Hycycles
Materials and components for Hydrogen production by sulphur based thermochemical cycles
(FP7 – Energy – 212470)

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Main topics:

Suitability of construction and catalyst materials for H₂SO₄ decomposition section

Material and design of H₂SO₄ decomposer (as heat exchanger)

Material and design of H₂SO₄ decomposer (as solar receiver-reactor)

Materials and design of SO₂/O₂ separator (membranes for enhancing the performance of SO₃ 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**.
Sulphur-Iodine Process

Water
H₂O
O₂
Heat
800–1200 °C
Hydrogen
H₂
Electrolysis (90°C)

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H₂SO₄ + H₂ → SO₂ + 2 H₂O
SO₂ + 2 H₂O + I₂ → SO₃ (aq) + 2 H₂
SO₃ (aq) + H₂O → H₂SO₄
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H₂SO₄ → H₂O + SO₃
SO₂ + ½ O₂ → SO₃
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“The Cycles of HycycleS”

Hybrid Sulphur Cycle
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)
Performance of long-term corrosion campaigns (SO$_2$, SO$_3$ rich, boiling H$_2$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 SO2-rich, SO3-rich and boiling sulphuric acid exposures.
• ‘In-house’ synthesized materials (metal oxide based) with high catalytic activity in terms of SO$_2$ production from H$_2$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 SO$_3$ dissociation mechanism
Modelling and design of SiC compact heat exchanger decomposer completed

Decomposer prototype manufactured by multi-step production process

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 H$_2$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 SO$_3$ decomposition
  - Validation with experimental data
- Control procedure for scale-up solar tower system
Separator for the Decomposition Products

High Temperature Membranes

Low Temperature Separation
• 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 H₂SO₄ 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
- H₂SO₄ conversions higher than 80 % and reactor efficiencies higher than 25 % achieved
- Completion thermodynamic models for multi-component solubility of SO₂ and O₂
- Feasibility experiments demonstrating oxygen transport from high temperature SO₂/O₂ 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
• “discovery of novel, efficient and cost-competitive materials, the development of new chemical processes and synthesis techniques, and the manufacture of critical components”

• “Research will focus on materials, components and sub-systems necessary for safe and efficient production of hydrogen through thermo-chemical decomposition of water”

• “Activities could include corrosion testing, thermal-hydraulics analysis, thermodynamic and mechanical, stress modelling, empirical validation and safety assessment.”

• “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”
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
• 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/