

# THE HYDROSOL PROCESS: SOLAR-AIDED THERMO-CHEMICAL PRODUCTION OF HYDROGEN FROM WATER WITH INNOVATIVE HONEYCOMB REACTORS.

C. Agrafiotis<sup>1\*</sup>, S. Lorentzou<sup>1</sup>, C. Pagkoura<sup>1</sup>, A.G. Konstandopoulos<sup>1,2,\*\*</sup>, M. Roeb<sup>3</sup>, M. Neises<sup>3</sup>, P.M. Rietbrock<sup>3</sup>, J.P. Säck<sup>3</sup>, C. Sattler<sup>3</sup>, P. Stobbe<sup>4</sup>, A.M. Steele<sup>5</sup>

<sup>1</sup>Aerosol and Particle Technology Laboratory (APTL), Chemical Process Engineering Research Institute, Center for Research and Technology-Hellas (CERTH/CPERI),  
P.O. Box 361,57001, Thessaloniki, Greece  
\*E-mail: chrisagr@cperi.certh.gr, agk@cperi.certh.gr

<sup>2</sup>Department of Chemical Engineering, Aristotle University,  
P.O. Box 1517, 54006, Thessaloniki, Greece

<sup>3</sup>Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR), Institut für Technische Thermodynamik,  
Solarforschung, D-51170 Köln, Germany

<sup>4</sup>Stobbe Tech Ceramics A/S, Vejlemosevej 60, DK-2840, Holte, Denmark

<sup>5</sup>Johnson Matthey Fuel Cells Centre, Sonning Common, RG4 9NH, Reading, United Kingdom

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## ABSTRACT:

The HYDROSOL research team has developed an innovative solar thermo-chemical reactor for the production of hydrogen from water splitting constructed from special refractory ceramic thin-wall, multi-channelled (honeycomb) monoliths that absorb solar radiation. The monolith channels are coated with active redox water-splitting materials capable to split water vapor passing through the reactor by “trapping” its oxygen and leaving in the effluent gas stream as product pure hydrogen. In a next step, the oxygen “trapping” material is solar-aided regenerated (i.e. releases the oxygen absorbed) and hence a cyclic operation is established on a single reactor/receiver system. Several solar campaigns proved not only the feasibility of solar hydrogen production by the HYDROSOL process but also the stability of the redox/support assemblies: cyclic, constant and continuous H<sub>2</sub> production was achieved exclusively at the expense of solar energy. The proposed concept holds significant potential for large-scale, emissions-free hydrogen production, particularly for regions of the world that lack indigenous resources but are endowed with ample solar energy.

**KEYWORDS:** thermochemical cycles, water splitting, honeycomb reactors, solar thermal, hydrogen

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## 1. Introduction

The harnessing of the huge energy potential of solar radiation and its effective conversion to chemical energy carriers such as hydrogen is a subject of primary technological interest. One of the reactions with tremendous economical impact because of the low value of its reactants is the dissociation of water (water splitting) to oxygen and hydrogen. However because of unfavorable thermodynamics interesting yields can only be achieved at very high temperatures imposing therefore technological difficulties to any ideas trying to couple solar energy as the driving energy for the reaction. The integration of solar energy concentration systems with systems capable to split water is of immense value and impact on the energetics and economics worldwide; by some is considered as the most important long-term goal in solar fuels production, to cut hydrogen costs and ensure virtually zero CO<sub>2</sub> emissions [1-3]. The current state of the art of solar chemistry for water splitting and hydrogen production is focused on the so-called redox pair cycles. These are two-step processes, based on redox materials that can act as effective water splitters at lower temperatures [4-6].

