



# Hycycles

Materials and components for **H**ydrogen production  
by sulphur based thermochemical **cycles**  
**(FP7 – Energy – 212470)**

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*German Aerospace Center (DLR) – Solar Research*

# 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

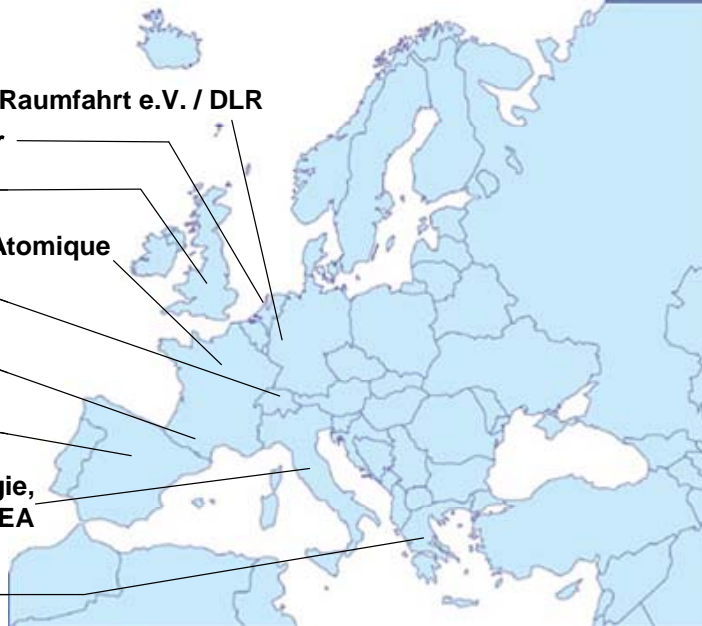
ETH Zürich

Boostec Industries

Empresarios Agrupados

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

Aerosol and Particle Technology  
Laboratory / CERTH-CPERI



## Main topics:

Suitability of construction and catalyst materials for  $\text{H}_2\text{SO}_4$  decomposition section

Material and design of  $\text{H}_2\text{SO}_4$  decomposer (as heat exchanger)

Material and design of  $\text{H}_2\text{SO}_4$  decomposer (as solar receiver-reactor)

Materials and design of  $\text{SO}_2/\text{O}_2$  separator (membranes for enhancing the performance of  $\text{SO}_3$  decomposition)

