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Solar Hydrogen Production by a Two-Step Cycle Based on Mixed Iron Oxides

A promising method for the conversion and storage of solar energy into hydrogen is the dissociation of water into oxygen and hydrogen, carried out via a two-step process using metal oxide redox systems such as mixed iron oxides, coated upon multi-channeled honeycomb ceramic supports capable of absorbing solar irradiation, in a configuration similar to that encountered in automobile exhaust catalytic converters. With this configuration, the whole process can be carried out in a single solar energy converter, the process temperature can be significantly lowered compared to other thermo-chemical cycles and the recombination of oxygen and hydrogen is prevented by fixing the oxygen in the metal oxide. For the realization of the integrated concept, research work proceeded in three parallel directions: synthesis of active redox systems, manufacture of ceramic honeycomb supports and manufacture, testing and optimization of operating conditions of a thermochemical solar receiver-reactor. The receiver-reactor has been developed and installed in the solar furnace in Cologne, Germany. It was proven that solar hydrogen production is feasible by this process demonstrating that multicycling of the process was possible in principle. [DOI: 10.1115/1.2183804]

Keywords: *hydrogen, redox system, honeycomb reactors, solar, thermochemical cycle*

Introduction

By far the most attractive reaction for the production of hydrogen is the thermal decomposition of water yielding directly pure hydrogen [1]. However, because of unfavorable thermodynamics, interesting yields can only be achieved at very high temperatures far above 2500 K, imposing therefore technological difficulties to any ideas trying to couple solar radiation as the driving energy for the reaction [2]. The current state of the art of solar chemistry for water splitting and hydrogen production is basically focused on processes for water splitting which are able to substantially lower that temperature level [3]. From all technological possibilities one of the most interesting is the thermochemical two-step water splitting process using redox systems. According to this idea, during the first step (water splitting) the reduced and therefore activated material (usually a metal oxide) is oxidized by taking oxygen from water and producing hydrogen according to the reaction:

$$MO_{\text{reduced}} + H_2O \rightarrow MO_{\text{oxidized}} + H_2 \qquad (1)$$

During the second step (regeneration) the material is reduced to be used again, delivering some of the oxygen of its lattice according to the reaction

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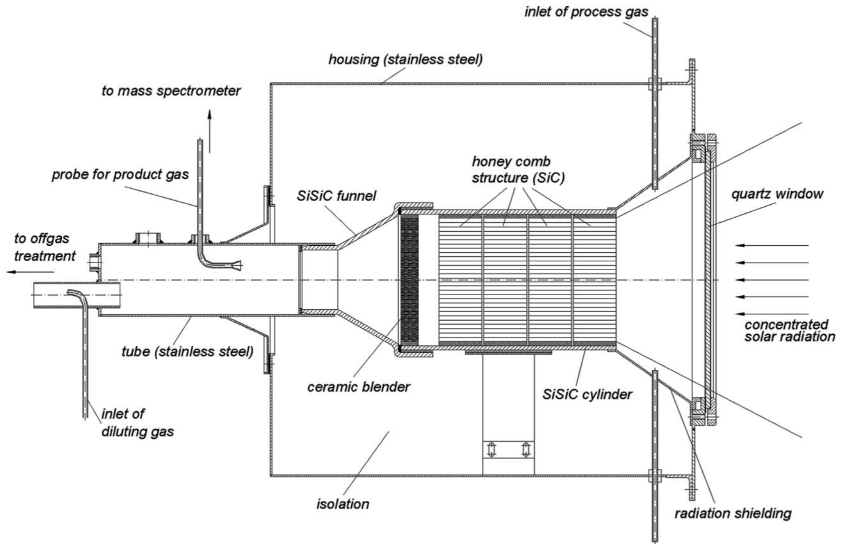

Fig. 1 Solar test reactor at DLR in Cologne, Germany

$$MO_{\text{oxidized}} \rightarrow MO_{\text{reduced}} + O_2 \quad (2)$$

Several redox systems have been investigated. A prominent example of a redox system applied during the testing is the following:

$$Mn_{0.5}Zn_{0.5}Fe_2O_4 + yH_2O \rightarrow Mn_{0.5}Zn_{0.5}Fe_2O_{4+y} + yH_2 \quad (3)$$

$$Mn_{0.5}Zn_{0.5}Fe_2O_{4+y} \rightarrow Mn_{0.5}Zn_{0.5}Fe_2O_4 + y/2O_2 \quad (4)$$

The evaluation of enthalpies for the investigated systems is in progress. For similar systems ($Mn_{0.5}Zn_{0.5}Fe_2O_4$) a thermodynamic evaluation provided enthalpies of +300 kJ/mol for the O_2 releasing step and between −35 and −68 kJ/mol for the water splitting step [4]. The advantage is the production of pure hydrogen without separation need of hydrogen and oxygen. The challenge is a two-step process consisting of a splitting and a regeneration step. The redox materials that have been evaluated consist of oxide pairs of multivalent metals (Fe_3O_4/FeO, Mn_3O_4/MnO [5]) or systems of metal oxide/metal (e.g., ZnO/Zn [6]) the most representative of which can be considered the Fe_3O_4/FeO system [7]. Water splitting is taking place at temperatures below 900 K while the reduction of the metal oxide, i.e., the regeneration, takes place at much higher temperatures (>2500 K [3]). The concept has been proven experimentally [8,9], however the regeneration temperatures are still high. The high temperatures of the reduction step impose a barrier towards integration of a two-step water splitting process and a concentrating solar system.

