

Solar thermochemical production of hydrogen – the carbothermic ZnO/Zn cyclic process

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ABSTRACT:

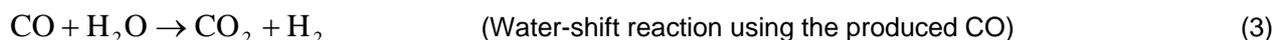
The two-step carbothermic ZnO/Zn cycle is one of the most promising routes for producing hydrogen by splitting water with the aid of concentrated solar energy. In a first endothermic step concentrated solar energy is used as the source of process heat to produce Zn and CO from ZnO and a carbon source, e.g. charcoal. The solar produced Zn can be stored and eventually transported before being exothermically reacted with steam to produce H₂ and ZnO. The produced CO may be exothermically shifted to H₂ by reaction with water, or used for onsite power production. The solar step has been successfully tested within the EU's R&D project SOLZINC on a pilot scale of 300 kW concentrated solar power, yielding up to 50 kg/h of 95%-purity Zn. The Zn in different physical forms can be used for hydrogen production. Several options have been investigated for this process on laboratory scale.

KEYWORDS: hydrogen, solar energy, zinc, thermochemical cycle, carbothermal reduction

INTRODUCTION

The direct splitting of water with concentrated solar energy as heat source faces tremendous problems in terms of material of construction of the reactor (temperature about 3000 K) and the need to separate the products H₂ and O₂ [1]. By working with metal-redox systems one can reduce the required temperature and can separate the production of O₂ and H₂. One of the most promising respective systems is ZnO/Zn [2, 3]. Research is performed on the solar dissociation of ZnO at temperatures of about 2000 K [4]. Major research topics include the choice of the construction materials of the solar reactor and the separation of the produced Zn from the Zn-O₂-offgas without significant re-oxidation. By mixing the ZnO with a small amount of carbon both issues can be drastically alleviated: the operation temperature comes down to around 1400 K and the Zn-CO-CO₂ off-gas composition is similar to the one existing in metallurgical processes, for which Zn separation is industrial practice. Since the process energy is delivered by the sun, only about 20% of the amount of carbon required for the traditional pyrometallurgical Zn-production is used.

The resulting carbothermic ZnO/Zn cycle can be described generally as follows:



In the endothermic step, concentrated solar energy is used as the source of process heat to produce Zn and CO from ZnO and a carbon source, e.g. charcoal. The solar produced Zn may be stored and eventually transported before being exothermically reacted with steam to produce H₂. Alternatively, it may be used to generate electricity in a Zn-air fuel cell. In both cases, ZnO is recovered and recycled to the solar reactor, thus closing the cycle. The produced CO may be exothermically shifted to H₂ by reaction with water, or used for onsite power production. Finally, the highly concentrated CO₂ off-gas may be sequestered. If the carbon used for the ZnO reduction originates from biomass, the process is fully renewable even without sequestration.