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

EU FP7 - ENERGY

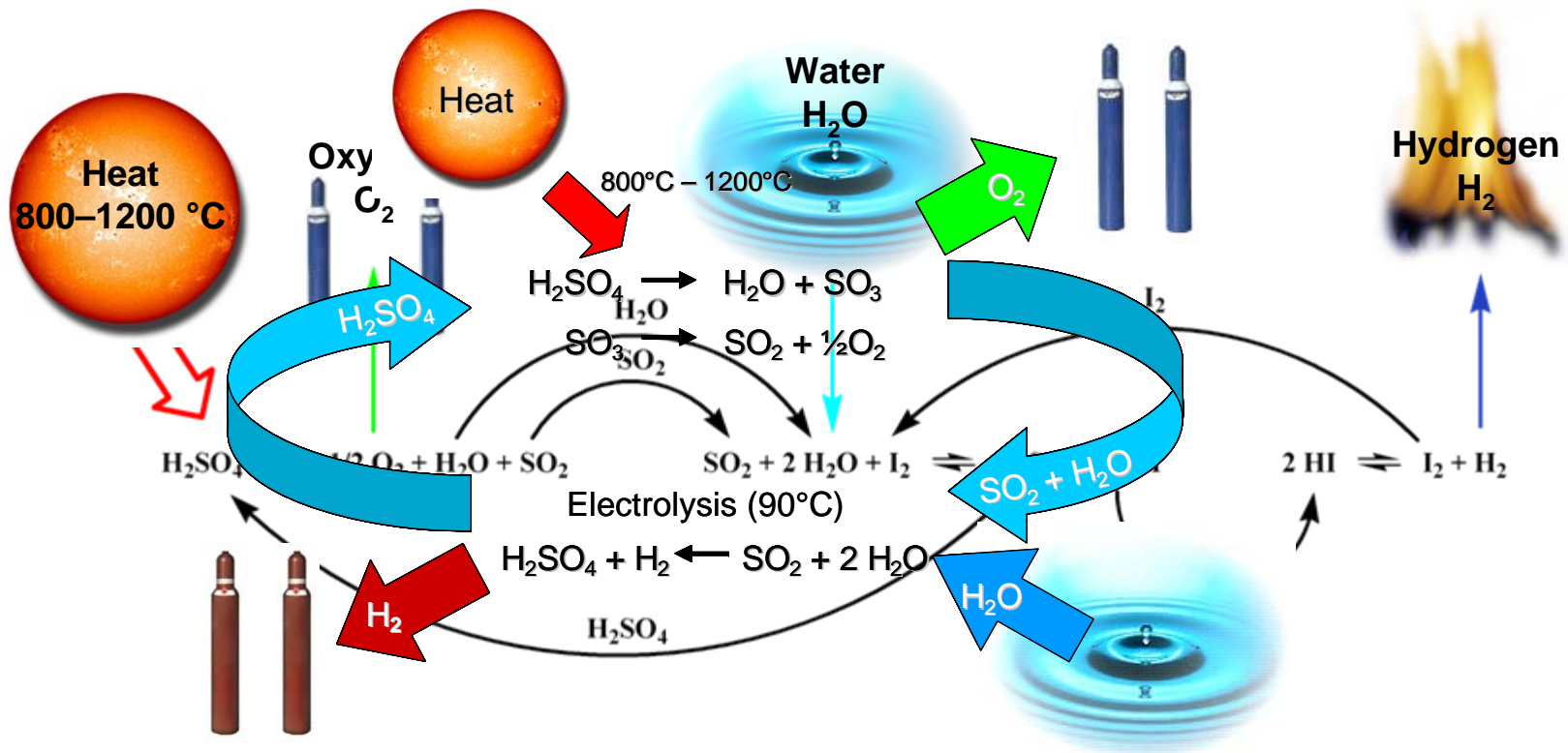
Duration: January 2008 – March 2011

# Objective

HycycleS will concentrate on providing **detailed solutions** for the design of specific key components, and in particular on the **materials needed**. Thus the focus of HycycleS is one of the most challenging sections of a dedicated hydrogen production plant: the high temperature section **for the thermal decomposition of sulphuric acid**.

# "The Cycles of HycycleS"

## Sulphur Sulphur Process

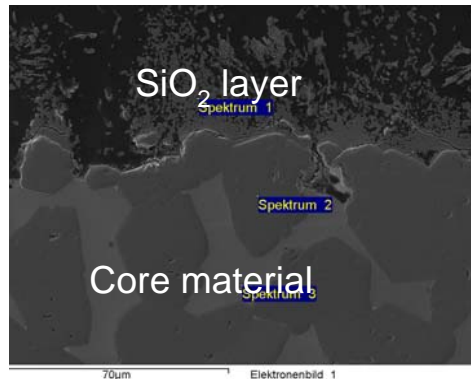
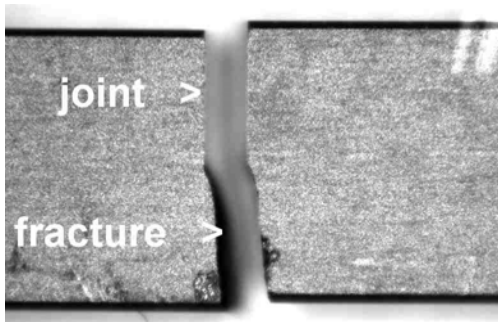
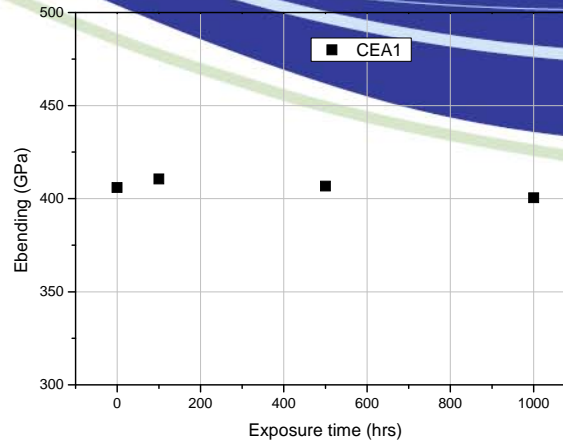
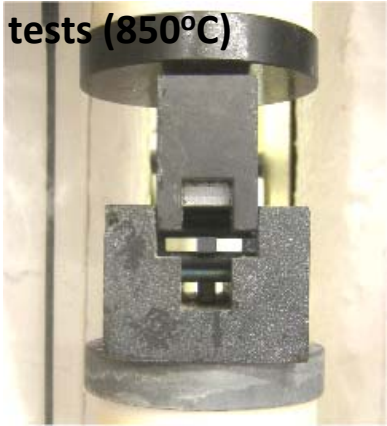