A crucial factor for the applicability of the reaction in technical processes is the stability of the redox system. Ehrensberger et al. showed that non-stoichiometric iron oxides and mixed manganese oxides form stable crystals that loose their activity over several consecutive cycles [10]. A major part of the work is to develop materials that do not show this behavior. The investigation of the materials (by x-ray diffraction, e.g.) is in progress and will be reported in a following paper.

The aim of the work is to exploit solar energy for the dissociation of water and the production of hydrogen. The basic idea is to combine a support structure capable of achieving high temperatures when heated by concentrated solar radiation, with a redox pair system suitable for the performance of water dissociation and at the same time suitable for regeneration at these temperatures, so that complete operation of the whole process (water splitting and regeneration of the metal oxide) can be achieved by a single solar energy converter. A highly compact reactor structure is that of a honeycomb monolith consisting of a plurality of channels on the surface of which active compounds can be coated. Such reactors made of advanced ceramics (Cordierite, SiC) find extensive application in automotive emission control [11,12]. SiC-based ceramics in particular have shown superior thermal properties [13,14] and can be coated with a variety of traditional and novel techniques [12,15]. Based on this experience, SiC has been used in an advanced solar volumetric receiver [16,17] with very good performance and it was selected to be the material for the solar water splitting reactor. Therefore, the four main tasks are:

- Development of novel and efficient oxide materials to carry out the water dissociation reaction, able to be reversibly oxidized and reduced within the temperature interval of 1073–1473 K. The mainstream materials of choice are based on the ferrite spinel family [18]. It is aimed to utilize the material activity caused by thermodynamic instabilities in the defect chemistry, which will be introduced on purpose into the crystal structures.
- Development of ceramic monolithic structures able to absorb efficiently concentrated solar radiation up to 1.5 MW/m^2.
- Integration of the redox material-coated monoliths on the solar reactor/receiver and development of a complete hydrogen fuel production unit based on solar energy.
- Evaluation of technical and economic feasibility of the whole process.

Testing of a Solar Reactor with Respect to Water Splitting Efficiency and Redox Material Regeneration Capability

To achieve these aims a solar test reactor was designed and built at the German Aerospace Center DLR, Cologne, Germany [19].

The reactor (Fig. 1) contains a ceramic support structure that is able to host different coated structures in order to compare different redox pair systems. The ceramic honeycombs tested were made from two kinds of silicon carbide: recrystallized and siliconized (Re-SiC and SiSiC, respectively). The housing is made of stainless steel and the reactor has a quartz window to allow a volumetric heating of a space closed to the environment.

The reactor is designed to withstand temperatures up to 1673 K. It is connected to an exhaust treatment system to analyze and thereafter dispose of the gases.

In a first step the reactor was qualified in the solar furnace of DLR in Cologne [19] as a test bed for different metal oxide-support assemblies [20].

