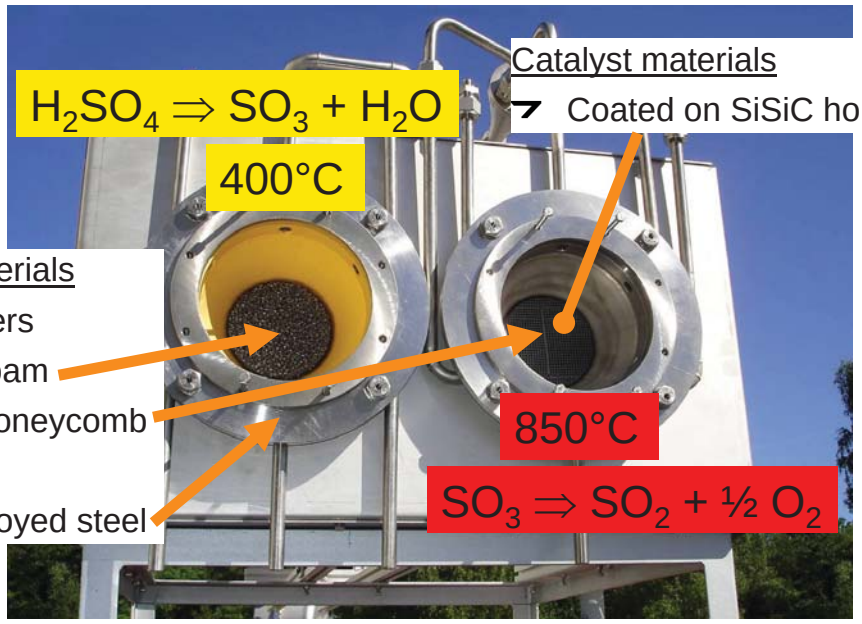


Front view of
evaporator and decomposer



Rear view

HycycleS solar reactor



Catalyst materials

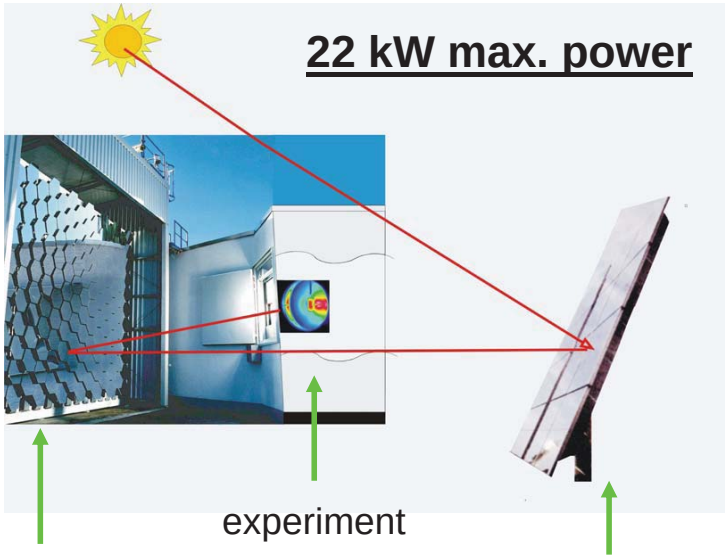
- Coated on SiSiC honeycomb

Construction materials

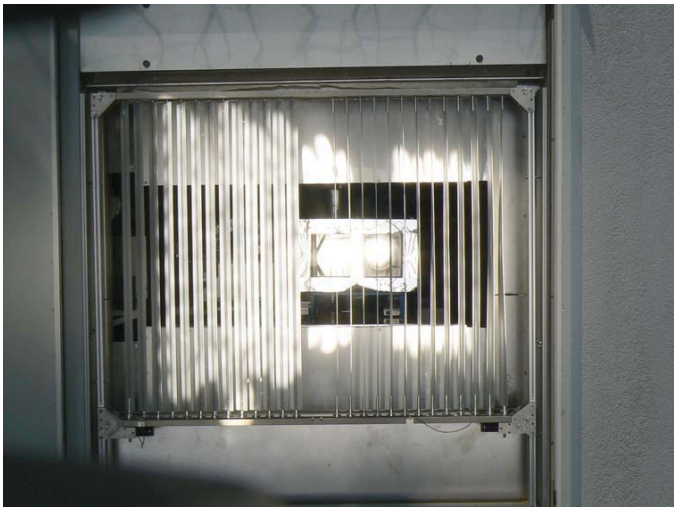
- Solar absorbers
  - SiSiC foam
  - SiSiC honeycomb
- Piping
  - High-alloyed steel

