Thermochemical Energy Storage

Overview on German, and European R&D Programs and the work carried out at the German Aerospace Center DLR

Dr. Christian Sattler
christian.sattler@dlr.de

Dr. Antje Wörner
antje.woerner@dlr.de

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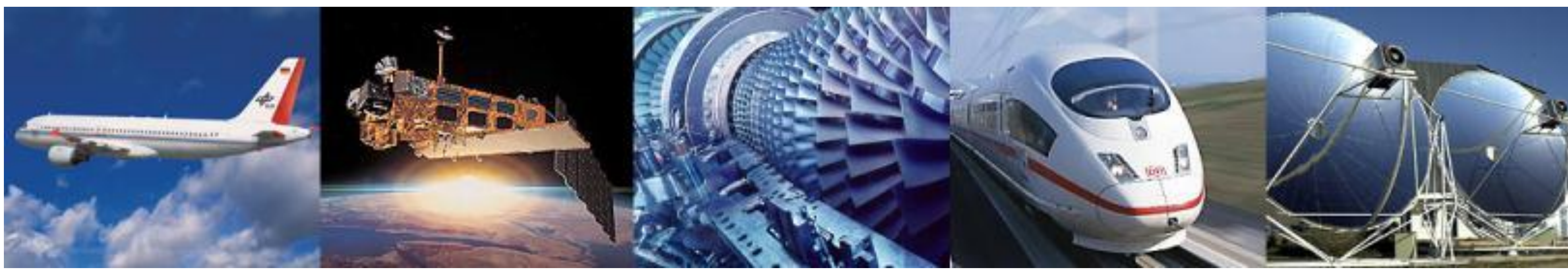
German Aerospace Center



– Research Institution
– Space Agency
– Project Management Agency

Research Areas

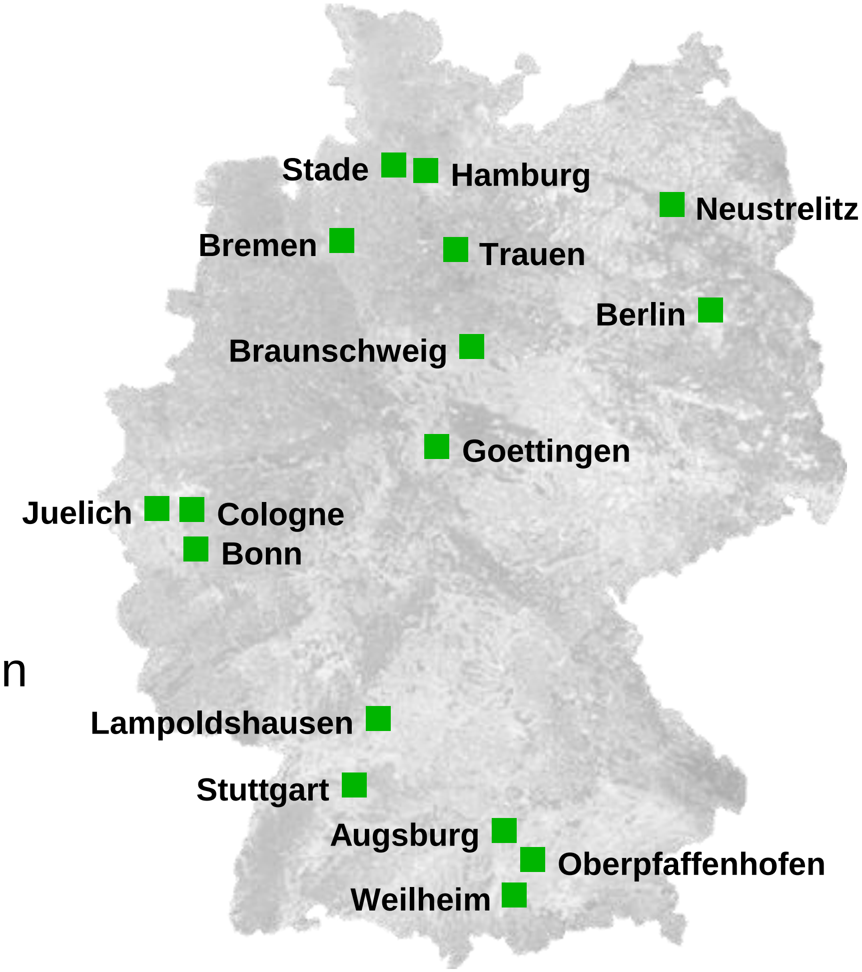
- Aeronautics
- Space Research and Technology
- Transport
- Energy
- Space Administration
- Project Management Agency

Locations and employees

7000 employees across
32 institutes and facilities at
■16 sites.

Offices in Brussels,
Paris, Washington, and Almería.

Permanent delegation at the
European Solar Test Centre
Plataforma Solar de Almería, Spain



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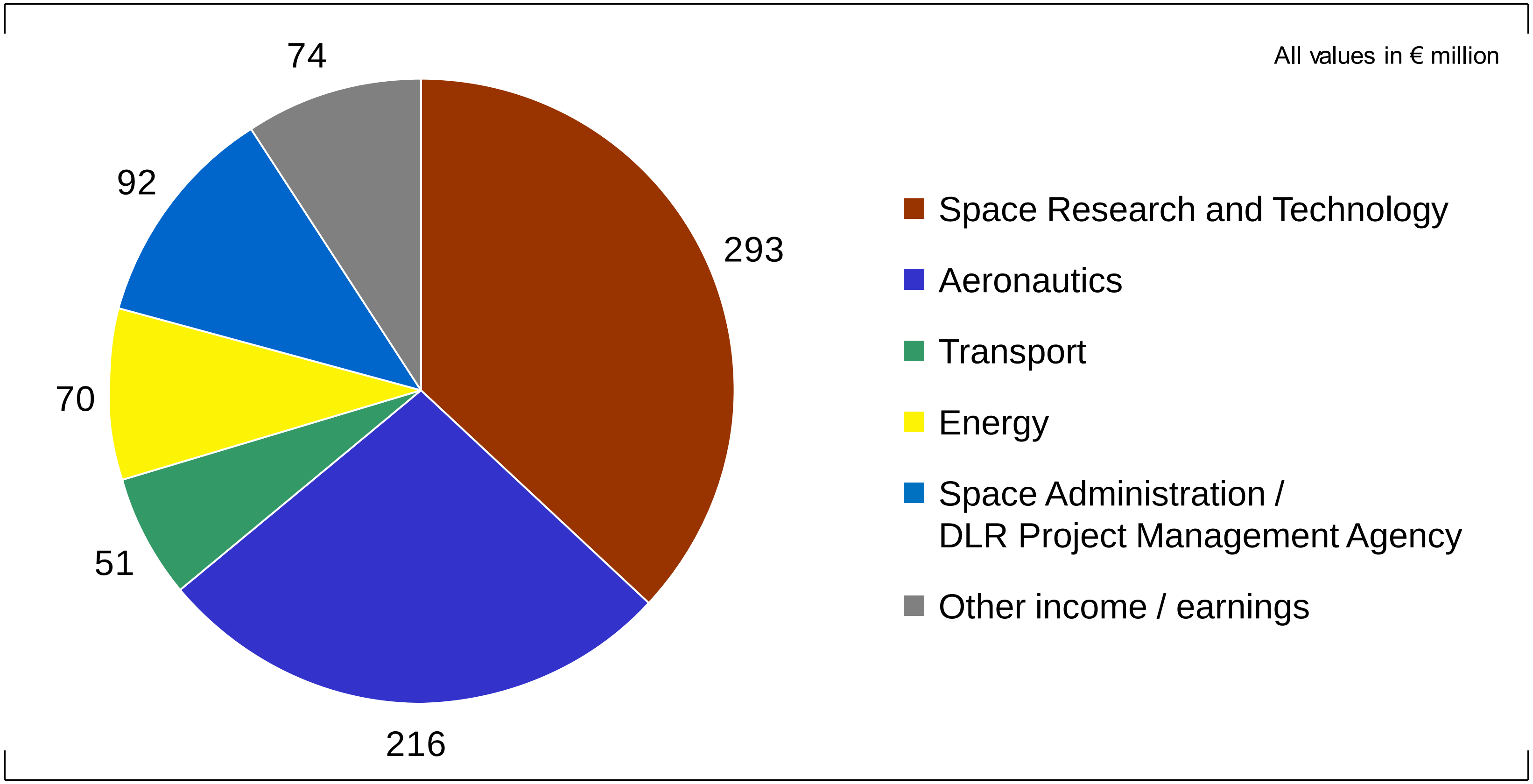
Total income 2011 – Research, operations and management tasks (excluding trustee funding from the Space Administration / DLR Project Management Agency): € 796 Mio.