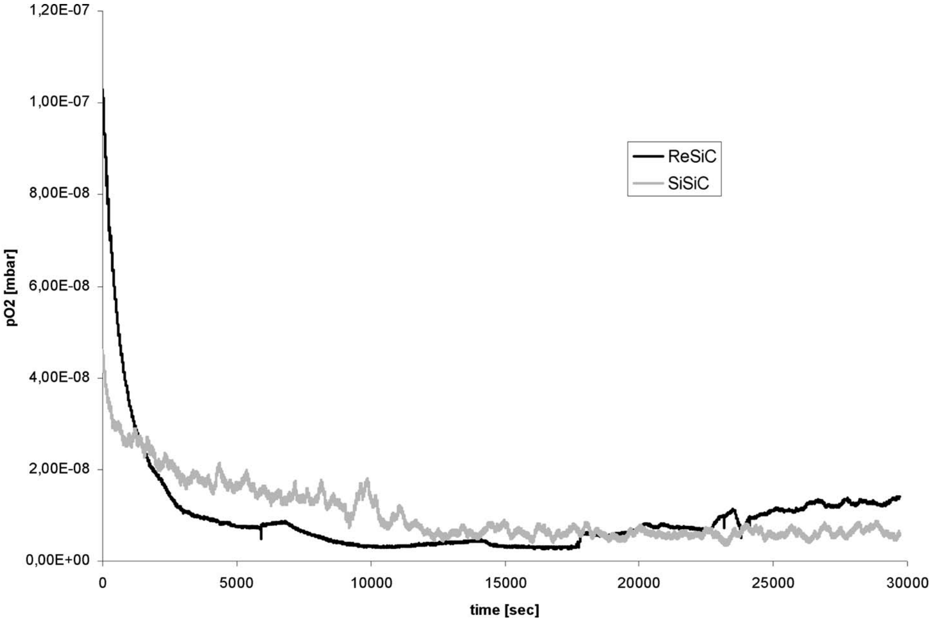

Fig. 2 Progress of O_2 signal provided by a mass spectrometer using a SiSiC monolith and a ReSiC monolith

Preparations. To enable the quantitative testing of coated honeycombs, the following actions were carried out:

- Implementation and qualification of reactor and peripherals
- Determination of operational limits with regards to temperatures, mass flows, solar input power, heating ramps and detection limits
- Elaboration of detailed experimental plan for the systematic performance of the tests
- Measurement of flux densities and flux distributions allowing thermal balancing and giving input for reactor simulation

Performance of Testing.

Testing of Uncoated Monoliths. The first measurements performed in the solar furnace concerned the calibration of a mass spectrometer (Pfeiffer Thermostar Quadrupol Mass Spectrometer) for the quantitative analysis of the produced gases. Therefore compound gases in accurately defined amounts, with the same quantitative gas composition as expected in the product gas, were measured. The scan time was 2 s. Systematic series of measurements regarding mass flow or concentration with the gases N_2+O_2 and N_2+H_2 were accomplished to determine the lower detection limit of the spectrometer for O_2 and H_2 and to provide calibration functions for the identification of the concentrations of these gases during operation with the coated honeycombs. The subsequent experiments concerned the effects of water vapor in the gas stream on the H_2O signal and on the H_2 signal. First, only water vapor was fed to the reactor and afterwards mixtures of steam and H_2. The resulting difference provided the contribution of pure H_2 to the relevant signal of the mass spectrometer by giving a correction function of the contributions from the splitting of water in the spectrometer. Finally, pure nitrogen was fed in to generate base lines for the relevant species H_2 and O_2.

A strong fluctuation of O_2 concentration in the exhaust (product) gas (Fig. 2) was observed when using siliconized silicon carbide (SiSiC) monoliths independently of whether the monoliths were coated or not. The fluctuation started at the time when the structure reached 1073 K and lasted for approximately 1 h, decreasing and gradually vanishing after about 2 h. The fluctuation varied in intensity from monolith to monolith [there are SiSiC monoliths with only minor grade of fluctuation]. This phenomenon was not observed when testing recrystallized silicon carbide (ReSiC) monoliths (Fig. 2).

These fluctuations have been interpreted as alternating oxygen absorption and desorption processes. They shall occur when residues of carbon or silicon are present on the surface of the monoliths after fabrication. The consequence of this observation is to pretreat the monoliths under oxygen-containing atmosphere to artificially age their surfaces and thereby render them inert.

Testing of Coated Monoliths. Monoliths coated with redox pair systems were tested subsequently—each in a separate experiment (Fig. 3). The replacement of a tested monolith was only possible after cooling of the whole reactor overnight. At the end of each test day, an abbreviated O_2 and H_2 calibration was carried out. Seven coated honeycombs were tested, four of them loaded with

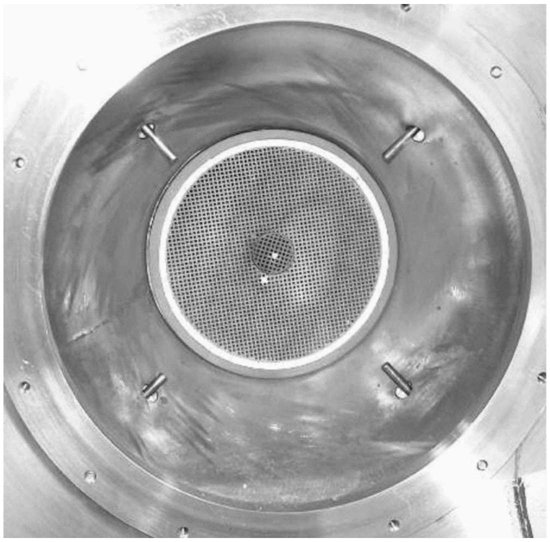

Fig. 3 Honeycomb coated with activated iron oxide in the center of the reactor, ready for testing