„Beam Down“ Optics

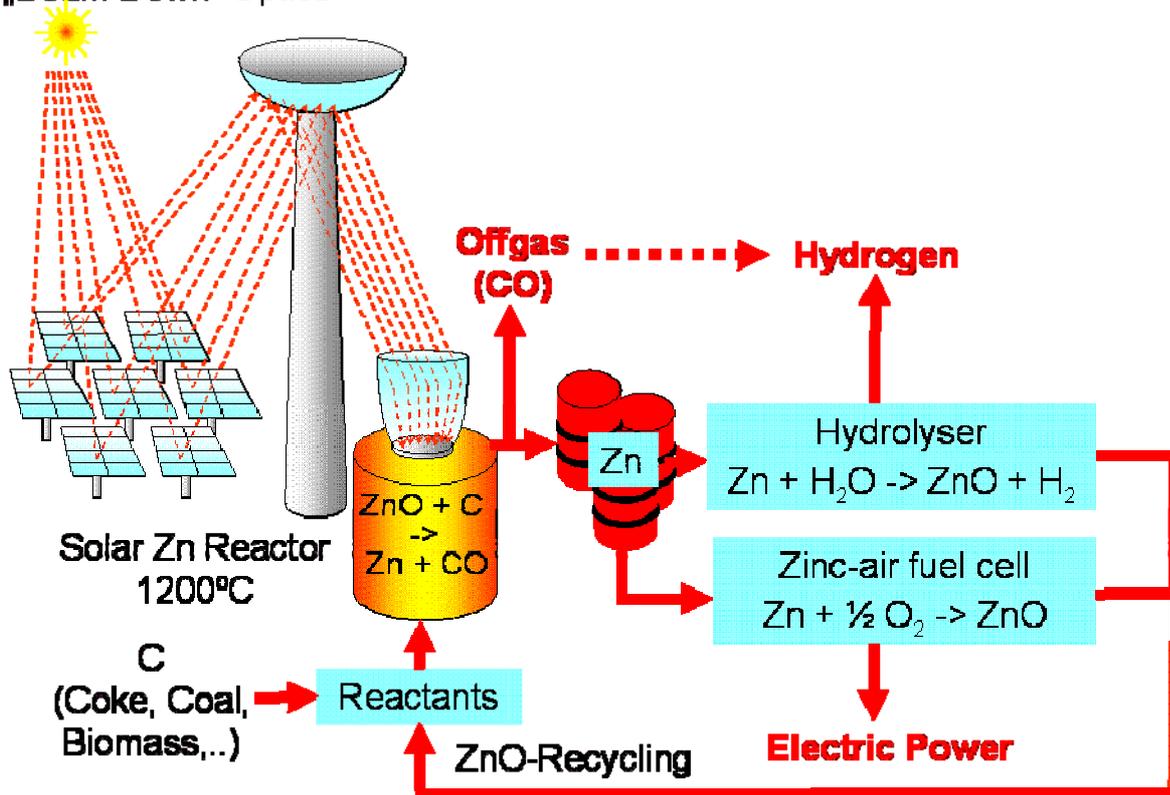


Figure 1: Schematics of carbothermic solar ZnO/Zn cyclic processes to solar hydrogen and to solar electricity.

The technical feasibility of the solar process step has been demonstrated for the first time at a pilot scale within the EU project SOLZINC, a cooperation of research institutes and industries from France, Germany, Israel, Sweden and Switzerland [5]. The pilot plant is located at the solar tower beam-down facility of the Weizmann Institute of Science. A mixture of industrial ZnO and charcoal is reacted to produce gaseous Zn and CO at about 1200°C. The power rating of the solar reactor is 300 kW of incoming concentrated solar radiation, sufficient to produce about 50 kg of Zn per hour.

This paper summarizes the findings from the solar operations of the pilot reactor and the associated equipment and describes options and scenarios for the non-solar exothermic reaction from Zn and water to produce hydrogen and ZnO.

The SOLZINC pilot plant

The pilot plant design is based on extensive investigations on 5 kW laboratory scale [6, 7]. The resulting key component of the plant, the solar reactor, is schematically shown in Fig. 3. It features two cavities in series, with the upper one functioning as the solar absorber, and the lower one as the reaction chamber. The upper cavity contains the 48-cm diameter aperture with a 12-mm thick quartz window mounted on a water-cooled copper ring, the 0.8-cm thick graphite or graphite/silicon carbide partition plates, and inlet/outlet ports for the inert carrier gas for window flushing. With this arrangement, the upper cavity protects the window against particles and condensable gases. The lower part, 140-cm in diameter and 0.8-m high, is a cylindrical cavity which contains the packed bed of ZnO-C mixture. The maximal initial height of the batch is 0.5 m, corresponding to about 500 kg of ZnO-C mixture for a full day operation, so that cooling and recharging of a new batch can be accomplished overnight.