Assembling of the solar reactor

Solar furnace of DLR in Cologne



Power regulation of the two chambers

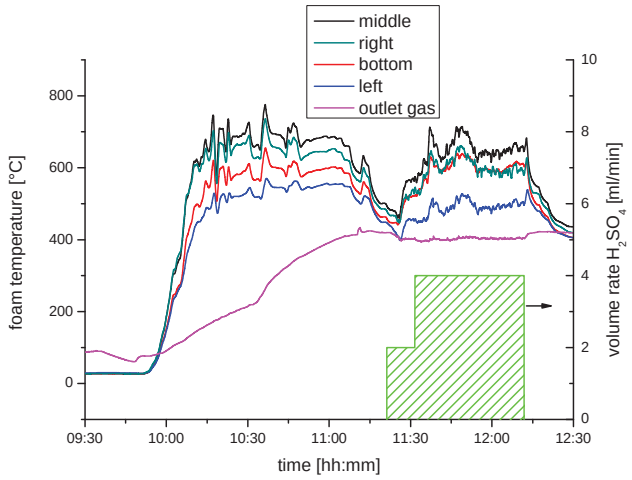


Segment shutter with 14 lamellae on each side

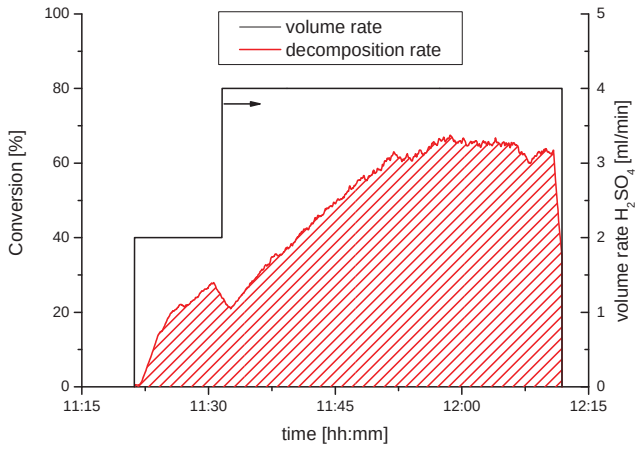
Receiver-Reactor during operation

Testing and qualification of the receiver-reactor

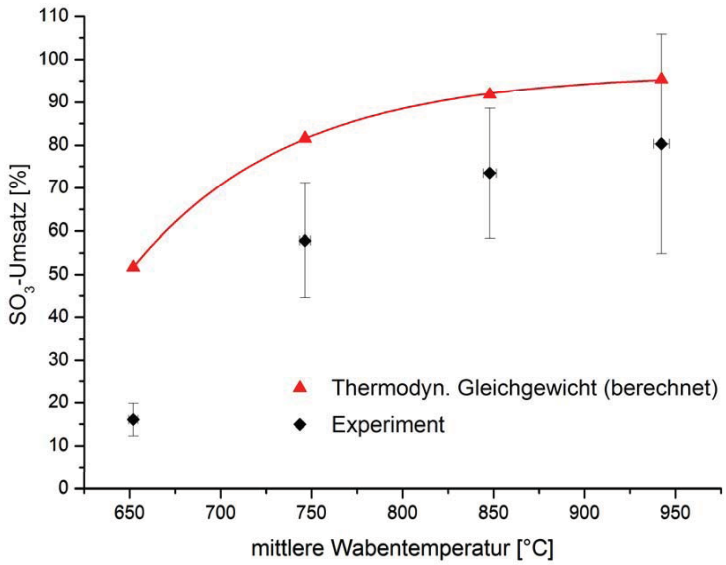
Temperature of the evaporator



Performance of the SO_3 decomposer



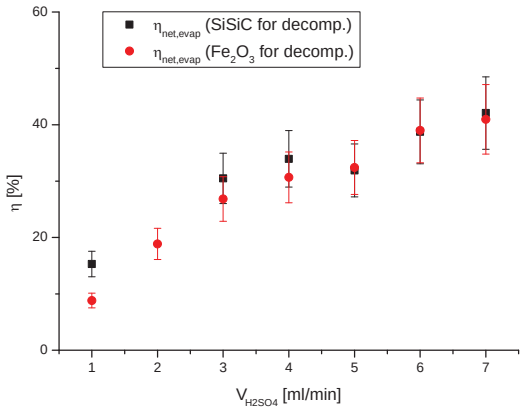
Conversion of SO_3: experiment and equilibrium



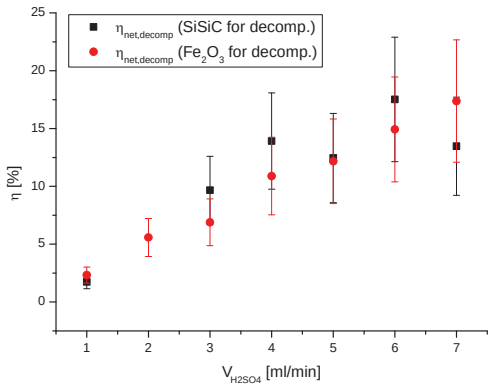
$$U_{SO_3} = \frac{\dot{V}_{SO_2;aus}}{\dot{V}_{SO_3;ein}}$$