# Cooperation beyond the consortium

- Associated International partners: Westinghouse, General Atomics, CSIRO
- International meetings, exchange and consultancy; cooperation on specific project related tasks
- Combination with IEA-HIA task 25 meetings and conferences: monitor and review the state of the art, to develop a common approach to evaluate those processes, to link the topic to further industrial representatives, and ensure a target oriented dissemination of the technology
- IEA implementing agreement SolarPaces
- Contribution to GenIV Initiative
- IPHE recognised project Thesis
- Cooperation with other European Projects (Extremat, Hydrosol)

# Stability of construction materials

High temperature tests (850°C)



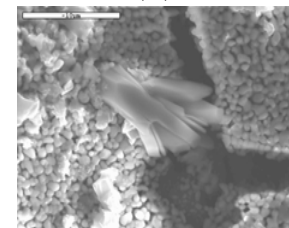
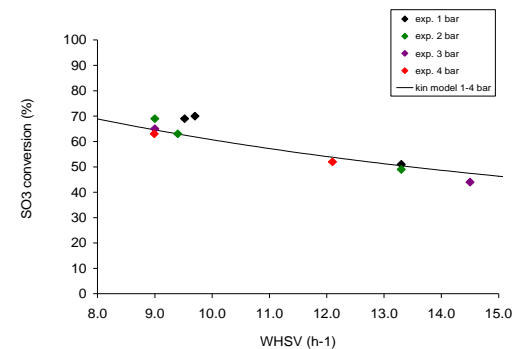
- Performance of long-term corrosion campaigns ( $\text{SO}_2$ ,  $\text{SO}_3$  rich, boiling  $\text{H}_2\text{SO}_4$ ) and post-exposure mechanical testing and inspection
- mainstream materials SiC-based as well as brazed samples
- The investigated SiC based materials are retained suitable for the intended application since they are not affected significantly by the  $\text{SO}_2$ -rich,  $\text{SO}_3$ -rich and boiling sulphuric acid exposures.

# Advanced catalysts and coatings for $\text{H}_2\text{SO}_4$ decomposition

- 'In-house' synthesized materials (metal oxide based) with high catalytic activity in terms of  $\text{SO}_2$  production from  $\text{H}_2\text{SO}_4$ :
- Coating of active materials in small- & large-scale SiSiC monoliths or fragments



- Satisfactory stability of samples coated with 'in-house' materials under 'long-term' operation
- Derivation of an empirical kinetic model
- Evaluation of the employed materials chemical stability
- Extraction of an  $\text{SO}_3$  dissociation mechanism

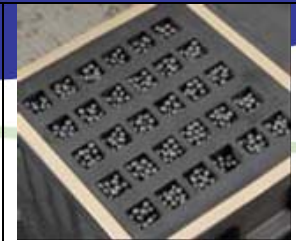


# Compact heat exchanger decomposer

- Modelling and design of SiC compact heat exchanger decomposer completed
- Decomposer prototype manufactured by multi-step production process