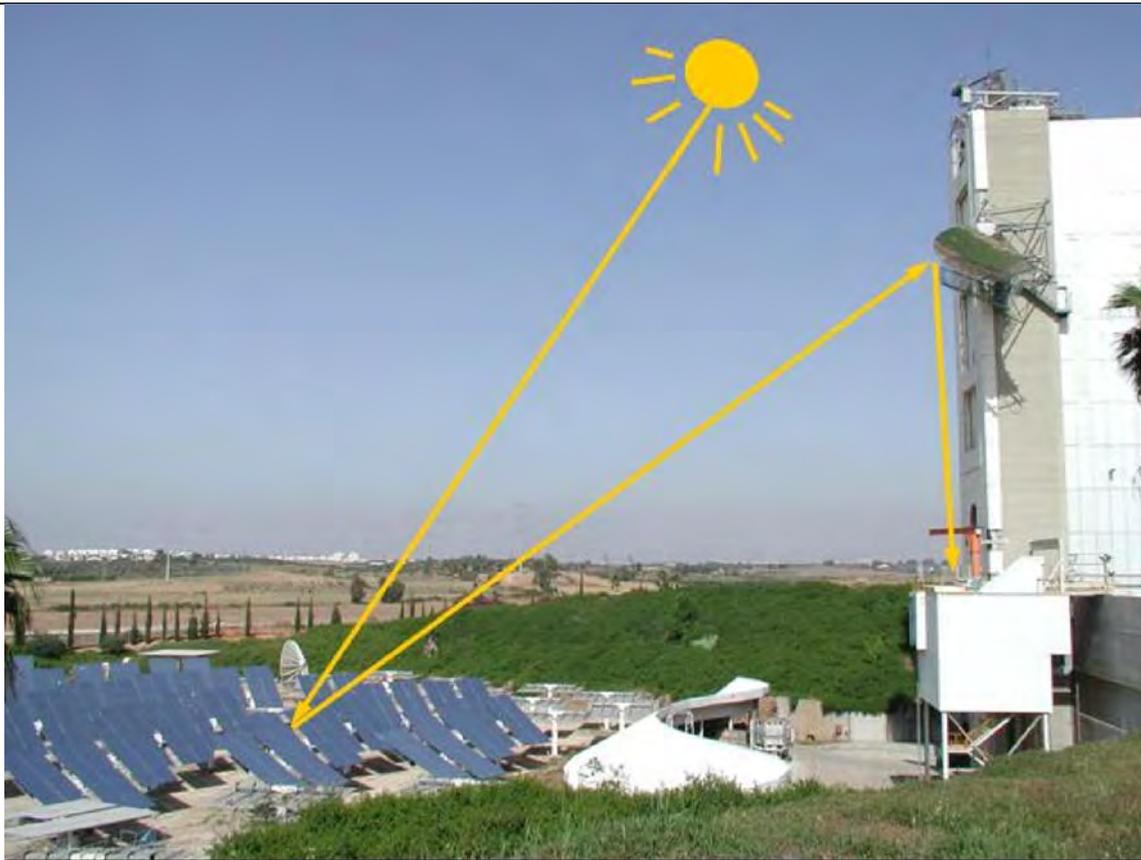


Figure 2: Optical configuration of the solar tower at WIS: Field of heliostats focusing sun rays onto a hyperbolic reflector at the top of the tower, which re-directs concentrated solar radiation to the solar reactor located on the ground level.