Reactor efficiencies

evaporator

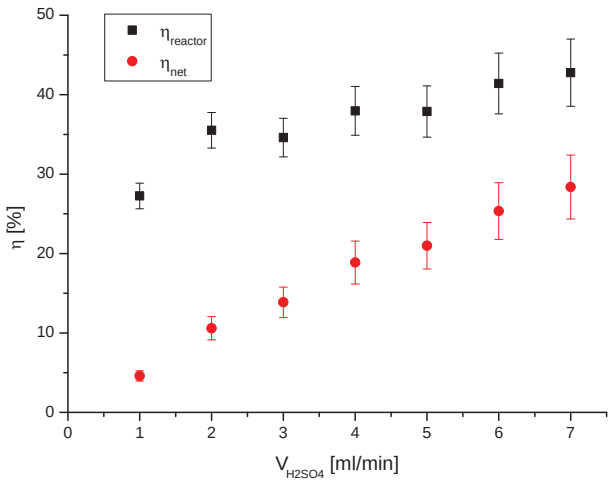


decomposer

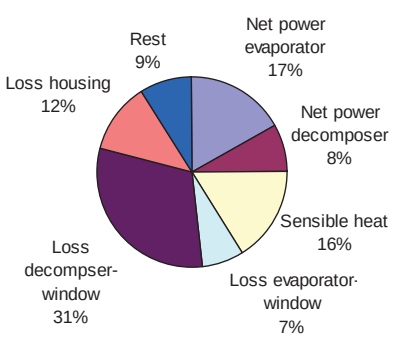


Reactor efficiencies

Total reactor



Energy Losses



$P_{S,evap}$	870 W
$P_{S,decomp}$	1141 W
Catalyst	Fe_2O_3
V_{H2SO4}	6 ml/min
$T_{hc,mean}$	852 °C
Conversion	82 %
$\eta_{net,evap}$	39 %
$\eta_{net,decomp}$	15 %

System Model of the Decomposer

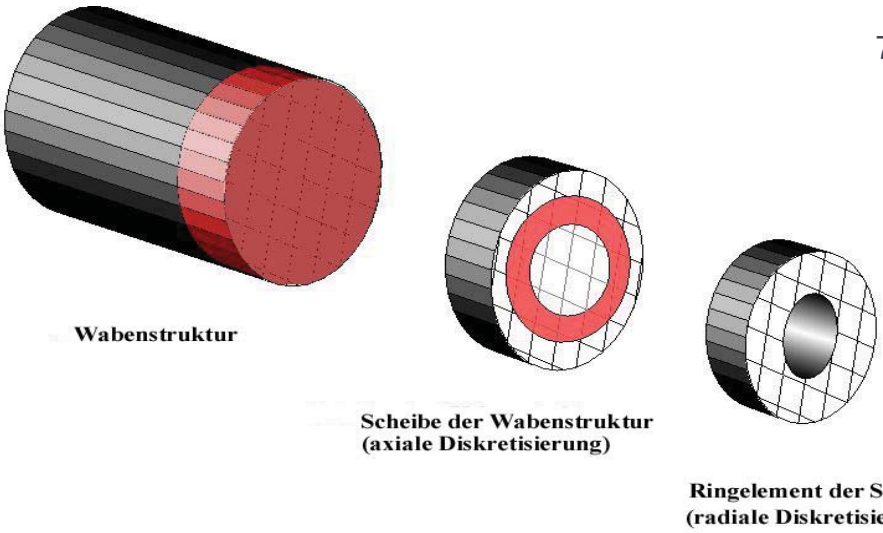
Discretisation of the Absorber

7 Ring elements x
10 Slices

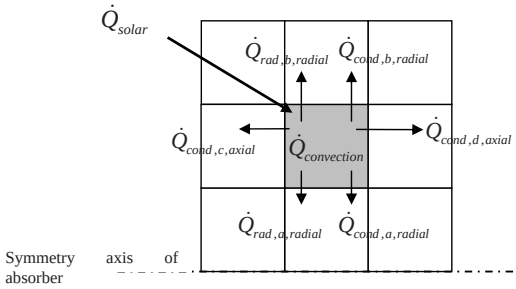
↓

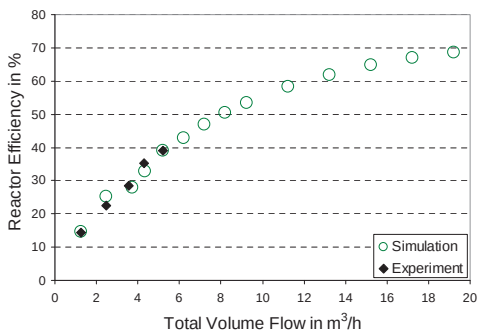
70 elements

20 cells
per element
for chemical reaction
modelling



Simulation of the SO_3 Decomposer





Heat balance of solid volume elements

$$0 = m \cdot c_p \cdot \frac{\partial T}{\partial t} + \dot{Q}_{cond,a,radial} + \dot{Q}_{cond,b,radial} + \dot{Q}_{cond,c,axial} +$$
$$+\dot{Q}_{cons,d,axial} + \dot{Q}_{rad,a,radial} + \dot{Q}_{rad,b,radial} + \dot{Q}_{solar} - \dot{Q}_{convection}$$