Supprimé :

Supprimé : promising way

Supprimé : production

The HYDROSOL monolithic honeycomb solar reactor, inspired from the well-known automobile catalytic converters [7], for performing these redox pair cycles for the production of hydrogen from the splitting of steam using solar energy was recently introduced [8]. The HYDROSOL reactor contains no moving parts and is constructed from special refractory (Silicon carbide) ceramic thin-wall, multi-channelled (honeycomb) monoliths, optimised to absorb solar radiation and develop sufficiently high temperatures. The monolith channels are coated with an active water-splitting material (usually the lower-valence form of a metal oxide) and the overall reactor looks very similar to the familiar catalytic converter of modern automobiles. When steam passes through the solar reactor, the coating material splits water vapor by “trapping” its oxygen and leaving in the effluent gas stream pure hydrogen (Eq. 1), without any need for expensive and complicated gas separation post-processing steps. In a subsequent step (Eq. 2), the oxygen “trapping” material is regenerated (i.e. releases the oxygen absorbed), by increasing the amount of solar heat absorbed by the reactor and hence a cyclic operation is established:



The inherent advantage of two-step thermochemical cycles is that the production of pure hydrogen and the removal of oxygen take place in separate steps, avoiding the need for high-temperature separation and the chance of explosive mixtures formation. In addition, with the HYDROSOL reactor configuration, with the active redox pair materials coated upon the substrate walls, the whole process can be carried out on a single solar energy converter, the process temperature can be significantly lowered compared to other thermo-chemical cycles and, last but not least, this reactor concept does not involve any circulation of (hot) solid reactants or products and therefore has no problems with the recovery of high temperature heat. Such redox-material-coated-honeycombs have achieved continuous solar operation water splitting – regeneration cycles in the temperature range 850–1200°C demonstrating the “proof-of-concept” of the proposed reactor design and producing the first solar hydrogen with monolithic honeycomb reactors [8,9]. The present work summarizes the work performed so far and highlights the current research efforts focussed on long-term material stability and scale-up of the solar reactor.

## 2. Redox Material Development

Four different routes were employed for the synthesis of iron-oxide-based redox water-splitting materials: Solid-State Synthesis (SSS), Self-Propagating High-Temperature Synthesis (SHS), Gel Combustion (GC) and Aerosol Spray Pyrolysis (ASP) [8]. These synthesis methods were chosen with the rationale to exploit particular characteristics of each one for the synthesis of products with “tunable” oxygen vacancies concentration. The synthesis details have been reported previously [8], therefore only the general reaction concepts are reported below, where A and B denote the bivalent dopant metals: Ni, Mn or Zn.

i) Solid state synthesis (SSS) involved powder mixing of the component oxides (or carbonates), pre-firing, milling, spray drying and calcination at high temperatures ( $\approx 1250^\circ\text{C}$ ). The products were doped spinel ferrites of the structure  $(\text{A}_x\text{B}_y\text{Fe}_z)\text{Fe}_2\text{O}_4$ .

ii) Self-Propagating High-temperature synthesis (SHS or Combustion Synthesis) of the targeted materials is based on the heat released from the reaction of iron metal powder (“fuel”) with oxygen (“oxidizer”) in the presence of the dopant metal oxides and of  $\text{Fe}_2\text{O}_3$  powder as a “thermal ballast/moderator” to control the synthesis temperature.

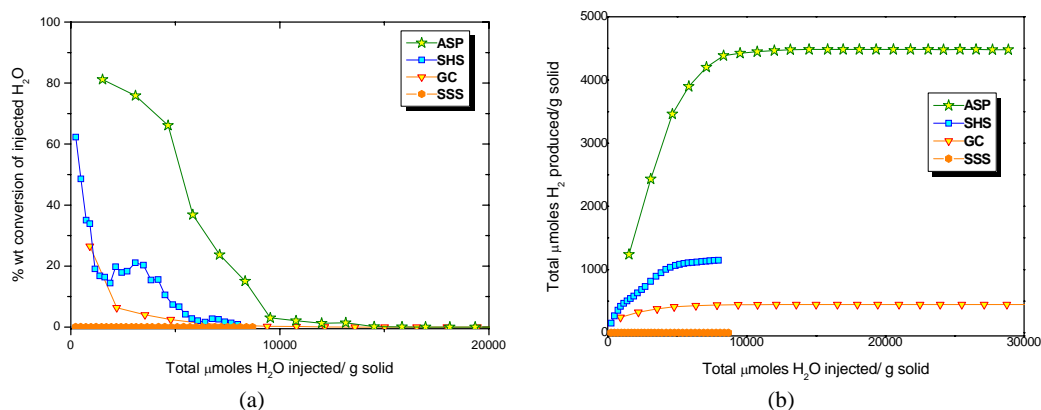
iii) Gel combustion (GC) is based on the reaction in aqueous solutions of nitrate salts  $\text{A}_x(\text{NO}_3)_y$  (“oxidant”) with amino-groups (“fuel”) to form explosive ammonium nitrate; upon heating the solution is first transformed to a gel which is then combusted to produce a very fine powder of spinel structure  $(\text{A}_x\text{B}_y\text{Fe}_z)\text{Fe}_2\text{O}_4$ .