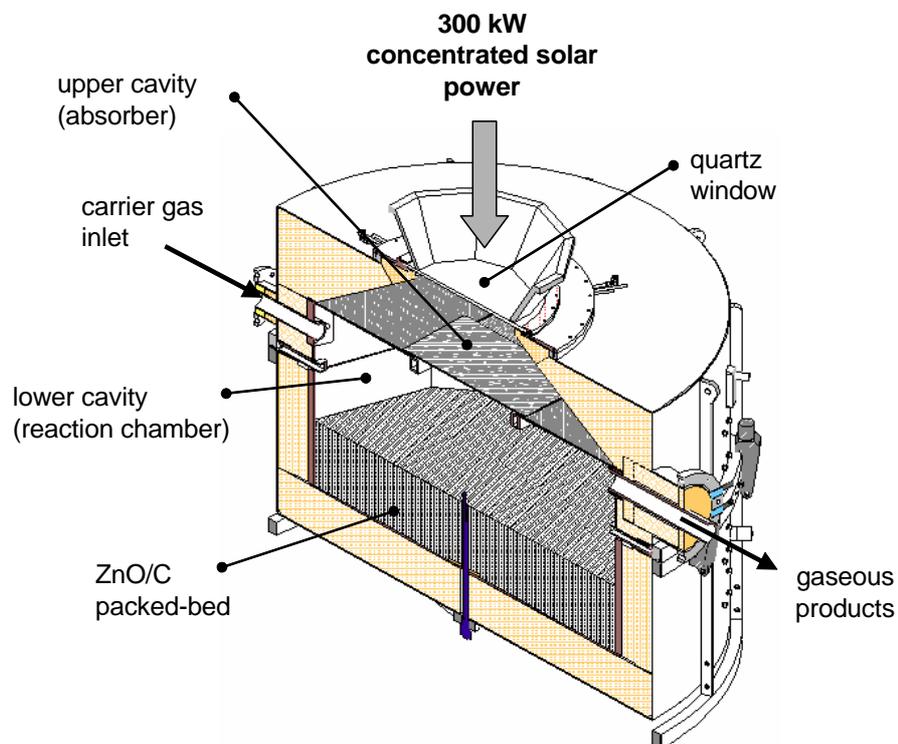


Figure 3: Schematic of the 300 kW solar chemical reactor: Solar absorber (upper cavity) and reaction chamber containing a ZnO-C packed bed (lower cavity) [8].

The main components of the SOLZINC pilot plant are schematically depicted in Fig. 4. Fig. 5 shows a photo of the plant in operation. The reactor's SiC off-gas exit pipe is electrically heated to prevent Zn condensation and extends into the quenching section, where it is mixed with recycled cold off-gas. In the quench/cooler section the Zn condenses and the coarser fraction of the resulting Zn dust is separated off in a cyclone. The fines remain in the gas and are mostly recycled back to the quench together with the product gas for further growth ("inner recycling loop"). A fraction of the gas behind the fan corresponding to the amount of new gas leaving the reactor passes a bag filter, where it is separated from the fine Zn-dust before leaving the plant. A fraction of this gas can be recycled back to the reactor to be used as a carrier gas ("outer recycling loop"). The fan speed and opening position of the valve in the inner recycling loop are used to control the pressure in the reactor and the gas flow rate in the inner recycling loop. Overall, more than 150 sensors for temperatures, pressures, flow rates, radiative power, gas analysis, etc. are used to monitor and control the process.

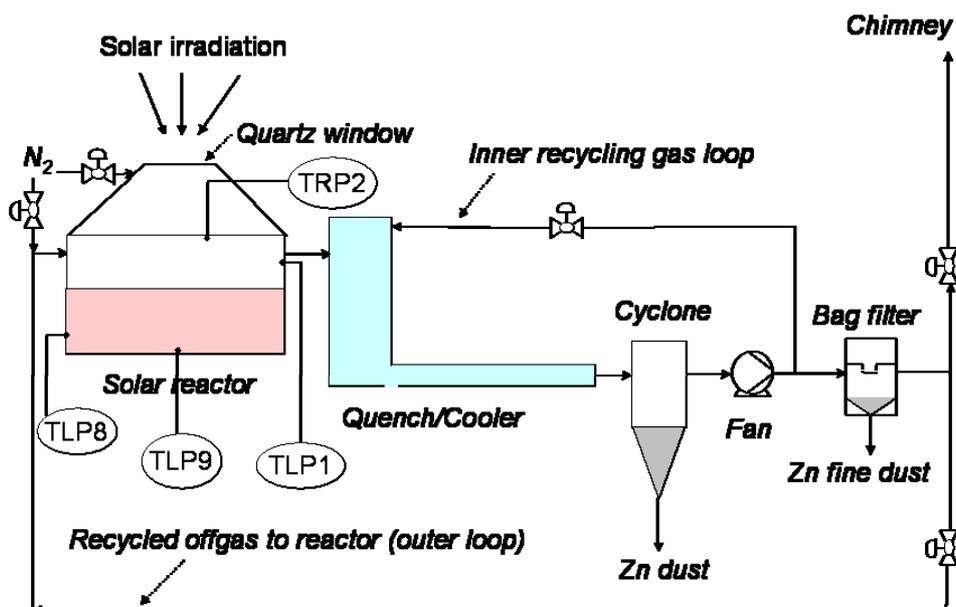


Figure 4: Flow diagram of SOLZINC solar chemical pilot plant: solar concentrating system, solar reactor, off-gas system, and some of the temperature sensors.



Figure 5: SOLZINC pilot plant in operation: The product gas of pilot solar reactor in the middle is quenched with recycled cold product gas in the vertical chamber on the right, before it passes a cyclone for separation of the Zn-dust.