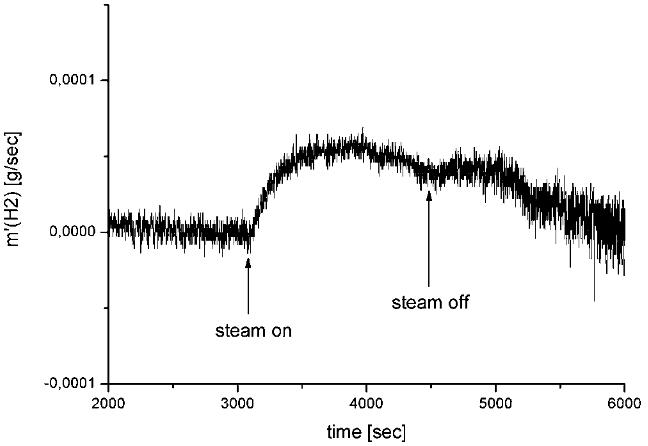

Fig. 4 Mass flow of hydrogen during splitting of water on Zn, Mn-doped iron oxide on ReSiC

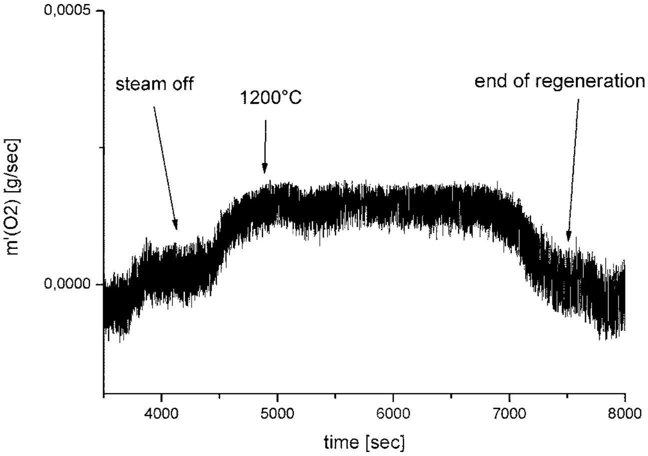

Fig. 5 Mass flow during release of oxygen (Zn, Mn-doped iron oxide on ReSiC)

self-propagating high-temperature synthesized (SHS) Zn, Mn-doped iron oxides and the other three with solid-state synthesized (SSS) activated iron oxide [20,21] (with different values of oxide loading).

The intention of the test program was the quantitative evaluation of capability for hydrogen production and metal oxide reduction by monitoring the progression of the two reaction steps—splitting of water vapor and regeneration of the metal oxide—by mass spectrometry. The basic procedure was to heat up the reactor to 1073 K and add water vapor for 20 min. Then the temperature was raised to 1473 K and maintained for 20 min that turned out as an appropriate time for both steps of the process. This procedure was repeated at least twice and for as long as the coating was regenerated and capable of splitting water.

The following procedure was employed: regeneration temperature was mostly 1473 K (sometimes higher if necessary). During the splitting step the temperature was gradually raised from 1073 to 1473 K (1. cycle: 1073 K, 2. cycle: 1173 K, 3. cycle: 1273 K, 4. cycle: 1373 K, 5. cycle: 1473 K). The amount of water vapor was varied in the splitting step. The quantity of hydrogen evolved was directly derived from the data provided from the mass spectrometer which itself was calibrated by supplying defined mixtures of N_2 and H_2.

Results. The first solar hydrogen was successfully produced by irradiating Zn, Mn-doped iron oxide coated on a ReSiC monolith at 1073 K in a mixture of steam and nitrogen (Fig. 4). The samples were coated with the reduced material and shipped under inert conditions to Cologne, therefore it was not necessary to activate them. The amount of hydrogen produced (8.23 mmol H_2/g oxide, the loading of one sample was 3.25 g oxide) corresponded very well to that produced in laboratory experiments performed with the metal oxide in the form of powders. After completion of the water splitting step the temperature was raised to 1473 K under flushing by pure nitrogen. This procedure initiated a release of 3.0 mmol of oxygen (see Fig. 5) per g oxide. Due to sintering of the oxide coating only one cycle could be operated.

Multicycling was possible when applying a coating of activated Fe_2O_3 on a SiSiC monolith. The coated monolith could perform six cycles at 1073 K with respect to solar water splitting and at 1473 K to be partly reactivated (Fig. 6). The last two cycles in Fig. 6 (cycle 7 and 8) suggested initially that the coating is significantly more active with respect to water splitting when increasing the splitting step reaction temperature (here 1473 K). However, further investigations showed that the hydrogen production at this elevated temperature is due to participation and thereby destruction of the support material and not desirable. The splitting temperature should not exceed 1273 K. Thus a maximum of six cycles can be stated for the set of coated monoliths tested so far. Although the kinetics of the reactions is relatively slow, this is favorable to the technical process. In the experiments the reduction step was completed after 10–15 min. This time is sufficient for a reliable operation even in a large scale reactor.