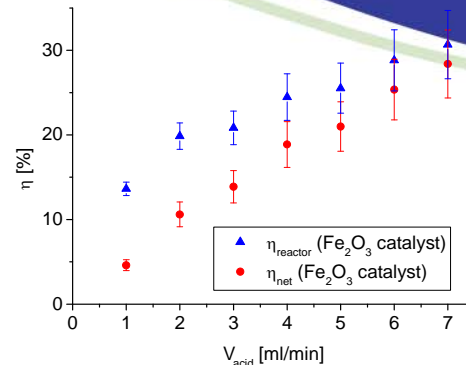
Prototype tested on clairette loop



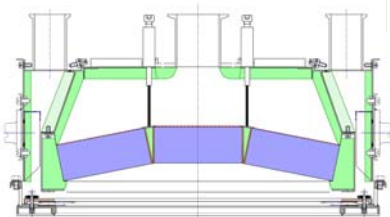
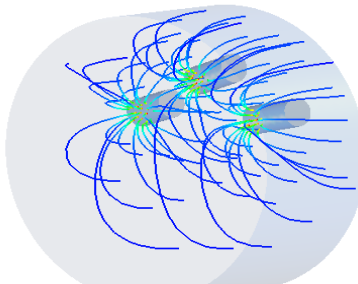
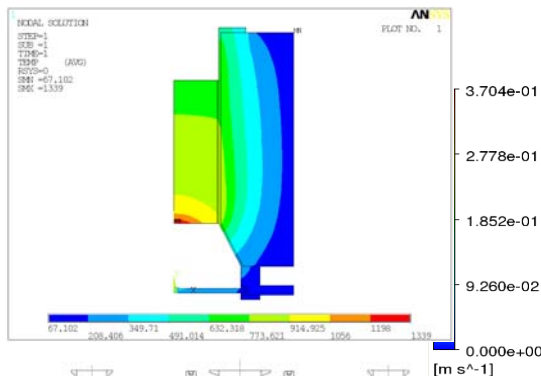
Bowls inside the channels

- Prototype installed at Clairette hot air loop in Grenoble
- tests have been run during 30 days with a hot inlet air temperature from 20°C up to 800°C
- Thermal performances are somewhat lower than predicted by models
- Good agreement between small mock-up and prototype results: non dimensional approach allows comparability

# Solar reactor as $\text{H}_2\text{SO}_4$ decomposer

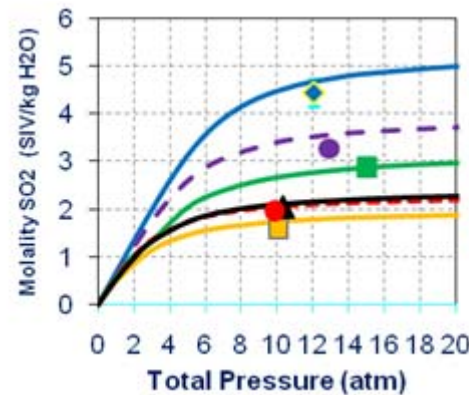
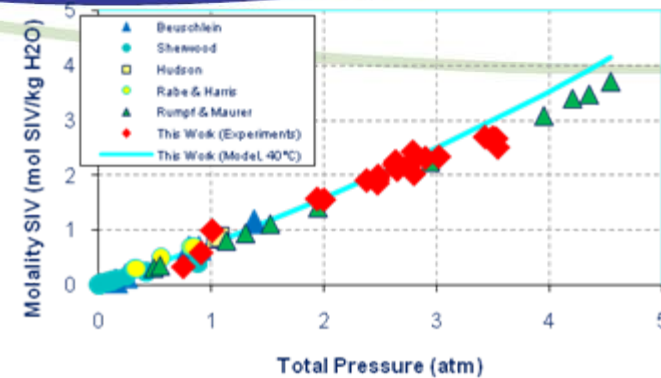
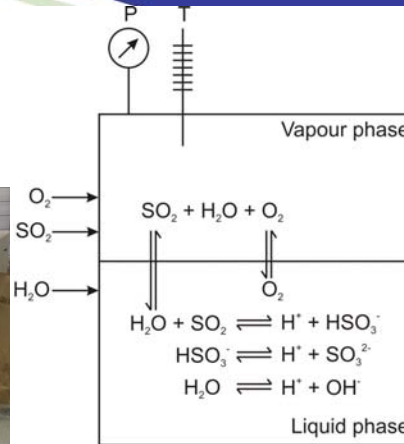
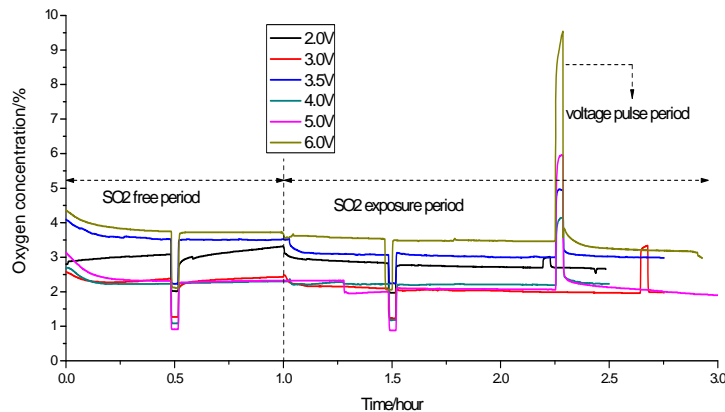
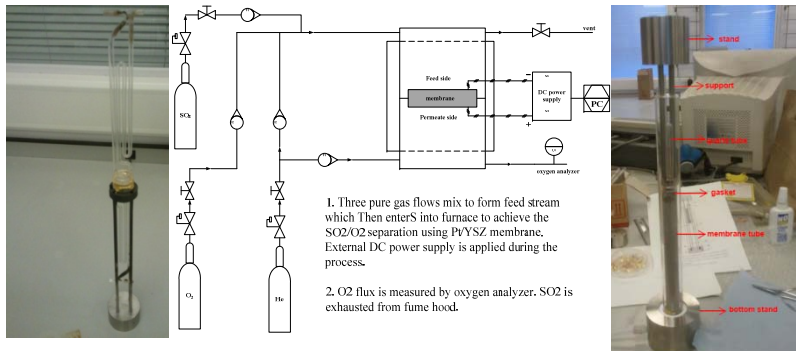