Participation in the Helmholtz Association

- Success in obtaining program-oriented funding
- Added value from support of the Helmholtz Association
- Helping to shape the organisational development process

HELMHOLTZ
GEMEINSCHAFT

AWI DESY dkfz. DLR DZNE Deutsches Zentrum für Neurodegenerative Erkrankungen in der Helmholtz-Gemeinschaft GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel

GSI GFZ Helmholtz-Zentrum Potsdam HZB Helmholtz Zentrum Berlin HZDR Helmholtz Zentrum Dresden Rossendorf Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung JÜLICH Forschungszentrum

KIT Karlsruher Institut für Technologie Helmholtz Zentrum für Infektionsforschung HelmholtzZentrum münchen Helmholtz Zentrum für Umweltforschung UFZ MDC IPP

National and International Networking

Customers and partners: Governments and ministries, agencies and organisations, industry and commerce, science and research

World

Europe

EADS, cnes, NLR, EREA, esa, ONERA, ECTRI

Germany

HELMHOLTZ GEMEINSCHAFT

Bundesministerium für Bildung und Forschung

Bundesministerium für Wirtschaft und Technologie

Bundesministerium der Verteidigung

LIEBHERR

SIEMENS, DIEHL, OHB TECHNOLOGY, AIRBUS, ASTRIUM AN EADS COMPANY

DLR Deutsches Zentrum für Luft- und Raumfahrt

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Energy

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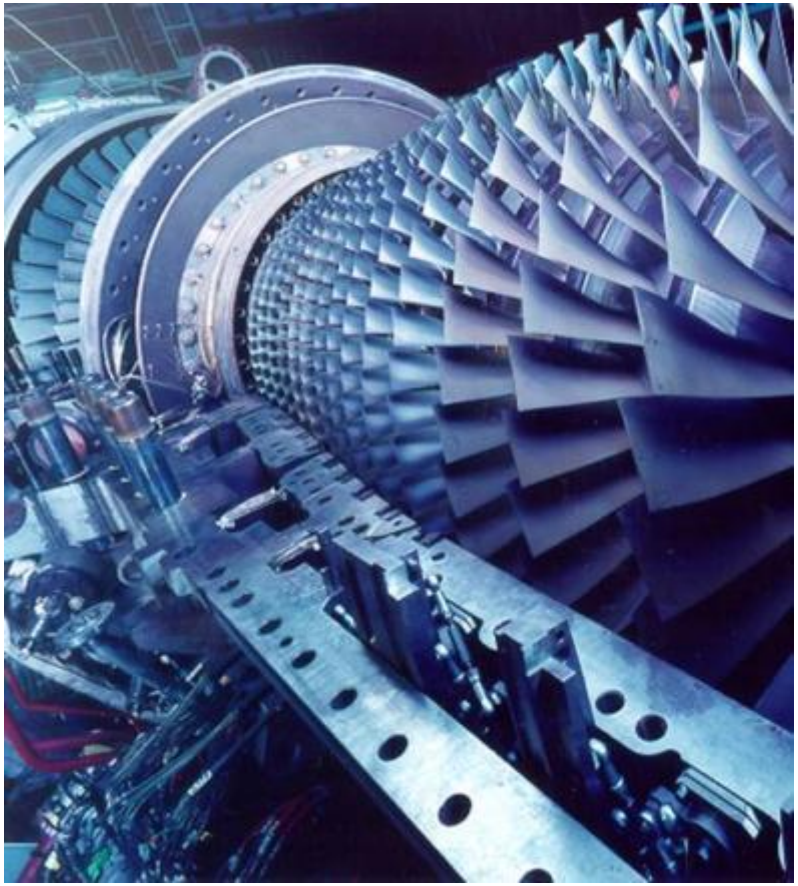
DLR Energy Research concentrates on:
- CO_2 avoidance by efficiency optimisation and renewable energies
- synergies within the DLR
- major research specific themes that are relevant to the energy economy

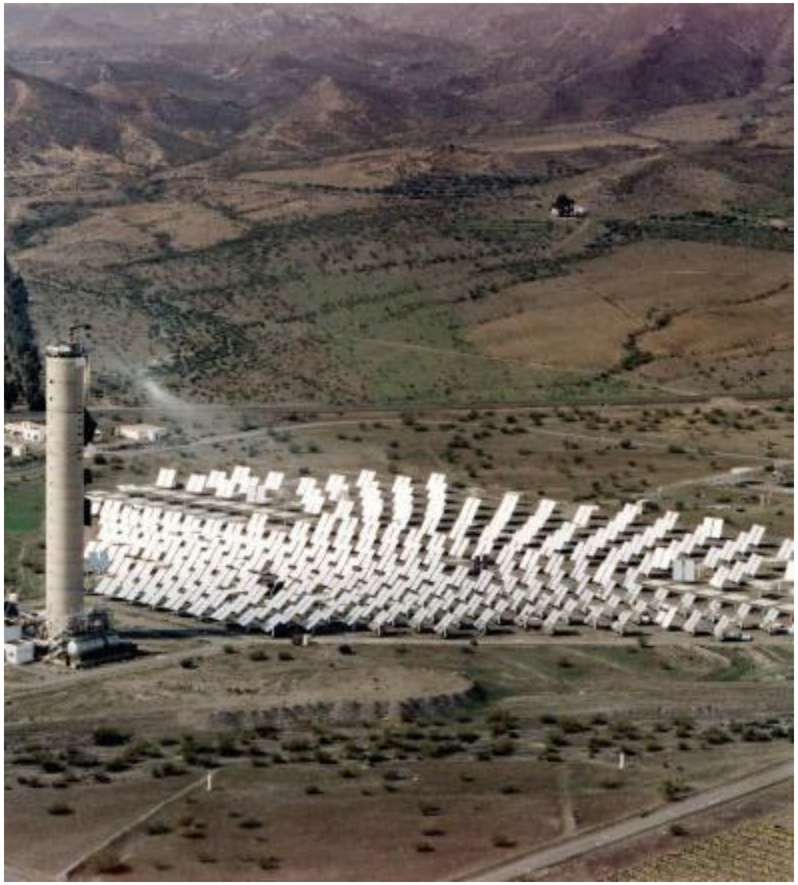


Energy Program Themes

- Efficient and environmentally compatible fossil-fuel power stations
  (turbo machines, combustion chambers, heat exchangers)

- Solar thermal power plant technology, solar fuels
  - Institute of Solar Research

- Thermal and chemical energy storage, High and low temperature fuel cells, Systems analysis and technology assessment
  - Institute of Technical Thermodynamics



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Strategic Basis

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Political view: SET-Plan (2007) European Strategic Plan for Energy Technology

- **Goals of the EU until 2020 (20/20/20)**
  - 20% higher energy efficiency
  - 20% less GHG emission
  - 20% renewable energy
- **Goal of the EU until 2050:**
  - 80% less CO_2 emissions than in 1990
- Actions in the field of energy efficiency, codes and standards, funding mechanisms, and the charging of carbon emissions necessary
- Significant research effort for the development of a new generation of CO_2 emission free energy technologies, like
  - Offshore-Wind
  - **Solar**
  - 2nd generation Biomass

Programs in Europe

- National Energy Research Programs in most of the European Countries (very different levels and aims)
- Joint Programs under the European Framework Programmes for Research and Technical Development (RFP)
  - Actual RFP is „FP7“ until the end of 2013 (few calls will be launched this year)
  - 2014 – 2020 „HORIZON 2020“
    - Wider focus than RFP: It will combine all research and innovation funding currently provided through the RFP, the innovation related activities of the Competitiveness and Innovation Framework Programme (CIP) and the European Institute of Innovation and Technology (EIT).