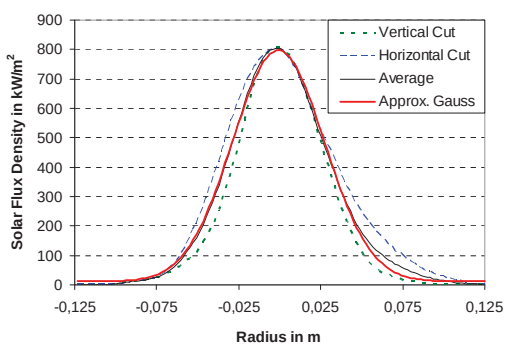
Heat balance of gas volume elements

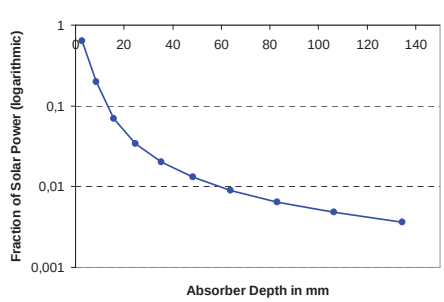
$$0 = \dot{m}_{in} \cdot h_{in} - \dot{m}_{out} \cdot h_{out} - \dot{Q}_{\text{reaction}} + \dot{Q}_{convection}$$

Kinetic model of SO_3 reduction

$$v_{[i]} = k \cdot \left(x_{SO_3,out[i-1]} \cdot c_{gas} \right)^{n_{SO_3}}$$
$$-k_{back} \cdot \left(\left(x_{SO_2,out[i-1]} \cdot c_{gas} \right)^{n_{SO_2}} \cdot \left(x_{O_2,out[i-1]} \cdot c_{gas} \right)^{n_{O_2}} \right)$$

Modelling of Radiation





Heat losses: Thermal radiation

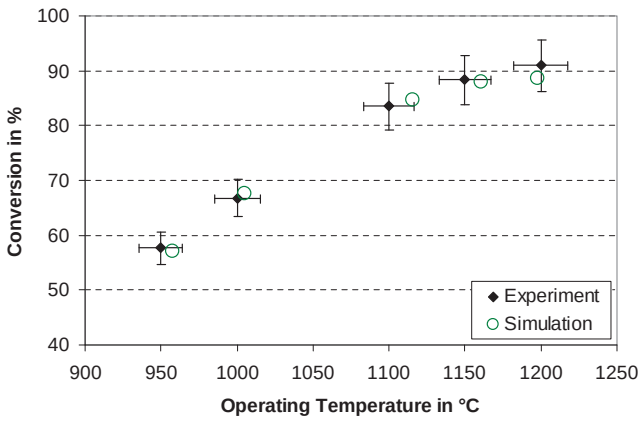
$$\dot{Q}_{TR} = \dot{Q}_{TR,\,conus} + \dot{Q}_{TR,\,window} + \dot{Q}_{TR,\,ambience}$$

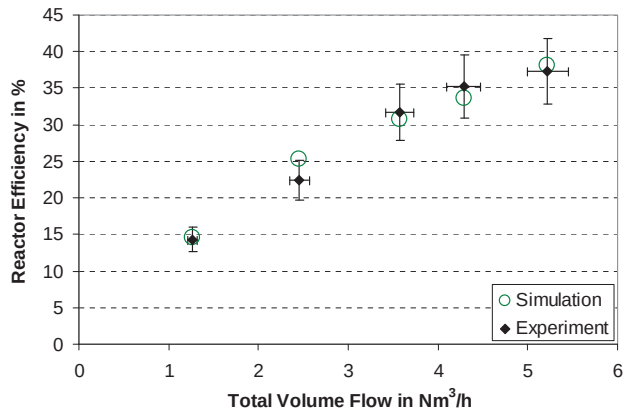
Thermal radiation through quartz window

$$\dot{Q}_{TR,\,ambient} = a_{\lambda<\lambda_{Grenz}} \cdot \phi_{12} \cdot \varepsilon_{Absorber} \cdot \varepsilon_{ambient} \cdot$$
$$\cdot C_S \cdot A_{Absorber} \cdot \left(T^4_{Absorber} - T^4_{ambient} \right)$$

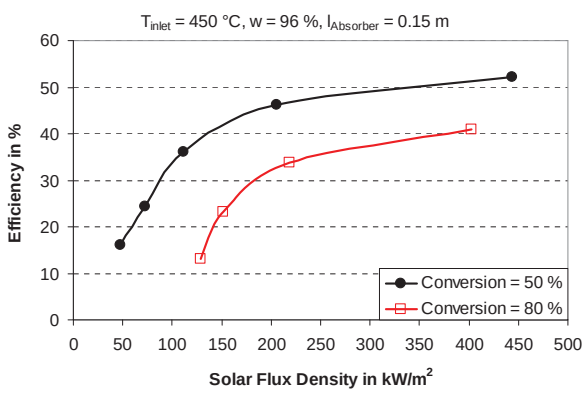
Validation: conversion and reactor efficiency

