

## 4 Task II: Solar Chemistry Research

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### 4.1 Nature of Work & Objectives

The primary objective of Task II – Solar Chemistry R&D – is to develop and optimize solar-driven thermochemical processes and to demonstrate their technical and economic feasibility at an industrial scale:

- *Production of energy carriers*: conversion of solar energy into chemical fuels that can be stored long-term and transported long-range. During this term, special focus is on solar thermal production of hydrogen and syngas.
- *Processing of chemical commodities*: use of solar energy for processing energy-intensive, high-temperature materials.
- *Detoxification and recycling of waste materials*: use of solar energy for detoxification and recycling of hazardous waste and of secondary raw materials.

**Organization and Structure:** The Task II Operating Agent, currently PSI, Switzerland, is responsible for organization, operation, and reporting. International solar chemical research, development and demonstration efforts are coordinated in cost, task and/or information-sharing activities by National Coordinators, making use of an efficient network, for the rapid exchange of technical and scientific information. The Task II Annual Meeting provides a forum for presenting and discussing major technological achievements.

The Task II Program of Work provides an up-to-date description of the national and international projects. When appropriate, Task II conducts a status review on novel technologies for assessing their technical and economical feasibility. Task II is continuously striving to stimulate public awareness of the potential contribution of solar chemistry to clean, sustainable energy services.

### 4.2 Status of Technology

This chapter provides a comprehensive overview of the many ways in which solar chemical technologies may be used for the delivery of clean, sustainable energy services. In 2008, special focus was on the solar thermal production of fuels (hydrogen and syngas) and

chemicals for the power, transportation and chemical sectors of the world energy economy.

In 2008, solar chemistry research was presented at two major international conferences:

- *14<sup>th</sup> SolarPACES International Symposium*, Las Vegas, NV (USA), March 4-7, 2008: 20 papers were presented on the topic of solar fuels.
- *ASME Energy Sustainability Conference (ES2008)*, Jacksonville, August 10-14, 2008: 11 papers were presented on solar chemistry and hydrogen production.

The most important achievements in 2008 are summarized with up-to-date information about project participation, objectives, status, and relevant publications.

### 4.2.1 SOLAR PRODUCTION OF ENERGY CARRIERS

#### SOLREF – Solar Steam Reforming of Methane Rich Gas for Synthesis Gas Production

**Participants:** DLR (D), APTL (GR), WIS (IL), ETH (CH), Johnson Matthey Fuel Cells Ltd. (UK), HyGear B.V. (NL), SHAP S.p.A. (I)

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**Funding:** EC funded project, cost shared:  
€ 2,100,000

**Duration:** April 1, 2004 - March 31, 2009

**Background:** The work proposed in SOLREF is based on the activities performed in the previous SOLASYS project, in which the technical feasibility of solar steam reforming was proven. Based on the experience and know-how acquired in SOLASYS, SOLREF will take solar steam reforming a significant step closer to industrialization.

**Purpose:** The main purpose of this project is to develop and operate an innovative 400-kW<sub>th</sub> solar reformer for such applications as hydrogen production or electricity generation. The new solar reformer is more compact and cost-effective than the previous SOLASYS reformer.

**Achievements in 2008:** Due to a delay in the manufacturing/certification of the reformer, the project is being extended to March 2009. In Fall 2008, the 400-kW<sub>th</sub> solar reformer was assembled at DLR and shipped to WIS. Figure 4.1 shows the solar reactor before shipping. It has now been assembled on the solar tower of WIS. The test campaigns will start early 2009.



Figure 4.1. SOLREF reactor assembled at DLR Stuttgart and ready for shipping to WIS.

Models based on computer tomography (CT) were developed by ETH. A CT-based methodology was applied to determine the fluid transport properties for flow across porous media (Ref. [4.1]). The effective thermal conductivity of reticulate porous ceramics (RPCs) was determined based on the 3D digital representation of their pore geometry obtained by high-resolution multi-scale CT (Ref. [4.2]). X-ray micro-tomography with a digital resolution of 30  $\mu\text{m}$  and synchrotron sub-micron tomography with a digital resolution of 350/700 nm was performed on catalyst-coated reticulate porous ceramics (Ref. [4.3]).

Better catalyst systems were developed by APTL in attempt to achieve cheaper catalysts than those selected for SOLREF.

**Publications:** [4.1]-[4.3]

## SOLHYCARB – High Temperature Solar Chemical Reactor for Co-production of Hydrogen and Carbon Black from Natural Gas Cracking

**Participants:** CNRS-PROMES (F), ETH (CH), PSI (CH), WIS (IL), CERTH/CPERI (GR), DLR (D), TIMCAL (B), SOLUCAR R&D (E), CREED (F), N-GHY (F)

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**Funding:** EC funded project, cost shared: € 2,000,000

**Duration:** March 1, 2006 – February 28, 2010

**Background:** The SOLHYCARB project addresses the solar thermal decomposition of natural gas for the co-production of hydrogen and Carbon Black (CB) as a high-value nanomaterial. This process avoids CO<sub>2</sub> emissions and saves fossil fuels compared to conventional H<sub>2</sub> and CB production methods (natural gas steam reforming and incomplete hydrocarbon combustion, respectively).

**Purpose:** Research is aimed at designing, constructing, and testing innovative solar reactors at various scales (10 kW<sub>th</sub> and 50 kW<sub>th</sub>) operating between 1400°C and 1800°C. The targeted results are: (1) CH<sub>4</sub> conversion over 80%; (2) off-gas H<sub>2</sub> yield over 75%; and (3) CB properties equivalent to industrial products. Research also focuses on solar reactor modeling, both separation of carbon nanoparticles from the gas-solid flow and hydrogen from the hydrogen-rich gas, characterization of CB, and the conceptual design of an up-scaled solar process.

**Achievements in 2008:** A multi-tubular solar reactor prototype (10 kW<sub>th</sub> scale) based on indirect heating was constructed and tested at CNRS-PROMES (Ref. [4.4]). The reactor features a cavity-type receiver (20 cm side) with a 9-cm-diameter aperture closed by a transparent quartz window which allows concentrated solar radiation to enter (Figure 4.2 and Figure 4.3). The reacting gas flows through four tubular reaction zones, each of which is made up of two concentric graphite tubes inserted vertically inside the cavity. A filtering system separates the CB particles at the reactor outlet. The off-gas composition is monitored online by specifically dedicated analyzers.