Experimental results

In most tests a 100 kg batch of industrial ZnO powder (Grillo 2011) mixed with 16 kg of industrial beech charcoal powder (Chemviron), forming a typical molar stoichiometry $\alpha=C/ZnO$ of 0.9, were distributed uniformly in the lower cavity, resulting in a 12-13-cm thick packed bed. Typically, the solar reactor was heated at a rate of about 10 K/min by successively introduction of heliostats until the desired temperature level was reached. The following table lists the major operational conditions of selected pilot experimental runs.

Experiment	A	B	C	D	E
Stoichiometry $\alpha= C/ZnO$	0.9	0.9	0.9	1	0.8
N_2 flow rate to upper chamber [Nm^3/h]	6	6	6	6	6
N_2 flow rate to lower chamber [Nm^3/h]	3	3	3-9	3-9	3-9
Outer recycled gas flow rate [Nm^3/h]	0-6	16	0-10	0-10	0-10
Inner recycled gas flow rate [Nm^3/h]	500	500	350	350	350
At maximum power input (plateau):					
$T_{lower\ cavity} = TLP1$ [K]	1440	1390	1450	1460	1470
Zn molar flow rate (maximal) [kmol/h]	0.64	0.44	0.67	0.7	0.61
Batch height after test [cm]	4	<1	<1	<1	<1

Table 1: Results of selected test operations

Figure 6 shows the time variation of the reactor temperatures during experiment C. Highest temperature of 1535 K is obtained on the partition wall (TRP2), while the temperature in the upper part of the reaction chamber is about 50-100 K lower, as predicted by radiation heat transfer modeling [9, 10]. The temperature at the SiC floor (TLP9) of the reactor indicates a high temperature gradient through the packed bed. Figure 6 also includes the Zn production rate – with peak at 0.7 kmol/h – determined from the oxygen balance: $\dot{n}_{Zn} = \dot{n}_{CO} + 2\dot{n}_{CO_2}$, where \dot{n}_i is the molar flow rate of species i , measured by GC. X-ray-diffraction analysis of samples collected in the cyclone and the bag filter indicated a Zn purity of about 95%

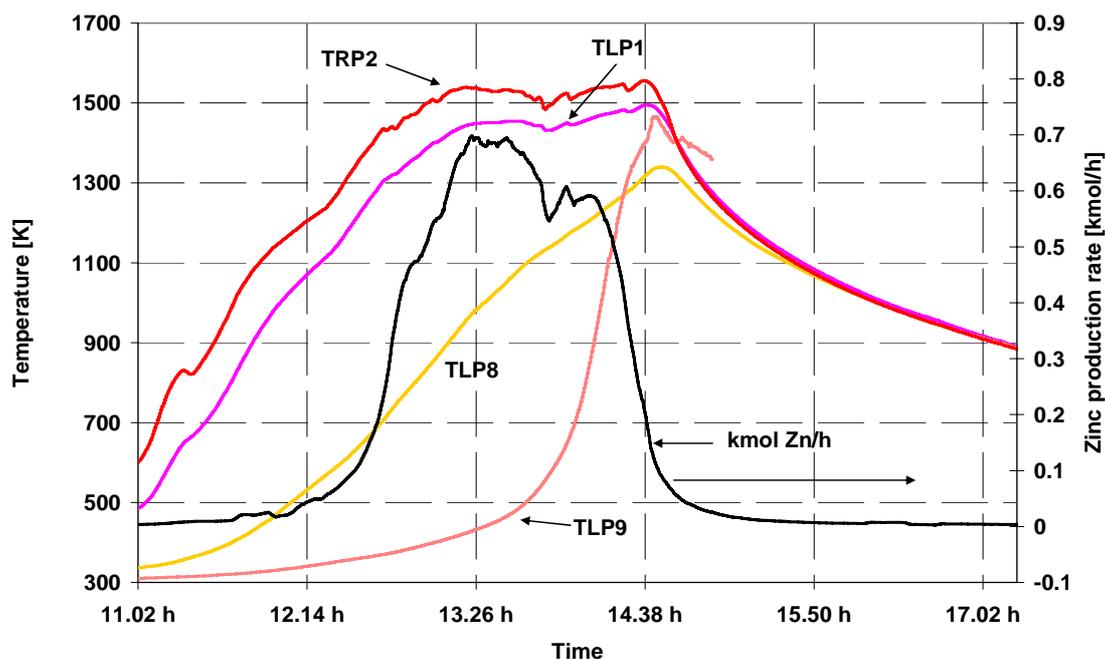


Figure 6: Temperatures and production rate during a typical test (Experiment C in Table 1). TRP2: partition plates; TLP1: reaction chamber; TLP8: SiC lateral wall; TLP9: SiC bottom plate. More details are given in Ref. [11].