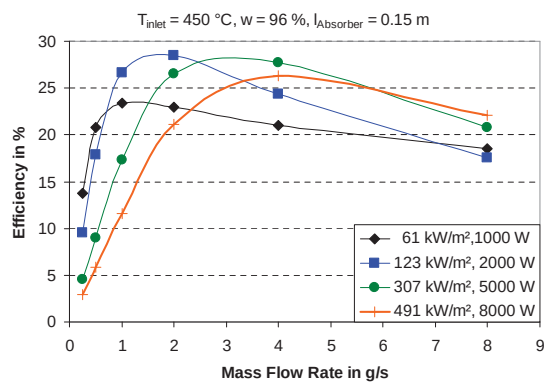
$$\eta_{\text{reactor}} = \frac{\dot{Q}_{net,reactor}}{P_{solar}} = \frac{\dot{Q}_{H_2SO_4-dissociation} + \dot{Q}_{SO_3-decomposition} + \dot{Q}_{sensible\ heat}}{P_{solar}}$$





Efficiency of the SO_3-decomposition





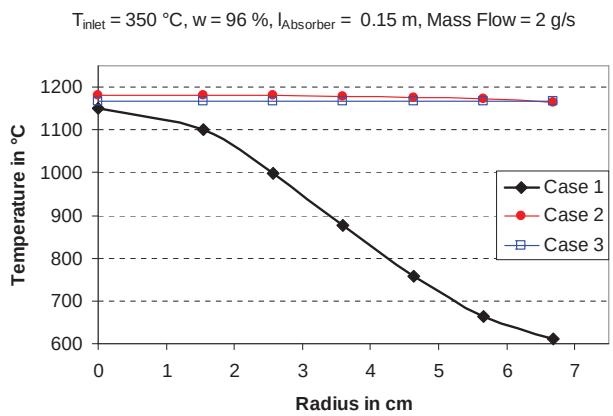
two different fixed minimum conversions

Case studies: Gradient of Solar Flux

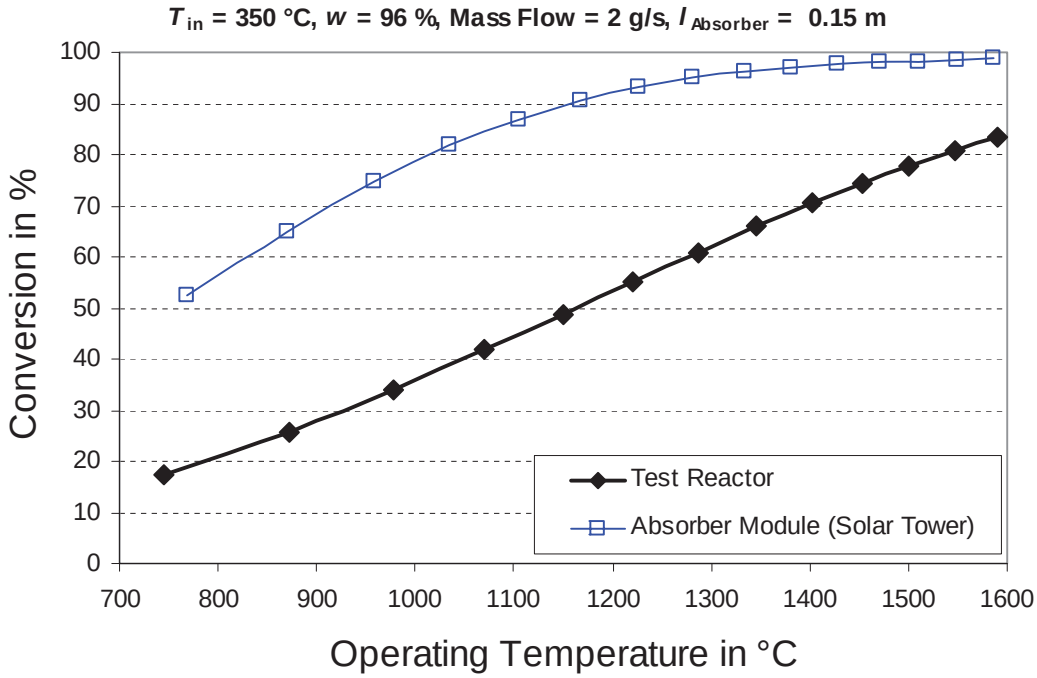
Case 1: The prototype test reactor as used in the solar furnace (Gaussian flux profile)

Case 2: Like case 1 but with an ideal homogeneous distribution of the solar flux density.

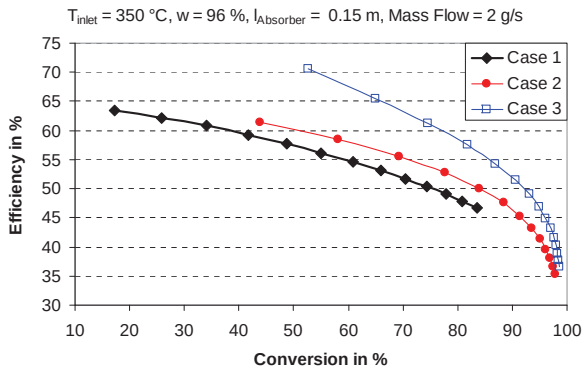
Case 3: Adiabatic absorber element of a large receiver-reactor on a solar tower.