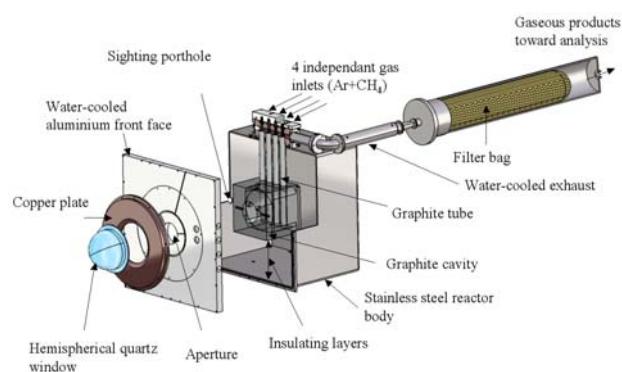


Figure 4.2. Diagram of the 10-kW solar reactor and filter developed at CNRS-PROMES.

The first test campaign was conducted at moderate temperatures (up to 1500°C). Gas composition at the reactor outlet, CH<sub>4</sub> conversion and H<sub>2</sub> yield, and the reactor thermal efficiencies were determined with respect to reaction temperature, residence time, gas flow rates, and feed gas composition. CH<sub>4</sub> conversion over 90% and H<sub>2</sub> yield of about 75% were measured (with 20% CH<sub>4</sub> in the feed gas and residence time of 18 ms),

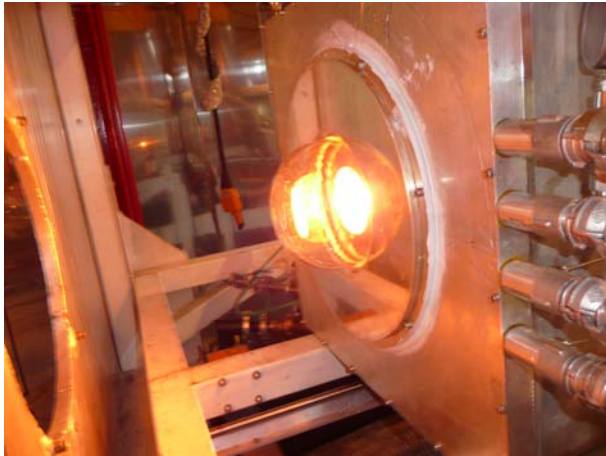


Figure 4.3. Close look at SOLHYCARB reactor aperture during cooling at CNRS-PROMES test rig.

but the CB contained polycyclic aromatic hydrocarbons (PAHs), and pyrocarbon was formed.

The second test campaign was performed at higher temperatures (1550-1800°C). Chemical conversion increased with temperature and gas residence time. Complete CH<sub>4</sub> conversion was achieved whatever the amount of CH<sub>4</sub> in the feed (up to 100%). H<sub>2</sub> yields were over 90%, and thermochemical efficiency was in the range 5-10%. Acetylene was the most important by-product with a mole fraction up to about 7%.

Thermal simulations for solar reactor modeling showed homogeneous temperature distribution inside the cavity receiver. The influence of the non-gray thermal radiation on the heating of Ar/CH<sub>4</sub> laminar flow was specifically investigated (Ref. [4.5]). The results showed that the temperature field is influenced markedly by radiation due to the participation of methane. Kinetic simulations were carried out with the Dsmoke calculation code using a detailed kinetic scheme for the wide range modeling of alkane transformation (Ref. [4.6]). Comparisons with experimental results between 1400°C and 1500°C showed good agreement for CH<sub>4</sub> conversion and off-gas composition.

Publications: [4.4]-[4.6]

### SYNPET – Hydrogen Production by Steam-Gasification of Petcoke and Vacuum Residue

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Funding: PDVSA-CIEMAT-ETH:  
 \$6,700,000

Duration: January 1, 2003 - June 30, 2009

Background: Hybrid solar/fossil endothermic processes make use of fossil fuels as the chemical source for H<sub>2</sub> production and of concentrated solar energy exclusively as the source of high-temperature process heat. PDVSA, CIEMAT and ETH have started a joint project to develop and test a 500 kW<sub>th</sub> solar reactor for steam gasification. In Phase 1, after in-depth studies of the thermodynamic and kinetic behavior, a small 5-kW<sub>th</sub> prototype was tested in the PSI Solar Furnace, Switzerland. The engineering design, experimentation, and modeling of the solar reactor were presented in [4.7]-[4.8], and literature cited therein. Phase 2 was devoted to the design, construction, modeling and optimization of a 500 kW<sub>th</sub> reactor (Ref. [4.9]-[4.10]). Construction was managed by CIEMAT, and it will be operated on the SSPS tower at the Plataforma Solar de Almería in 2009.

Purpose: The project aims at experimental demonstration of the technology in a 500-kW<sub>th</sub> solar reactor of heavy crude oil solid derivatives, such as petcoke.

Achievements in 2008: During 2008, the installation of the 500-kW<sub>th</sub> Solar Gasification Plant on top of the SSPS/CRS tower at the Plataforma Solar de Almería was finalized. The receiver-reactor was placed at the 40 m platform of the SSPS tower. The pilot plant consists of the cavity reactor, upstream and downstream equipment, and measurement systems. A schematic layout of the plant is shown in Figure 4.4. The installation includes a multi-screw feeder and a mixing tank, as well as valves, flow meters and pumps. In the mixing tank, coke is mixed with water to form the slurry, which is conveyed to the entrance of the reactor by a pump. The coke reacts with steam at a temperature of 1100 -

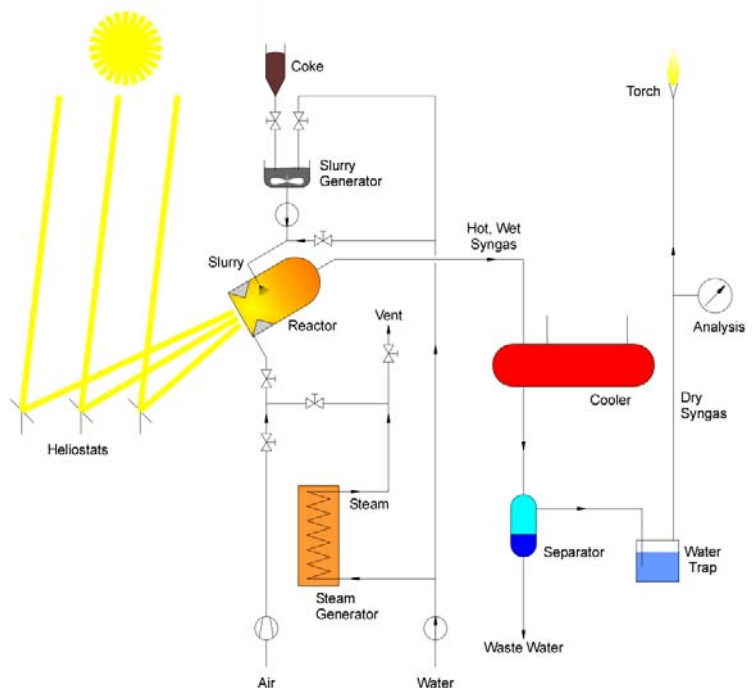


Figure 4.4. Schematic of the solar plant layout for the steam-gasification of petroleum coke at the Plataforma Solar de Almería.