iv) Aerosol spray pyrolysis (ASP) employs the atomisation of a metal precursor salts solution in a spray of fine droplets that is subsequently passed through a hot-wall reactor where it transforms within a very short time to ultra-fine, nanostructured spherical particles [10].

The first “screening” of the synthesized material compositions with respect to water splitting activity was performed in a laboratory unit described in detail previously [11] and subsequently in a scaled-up testing rig version consisting of a 20-mm-diameter quartz glass tubular reactor enclosed within a high-temperature programmable furnace capable of reaching temperatures of  $1500^\circ\text{C}$ . A bed of the redox material powder to be tested was placed in the middle of the reactor and subsequently heated under inert atmosphere (Nitrogen) to the water-splitting testing temperature. When this

temperature was reached, steam was introduced to the reactor, either by successive intermittent injections of water in the Nitrogen stream flowing continuously over the heated sample by a microliter syringe or continuously with the aid of a manometric water pump and a heated evaporation line. The effluent, after passing through a water trap, was diverted to the analysis rig, consisting of an MS detector, a CO and a CO<sub>2</sub> analyzer. Each water-splitting experiment lasted until Hydrogen could not be further detected in the effluent stream; thereafter the steam flow was switched off, the reactor was cooled down and the redox materials were collected for ex-situ characterization. The quantities of unconverted water and of produced Hydrogen were calculated based on the areas of the corresponding MS peaks.

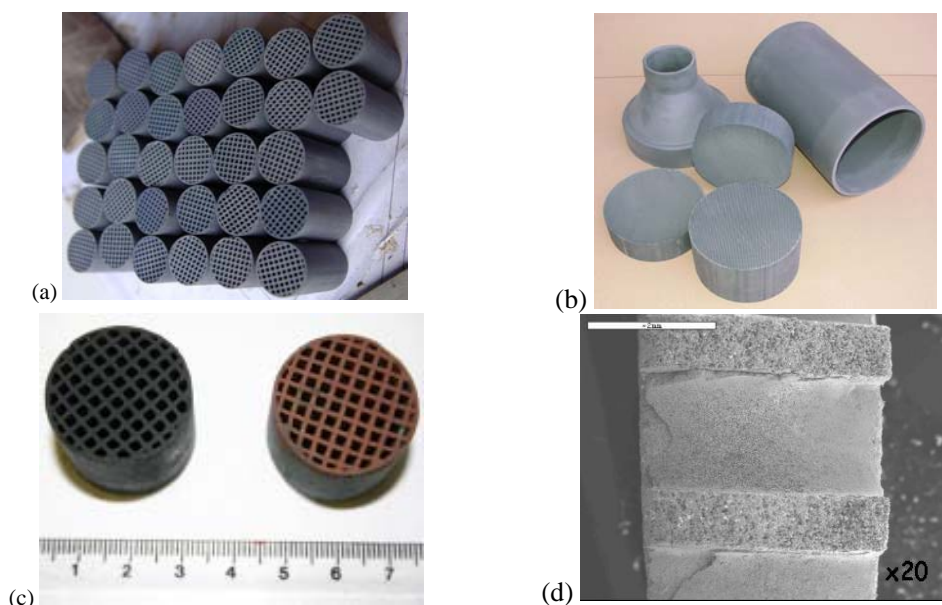
These experiments have shown that systems from all the synthesis routes were able to split water and generate hydrogen as the only product, at temperatures as low as 800°C and could be repeatedly regenerated under inert atmospheres at temperatures below 1200°C [8]. The “best” products from each synthesis route are compared with respect to water-to-hydrogen conversion and total hydrogen yield in Figs. 1a, 1b respectively. Both SHS and ASP materials exhibited very high water conversions (amount of water converted/total amount of injected water) at 800°C – 57% and 81% respectively. Overall the ASP materials exhibited both the highest water conversion and hydrogen yield.