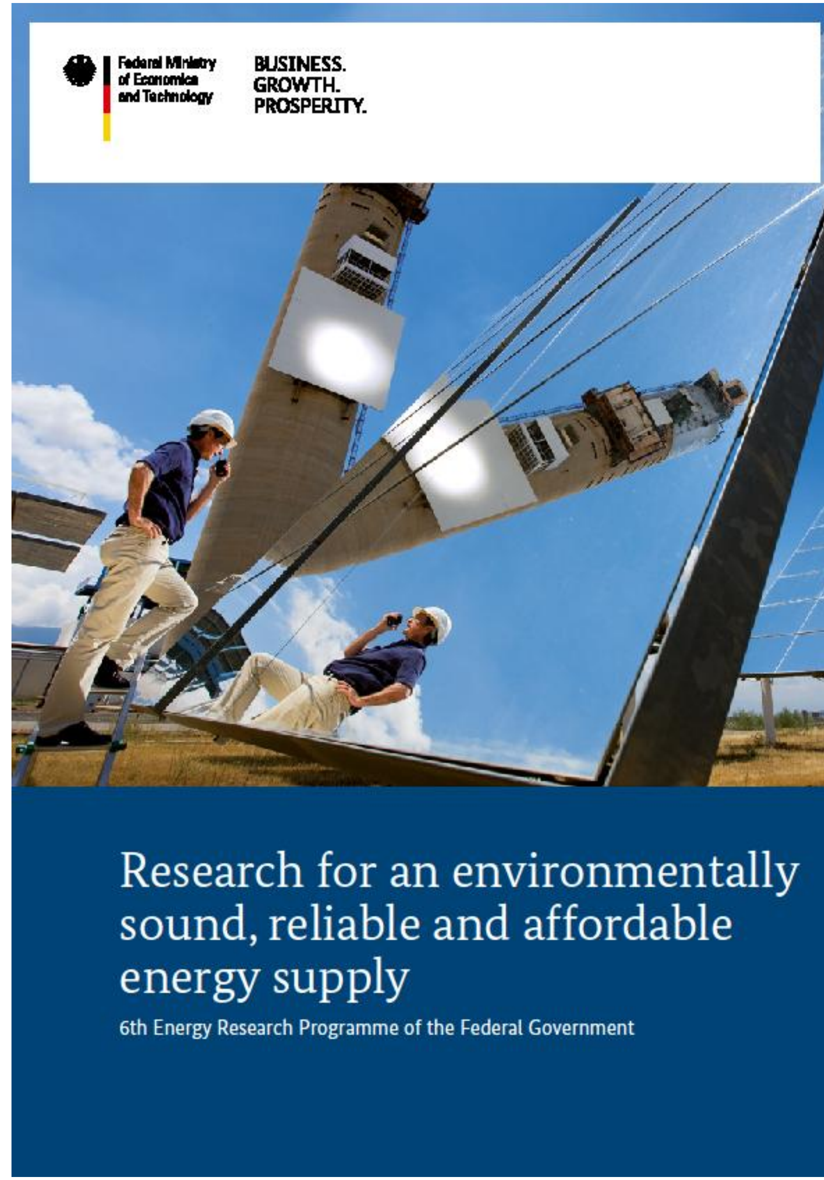
HORIZON 2020

- Budget Issues! Negotiations are going on – Result is open,
- Proposals between € 40 bn and €110 bn
- Main Topics
  - Strengthen the EU's position in science. European Research Council (ERC) Person related basic research (33%)
  - Strengthen industrial leadership in innovation (24%)
  - address major concerns shared by all Europeans such as climate change, developing sustainable transport and mobility, making renewable energy more affordable, ensuring food safety and security, or coping with the challenge of an ageing population (43%)
- In the energy sector storage will be a major topic
  - Workshops by the European Commission with experts and stakeholders prepared this in 2011

Programs in Germany

- 6th Energy Research Programme (3.5 billion euros for the period 2011-2014).

- The Programme focuses on key topics relating to the restructuring of Germany's energy supply, i.e.
  - renewable energies,
  - energy efficiency,
  - storage and grids.



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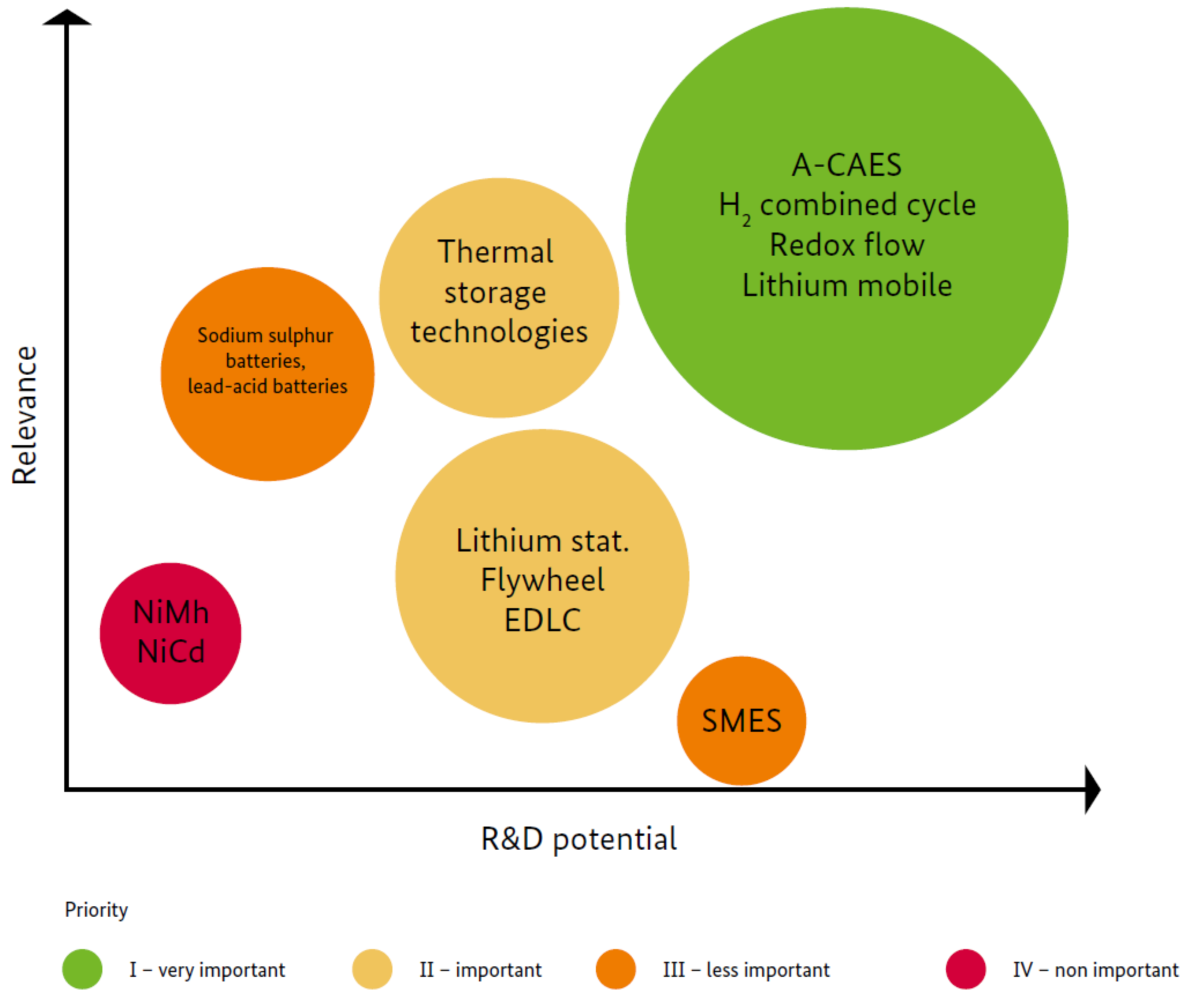
6th Energy Reserach Programme



Programs in Germany

- 6th Energy Research Programme
    - Federal Ministry for Economics and Technology (BMWi)
        - Energy Storage Program
    - Federal Ministry of the Environment (BMU)
        - CSP Program
    - Federal Ministry of Transportation (BMVBS)
        - NOW (National Organization for Hydrogen)
    - Federal Ministry of Education and Research (BMBF)
        - Energy Storage Program

- Basic Funding of the research institutions (e.g. Helmhotz by BMBF and BMWi)
- Programs of the federal states

Thermochemical Energy Storage

Work at DLR

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Reversible Gas-Solid-Reactions

$$AB \underset{\text{exothermal}}{\overset{\text{endothermal}}{\rightleftharpoons}} A + B$$

- High storage density
- Lossless long-term storage possible
- Possible heat transformation
- Large temperature range (RT to > 1000 °C)
- Detachment of storage capacity and thermal power
- Cost efficient storage materials