Table 1 summarizes the main results of the first test campaign. Except the first monolith tested, all coated samples were able to split water at least once. The monoliths coated by activated iron oxide are capable of multicycling (up to six cycles).

In conclusion, it can be stated that solar thermo-chemical splitting of water and hydrogen production was successfully demonstrated several times. The release of oxygen from the redox coating was also realized by using solar energy. Multicycling of the process is possible in principle. The amounts of hydrogen produced correspond very well to laboratory results on the redox systems in the form of powders indicating that the iron oxide as coating is almost as active as the powder in laboratory tests. ReSiC was proven more suitable in these tests compared to SiSiC, due to its resistance towards higher temperatures, lower tendency of absorption/desorption of oxygen, lower tendency of reactions with the coating and easier fabrication of monoliths with a higher number of channels per unit area.

Table 1 shows that because of the limited number of samples tested the obtained results are not sufficient to calculate reproducible solar energy conversion efficiencies that will be a focus of the next test campaigns. A decrease of the overall efficiency of the process will occur if one takes into account the energy required to

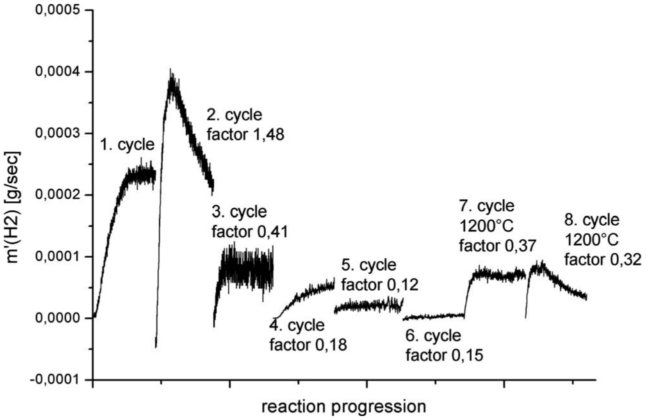

Fig. 6 Mass flow of hydrogen produced during subsequent splitting steps (activated Fe_2O_3 on SiSiC)

Table 1 Quantitative evaluation of the test campaigns a (top) and b (below)

No	Coating	Loading [g]	Loading/Support [g/g]	Support material	Cycles
1	Zn, Mn-doped FeO	5.94	0.131	SiSiC	7
2	"	3.25	0.273	ReSiC	7
3	Act. Fe_2O_3	3.20	0.071	SiSiC	3
4	"	5.32	0.124	SiSiC	10
5	"	3.08	0.073	SiSiC	3
6	Zn, Mn-doped FeO	1.34	0.134	ReSiC	6
7	"	11.23	0.250	SiSiC	4
8	Act. Fe_2O_3	3.18	0.071	SiSiC	3

No	Number of cycles with H_2 formation	Quantity (H_2)max per cycle [mmol]	Quantity (H_2) per g(oxide) [mmol/g]	Quantity ratio (H_2) of subsequent cycles
1	0	0	0	-
2	1	26.8	8.2	-
3	3	*	*	1 : 0.19 : 0,20
4	8 (incl.1200°C)	163	30.6	1 : 1.48 : 0.41 : 0.18 : 0.12: 0.15 (:0.37 : 0.32)*
5	3	29.8	9.7	1 : 0.45 : 0.09
6	5	*	*	0.08 : 1 :0.05 : 0.01 : 0.1
7	2	23.4	2.1	1 :0.1
8	3	*	*	-

recycle/separate the inert gas (such as nitrogen) needed to provide inert atmosphere for the reduction step. Depending on the size of the plant, pressure swing absorption or membrane methods will be applied to separate the released oxygen and to purify the nitrogen, methods needing about 0.25 kWh/Nm^3 nitrogen. The exact value depends on the required purity of the nitrogen, which is still an object of investigation. Preliminary calculations indicate that, in general, a reduction of efficiency of about one fourth is expected by the need to use pure nitrogen as flushing gas. This reduction can be counterbalanced by improvements in the overall reactor design and operation that can maximize hydrogen production during the water-splitting step and minimize heat losses during the entire continuous operation. However, a recent investigation [22] shows a release of oxygen in similar redox systems that can reach nearly 100% under airflow conditions. This opens up the perspective to avoid inert gas completely or at least minimize the required amount.

Nevertheless, the obtained results are very encouraging with respect to the feasibility of the process investigated. The concept appears to be ready for scale-up after some further improvement of the stability of the coating and calculations of kinetics and efficiency.

Currently, doped-iron-oxide-based redox pair materials synthesized via several routes (solid-state synthesis, combustion synthesis and aerosol spray pyrolysis) have been proven capable of splitting water at relatively low temperatures (1073 K) with water conversions up to 80% and hydrogen being the only reaction product. This is the case for the redox pair materials both as powders as well as coatings on a ceramic support [20].