**Figure 1: Comparison of “best” redox powders from each synthesis route with respect to: (a) water conversion and (b) total Hydrogen yield.**

### 3. Manufacturing and coating of honeycomb solar receivers

Several series of small-scale (Ø25x50 mm) and large-scale (Ø144x200 mm) monolith extruded multi-cell SiC supports were produced (shown in Figs. 2a and 2b respectively) and coated with the synthesized materials via the “washcoating” technique employed for the coating of automotive catalysts, in which the porous supports are impregnated in a slurry of the coating powder [7]. With subsequent drying and firing at the temperature range 500-800°C, an adherent oxide layer is formed on the walls of the support. However, in the particular case, this “adhesion” firing had to take place under oxygen-free atmosphere (inert) in order to prevent oxidation of the redox material that would destroy its oxygen-deficiency and consequently its water-splitting ability. The coated honeycombs (Figs. 2c, 2d) were employed for the experimental campaigns in the solar furnace to demonstrate the “proof-of-concept” of the proposed approach and to “screen” redox material formulations.



**Figure 2: (a) Small-size and (b) large-size, extruded SiC honeycombs (carriers) and cast parts (housing vessel), (c) typical coated small-size honeycombs before (black material: “reduced state”) and after solar water-splitting (red material: “oxidized state”), (d) “top” view SEM photograph of coated honeycomb channels.**

#### 4. Solar Reactors

Two reactors have been developed for different purposes. The first reactor built (Fig. 3a) was designed and constructed to monitor the performance and feasibility of solar chemical hydrogen production by redox systems coated on ceramic support structures. This receiver-reactor is the central element of a so-called mini-plant operated in the operational room of the Solar Furnace at DLR facilities, in Cologne, Germany, that is capable of absorbing solar radiation provided by a solar furnace and at the same time of carrying out the necessary process steps at the required temperatures. This reactor was mainly designed for the investigation of the general feasibility of both steps of the process and for screening different “families” and “generations” of redox pairs coated on small-scale honeycombs as depicted in Fig. 3b. Both steps of the thermochemical cycle were successively performed in the same reactor, the first requiring the supply of pure steam and the second (oxygen releasing) the supply of pure inert gas, i.e. nitrogen.

The first solar campaign demonstrated the in-principle-feasibility of water splitting by the proposed method. The first solar hydrogen was successfully produced by irradiating a redox material coated on a SiC monolith at 800°C in a mixture of steam and nitrogen, whereas after completion of the water splitting step and by raising the operating temperature to 1200°C under flushing by pure nitrogen, a release of oxygen was initiated. The second campaign proved the feasibility of multi-cycling, i.e. a periodic and alternating performance of water splitting and regeneration of the redox system. Not only the reactor was capable for producing hydrogen from steam at the expense of solar energy alone, but multi-cyclic operation (water splitting and redox material regeneration) at the temperature range 800-1200°C was successfully demonstrated several times and for several of the redox materials synthesized [9] that were capable of achieving up to 14 cycles of Hydrogen production.

The main objectives of the third campaign were on the one hand large monoliths (Ø144 x200 mm) testing for the demonstration of continuous production of hydrogen and on the other hand, further improvement of the coated monoliths with respect to multi-cycling capability and the amount of H<sub>2</sub> produced. In particular, the stability of coating/support assembly was to be improved compared to the second campaign focussing on the lifetime of the coating. The results were quite encouraging. One of the samples was irradiated in a long-term operation over five days and it evidenced activity in terms of water splitting after 40 cycles. The portions of the hydrogen emerged slightly decreased over the very first cycles to reach an almost constant level over all following cycles. Even more cycles would have been possible; the experiments were discontinued due to the end of the campaign. A very relevant