1400°C to produce a raw fuel gas and un-gasified material. At the exit of the reactor, the product gas is simply cooled down by water in a standard TEMA-type BEU heat-exchanger to sufficiently reduce the temperature for accomplishing the requirements of the torch. For this plant, syngas production of around 100 to 180 kg/h has been estimated.

In 2009, it is planned to demonstrate the feasibility of solar gasification, determine critical process parameters, identify possible difficulties, and finally get a solid database for scale-up in Phase 3 of the project.

Publications: [4.7]-[4.10]

## STCH – Solar-Powered Thermochemical Production of Hydrogen from Water

Participants: University of Nevada Las Vegas (UNLV), University of Colorado (UC), Sandia National Laboratories (SNL), National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), General Atomics (GA)

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Funding: U.S. DOE funded project,  
cost shared: \$13,005,000

Duration: June 25, 2003 - November 30, 2008,  
continuing

Background: Hundreds of thermochemical cycles to split water have been proposed. The feasibility of these processes can be assessed through thermodynamic analysis and experimentation. There is a need to evaluate these cycles in order to identify the most feasible and economical for further investigation. The most promising cycles should be demonstrated.

Purpose: Quantify cycle thermodynamics, reaction kinetics, reactant/product equilibrium quantities for each cycle step, and process economics for current thermochemical cycles. Ultimately, demonstrate integrated pilot plant designs, including on-sun testing for up to three competitive cycles.

Achievements in 2008: Five thermochemical cycles are currently under active study in the STCH. These include: (1) zinc oxide and cadmium oxide volatile metal oxide cycles, (2) sodium manganese and cobalt ferrite non-volatile metal oxide cycles, and (3) hybrid copper chloride cycle. In addition, a solid particle receiver is being constructed to interface to hybrid sulfur (HyS) and sulfur-iodine (SI) cycles.

Zinc Oxide – An experimental study of the thermal dissociation of ZnO particles (1<sup>st</sup> step) in an aerosol flow was completed (Ref. [4.11]). Experiments were performed at temperatures between 1600°C and 1750°C and residence times between 1.11 s and 1.78 s. The net conversions after recombination had a maximum value of 18%, with a mean value of 8%. Surface area of prod-

uct particles, which ranged between 5 nm and 70 nm, were expected to increase the rate of the Zn hydrolysis step of the cycle.

The hydrolysis of zinc powder (2<sup>nd</sup> step) was studied in an aerosol to determine whether high conversions are feasible at short residence times and high dispersions (Ref. [4.12]). Zinc particles with an average size of 158 nm reacted with water vapor to form hydrogen and zinc oxide in an aerosol flow tube reactor at ambient pressure (82 kPa) between 380°C and 540°C and 3% water concentration. The highest conversion observed in the flow system was about 24% at 540°C and a gas residence time of ~0.6 s. Non-isothermal thermogravimetric analysis (TGA) indicated that complete conversion of Zn to ZnO could be achieved for longer residence times.

Significant progress has been made toward constructing and testing a new multi-tube reflective wall solar reactor (Figure 4.5). Validation and testing of the power and flux profile was done using the High Flux Solar Furnace (HFSF), capable of producing 2500 suns concentration, at the National Renewable Energy Laboratories (NREL). A new secondary concentrator has been constructed that produces up to 3000 suns. Both ray tracing and multi-physics models have been developed to simulate the performance of the HFSF test facility.

A three-dimensional computational fluid dynamics model of the multi-tube aerosol flow reactor is being developed using the finite-volume models in the commercial Fluent software. Simulations done for small reacting and non-reacting particles entrained in either a single inert gas or a mixture of gas species showed that the aerosol mixture in the flow tubes reached temperatures up to about 1377-1477°C.

Cadmium Oxide – A rotary kiln reactor was designed and constructed to improve the hydrolysis reaction of molten cadmium. Design modifications for a thermogravimetric analyzer (TGA) were completed to permit measurements of recombination rates during the dissociation of CdO; first measurements show a recombination of 30-40% for temperatures in the range 1000°C to 1475°C.

A window-closed reactor was designed for CdO dis-

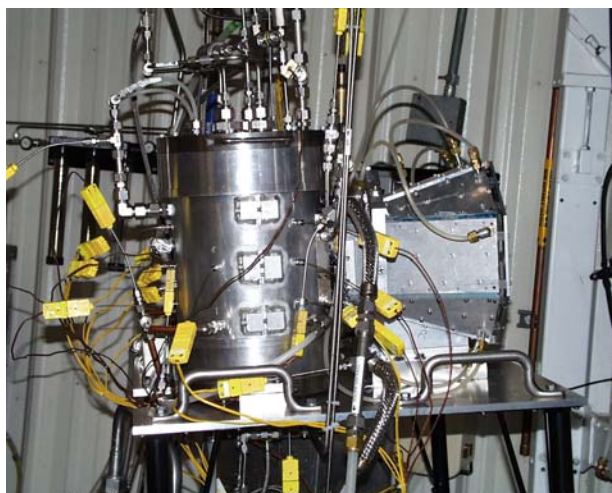


Figure 4.5. Multi-tube reactor installed and tested at NREL

sociation to prevent loss of Cd vapor. Modeling studies addressing the effect of negative pressure differential showed that the decomposition temperature could be reduced from 1500°C to 1255°C for operating pressures around 0.1 bar.

A CdO flow sheet for a 24-hr plant was developed. The thermal efficiency of the initial flow sheet was found to be 48.3% (LHV). Further optimization is expected to increase this predicted efficiency. A CdO central plant concept solar field has been developed to make use of a beam-down collector/concentrator to permit ground-level operation of all chemical processes.

**Ferrites** – Continuing ferrite feasibility work focuses on two areas: (1) evaluation of transport mechanisms and reaction rates for the water oxidation reaction and (2) fabrication of large-surface reactive structures (Ref. [4.13]). Performance of the ferrite cycles ultimately depends on improvements in the chemistry and on fabricating reactive structures that provide a good interface with concentrated solar energy and a large surface area for the reaction. Although the project had relied on Robocasting, a rapid prototyping technique for ceramics, to produce reactive structures, research has recently been employing other techniques to increase the reactive area of the materials beyond the capability of Robocasting and improve their manufacturability.

Construction of the CR5 reactor has been completed. The system is scheduled for first on-sun testing in Sandia's solar furnace facility. A recent image of the CR5 system is shown in Figure 4.6.