The thermal efficiency of the solar reactor, defined as the ratio of the reaction enthalpy gain to the solar power input, amounts to about 30%. Losses are mainly due to re-radiation through the aperture and heat conduction through the walls. Higher efficiencies are expected for larger industrial plants. The conceptual design and economic analysis of a 5 MW chemical plant is in progress.

Further and more detailed results of the pilot experimentation can be found in Ref. [11].

Scenarios of solar hydrogen production via carbothermic ZnO/Zn cyclic process

Principally two different modes for using the SOLZINC-process for hydrogen production can be distinguished:

a) In situ production at the exit of the solar reactor by introducing steam as a quenching gas into the Zn-containing offgas. Figure 7 sketches a respective solution.

b) Production of hydrogen from solar produced Zn after storage (normally as a solid) and eventually transport of the material (see Fig. 8). Sub-scenarios range from 24h continuous H₂-production at the solar site (day/night storage) to far distance transport of the produced Zn prior to the hydrolysis (preferentially using sea freight).

In addition, in any case, in situ hydrogen can be produced by reacting the CO in the off-gas with steam (shift reactor, eq. (3)).

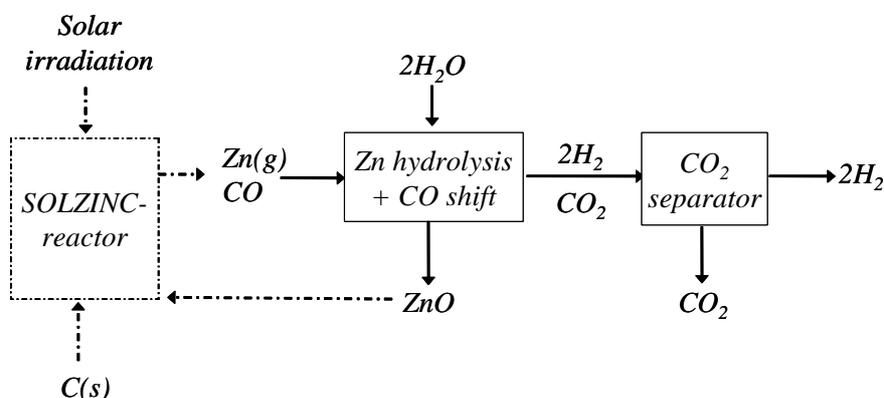


Figure 7: Path (a) to solar hydrogen: *in-situ* generation of hydrogen at the solar Zn plant from the off-gas consisting of gaseous zinc and carbon monoxide.

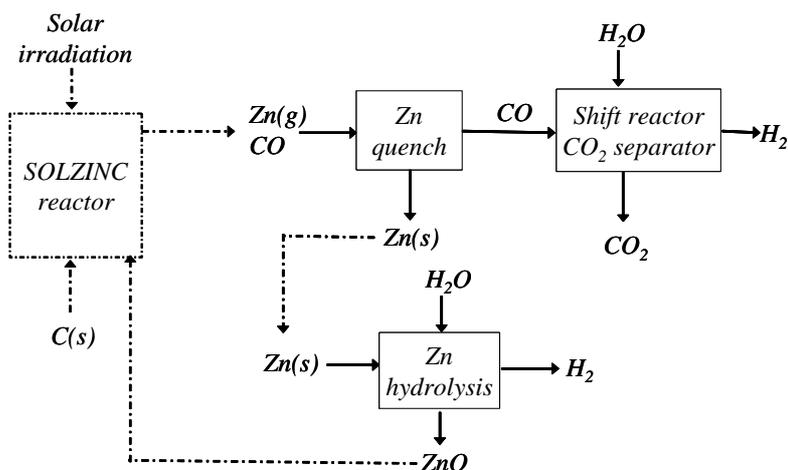


Figure 8: Path (b) to solar hydrogen: Storage (and potential transport) of Zn and subsequent hydrogen production on demand. Potential additional *in-situ* hydrogen production at the solar plant via water-gas shift reaction (alternative: *in situ* electricity production).