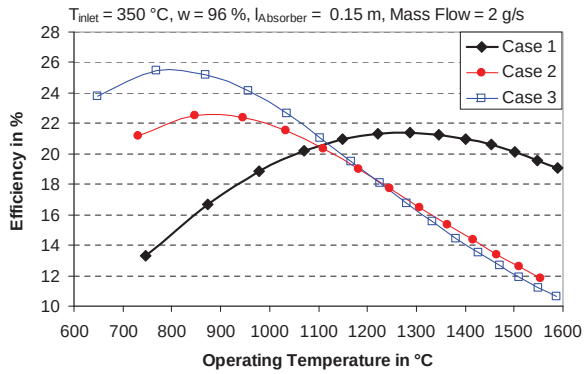


Higher Conversion in a Large Scale Receiver-Reactor



Case Studies: Efficiency

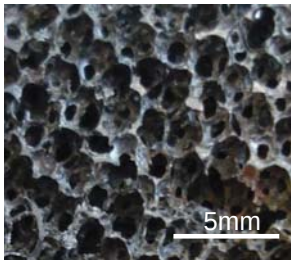




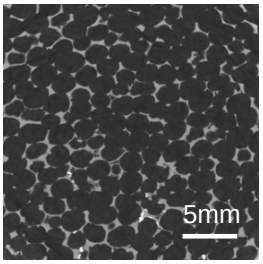
Model of the evaporator (ETH)

Foam characterization by CT and digitalisation

- SiSiC sample (uncoated, 20ppi → d_{nom} = 1.27mm):

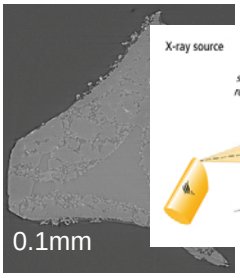


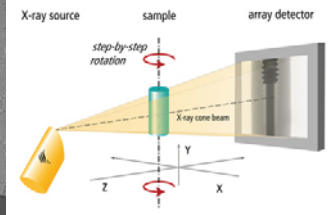
photo



micronCT

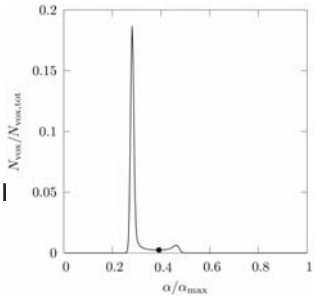
3D rendered



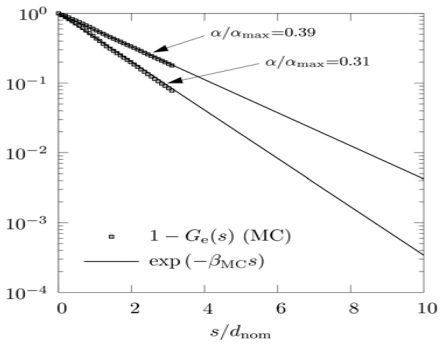


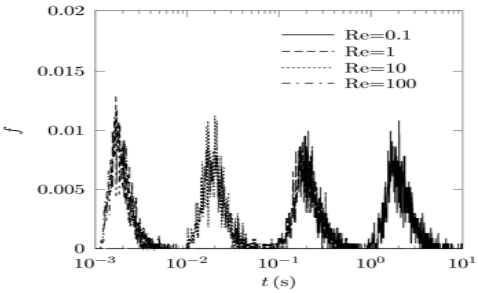
submicronCT

l poi



Characterisation of the foam



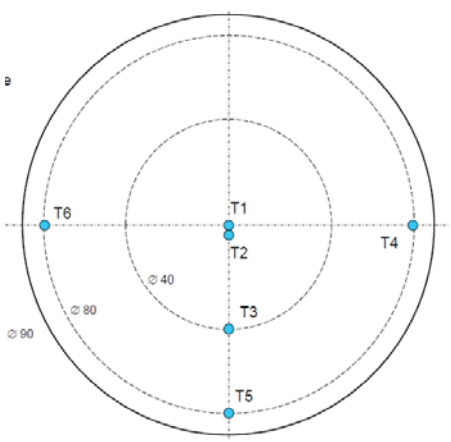


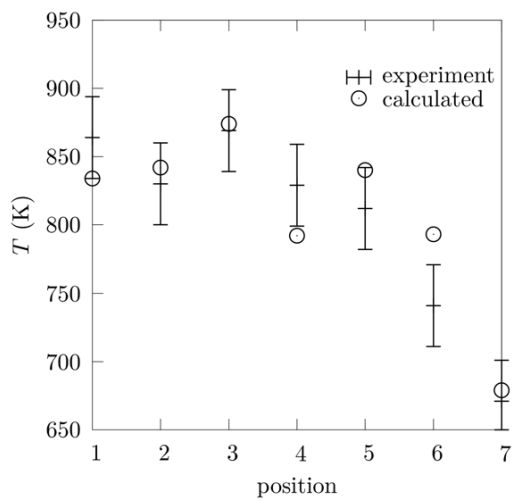
- Geometrical Characterisation
- Radiative Characterisation
- Convective Characterisation
- Heat Transfer Characterisation
- Mass Transfer Characterisation