**Copper Chloride** – The Cu-Cl cycle was selected as the most promising alternative thermochemical cycle under the Nuclear Hydrogen Initiative. The conceptual process design for the three-reaction Cu-Cl cycle was completed. It consists of four operating units: The electrolyzer, crystallizer, hydrolysis reactor, and oxychloride decomposition reactor. The current Aspen flow sheet is shown in Figure 4.7. So far, the nebulizer hydrolysis reactor has been designed, fabricated and successfully tested. The slurry  $\text{CuCl}_2$  goes from the crystallizer to the

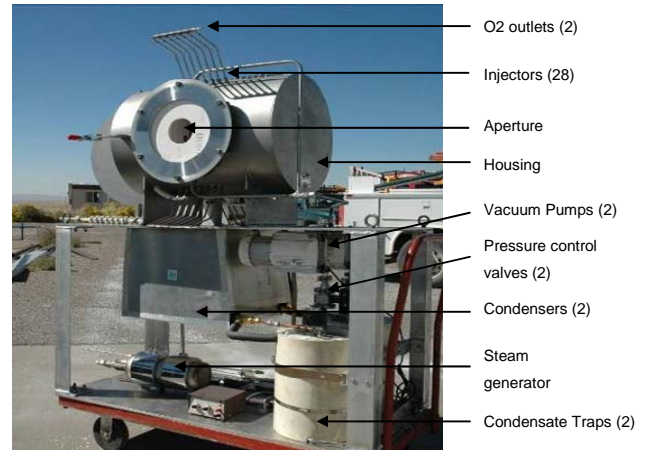


Figure 4.6. Recent image of the CR5 system.

hydrolysis reactor at 22 bar where it is sprayed into a superheated (400°C) steam environment at 1 bar. The  $\text{CuCl}_2$  forms a free jet. As the jet expands it sucks the superheated steam into the jet resulting in high mass and heat transfer between the  $\text{CuCl}_2$  in the jet and the steam. The  $\text{CuCl}_2$  is converted into  $\text{Cu}_2\text{OCl}_2$  and HCl. The HCl and un-reacted steam leave the hydrolysis reactor to be cooled and are fed to the cathode of the electrolyzer, where hydrogen is produced.

Dry, free flowing solid  $\text{Cu}_2\text{OCl}_2$  accumulates at the bottom of the hydrolysis reactor and is then transferred to the oxychloride decomposition reactor at 550°C where it decomposes into molten  $\text{CuCl}$  and oxygen. The heat is recovered from the molten  $\text{CuCl}$  in a direct heat exchanger where the  $\text{CuCl}$  is granulated while raising steam. The solidified  $\text{CuCl}$  then goes to the anode feed tank where it is dissolved in an HCl- $\text{CuCl}_2$  solution. At the anode of the electrolyzer,  $\text{CuCl}$  is oxidized to  $\text{CuCl}_2$ , which goes to the crystallizer.

A CuCl cycle plant producing 125 MT  $\text{H}_2$ /day requires 210 MW of thermal energy and 87.8 MW of electrical energy, resulting in an efficiency of about 40-42% (LHV). A preliminary H2A cost analysis has been completed.

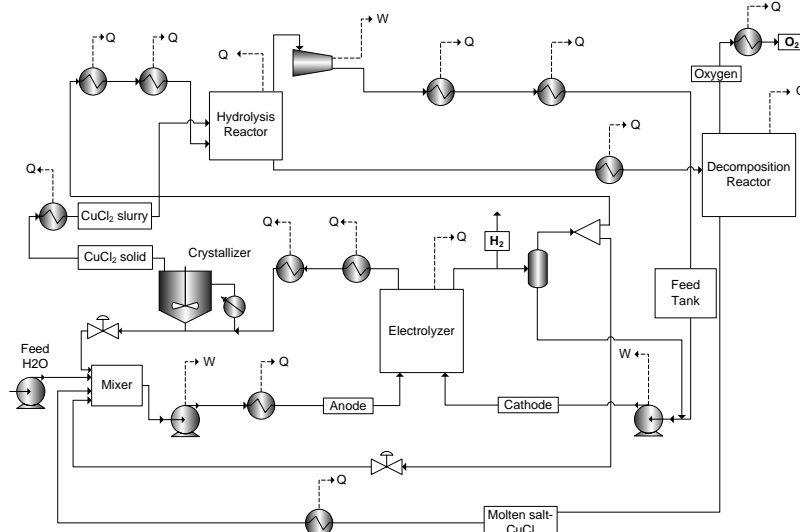


Figure 4.7. Aspen Plus™ flow sheet for the CuCl cycle.

**Solid Particle Receiver** – The solid particle receiver (SPR) is a direct absorption receiver, in which solar energy heats a curtain of falling ceramic particles to a temperature in excess of 1000°C (Ref. [4.14]). On-sun testing of the 10 m tall receiver was conducted on top of a power tower at Sandia National Laboratories in early 2008. The test plan included three mass flow rates and three input power levels. During some tests winds exceeded 30 mph. A schematic drawing and photograph of the SPR are shown in Figure 4.8.

Particles entered through a hopper in the top of the receiver that provided sufficient storage for five-minute or more tests, depending on the flow rate. A distance of about 3.9 m was directly heated within the cavity. Receiver performance can be evaluated by considering the tem-

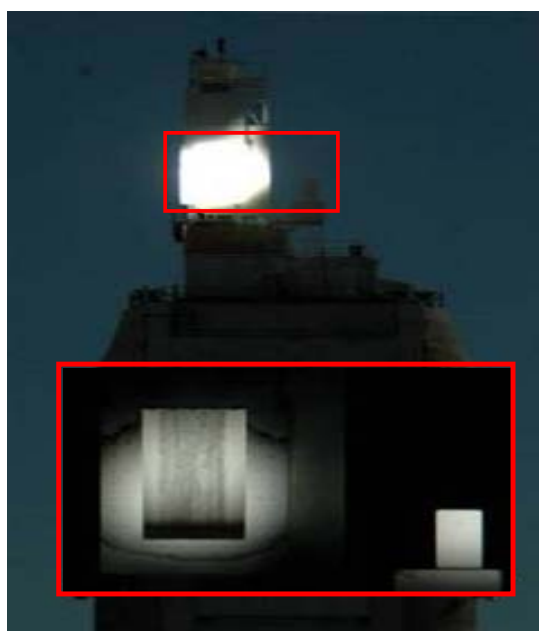
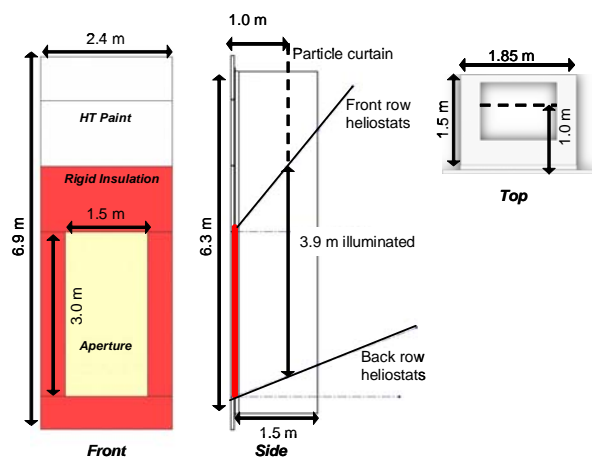