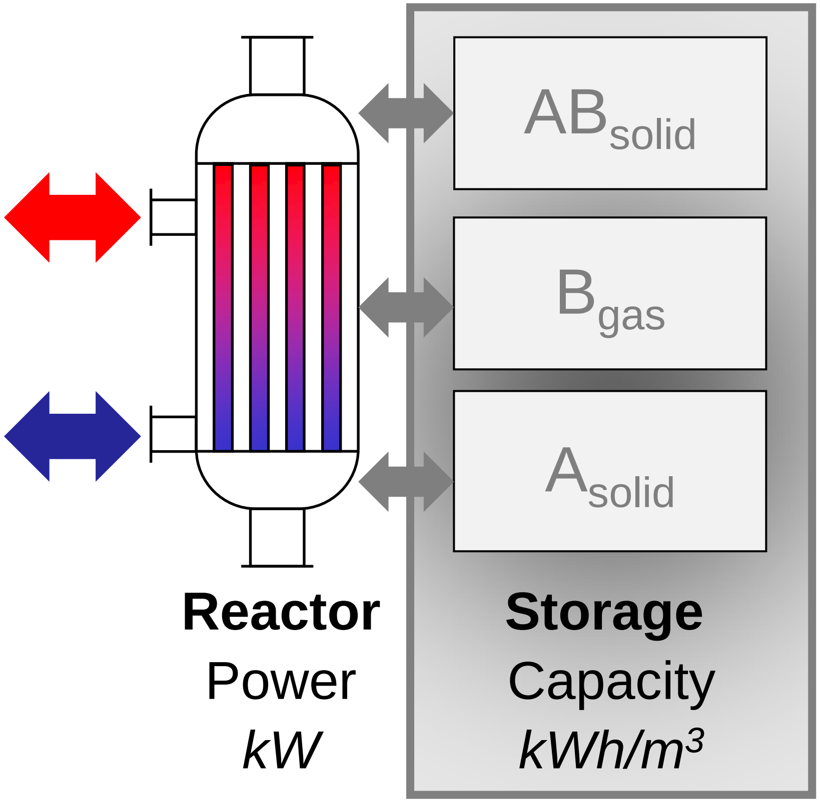
- Reactions:
  - Dehydration: $CaCl_2{*}6H_2O = CaCl_2 + 6\,H_2O$
  - Metalhydroxide/Metaloxide: $Ca(OH)_2 = CaO + H_2O$
  - Redox cycles of Metaloxides: $2\,MnO_2 = Mn_2O_3 + \frac{1}{2}\,O_2$

Requirements for TCS Storage System

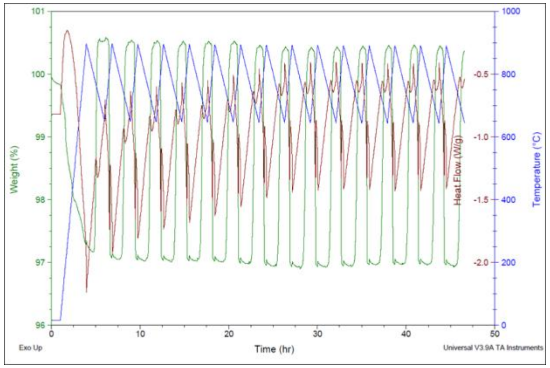
- **Closed loop operation** requires storage of gaseous reactant
- **Open loop operation** possible for steam or oxygen reaction systems

- Transport of solid reactant enables **detachment of power from capacity**

- **Integration** of storage system with process important



Requirements for TCS Reaction System and Storage Material



- High enthalpy of reaction
- Complete reversibility and cycling stability
- Suitable thermodynamics and sufficient reaction kinetics
- Long-term stable and superior thermo-physical and mechanical properties

- High availability of material at low cost
- Non-toxicity of material
- Positive LCA

→ Amount of „useful“ cycles determines the amortization periode

  - Seasonal storage
  - Day / Night storage
  - Continuous operation (sorption system)

Limestone quarry Hahnstetten

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

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CeraStorE

Joint Research Facility by DLR‘s Institutes of

-Material Research

-Fiber ceramics, redox materials

-Solar Research

-Solar fuels and reactor development

-Technical Thermodynamics

-Thermal- and thermochemical storage

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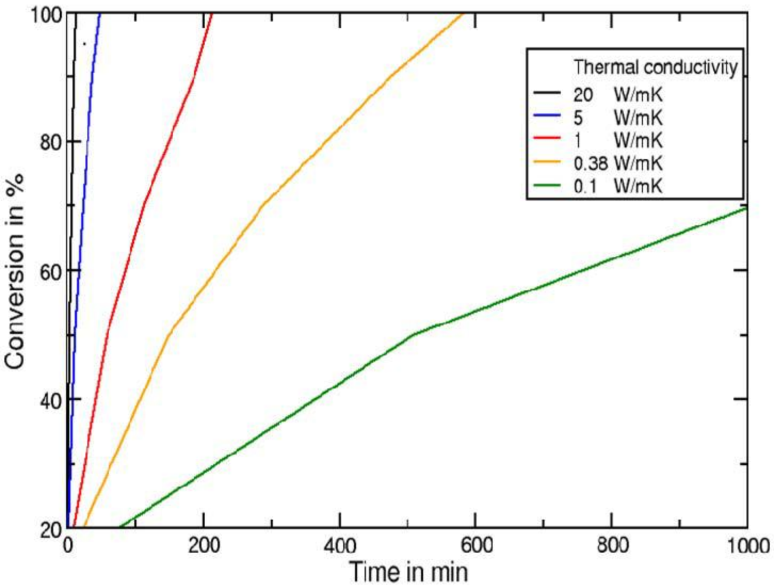
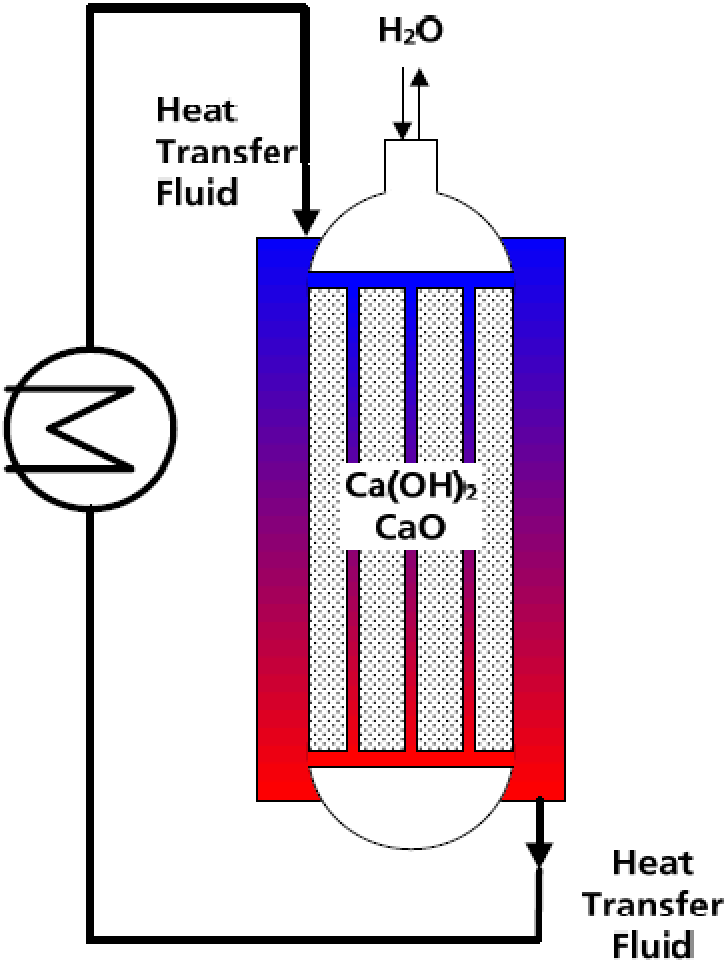
CaO/Ca(OH)$_2$ system

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

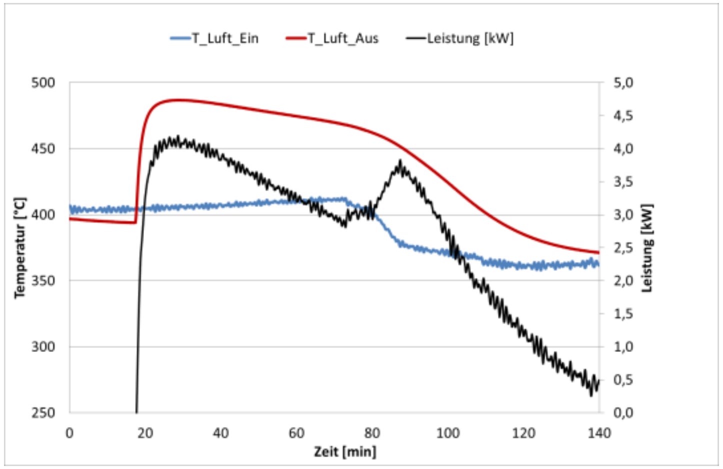


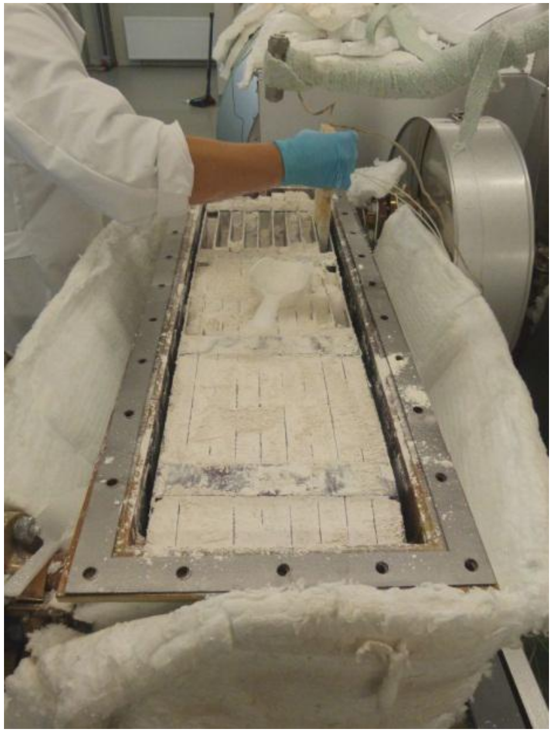


F. Schaube et al., High Temperature TC Heat Storage for CSP using Gas-Solid Reactions, Proceedings of SolarPaces 2010, Perpignan, France (2010)