- Development and operation of a scalable prototype
  - FEM analysis
  - trouble-free operational > 50 h
  - conversions > 80 %
  - reactor efficiency > 25 %
- Continuum model of foam vaporiser
  - Computer tomography
- Modelling of  $\text{SO}_3$  decomposition
  - Validation with experimental data
- Control procedure for scale-up solar tower system



# Separator for the Decomposition Products

## High Temperature Membranes



Expt. 37, 8.6% SO<sub>2</sub>, 1.56% O<sub>2</sub>

Expt. 34, 6.52% SO<sub>2</sub>, 1.39% O<sub>2</sub>

Expt. 8, 5.36% SO<sub>2</sub>, 2.12% O<sub>2</sub>

Expt. 6, 4.10% SO<sub>2</sub>, 1.56% O<sub>2</sub>

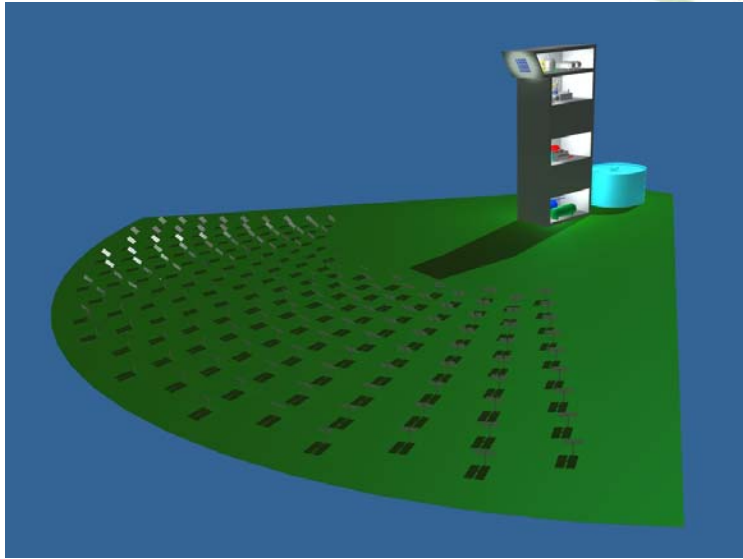
Expt. 7, 3.92% SO<sub>2</sub>, 1.36% O<sub>2</sub>

Expt. 35, 3.41% SO<sub>2</sub>, 1.67% O<sub>2</sub>

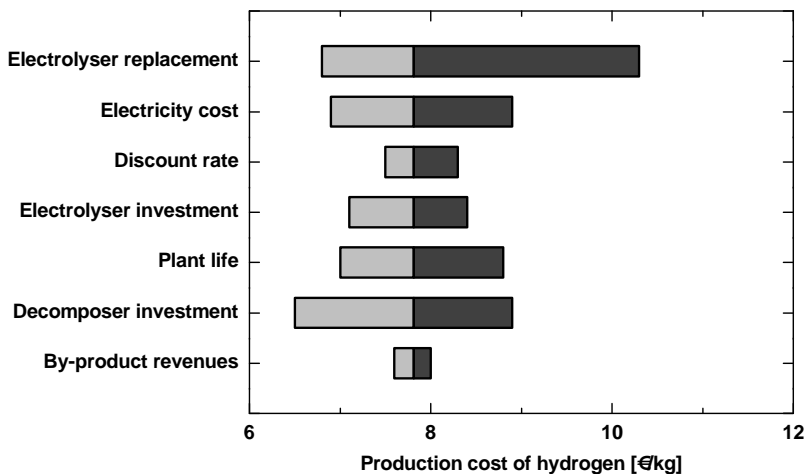


## Low Temperature Separation

# Techno-economics



- Flowsheet for solar HyS process refined and completed
- All Components including the solar field were sized for a nuclear HyS and SI process and a solar HyS process
- Investment, O&M cost, production cost were analysed → considerable higher than initial target
- 50 MW solar tower plant for hydrogen production by HyS cycle defined and depicted
- Investment, O&M cost, production cost were analysed
- Thorough safety analysis was carried out for respective nuclear and solar power plants



