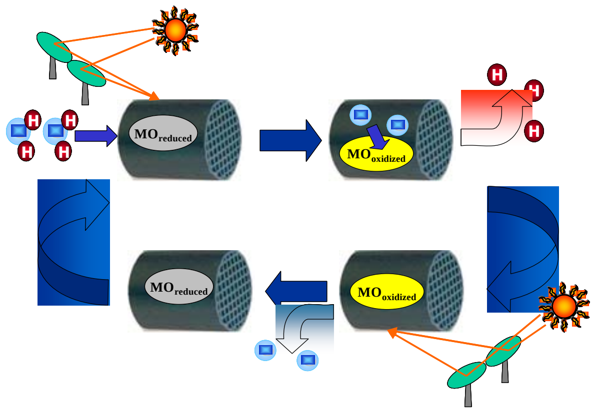
Hydrosol Cycle

Process principle

The HYDROSOL research team has developed an innovative solar thermo-chemical reactor for the production of hydrogen from water splitting resembling to the familiar catalytic converter of modern automobiles[1]. The reactor contains no moving parts and is constructed from special refractory ceramic thin-wall, multi-channeled (honeycomb) monoliths that absorb solar radiation. The monolith channels are coated with active redox water-splitting materials capable of splitting water vapor passing through the reactor by “trapping” its oxygen and leaving the effluent gas stream as pure product hydrogen. In the next step, the oxygen “trapping” material is regenerated using solar energy to release the absorbed oxygen and hence a cyclic operation is established on a single reactor/receiver system. With this concept, the full thermochemical cycle can be performed continuously on a single solar reactor/receiver system with the water-splitting material immobilized upon the honeycomb walls avoiding the need for continuous powder feeding and collection from the reactor.

The Hydrosol process is one of the most promising processes for a completely environmentally-friendly and sustainable way of hydrogen production as both reactants and primary energy sources are renewable and carbon-free.



$$Me_xO_y + H_2O \rightarrow MeOox + H_2 \qquad (1)$$

$$MeOox \rightarrow Me_xO_y + O_2 \qquad (2)$$

Current status :

- Chemistry reactions all demonstrated at lab and pilot scale,
- Materials candidates selected and tested,
- On site demonstration plant is being finalized and ready for testing at a 100 kW scale.

Advantages :

- No pollutants nor CO_2 emissions: only water and oxygen are released,
- Reactants are unlimited: water and solar energy,
- No rotating/moving parts in the reactor; no circulation of (hot) solids required,
- Inexpensive materials used.

Challenges :

- Temperatures required: 800 to 1200 °C,
- Redox material coating adhesion and stability,
- Suppression of inert carrier gas,
- Loss of activity of redox metal

HYDROSOL thermochemical cycle

Process description: 2 steps

(1) Hydrogen Production by water splitting and metal oxide oxidation: 800-1000 °C

(2) Regeneration of the redox material: metal oxide thermal reduction: 1000-1200 °C

Heat source : Solar

Materials :

- Iron-oxide-based redox materials
- Silicon carbide as substrate / reactor

Total efficiency:
40 %

Cost evaluation :
€ 6.7 /kg H_2 [7]
In the future: between 3.5 and 12.8 €/kg

Flow-sheet

A basic flow sheet has been put forward[2] as a starting point for a commercial plant concept (only one reactor is represented). For a process to be feasible both technically and economically, it is necessary to recover heat and materials as far as technically possible and economically reasonable. With respect to materials, loops are envisaged for water/ steam that will not be 100% converted in the reactor and for nitrogen applied as a pure flushing gas which is contaminated by oxygen released during the regeneration step. The separation of hydrogen and the remaining steam is performed in a combined condenser/heat exchanger by condensation of the steam. The recovered water is recycled, mixed with fresh feed water, and fed to the steam generator. The contaminated nitrogen is re-purified using cryogenic or pressure-swing methods, depending on the plant size. Heat recovery is important as it is possible to use the energy content of the hot product gases (700-1200 °C) of both reaction steps. This is done by 2-step heat exchangers. The heat is used to pre-heat the feed gases, steam and nitrogen, or for the evaporation of feed water.