Hydrogen production by reacting zinc with steam

The reaction rates of Zn with steam depend strongly on the form of Zn (surface area, morphology, impurities). Hence different types of hydrolyses reactors are envisioned.

Both for solid and liquid Zn, the reaction with steam is hindered by a growing ZnO layer covering the unreacted Zn. In studies of Zn oxidation with air, it was found that the diffusion of Zn through the ZnO layer is rate limiting and the oxidation reaction occurs mainly on the outer surface [12]. Similar mechanism is expected for the reaction of Zn with steam that is of interest here. Laboratory scale tests have been performed with a variety of Zn-forms:

Hydrogen via zinc-nanoparticles

When Zn vapours are mixed with steam, nanoparticles can be formed, which simultaneously react with the steam to form hydrogen and ZnO [13, 14]. The large surface to volume ratio of the nanoparticles allows for a nearly complete conversion of Zn to ZnO. No external energy is required. Details of the current development status can be found in [15]. One interesting application of this process is the direct hydrogen production at the exit of the solar reactor. The same principle may also be used after storage of Zn. In this case Zn nanoparticles produced at the exit of the solar reactor have to be dispersed again or - easier to handle - more coarse Zn has to be evaporated for the formation of nanoparticles. The energy released by the exothermic hydrolysis reaction is larger than the energy required for heat up and evaporation of the Zn.

Hydrogen from zinc-dust

The reaction of Zn-dust (typical size a few μm) with steam has been tested using thermo-gravimetry. For some samples a significant reaction was observed in these exploratory tests [16]. Recently, experiments for the production of H_2 from the solar produced Zn dust from the pilot plant have been conducted. First results are promising. These tests are in progress and further study is needed prior to publication.

Hydrogen from zinc powder

Zn powder is widely produced by atomization of liquid Zn and has a typical particle size of 100 μm [17]. It is often used for battery applications, in which its reaction with water (electrolyte) is undesirable. For this reason Zn powder is typically including small amounts of additives that strongly reduce the reactivity of the Zn in air [18] as well as in water. Hydrogen production tests with standard Zn powder did result in small reaction rates only [19]. Tests for hydrogen production that take the influence of impurities into account are planned for the near future.

Hydrogen from liquid zinc

Experiments have been performed in which steam has been bubbled through liquid Zn [20]. By stirring the Zn-melt the rates could be increased [21]. Again rate limiting is the formation of a ZnO-layer around the bubble. The reacted ZnO floats on top of the liquid Zn. An industrial process would include a scrapper, cleaning periodically the Zn(l)-surface. This liquid-Zn process could be used after storage of Zn(s), e.g. as bulk Zn, eventually transport and re-melting. It might also be used for a short time (day-night) intermediate storage of Zn(l) on site, e.g. to allow for an 24h solar hydrogen supply. One might, e.g., make use of the H_2 from the shift reaction produced during the solar operation and store all the produced Zn as a liquid for reaction with steam after sunset.

Conclusions and Outlook

The EU's R&D project SOLZINC accomplished a pioneer technology demonstration of a pilot-scale solar chemical plant for the production of Zn by solar carbothermic reduction of ZnO. Its testing at a 300 kW scale in a solar concentrating facility at the 1300–1500 K range yielded up to 50 kg/h of 95%-purity Zn with energy conversion efficiency (ratio of the reaction enthalpy gain to the solar power input) of about 30%. The pilot plant is available for further improvements.

Several options to produce H_2 from Zn exist. The respective processes still have to be developed on industrial scale. Main difference is the form of Zn used. Fortunately we are able to design different types of off-gas systems for the carbothermic solar reactor, for production of either bulk or liquid Zn, Zn dust or Zn powder. Therefore, an overall process optimization will be possible depending on the results of the further investigations of the different hydrolyses processes.

Overall the SOLZINC process provides an efficient thermochemical route for the storage and transportation of solar energy and the production of solar hydrogen.

Acknowledgments

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