The next efforts involve the execution and optimization of a test program for continuous water splitting and redox material regeneration in the solar reactor/receiver. The range of working conditions will be explored and the overall reactor performance will be evaluated as well as solar energy conversion efficiencies calculated, before a final technical and economic evaluation of a solar plant for the production of solar hydrogen.

Technical Evaluation

A preliminary evaluation of technical and economic aspects of the process developed was done by a design study of a plant for solar water splitting in a commercial scale of hydrogen production by the two-step “HYDROSOL” process.

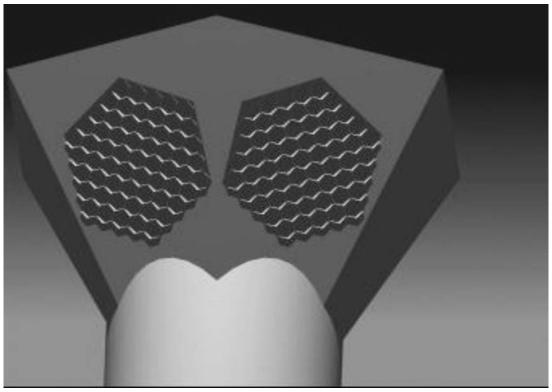

Fig. 7 Design of a faceted receiver on a solar tower

First, a setup of a plant concept was defined. A set of flow sheets for the (chemical) part of the process was generated. From this point simulations were carried out to generate and select experimental and simulation data providing a basis for the design study.

Plant Concept. The setup of a plant concept intensively corresponds to the design of a continuously operating reactor serving as a model reactor in commercial scale. The decision was taken in favor of a reactor concept with modular setup and with fixed position. Regarding commercial scale, the solar heating of the process cannot be done by a solar furnace, which is a research instrument.

The temperature level of up to 1200°C in combination with a mass production of hydrogen can only be realized by using a solar tower system, a so-called central receiver system consisting of a set of tracked mirrors (heliostat field), a tower, and a receiver. A sketch of the faceted receiver on the solar tower is shown in Fig. 7, and a simulation of the heliostat positions with respect to the tower in Fig. 8.

Different parts of the receiver area will be used for different heat demands in the process. In particular, the edge part with comparably low solar flux will be used for the evaporation of water. Differences of solar irradiation during daytime will be compensated by adjustment of mass flows and by a special flexible partitioning of the modular receiver.

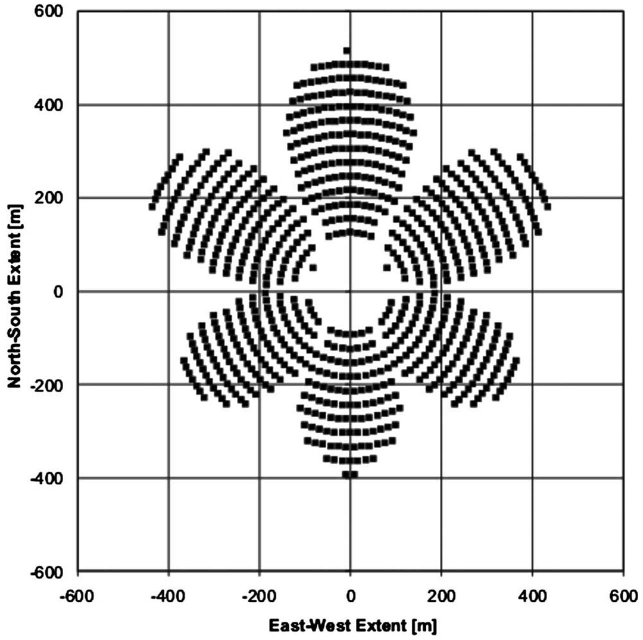

Fig. 8 Simulation of heliostat field. Heliostat positions relating to tower (25 MW_{th}).

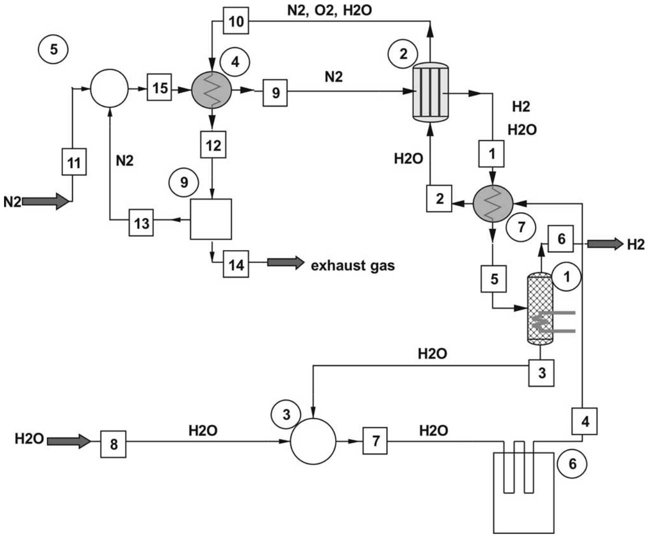

Fig. 9 Basic flow sheet of the water splitting process: (1) condenser, (2) receiver reactor, (3) valve, (4) heat exchanger (two stages), (5) valve, (6) steam generator, (7) heat exchanger (two stages)

Flow Sheets. Two versions of the flow sheet have been generated and used for the layout of solar model plants. The first one is based on an equal temperature level for both process steps, the second one on alternating temperature levels of 1073 and 1473 K. Figure 9 provides the basic flow sheet for the process applying equal temperature levels for both steps.