Development of a continuum model

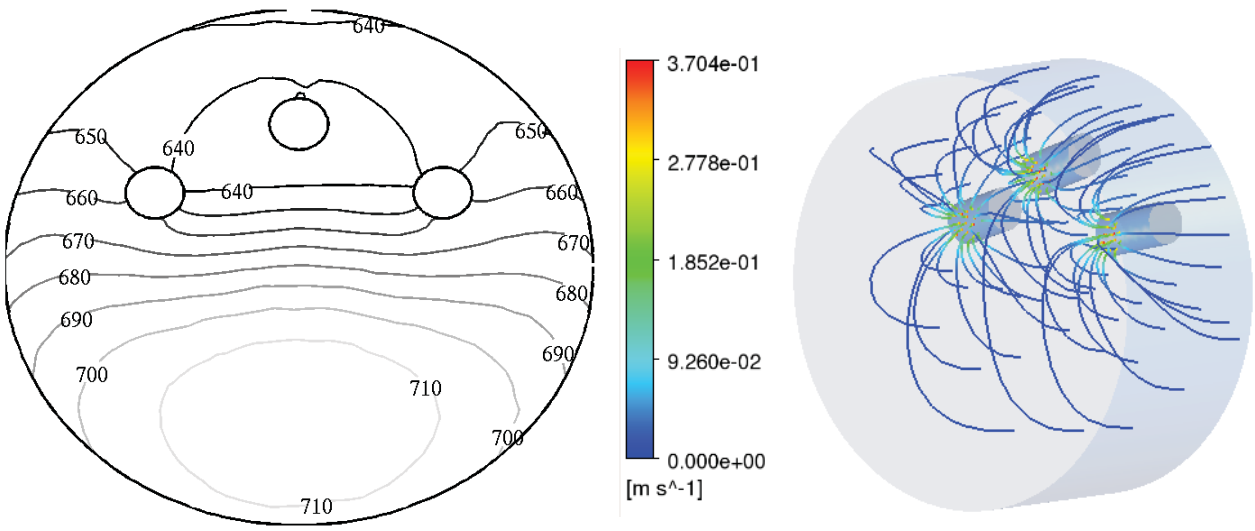
- Continuum model based on
  - Energy conservation, solid and fluid
  - Mass- & Species conservation, fluid
  - Momentum conservation, fluid
- will be able to predict: optimum and maximal mass flow of acid
- Variations in:
  - position of acid inlet
  - porosity and nominal diameter of foam
  - solar input
  - …
- lead to a deeper understanding of the process and its optimization for maximum solar-to-chemical energy conversion efficiency