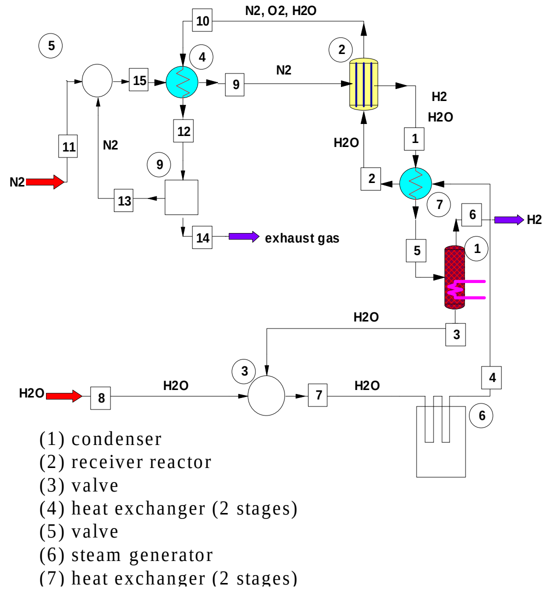


Fig 1: Basic flow sheet of water splitting process[2]

Experimentations, existing prototypes

Non-solar, lab-scale water-splitting/regeneration tests have been performed at Aerosol and Particle Technology Laboratory (APTL) in Greece and Johnson Matthey (JM) in UK. Pilot-scale solar tests were run in the facilities of the German Aerospace Centre (DLR) in Cologne, Germany, under real solar conditions using the available solar furnace. The first solar reactor built (Fig. 2a) was designed and constructed to monitor the performance and feasibility of solar hydrogen production by redox systems coated on ceramic supports. Both steps of the thermochemical cycle were successively performed at the required temperatures in the reactor in a multi-cyclic process[2]. The second solar reactor constructed - ("Conti" reactor) - was a dual-chamber reactor with fixed honeycomb absorbers designed to be capable of continuous hydrogen production (Fig. 2b). The modular set-up allows for essentially continuous production of solar hydrogen, because one part of the available modules split water while the other is being regenerated. After completion of the reactions, the regenerated modules are changed to the splitting process and vice versa by switching the feed gas. This reactor concept is amenable to straightforward scale-up due to the lack of movable parts and its modularity. Several campaigns proved the capability of the "Conti" reactor both reliably to operate the HYDROSOL cyclic process quasi-continuously and I ters of the long-term stability of the redox-coated honeycomb systems: 53 cycles of solar hydrogen generation with the same redox coating were performed during a 5-day campaign[3,4]. More recently, a dual-chamber, large-scale demonstration reactor has been built (Fig. 2c) and is coupled with the solar platform facilities of CIEMAT on the Plataforma Solar Almeria (PSA), Spain[4]. The demonstration plant, with a capacity of 100 kW is expected to validate the technical feasibility of the process in a real environment.

Fig 2a: First solar reactor

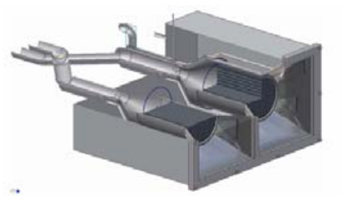


Fig 2b: Conti reactor

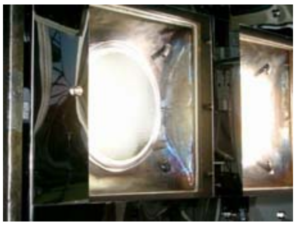


Fig 2c: dual chamber

Description of heat sources

HYDROSOL utilises heat produced by concentrated solar radiation. For mass hydrogen production on a commercial-scale level, the temperatures required can only be realized on so-called central receiver systems consisting of a set of sun-tracking mirrors (heliostats), a solar tower and a receiver (i.e. the same configuration employed in solar thermal power plants). The different and alternating operating temperature requirements of the two process steps are achieved in such a system by partitioning the heliostat field and using different flexible groups of heliostats: i.e. some of those providing a base load and others switching their focus alternatively between the two different focal positions after each half-cycle from one chamber to the other in tandem with the switchover of modules from one process step to the other.

Materials

The solar reactors consist of ceramic multi-channelled honeycombs coated with active redox materials. The honeycomb structure is made of advanced silicon carbide (SiC) that exhibits a high melting point, excellent thermal shock resistance and enhanced absorbance due to its naturally black colour coupled with its high thermal conductivity that enable the collection of solar heat and the effective heating of gases inside the honeycomb channels[5]. The active redox materials used are mainly iron-based mixed oxides, synthesized via short-time synthesis routes such as combustion and aerosol techniques and coated on the monolith with a variety of traditional and novel techniques.