Figure 4.8. Top: Schematic drawing of the SPR. Bottom: The SPR during testing on top of Sandia's power tower. The inset region shows a detailed view of the particle curtain as it falls through the aperture.

perature change in the particles and the ratio of heat absorbed to heat incident on the aperture (receiver efficiency). A maximum particle temperature change of 247°C and maximum receiver efficiency of about 57% were measured.

Publications: [4.11]-[4.14]

## Hydrogen Production from Solar Thermochemical Water-Splitting Cycles

Participants: CNRS-PROMES (F), CNRS-IEM (F)

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Funding: CNRS

Background: The production of hydrogen from solar-driven thermochemical cycles is under investigation. A

preliminary screening identified the most promising metal-oxide redox cycles (Ref. [4.15]). Two and three-step cycles involving high-temperature solid-gas reactions are being considered. Innovative mixed-metal oxide systems are also being developed. Each cycle step requires thorough investigation of the chemical reaction systems and design and performance assessment of innovative solar reactor concepts.

Purpose: (1) Identify and investigate novel multi-step cycles for hydrogen production; (2) determine the characteristics of the solid-gas reactions involved in the cycles and propose kinetic rate laws; (3) design, manufacture, and operation of a solar reactor prototype for continuous-mode reduction reactions; (4) simulate reactor operation under steady-state and transient conditions; (5) evaluate the overall energy efficiencies of the solar chemical processes.

Achievements in 2008: Two-step cycles operating below 1700°C were investigated, and the innovative SnO<sub>2</sub>/SnO system was proposed (Ref. [4.16]). Like ZnO/Zn, it is one of the volatile systems, because the solar thermal reduction step between 1500°C and 1700°C produces Zn or SnO vapor which later condense as nanoparticles. Dilution and quenching with a neutral gas favors the reaction yield. The reaction kinetics, found by TGA, increase when the temperature is raised or pressure is lowered.

A high temperature reactor prototype (cavity-type rotating receiver absorbing solar radiation) was designed, constructed, and operated. The solid reactant is continuously injected in a controlled atmosphere, and the particles produced are recovered in a filter downstream for hydrolysis. The solar reduction of ZnO was accomplished as a function of pressure and inert gas flow rate, and the Zn yield in the collected product was up to 90%.

The water-splitting step employs the reduced species that react efficiently with water to produce H<sub>2</sub> in the range 450-600°C. Experiments characterized the hydrolysis step in a fixed-bed reactor and determined the kinetic rate laws. The hydrolysis of Zn nanoparticles hardly yielded 60% H<sub>2</sub>, whereas SnO hydrolysis was almost complete, but the reaction took longer (Figure 4.9 and Figure 4.10).

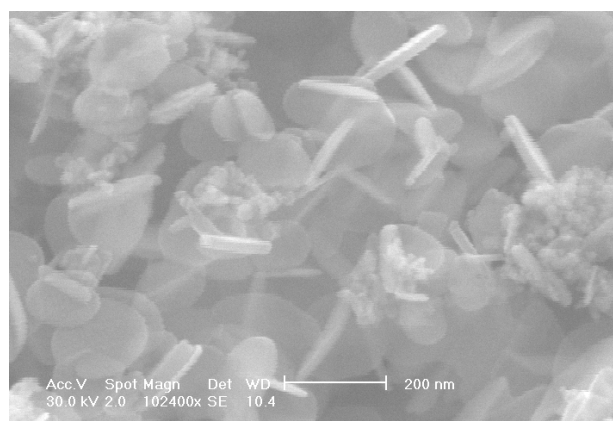


Figure 4.9. Solar-produced SnO nanoparticles.

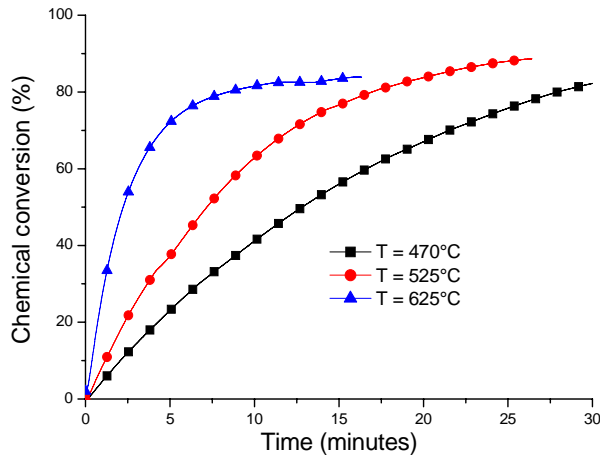


Figure 4.10. Chemical conversion of SnO hydrolysis at different temperatures.

Furthermore, three-step cycles involving mixed cerium oxides and alkali hydroxides were experimentally demonstrated. The high-temperature synthesis of reduced cerium-based mixed oxides ( $\text{Ce}_2\text{Ti}_2\text{O}_7$ ,  $\text{Ce}_2\text{Si}_2\text{O}_7$ ,  $\text{CeFeO}_3$ ,  $\text{CeVO}_4$ ,  $\text{CeNbO}_4$ ) was performed in a lab-scale solar reactor at 1400–1500°C. The activation reaction with NaOH or KOH produced up to  $1.94 \text{ mmol H}_2 \text{ g}^{-1}$  in the range 500–600°C.

A numerical unsteady-state model was developed to simulate the effect of transient conditions on solar reactor operation (Ref. [4.17]). On the basis of real solar irradiation data recorded at CNRS-PROMES (Odeillo, France), the daily and yearly Zn production was assessed for a 50-MW<sub>th</sub> solar reactor, resulting in hydrogen production of about 1100 kg per day of operation.

Energy efficiency analyses of large-scale solar tower plants were performed. The global solar-to-hydrogen energy conversion efficiency for iron and zinc oxide cycles was estimated at about 20% with currently available data, by including the main losses occurring in the solar concentrating system, the solar receiver-reactor, and the chemical process itself.