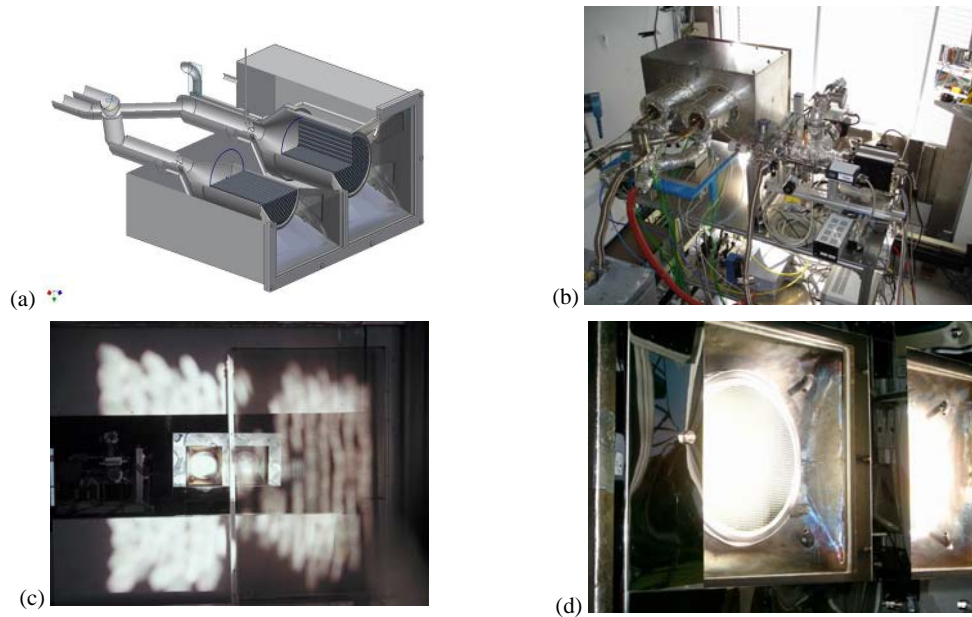
observation was that the structure including the coating remained in good conditions throughout all cycles only exhibiting a minor detachment of the coating after dismounting.



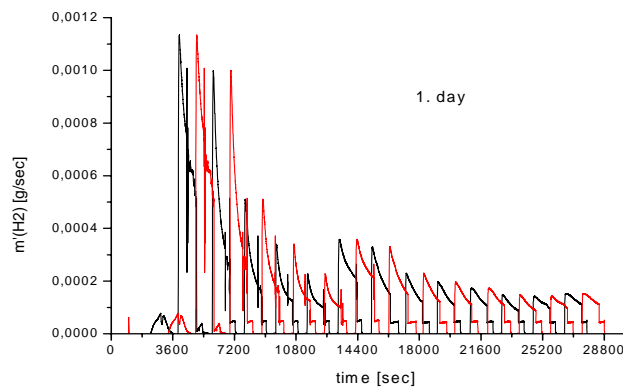
**Figure 3: (a) Front view of the first solar water-splitting receiver-reactor, (b) Small-scale honeycomb coated with redox material (black) in the centre of the reactor ready for testing.**

The second reactor constructed, was designed with the purpose to be capable for continuous hydrogen production [12]. Different approaches of receiver-reactors have been analysed and compared. The final decision was in favor of a multi-chamber reactor with fixed honeycomb absorber allowing a modular set-up. This concept exhibits the possibility of a straightforward scale-up due to the lack of movable parts and due to its modularity. The modular set-up itself allows for a continuous provision of solar hydrogen, because one part of modules splits water while the rest is being regenerated. After completion of the reactions the regenerated modules are switched to the splitting process and vice versa by switching the feed gas. The thermochemical cycle is made up of two process steps performed at different temperature levels with different heat demand. This general design concept has been transferred into a detailed design of the so-called “conti reactor” represented in Fig. 4. The test programme aimed at exploring suitable operation conditions to verify the concept of a continuous hydrogen production in the “conti reactor”.