Expected efficiency

Kolb and Diver[6] performed an independent screening analysis to identify concentrating solar power (CSP) concepts that produce hydrogen with the highest efficiency (cf. document, “screening analysis of solar thermochemical hydrogen concepts”). Several CSP concepts were identified that have the potential to be much more efficient than today’s low-temperature electrolysis technology. They combine a central receiver or dish with either a thermochemical cycle or high-temperature electrolyser that operate at temperatures > 600 °C. The solar-to-hydrogen efficiencies of the best central receiver concepts exceed 20 %, significantly better than the 14 % value predicted for low-temperature electrolysis. Ferrite cycles like HYDROSOL are between 23 and 25 % and therefore potentially some of the most efficient, but the higher temperatures needed must be taken into account.

Cost evaluation

For solar thermochemical hydrogen generation based on metal oxides, a 50 MW plant has been modeled. It consists of a 176 m high tower and a round field of 3199 heliostats each with a reflective surface of 121 m^2. Due to a fragmentation of the receiver reactor area the heliostat field is subdivided into eight different subfields in which the respective mirrors aim at their dedicated aperture. The metal oxide based cycle has higher O&M costs compared with other processes like solar electricity plus electrolysis. This is because the redox system must be periodically renewed and the price is based on a custom-made product today. Also, the N_2 flushing gas has to be replaced and separated constantly. However, the metal oxide based cycle produces the greatest amount of hydrogen because of its very high efficiency with an HPC of 6.7 €/kg [7]. In the future, this cycle will yield an HPC in a range between 3.5 and 12.8 €/kg, mainly caused by the high demand of the metal Oxide.

IEA/HIA task 25 : High Temperature Hydrogen Production Process

Hydrosol cycle

Contacts :

- Athanasios Konstandopoulos, APTL, agk@cperi.certh.gr
- Christos Agrafiotis, APTL, chrisagr@cperi.certh.gr
- Martin Roeb, DLR, Martin.Roeb@dlr.de
- Christian Sattler, DLR, Christian.Sattler@dlr.de
- Per Stobbe, STC, per.stobbe@stobbe.com
- Andrew Steele, JM, steela@matthey.com
- Antonio Lopez, CIEMAT,

https:// www-prodh2-task25.cea.fr

Main initiatives

HYDROSOL: Catalytic Monolith Reactor for Hydrogen Generation from Solar Water Splitting (ENERGY ENK6-CT-2002-00629)

HYDROSOL 2: Solar Hydrogen via Water Splitting in Advanced Monolithic Reactors for Future Solar Power Plants (SES6-2004-020030): http://www.hydrosol-project.org

Participating Organizations:

APTL/CERTH/CPERI, (Coordinator Greece): http://apt.cperi.certh.gr

DLR, (Germany): http://www.dlr.de

STC, (Denmark): http://www.stobbe.dk

CIEMAT, (Spain): http://ciemat.es

JM, (U.K.): http://www.matthey.com

Awards - International recognition

07/05/2007: Descartes Prize for Collaborative Scientific Research 2006 "...In recognition of the outstanding scientific and technological achievements through collaborative research in the field of science...".

13/06/2006: International Partnership for the Hydrogen Economy (IPHE) Technical Achievement Award, (IPHE), "...HYDROSOL's selection by the IPHE Awards Committee recognizes the significant potential it holds for large scale, emissions free hydrogen production...".

16/06/2005: Global 100 Eco-Tech Award, Japan Association for the 2005 World Exposition, "...In recognition of your outstanding contribution to the resolution of global environmental problems and to the creation of a sustainable future...".

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[6] G.J. Kolb, R.B. Diver "Screening Analysis of Solar Thermochemical Hydrogen Concepts" SANDIA Report SAND2008-1900, Unlimited Release, printed March 2008.

[7] D.Graf, N. Monnerie, M. Roeb, M. schmitz, C. Sattler "Economic comparison of solar hydrogen generation by means of thermochemical cycles and electrolysis",International Journal of Hydrogen Energy (2008), doi:10.1016/j.ijhydene.2008.05.086