Publications: [4.15]–[4.17]

## Solar Hydrogen Production from a ZnO/Zn Thermochemical Cycle

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Funding: BFE-Swiss Federal Office of Energy, PSI, ETH

Duration: January 1, 2003 - December, 2011

Background: Hydrogen production from water using solar energy in a two-step thermochemical cycle is being studied. The first, endothermic step is the thermal dissociation of ZnO(s) into Zn(g) and O<sub>2</sub> at temperatures above 2000 K using concentrated solar energy as the source of process heat. The second, non-solar, exother-

mic step is the hydrolysis of Zn at 700 K to form H<sub>2</sub> and ZnO(s); the latter separates naturally and is recycled to the first step.

Purpose: (1) Solar chemical reactor technology for the production of Zn by thermal dissociation of ZnO; (2) solar chemical reactor modeling using CFD and Monte Carlo ray-tracing simulations; (3) fundamental research on the reoxidation and quenching of Zn(g); (4) production of H<sub>2</sub> by hydrolysis of Zn.

Achievements in 2008: The proposed solar chemical reactor concept is based on a rotating cavity-receiver lined with ZnO particles that are held by centrifugal force and directly exposed to high-flux irradiation (Ref. [4.18]). A set of 15 experimental runs were performed with the 10 kW<sub>th</sub> reactor prototype at PSI's High Flux Solar Simulator (HFSS). The number of feed cycles was varied between one and three. The maximum power input was set between 9.1 kW<sub>th</sub> and 11.6 kW<sub>th</sub> in order to obtain the desired cavity temperatures in the range 1757–2001 K. A typical experiment lasted from 50 to 90 min after heating up. The Ar flow rate was in the range of 7–28 l<sub>N</sub> min<sup>-1</sup> for purging the reactor window and aperture, and 30–90 l<sub>N</sub> min<sup>-1</sup> for quenching the product gases. The maximum Zn content of the quenched products was 44.9%, and the maximum Zn content of the filtered products was 51.1%, as determined by dissolution of the products in HCl with the measurement of evolved H<sub>2</sub>.

Figure 4.11 shows the Zn yield  $X_{\text{Zn, QS}}$  in the quenching section as a function of Zn partial pressure  $P_{\text{Zn, QS}}$  for the 15 experimental runs (Ref. [4.19]).  $X_{\text{Zn, QS}}$  is found to increase with decreasing  $P_{\text{Zn, QS}}$ . Two distinct regions of  $X_{\text{Zn, QS}}$  are observed. Almost constant Zn yield  $X_{\text{Zn, QS}} \sim 14\%$  is found for  $P_{\text{Zn, QS}}$  in the range 370–600 Pa. Hence, the quenching device is inefficient at these Zn partial pressures. For  $P_{\text{Zn, QS}} < 370$  Pa,  $X_{\text{Zn, QS}}$  increases approximately linearly with decreasing  $P_{\text{Zn, QS}}$ . The maximum Zn yield of about 45% was measured at Zn partial pressure of 42 Pa. Zinc yield exceeding 90% was obtained

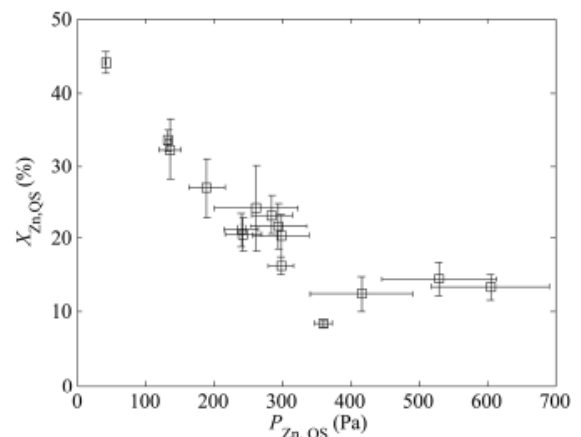


Figure 4.11. Zinc yield  $X_{\text{Zn, QS}}$  of quenched products as a function of zinc partial pressure  $P_{\text{Zn, QS}}$  in the quench section. Error bars account for the uncertainty of recovered and quenched particles. From [4.19].

with a sophisticated quenching device, which was tested in a solar thermogravimeter (TG) and previously described in [4.20].

The net Zn yield increased with decreasing Zn partial pressure in the quenching section, in agreement with a kinetic model for the separation of a mixture of Zn vapor and oxygen [4.21].

A transient heat transfer model was developed for analyzing the thermal performance of the solar reactor prototype for the solar-driven dissociation of ZnO in the 1600–2130-K range [4.22]. The model couples radiation, convection, and conduction heat transfer to the reaction kinetics for a shrinking domain and simulates a transient ablation regime with semi-batch feed cycles of ZnO particles. A set of four experimental runs with 3, 5, 7, and 9 consecutive feed cycles was used to validate the reactor model. Figure 4.12 shows the experimentally measured (solid curves) and numerically calculated (dashed curves) temperatures halfway along the reactor cavity at locations  $T_{B,1}$ ,  $T_{B,2}$ ,  $T_{K,1}$ , and  $T_{K,2}$  for the run with 9 consecutive feed cycles. Also indicated are the measured power input  $P_{\text{solar}}$  and the calculated ZnO dissociation rate. The temperature agreement is reasonably good at all locations. As expected, temperatures dropped during ZnO feeding due to the interruption of  $P_{\text{solar}}$  and the addition of fresh ZnO particles. Discrepancies are attributed to slow and partial mixing of hot residual and cold fresh particles (not modeled).

Conduction losses in the water-cooled quenching unit and radiation losses in the annular outlet were identified as the main reasons for low efficiency of about 3%. Model calculations predict that the solar-to-chemical conversion efficiency of the prototype reactor can be increased up to 17% by downsizing the cavity outlet and by removing outlet water-cooling. Scaling up the reactor to 100 kW and 1000 kW nominal solar power input could potentially reach maximum solar-to-chemical conversion efficiencies over 50%, mainly as a result of higher reaction rates at higher operating temperatures and lowered conduction losses through opti-

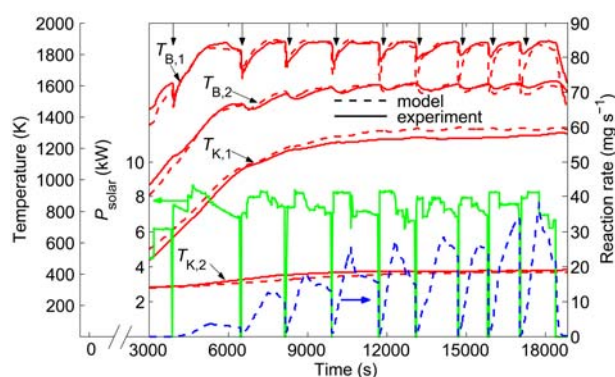


Figure 4.12. Experimentally measured (solid curves) and numerically calculated (dashed curves) temperatures, measured radiation power input, and numerically calculated ZnO dissociation rate as a function of time for the experimental run with 9 feed cycles. The top arrows point out to the times when the batch feeding of ZnO took place. From [4.19].

mization of the geometry to minimize water-cooled components (Ref. [4.22]).