$CaO/Ca(OH)_2$

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

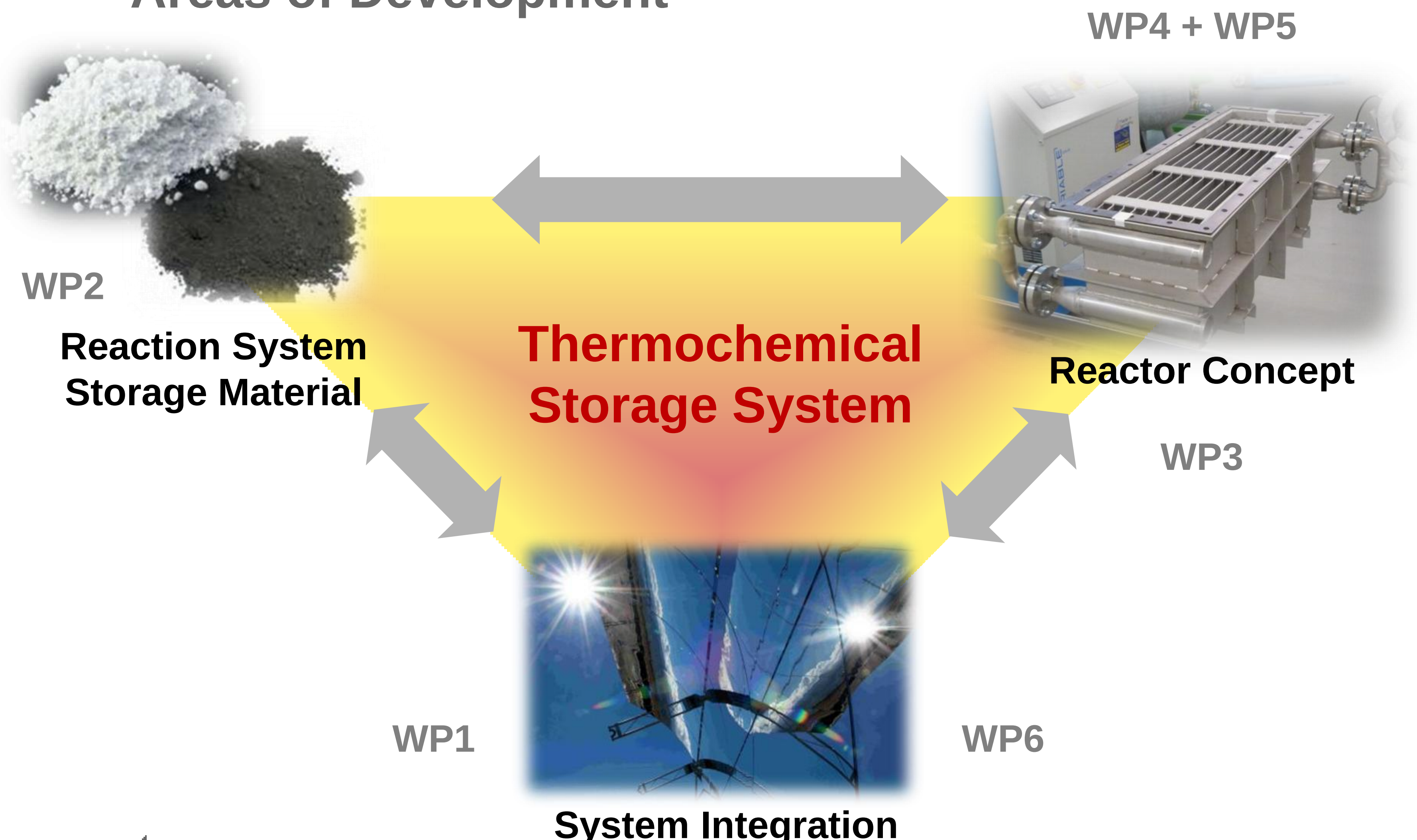




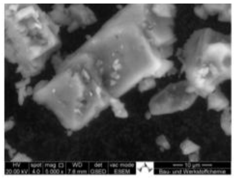
TCSPower Project

- FP7 European project 2011 – 2015
- **Storage materials** with improved functionality in regard to reaction kinetics, thermo-physical and mechanical properties
- **Dynamic simulation tool** for the design of a TCS reactor with improved performance (heat and mass transfer, charging/discharging behaviour)
- Suitable **reactor concept** being experimentally proven and evaluated in laboratory scale
- Proof-of-principle **pilot-scale thermochemical reactor** (10 kW, 100 kWh)
- **Overall process concept** for the integration into the CSP plant,
- **Strategy for up-scaling** to commercial scale and **techno-economic evaluation** of thermochemical storage systems