The concept of the conti receiver/reactor has proven to be successful. The approach to the operation of the reactor is generally practicable and very reliable to attain a continuous process and production of hydrogen. The necessary switch of solar flux density was realised in practice by a movable diminisher. The necessary switch of feed and product gas was realised by a 4-way-valve. This way of operation is transferable to a solar tower application in principle. Fig. 5 presents the quasi-continuous production of hydrogen in 13 subsequent cycles during the first day of solar testing of two large coated monoliths in the conti reactor. Another 10 cycles were carried out during the following day. A subsequent campaign proved 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, proving the capability of the “conti” reactor to reliably operate the HYDROSOL two-step water splitting process quasi-continuously.



**Figure 4: The dual-chamber (“conti” reactor) for continuous solar hydrogen production: (a) vertical-horizontal cut, (b) rear view of the reactor with necessary peripherals and (c), (d) front view of the reactor, in operation at the solar furnace facility.**



**Figure 5: Campaign with the “conti” reactor; first quasi-continuous production of hydrogen: mass flow of hydrogen for 13 cycles during the first day of testing of two coated monoliths.**

## 5. System scale-up

The next steps involve the development and build of an optimized pilot plant (100 kWth) for solar Hydrogen production based on this novel reactor concept, involving further scale-up of the HYDROSOL technology and its effective coupling with solar platform concentration systems, in order to exploit and demonstrate all potential advantages. Specific challenging problems currently addressed include:

- enhancement and optimisation of the metal oxide-ceramic support system with respect to long-time stability under multi-cycle operation (more than 100 cycles)
- development and construction of a complete pilot dual absorber/receiver/reactor unit in the 100 kWth scale for solar thermochemical splitting of water
- effective coupling of this reactor to a solar heliostat field and a solar tower platform for continuous solar Hydrogen production within an optimized pilot plant.

The first scaled-up version of the solar reactor/receiver currently under construction is shown in Fig. 6. It involves a dual-reactor unit, each part assembled from 9 square-shaped SiC honeycomb pieces with dimensions 146x146 mm. The unit is going to be coupled with the solar tower platform of Plataforma Solar of Almeria, Spain and to the respective solar heliostat field, for test operation for continuous solar Hydrogen production.



Figure 6: Next generation of HYDROSOL solar reactors.

## 6. Conclusions

The HYDROSOL team has proposed and developed an innovative solar reactor for the production of hydrogen from the splitting of steam by a two-step thermochemical cycle using solar energy. The basic idea behind the HYDROSOL technology, i.e. that of combining a support capable of achieving high temperatures when heated by concentrated solar radiation, with a redox pair system suitable for water dissociation and at the same time for regeneration at these temperatures, and therefore perform both steps of the thermochemical cycle on a single solar energy converter was successfully put into practise. The necessary redox pair powder materials synthesized via un-conventional routes (combustion synthesis and aerosol spray pyrolysis) have been proven capable of splitting water at relatively low temperatures (800 °C) with high water conversions and Hydrogen being the only reaction product. The evaluation of the redox materials on the solar reactor proved the feasibility of solar hydrogen production by the HYDROSOL process and the stability of the redox/support assemblies: multi-cyclic solar thermo-chemical splitting of water was successfully demonstrated: the reactor produces hydrogen by cyclic operation exclusively at the expense of solar energy; up to 52 cycles of constant hydrogen production were operated in a row in a five-days campaign.

The project is the world's first closed, solar-thermochemical cycle in operation that is capable of continuous hydrogen production and seeks to develop a cost effective and efficient means of producing hydrogen from solar energy that is expected to proceed with the ongoing commercialization of solar thermal applications (in particular power plants). The developed technology not only produces hydrogen - a "clean" fuel considered to be the energy source of the future with the advancement of fuel cell technology - but employs entirely renewable and abundant energy sources and raw materials - solar energy and water respectively -without any CO<sub>2</sub> emissions, in an entirely "clean", natural and environmentally friendly way. It holds, thus, a significant potential for large-scale, emissions-free hydrogen production, particularly for regions of the world that lack indigenous resources but are endowed with ample solar energy. Based on these results, the next efforts involve further scale-up of the technology and its effective coupling with solar concentration systems like solar towers in order to demonstrate large-scale feasibility of a solar plant for the production of solar Hydrogen. The target is a sustainable energy supply through zero emission process production of hydrogen by solar energy that in the long term will promote economic development and people's quality of life, especially in many economically depressed Mediterranean regions with sufficient insolation.

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