Validation of model using experimental data from solar furnace campaigns

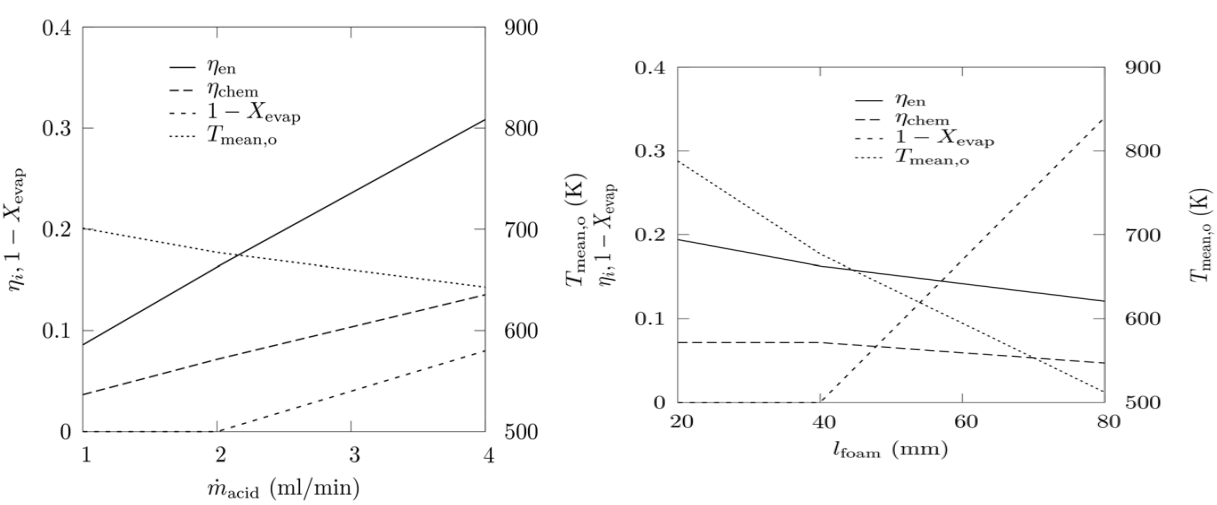




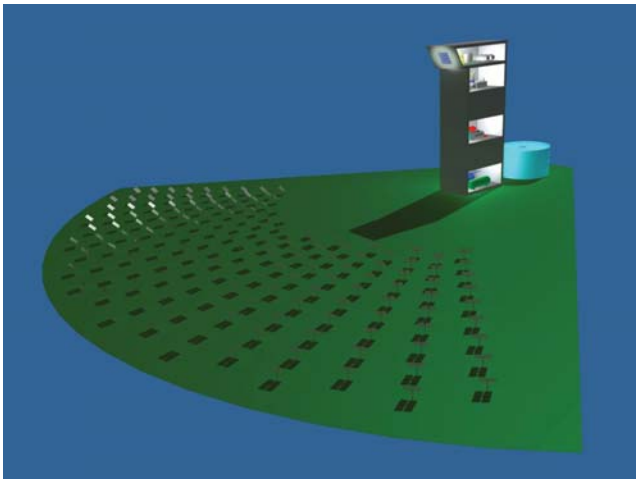
Temperature maps and flow regimes of the foam vaporiser

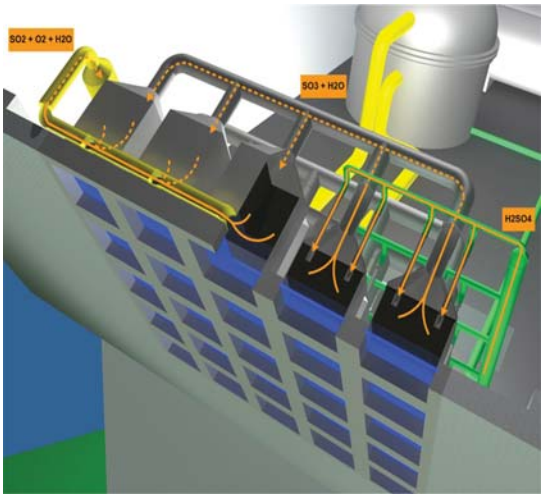


Influence of process parameters on reactor's energetic and chemical efficiency and mean outlet temperature

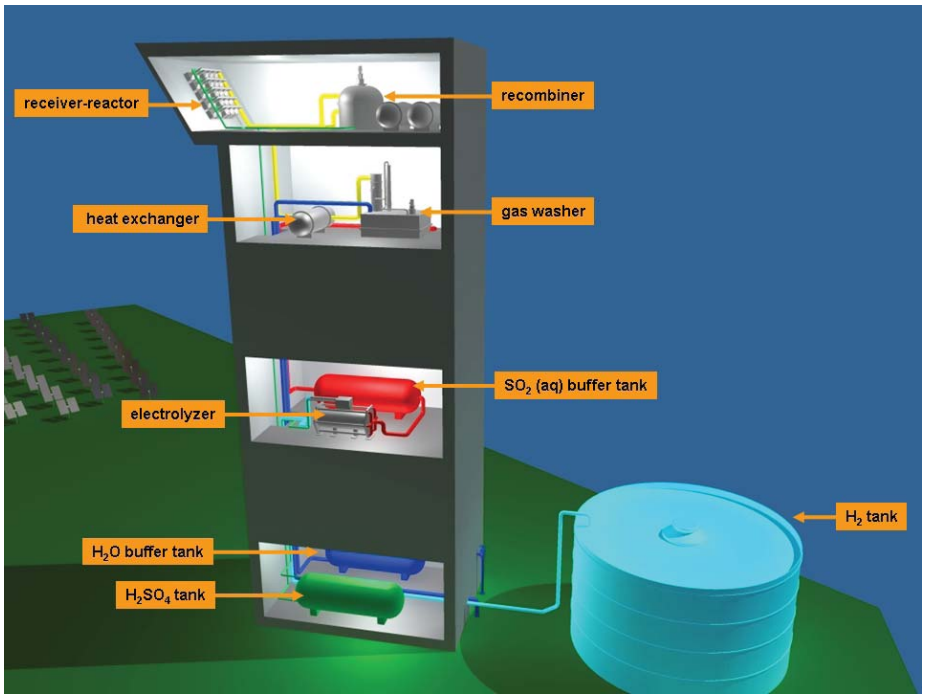


Scale-up





Implementation in to a Solar Tower



Summary

- Volumetric Receiver-Reactors well suited for thermochemical hydrogen production
- Observed yield close to therodynamic limits
- Efficiency of the reactor can still be drastically improved (Slow kinetics, high re-radiation losses)
- Materials: Optimum solutions by far not yet reached for redox materials, catalysts, construction materials
- A bunch of capable reactor and process models developed and now avaiable for a broad variety of purposes and applications
- The more one gets into the details of process design, the higher are the production cost

Acknowledgements

The authors acknowledge the co-funding of the European Commission for the projects HYTHEC, HycycleS, HYDROSOL, HYDROSOL-2 and HYDROSOL-3D.

Many thanks for your attention!