Areas of Development



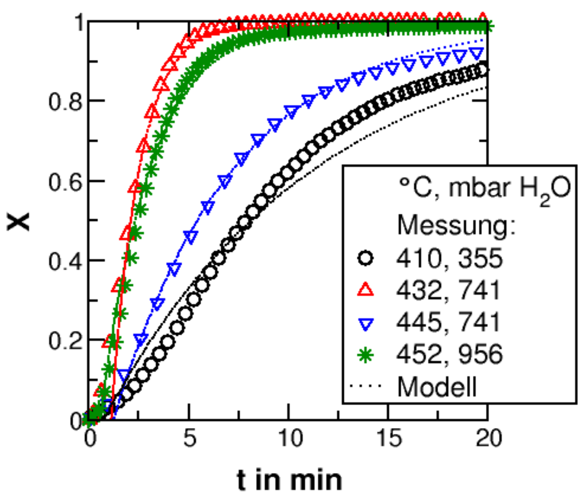
Selected Reaction Systems



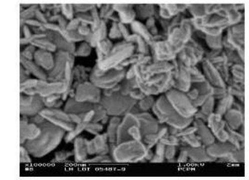
Calcium Hydroxide

$Ca(OH)_2 + \Delta H \leftrightarrow CaO + H_2O$

T_{eq} = 507°C at 1 bar
ΔH = 100 kJ/mol
Storage density*) = 410 kWh/m^3

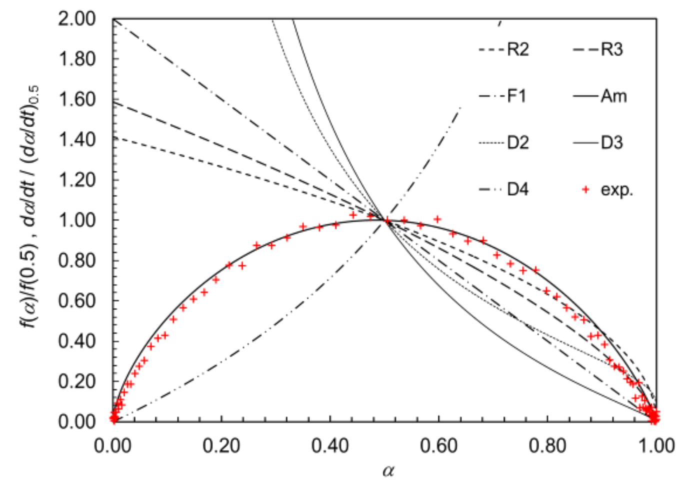


Manganese Oxide



$6\ Mn_2O_3 + \Delta H \leftrightarrow 4\ Mn_3O_4 + O_2$

T_{eq} = 980°C at 1 bar
ΔH = 31.8 kJ/mol
Storage density*) = 126 kWh/m^3

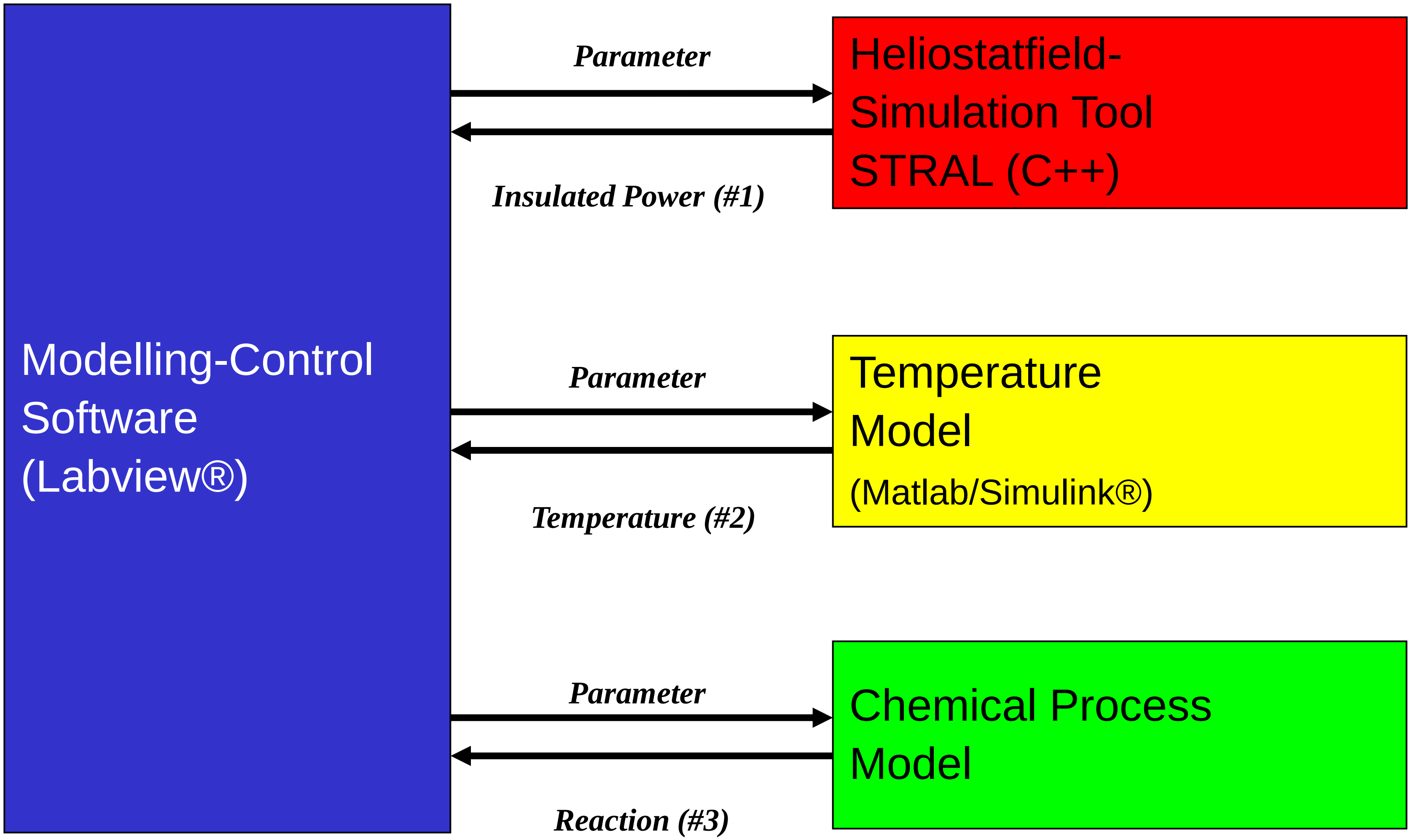


*) open loop, bulk porosity ε = 0.5

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
- Demontration 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 the EU
- Presentation of a suitable strategy for the introduction of the technology into the market.

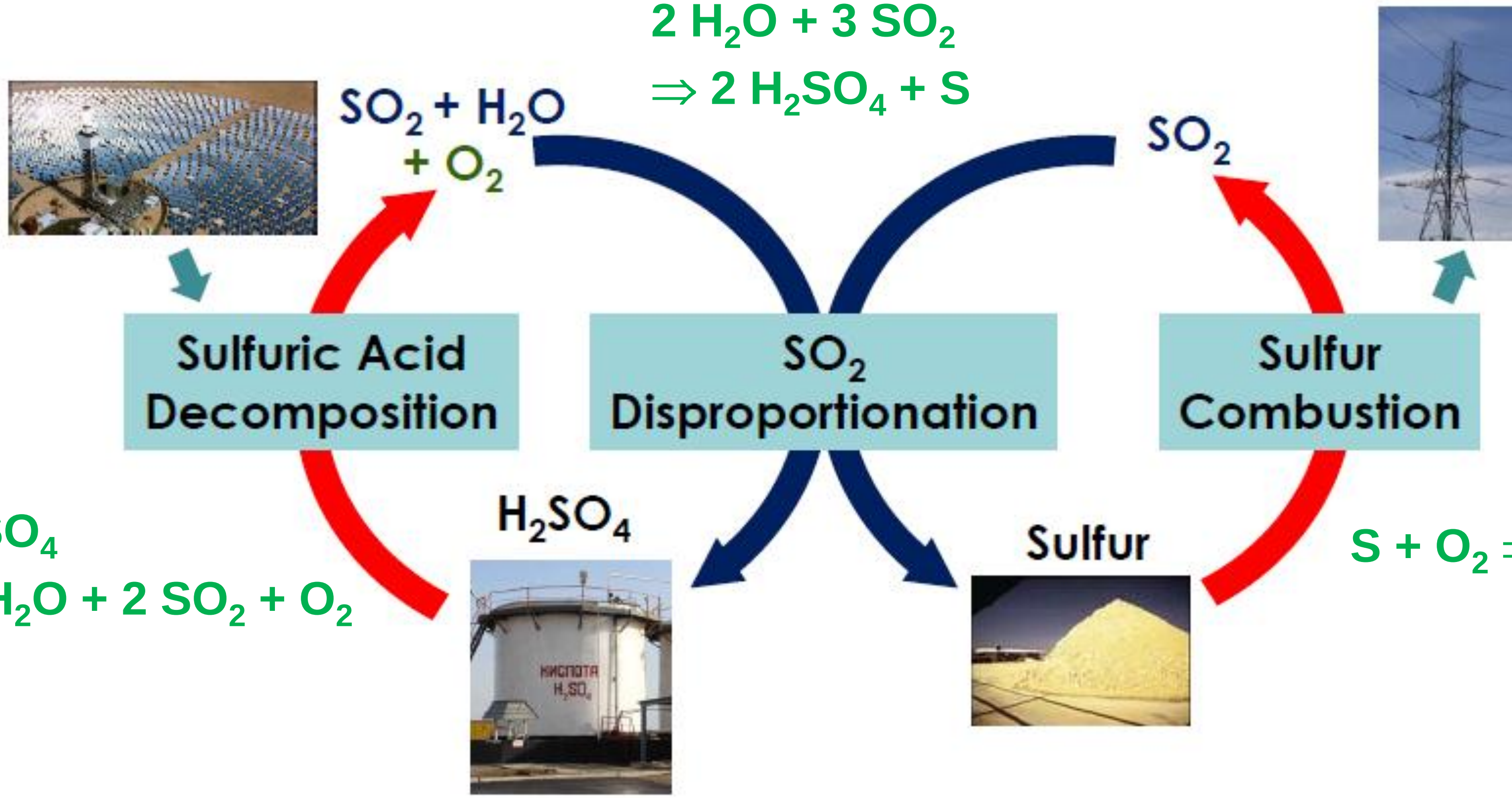
Modelling of a solar chemical plant



Pilot Plant arranged on the research platform of the ST Jülich (artist view)