Hydrogen production by steam-hydrolysis of zinc as the second step of the two-step water-splitting thermochemical cycle based on ZnO/Zn redox reactions was investigated [4.23]. The hydrolysis reactor consists of a hot-wall tube containing a steam-quenched Zn(g) flow that co-produces H<sub>2</sub> and Zn/ZnO nanoparticles. The effects of the quenching gas flow rate and reactor wall temperature on the Zn-to-ZnO chemical conversion and particle yield were examined. Solid products were characterized by X-ray diffraction, N<sub>2</sub> adsorption, and SEM microscopy. Quench rates of  $26 \times 10^4$  K/s yielded conversions of up to 95% at the expense of low particle yield due to significant wall deposition followed by hydrolysis. In contrast, operation at quench rates up to  $10^6$  K/s led to increased particle yield but lower conversion.

In another study, the hydrolysis rate of Zn particles by up to 50 mol% water vapor in Ar gas was measured by thermogravimetric analysis (TGA) at atmospheric pressure and 330–360°C and quantified by a core-shell model (Ref. [4.24]). A ready-to-use equation for the calculation of ZnO and H<sub>2</sub> formation during Zn hydrolysis was proposed and compared to literature data revealing enhanced hydrolysis rates for submicron Zn particles.

Publications: [4.18]-[4.24]

## HYDROSOL-2 – Solar Hydrogen via Water Splitting in Advanced Monolithic Reactors for Future Solar Power Plants

Participants: CERTH/CPERI (GR), DLR (D), Stobbe Tech (DK), Johnson Matthey Fuel Cells Ltd. (UK), CIEMAT (E)

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Funding: EC (FP6), DLR

Duration: November 1, 2005 - October 31, 2009

Background: A promising new method for solar-heated two-step water-splitting thermochemical processes operating at temperatures below 1500 K is being developed (Ref. [4.25]). It includes a support structure that can reach high temperatures when heated by concentrated solar radiation, combined with a redox system capable of water dissociation and suitable for high-temperature regeneration at the same time. The feasibility of this technology was previously demonstrated in the HYDROSOL project. A pilot-scale solar reactor was designed, built and operated in the DLR solar furnace facility in Cologne (Germany), and produced continuous “solar hydrogen”.

Purpose: (1) Develop an optimized pilot plant (100 kW<sub>th</sub>) based on this innovative reactor concept and test it at the Plataforma Solar de Almería (PSA, Spain);

(2) further scale up this technology and demonstrate effective combination with solar concentrating systems; (3) provide stable metal oxide/ceramic support assemblies capable of performing at least 50 water-splitting cycles in a row; (4) decrease the temperature level of the regeneration step considerably below 1500 K; (5) optimize the efficiency of water-splitting and oxygen-releasing steps; (6) develop a solar field control strategy.

**Achievements in 2008:** The 100-kW<sub>th</sub> pilot plant, including all peripheral systems like gas feeding, steam generator, mass flow controller, IR camera, flux measurement system, and analytics necessary for the two-step thermochemical water-splitting process, has been erected and installed on an experimental platform on the PSA SSPS tower. The plant was inaugurated at the end of March 2008. The following summer, its thermal behavior and characteristics were extensively tested (Figure 4.13). The effects of different operating parameters such as mass flow, gas preheating, and heliostat selection were investigated to define appropriate operating ranges and to find and demonstrate process control strategies. It was found that the process was controllable only by focusing and defocusing heliostats. The thermal tests made it possible to optimize and finally prove the process strategy and demonstrated the feasibility of the control concept implemented. It was shown that rapid changeover between the modules benefits process performance significantly.



Figure 4.13. 100 kW<sub>th</sub> dual chamber pilot reactor during thermal testing at the SSPS tower at PSA.

In November 2008, the absorber was replaced and honeycombs coated with redox material based on ferrites were inserted. This allowed hydrogen production by water splitting to be tested for the first time. The tests were successful – some first cycles were run without problem. Significant amounts of hydrogen were produced with steam conversion of up to 30%.

**Publications:** [4.25]

## HycycleS – Solar Production of Hydrogen by the Sulfur-Iodine and Westinghouse Thermochemical Cycles

**Participants:** DLR (D), CEA (F), University of Sheffield (UK), CERTH/CPERI (GR), JRC (NL), ENEA (I), ETH (CH), Empresarios Agrupados (E), BOOSTEC (F)

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**Funding:** EC (FP7), DLR

**Duration:** January 1, 2008 - December 31, 2010

**Background:** Solar energy is expected to play a major role in the production of future transportation fuels. In particular, solar thermochemical processes offer the potential of highly efficient mass hydrogen production at a competitive cost. Although most of these processes have been evaluated in theoretical studies, the technology is not yet ready for application. The highest worldwide priority is currently the sulfur-based cycles, i.e., the sulfur-iodine (SI) and hybrid sulfur (HyS) cycle, because they can be operated at temperatures at which it is possible to use concentrated solar radiation as the process heat source. However, high temperatures and corrosive environments in their key steps present major challenges. The severe operating conditions require advanced materials as well as special design and fabrication methods for key components common to both cycles, including oxygen separator, H<sub>2</sub>SO<sub>4</sub> evaporator, and SO<sub>3</sub> decomposer. The latter has to withstand the highest temperature in the cycles, which is over 850°C and is one of the main foci of HycycleS.

**Purpose:** Development and improvement of materials and key components for H<sub>2</sub>SO<sub>4</sub> decomposition by: (1) recommendations for suitable materials and catalyst/support systems needed for key components of sulfuric acid decomposition; (2) construction and test operation of a solar receiver-reactor for H<sub>2</sub>SO<sub>4</sub> evaporation/decomposition ready for scale-up; (3) realization and verification of the feasibility of a compact SiC plate heat exchanger as an H<sub>2</sub>SO<sub>4</sub> decomposer; (4) detailed understanding of transport properties and reaction performance of porous ceramic structures as reaction containment for the solar decomposition of H<sub>2</sub>SO<sub>4</sub>; (5) development of stable and reliable membranes for use in a separation step to significantly increase the conversion of SO<sub>3</sub> to SO<sub>2</sub>.