Experimental Data as Input. The experimental campaigns have been evaluated not only regarding the feasibility of water splitting and oxide regeneration but also to generate a data base as a starting point for the modeling of a scale-up of the process. The following issues are the most important for that purpose.

The thermal behavior of the mini plant including receiver-reactor and all peripherals operated in the solar furnace in Cologne has been intensively analyzed by experiments. Beyond that, calculations have been applied for parameters not directly accessible by measurements. Important parameters for a technical and economic evaluation are thermal losses and net power available for the reactions. The major contribution to losses and power consumption are caused by the high temperature endothermic step of catalyst regeneration. Therefore, the thermal balancing of the reactor is exemplarily shown for an absorber temperature of 1473 K and nitrogen as feed gas. The balancing was done at or near thermal equilibrium of the reactor. There are three contributions to the thermal losses of the mini plant:

- Convective losses at the housing,
- Re-radiation losses trough the window,
- Heat transfer to the product/exhaust gas.

The third contribution will be recovered to a far extent in an optimized or commercial process. The experiments and calculations provided the results shown in Table 2.

Therefore, solar energy input beyond 3.5 and 5.1 kW, respectively, is available to run the regeneration reaction in the reactor. Thus an upper limit of 80% of the incoming radiation may be used for that reaction. More than 95% of the process energy is required in the highly endothermic regeneration step. The reaction enthalpy of 300 kJ/mol is assumed for that step according to [4]. Energy losses during the exothermal splitting step are largely compen-

Table 2 Thermal balancing of mini plant at $T_{Absorber}=1473$ K

Contribution	Minimum [kW]	Maximum [kW]
Convection at reactor housing derived from surface temperature distribution of the housing	0.7	1.0
Re-radiation measured by blackbody absorber in front of the reactor aperture	2.0	2.5
Heat in exhaust/product gas $=c_p$(product gas)*T(product gas) - c_p(feed gas) * T(feed gas)	0.8	1.6
Overall losses without heat recovery	3.5	5.1
Overall losses with heat recovery from product gas ($\eta = 70\%$)	2.9	4.6
Solar input power from solar furnace	25.0	25.0
Max. available solar power for chemical reaction	20.1	21.4

sated by the reaction heat. Additionally 70% solar field efficiency has to be considered and 0.35 kW (solar) are needed for the regeneration of 1 Nm^3/h of nitrogen contaminated by oxygen. This leads to a rough estimation of an overall efficiency of up to 40% (ratio of higher heating value of produced hydrogen and solar input). The value has to be refined by determining potential receiver efficiencies by experiments, in particular using a continuous operating reactor, by analyzing all unit operation represented by the process flow sheet, and finally by annual balancing of the operation of an optimized model plant.

A transient evaluation of the whole process is a demanding task. At the moment a model is being developed to investigate the dynamic behavior of the receiver-reactor for an operation with alternating conditions, in particular alternating temperatures.

Economic Evaluation

Starting with these basic considerations a first calculation was performed with the following considerations for a solar plant (Fig. 10):

- solar only operation
- sited in Almería, Spain
- regeneration temperature: 1473 K, splitting temperature 1073 K
- yield of hydrogen with respect to steam injected: 35%
- sevenfold surplus of nitrogen needed for the regeneration
- size of heliostat field (90,000 m^2 north field)
- 150 Euro per m^2 of mirror area installed