Thermochemical cycle for sulfur-based seasonal heat storage

$2\ H_2O + 3\ SO_2$
$\Rightarrow 2\ H_2SO_4 + S$

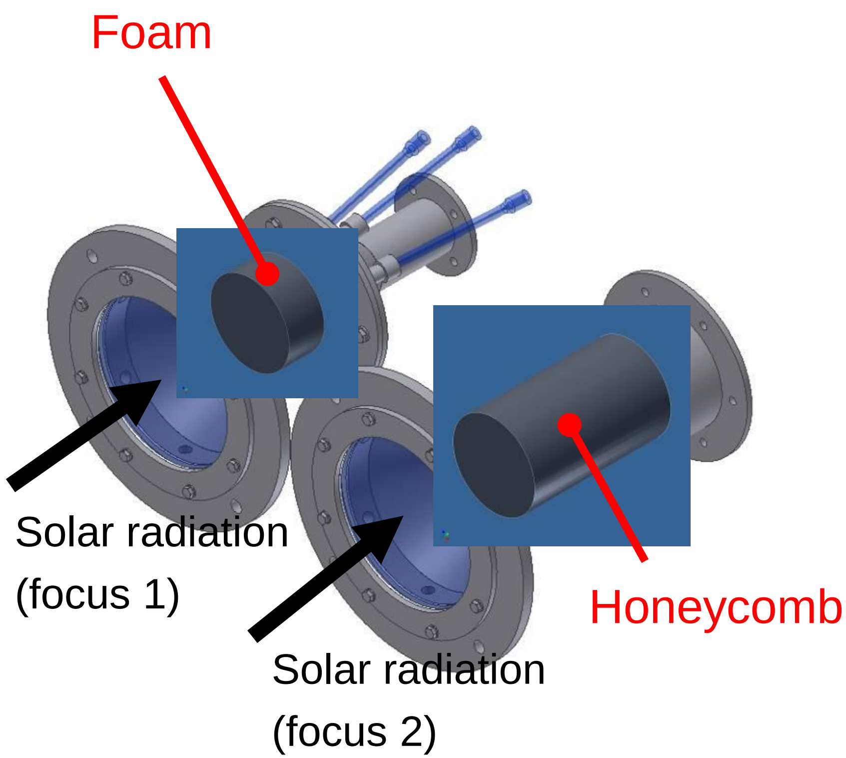


$2\ H_2SO_4$
$\Rightarrow 2\ H_2O + 2\ SO_2 + O_2$

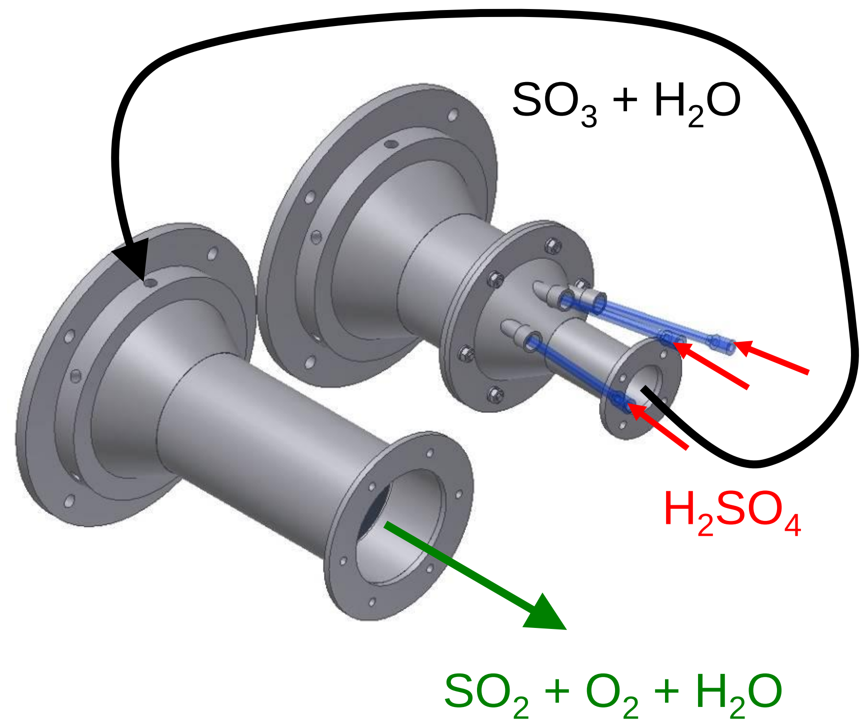
$S + O_2 \Rightarrow SO_2$

Source: General Atomics

Design of two-chamber solar reactor

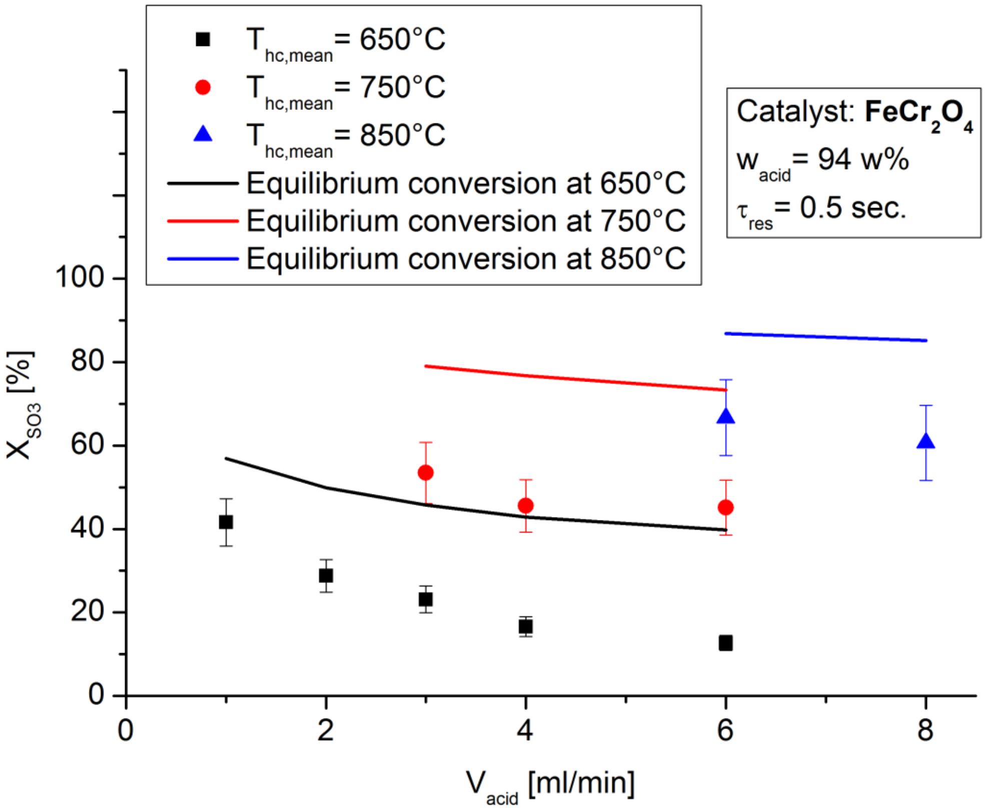


Front view of evaporator and decomposer



Rear view

Experimental results:
Conversion of SO_3 vs. honeycomb temperature



$$X_{SO3} = \frac{\dot{n}_{SO2,out}}{\dot{n}_{SO3,in}}$$

New catalyst required at low temperature (e.g. vanadium oxide, platinum)

State of work

- Development of solar reactor for decomposition of sulfuric acid
- Experimental analysis of SO_3 conversion at different temperatures
    - New catalysts required at T < 700 °C

- Modeling of SO_3 decomposition chamber of reactor
- Adaptation of an existing Dymola/Modelica finite volume model
- Validation with experimental results
    - Good modeling of thermal behavior of reactor
    - Model of chemical reaction only valid at elevated acid flow rates
- Simulation of transient behavior
    - Adequate prediction of experimental values

- Optimization of reactor performance: conversion > 80%, efficiency > 50%
- Development of a reactor model in Aspen Custom Modeler®
- Integration of model into system flowsheets of HyS/sulfur cycle

Conclusion and Outlook

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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

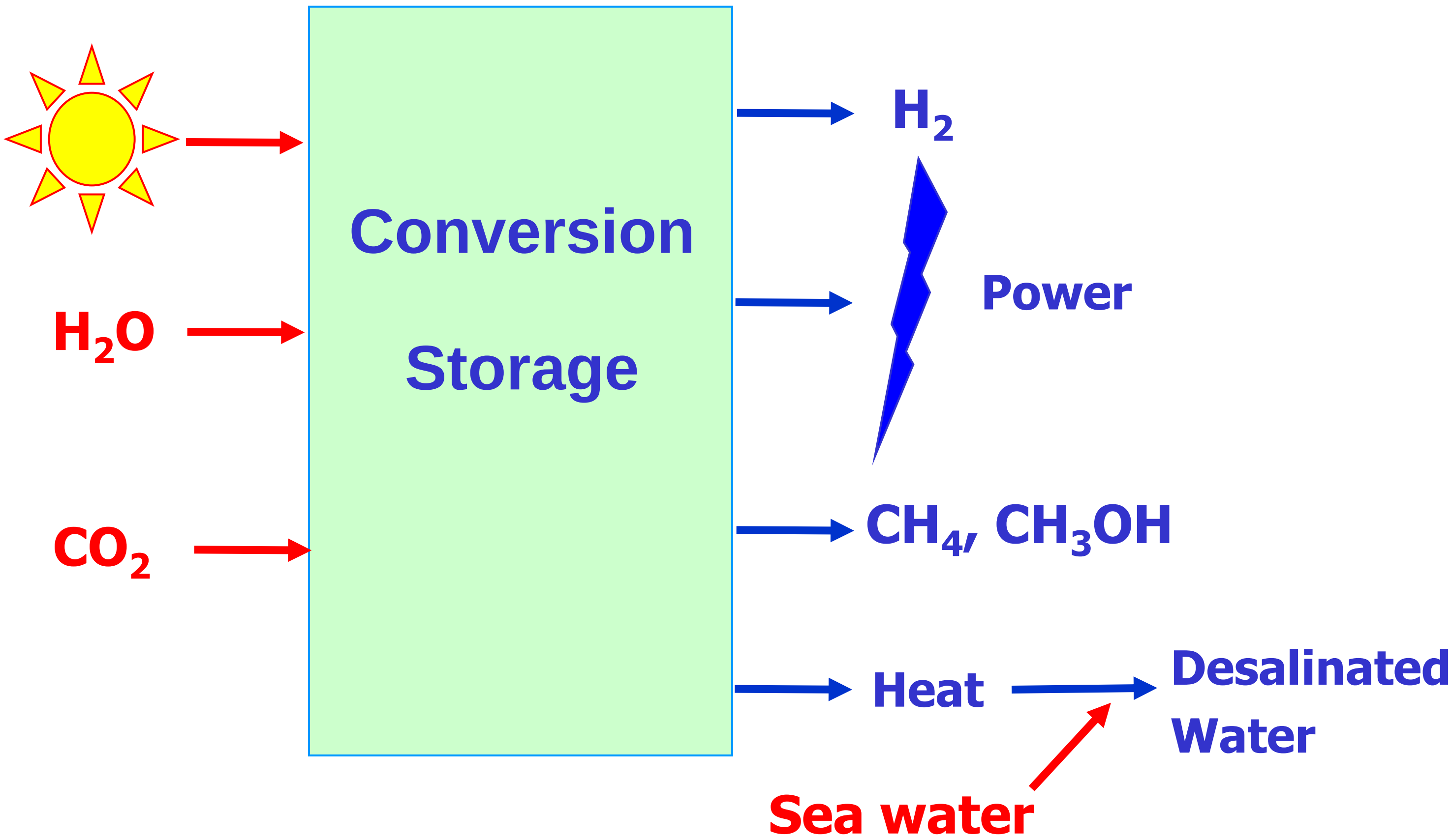
  - **Technically it offers several advantages** like
    - potentially high storage density,
    - lossless long-term storage