**Achievements in 2008:** A major solar reactor concept was developed in the previous FP6-project HYTHEC. The porous absorber reactor was dedicated to the second step of the reaction, which is the reduction of sulfur trioxide, SO<sub>3</sub> (Ref. [4.26]). In HycycleS, this reactor concept is being further pursued and extended to the entire H<sub>2</sub>SO<sub>4</sub> decomposition process including both the high temperature dissociation and the evaporation step.

A prototype receiver-reactor was designed and simulated and will subsequently be tested in the solar furnace to prove the feasibility of the concept, to investigate the

process behavior, and to refine available experimental data for design studies and process simulation. The development of a multi-chamber reactor is of primary interest to examine the evaporation and  $\text{SO}_3$  reduction processes separately. This allows optimization of both process steps to be highly independent.

The thermostructural integrity of the planned reactor was evaluated and predicted by FEM modeling for final design and proof of design.

As a core part of the receiver-reactor, absorber structure was analyzed in depth (Figure 4.14). Computer tomography in conjunction with numerical techniques was used to determine the morphological characteristics and the effective heat/mass transfer properties of the foam, such as extinction coefficient, scattering function, thermal conductivity, interfacial heat transfer coefficient, permeability, Dupuit-Forchheimer coefficient, tortuosity and residence time distributions, and dispersion tensor.



Figure 4.14. Lab rig for ageing tests: development of catalyst/substrate combinations for solar  $\text{SO}_3$  reduction.

A pre-design of a compact heat exchanger as an  $\text{SO}_3$  decomposer has been completed. Various mock-ups are being built to investigate other design challenges.

A review of high-temperature oxygen separation membrane materials, identified from previous work on fuel cells, has been undertaken. A pre-screening provided some candidate materials which are going to be tested in 2009.

Publication: [4.26]

### **SOLTERH – Solar Thermochemical Production of Hydrogen by Water-Splitting Processes**

Participants: Solúcar Energía S.A. (E), Hynergreen Technologies S.A. (E), CIEMAT-PSA (E)

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Funding: Spanish Ministry of Science and Education (PROFIT): € 770,000

Duration: January 1, 2004 - December 31, 2008

Background: Thermochemical cycles are expected to be a cost and energy-efficient way to produce large amounts of hydrogen. Two-step water splitting processes based on ferrites are considered very attractive candidates since there is no phase transformation during the redox cycle. A study has been begun at the CIEMAT to identify critical factors for developing this technology [4.27]. For example, the choice of directly-irradiated volumetric receivers versus cavity receivers for solar driven catalytic reactions is still a key decision in technology development. This project seeks to solve the technical problems encountered in cavity receivers for driving solar heterogeneous reactions.

Purpose: Design, construction, and testing of innovative solar particle receiver-reactors at different scales (1 to  $5 \text{ kW}_{\text{th}}$ ) at operating temperatures of about  $800\text{-}1200^\circ\text{C}$ .



Figure 4.15. Photograph of the rotating cavity reactor at the PSA solar furnace.

Achievements in 2008: A considerable effort has been made throughout the year to demonstrate an advanced rotary kiln for gasification applications based on industrial experience.

The solar rotary kiln is shown in Figure 4.15. It features a refractory-lined steel cavity about 470-mm long with a 370-mm internal diameter, inclined about 2 degrees to the horizontal and rotating at about 10-50 rpm. Granular material is fed into the reactor and is moved during operation by the combined effects of rotation and gravity.

In parallel, the activity of five commercially available ferrites with different compositions was evaluated in the lab. In these tests, the potential cyclability of  $\text{NiFe}_2\text{O}_4$  was confirmed, making it possible to employ this material for several hydrogen production cycles. In view of this, it was selected as the first candidate for solar experiments.

Publication: [4.27]

## PHYSICO2 – Clean Hydrogen Production by Carbon Dioxide Free Alternatives

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**Funding:** The Community of Madrid: € 2,017,000

**Duration:** January 1, 2006 - December 31, 2009

**Background:** The PHISICO2 project (Clean production of hydrogen: CO<sub>2</sub> emission-free alternatives) progresses in solving current technological and economic limitations by exploring different processes for clean hydrogen production, essential to future transition towards a hydrogen economy. The alternatives in this project feature prevention of CO<sub>2</sub> as a hydrogen by-product by using renewable energy sources to power its generation. The research in this project considers hydrogen production (1) from decomposition of natural gas assisted by heterogeneous catalysts; (2) by water photodissociation; (3) from water through solar-thermal processes based on thermochemical cycles.

**Purpose:** Evaluation and optimization of three different processes for clean, carbon dioxide-free emission hydrogen production.

**Achievements in 2008:** In previous work, the ferrites under consideration were usually synthesized in the laboratory by various preparation methods and assayed for the thermochemical cycles under different reaction conditions. Some examples of materials which have been studied by the CIEMAT are metal-doped ferrites with the chemical formula  $M_{0.25}Mn_{0.75}Fe_2O_4$  (M: Mn, Co, Ni, Cu) [4.28]. However, since the figures of merit have not yet been established for this process, it is difficult to compare their activity with reports in the literature.

Therefore, commercially available ferrites such as nickel, zinc, copper, nickel-zinc, and copper-zinc ferrites were used as the reference standard for evaluating their feasibility for solar hydrogen production [4.29]. In addition to basic chemical and structural characterization, a study on hydrogen production and potential cyclability is currently underway.

Among the samples studied, NiFe<sub>2</sub>O<sub>4</sub> appears to be the most active material both for net hydrogen production and cyclability. The results of four cycles with the NiFe<sub>2</sub>O<sub>4</sub> ferrite are summarized in Table 4.1. The oxygen release decreases from the first cycle to the second one and so on. This may be due to the fact that, in the first three cycles, part of the activated ferrite was not re-oxidized during the water-splitting steps; however, the fully oxidized state is completely recovered in the fourth

hydrolysis cycle. Indeed, the average molar ratio of H<sub>2</sub>/O<sub>2</sub> produced throughout the four cycles is essentially stoichiometric. This nickel ferrite is proposed as possible reference material. Regarding the rest of the tested ferrites, NiZn shows the highest hydrogen production in the first cycle.

Table 4.1. Water dissociation results for four cycles with the Ni-ferrite

Cycle no.	O <sub>2</sub> (mmol/g ferrite)	H <sub>2</sub> (mmol/g ferrite)	H <sub>2</sub> / O <sub>2</sub> molar ratio
1	0.55	0.63	1.15
2	0.35	0.54	1.54
3	0.29	0.57	1.97
4	0.34	1.48	4.35
<b>Total</b>	1.53	3.22	2.10
<b>Average</b>	0.38	0.81	2.10

**Publications:** [4.28]-[4.29]

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