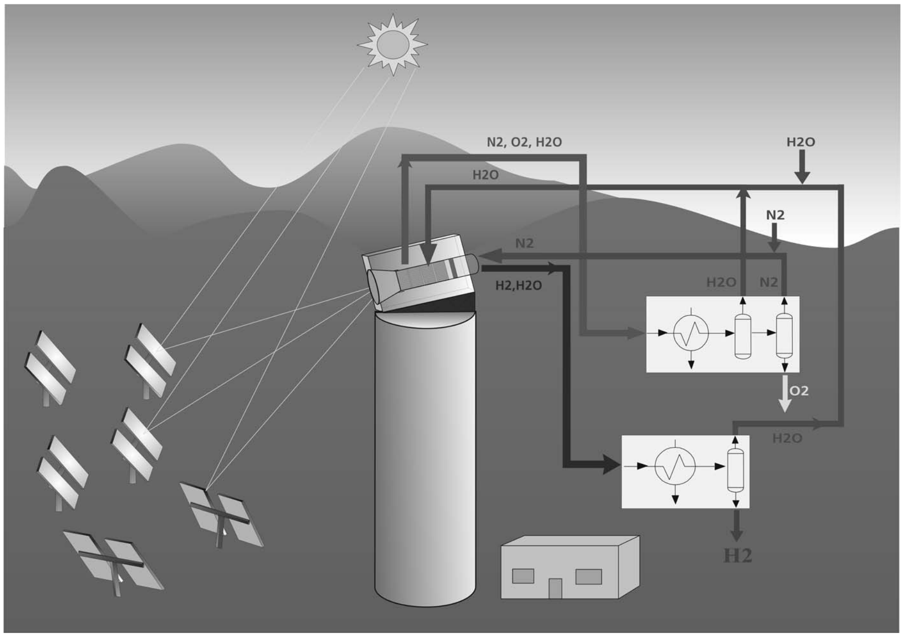

Fig. 10 Scheme of plant concept with integrated simple flow sheet

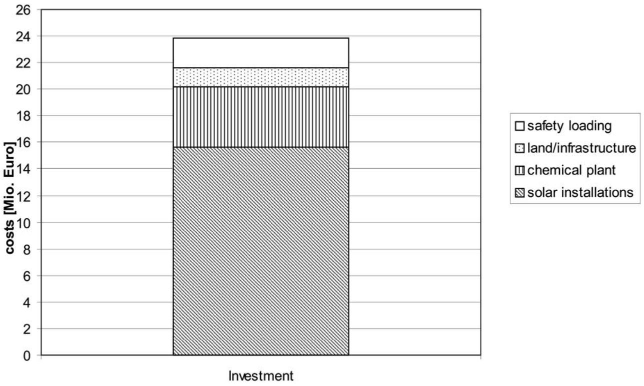

Fig. 11 Investment costs

- losses of 1% of flushing gas during recycling
- annual production: 65.5 GW h of hydrogen low heating value (LHV)
- 1500 Euro per kg of metal oxide (coated)

Using these boundary conditions the investment costs and operating costs of such a facility have been calculated (Figs. 11 and 12). The duration of depreciation is ten years; the interest rate is 6%. On this basis the production cost for hydrogen are 0.18 Euro/kW h (LHV), accordingly.

Sensitivity analyses were performed indicating that major reduction of the production costs (see Figs. 11 and 12) is possible and likely due to the following parameters:

- reduction of price of the metal oxide
- enhancement of its reaction characteristics
- operation at temperatures lower than 1200°C
- reduction of the necessary amount and purity of nitrogen
- potential co-generation of hydrogen and electric power

Conclusions

A solar reactor based on ceramic refractory honeycomb structures coated with active redox materials was constructed. Its capability of achieving a uniform temperature profile of 1473 K was demonstrated. Solar thermo-chemical splitting of water and hydrogen production was successfully demonstrated up to ten cycles. The release of oxygen of the iron-oxide-based coating was realized by using solar energy. Multicycling of the process is possible in principle. The amounts of hydrogen produced correspond very well to the laboratory experiments with the oxides in the form of powders. The redox pair materials as coatings are almost as active as the powders.

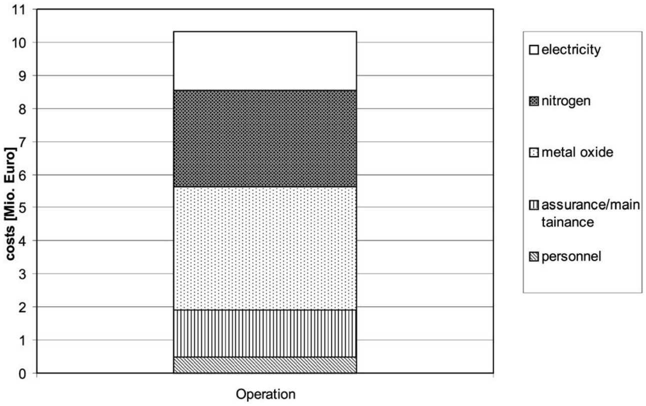

Fig. 12 Operational costs

The analyses indicate that there is potential to reduce the production cost of hydrogen down to 10–12 Eurocent/kW h. Reduction of cost for the installation of the solar part of the plant, which is expected to proceed with the ongoing commercialization of solar thermal applications (in particular power plants), may provide even lower cost.

Acknowledgment

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Nomenclature

ReSiC = recrystallized silicon carbide
SiSiC = siliconized silicon carbide
SSS = solid-state synthesis
SHS = self-propagating high-temperature synthesis

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