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

- **Further research cooperation with USA partners would use synergies and accelerate the developments**

Future Solar Thermal Plants – more than power!

Production of fuels (renewable H_2 and CH_4 / CH_3OH),
Recycling of CO_2, Power Production, Process Heat and Desalination (H_2O)



Acknowledgement

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

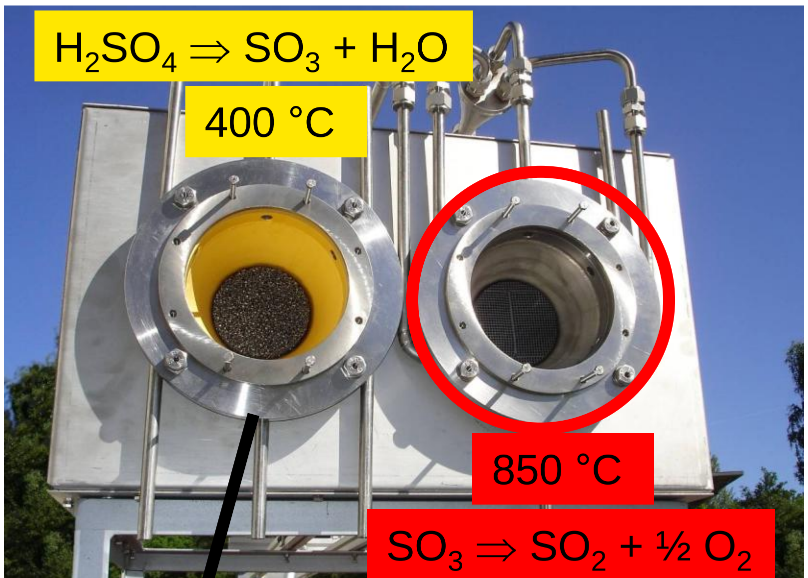
- Thanks to all colleagues and partners who provided various contributions to this work.

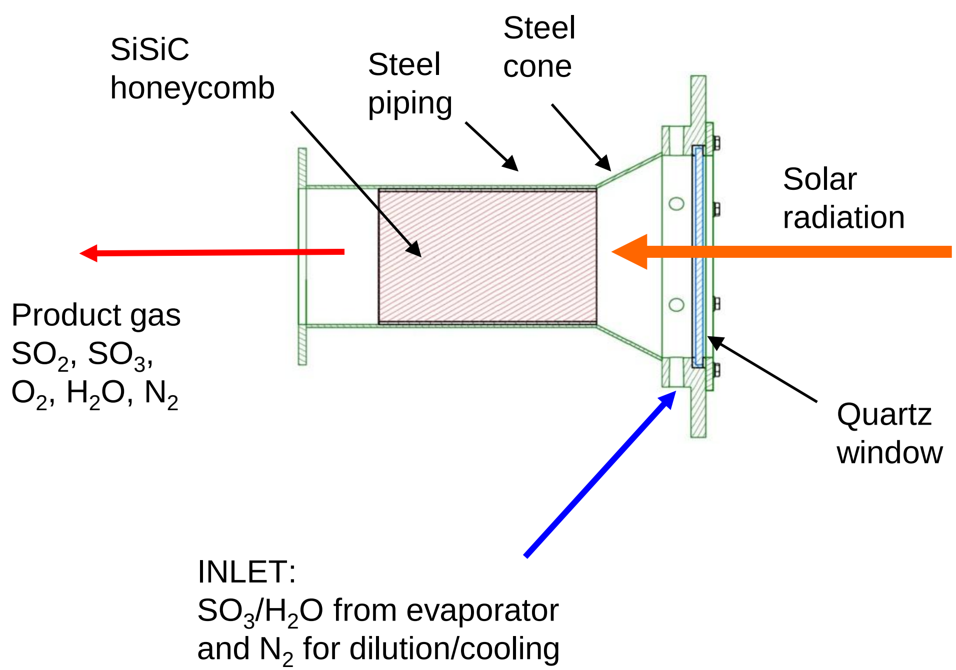
DLR H_2 Aircraft
ANTARES

Thank you very much for your attention!

Model of chamber for decomposition of SO_3

SO_3 decomposition chamber



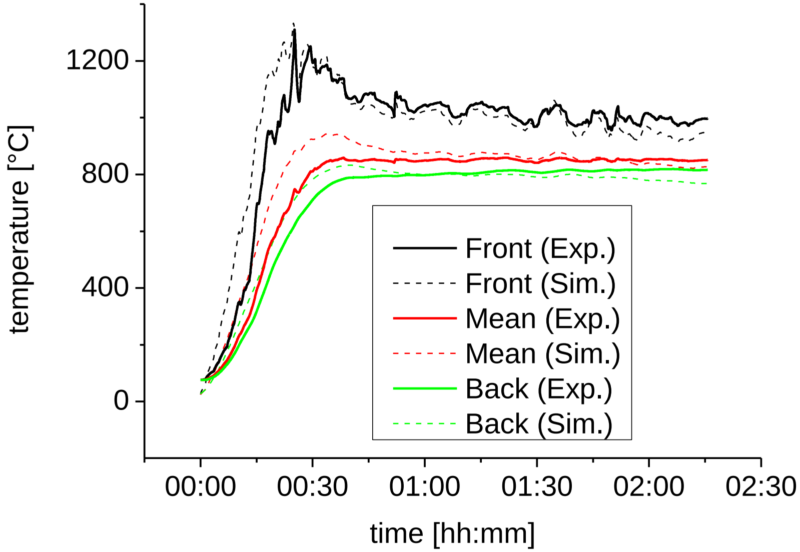


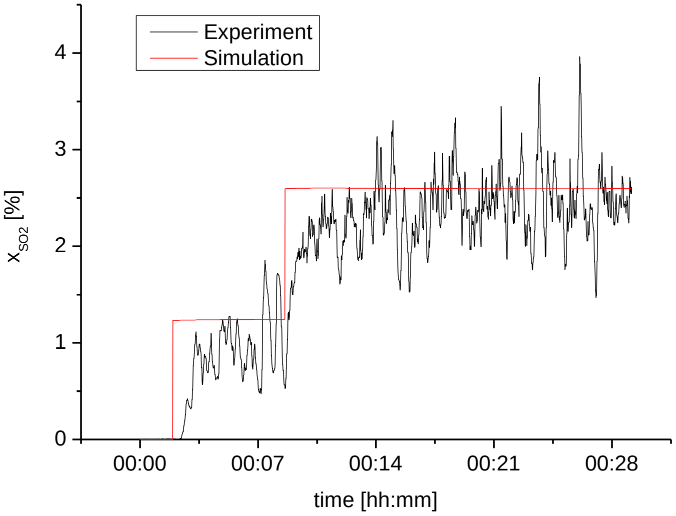
Model of evaporator presented by

Haussener, et al. at ASME Conference, Puerto Rico, 2012

Noglik, et al., International Journal of Energy Research, 2011

Validation of model:
Dynamic modeling of temperature and conversion





- Mean honeycomb temperature: 850 °C
- Acid volume flow rate: 4 ml/min (50 w-%)

- Mean honeycomb temperature: 850 °C
- Acid volume flow rate: 5 ml/min (50 w-%)