# Milestones/Achievements

- Suitable construction material and joining technique for key components identified
- Decay of flexural strength of material for decomposer only marginal after treatment under rel. conditions
- Active and stable catalysts for  $\text{H}_2\text{SO}_4$  decomposition developed and qualified
- heat-exchanger prototype designed, built and experimentally tested
- In-depth characterisation and modelling of porous absorber structures
- trouble-free operation of the solar receiver-decomposer
- $\text{H}_2\text{SO}_4$  conversions higher than 80 % and reactor efficiencies higher than 25 % achieved
- Completion thermodynamic models for multi-component solubility of  $\text{SO}_2$  and  $\text{O}_2$
- Feasibility experiments demonstrating oxygen transport from high temperature  $\text{SO}_2/\text{O}_2$  mixtures through suitable membrane system
- Scale-up scenario developed and depicted by multiplying the solar receiver-reactor module on top of a solar central receiver system

# Dissemination/Training

- 6 dissertations and numerous Diploma/Master-Thesis completed
- >10 paper in peer-reviewed journals; >20 conference contributions and invited speeches
- Interviews and Reports for internet-portals for a broader public
- Contribution to train young scientists within the Sollab-Alliance and SFERA-Initiative (Doctoral Colloquia and Winterschools)
- Project Web-site: [www.hycycles.eu](http://www.hycycles.eu)

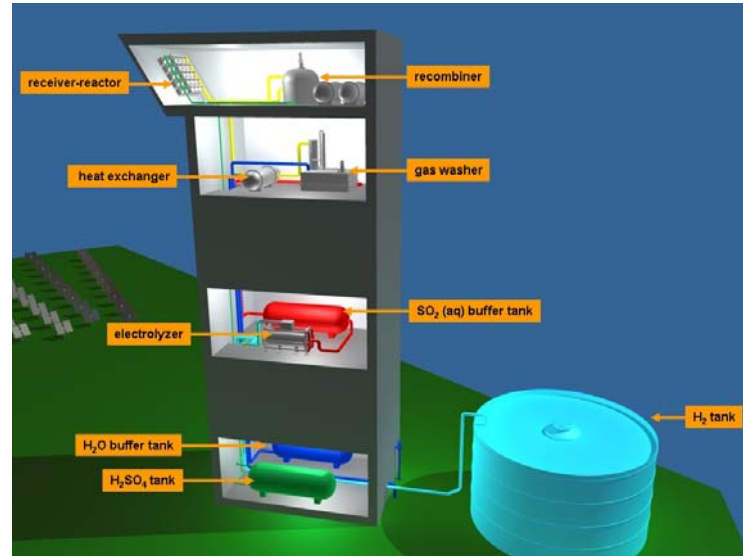


# *Alignment to FP7 Cooperation Work Programme 2007: Energy*

- “discovery of novel, efficient and cost-competitive materials, the development of new chemical processes and synthesis techniques, and the manufacture of critical components” **DONE**
- “Research will focus on materials, components and sub-systems necessary for safe and efficient production of hydrogen through thermo-chemical decomposition of water” **DONE**
- “Activities could include corrosion testing, thermal-hydraulics analysis, thermodynamic and mechanical, stress modelling, empirical validation and safety assessment.” **DONE**
- “Improve the durability and efficiency of critical components and subsystems, and in general, to prove the technical viability of promising thermo-chemical cycles for water splitting” **DONE**

# Future Perspectives

- Technology ready for field demonstration:



- Spin-offs:
  - Joining technology for ceramic components
  - Models for sulfuric acid processing and solar applications
  - Catalysts/materials for use in harsh environment

# Acknowledgement

- European Commission for supporting our Hydrogen research within HYCYCLES
- All the consortium members and International Partners for their significant contributions and the excellent collaboration



Thank you for your attention!

<http://www.hycycles.eu/>