Proceedings ISES 2003, Göteborg, June 14-19, 2003

SOLAR CARBOTHERMIC PRODUCTION OF ZINC AND POWER PRODUCTION VIA A ZNO-ZN-CYCLIC PROCESS

M. Bruesewitz and G. Semrau
Zoxy Energy Systems AG, Oberderdingen, Germany
M. Epstein and I. Vishnevetsky
Weizmann Institute of Science, Solar Reaserch Unit, Rehovot, Israel
U. Frommherz, S. Kräupl, R. Palumbo and C. Wieckert
Paul Scherrer Institute, Solar Process Technology, Villigen, Switzerland, +41 56 310 4407, christian.wieckert@psi.ch
G. Olalde and J.-F. Robert
CNRS, Institut de Science et de Genie des Materiaux et Procedes, Odeillo, France
T. Osinga and A. Steinfeld
ETH-Swiss Federal Institute of Technology, Mechanical and Process Engineering, Zurich, Switzerland
S. Santén
ScanArc Plasma Technologies AB, Hofors, Sweden

Abstract – The reduction of ZnO with a carbonaceous material using concentrated solar radiation as energy source is an innovative concept (1) for the storage of solar energy in Zn as a "solar fuel" prior to its use for the production of electricity in Zn-air fuel cells or of hydrogen by splitting water with Zn. In both cases ZnO is formed, which can be reprocessed to Zn in the solar plant, creating a cyclic process (2) for the production of metallic Zn as a commodity with drastically reduced CO_2-emissions compared to conventional fossil-fuel based Zn-production. This paper gives an overview over the SOLZINC-project, in which we investigate the scientific and technological problems of scaling up this novel technology. Based on the small scale investigations a batch process (1 batch per day) using a concentrated beam down radiation heating the ZnO-C mixture has been selected for upscaling. The choosen furnace concept using concentrated solar irradiation to react ZnO and a solid carbon material to produce gaseous Zn has been further optimized on 5-10 kW scale. The necessary input data for upscaling have been generated. The results with respect to operation temperature requirements, overall reaction rates, choice of specific C-material for reduction and of construction materials of the furnace are used to design and build a pilot plant at a scale of several hundred kW. The use of Zn-dust as to be produced from the offgas of the solar reactor for mechanically rechargable Zinc-air fuel cells has been demonstrated.

1. INTRODUCTION

Intermittent solar energy can be converted into a storable and transportable fuel via the production of Zn from ZnO using concentrated solar radiation as the source of high-temperature process heat (Steinfeld and Palumbo, 2001; Bilgen, Ducarroir et al, 1977). The energy content of zinc can be recovered as electricity in zinc-air fuel cells (Iliev, Kaisheva et al, 1997). These cells operate in a battery like fashion at ambient temperature with KOH as the electrolyte. Zinc can also be reacted with water in an exothermic reaction for producing high-purity hydrogen for H_2-O_2 PEM fuel cells (Berman and Epstein, 2000). In both power-generating routes, the chemical product is ZnO, which is recycled to the solar reactor. Thus, Zn serves as the chemical energy carrier for storing and transporting solar energy.

While the thermal dissociation of ZnO requires operating temperatures above about 1750ºC (Möller and Palumbo, 2001) the use of carbonaceous materials as reducing agents (e.g. coal, coke, biomass, or natural gas) allows operation at much more moderate temperatures, in the range of 1000-1400 ºC, but at the expense of releasing CO_2. Nevertheless, compared to the conventional fossil-fuel-based production of Zn, the solar-driven carbothermic processes can reduce CO_2 emissions by a factor of 5. If biomass is used as a reducing agent, the process has basically zero net CO_2 emissions, if the production rate of biomass can be matched to its use as a reducing agent. Furthermore, the development of solar carbothermic ZnO reduction processes can profit from the traditional pyro-metallurgical know-how (Graf, 1996).

Carbothermic ZnO-reduction has been successfully demonstrated in different 5 kW-scale solar reactor prototypes (Adinberg and Epstein, 2002; Kräupl and Steinfeld, 2003).

2. THE SOLZINC PROJECT: OBJECTIVES, METHODOLOGY AND CONSORTIUM

2.1 Objectives

The key objective of SOLZINC is to develop and to experimentally evaluate a solar carbothermic ZnO-reduction process at a pilot scale. In addition, the project includes the investigation of the cyclic process including the interfaces of mechanically rechargeable Zn-air fuel cells with the solar process. Figure 1 sketches the process steps under investigation in SOLZINC. As indicated in the Figure the strongly simplifying overall net chemical reaction for a stoichiometric carbothermic reduction of ZnO, using C as reducing agent reads

$$ZnO + C \rightarrow Zn(g) + CO \qquad (1)$$

Clearly the project results will be of interest for other process options as the production of hydrogen from Zn and the production of Zn as a commodity with very low CO_2-emissions.

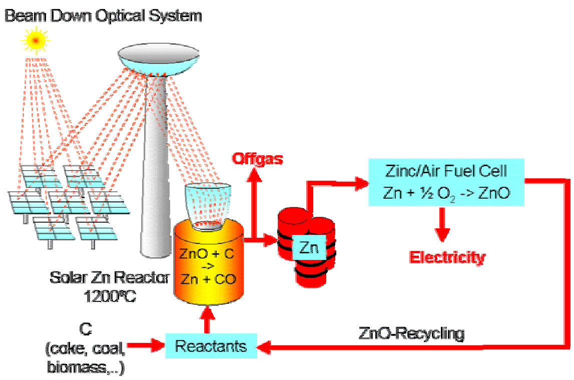

Figure 1: Process investigated in the Solzinc-project (solar reactor and cyclic ZnO-Zn process to electricity).

2.2 Project phases

The project has three major phases:

(1) Laboratory phase. At projects start selection of the solar reduction technology that - based on all available previous experience – is the most promising for scaling up to commercial size. The chosen process and the reactor design are further optimized. This includes laboratory tests on a 5 kW scale.

(2) Upscaling: test of optimized technology in pilot scale of several hundred kilowatts solar input.

(3) Conceptual Design: design a multi-MW scale demo unit for solar plant as well as for components of cyclic process for electricity production, based on results from phases 1 and 2.

2.3 Consortium

The consortium partners and their main roles are listed in Table 1.

3. LABORATORY TESTING

3.1 Choice of solar concept

Early in the project we decided to use solid carbon materials as reductant (not the alternative gaseous hydrocarbons like methane) and selected a "two cavity reactor concept" for ZnO+C(s) using beam down optics for optimization and upscaling (Wieckert, Epstein et al, 2002): a fixed bed of the ZnO-C mixture is indirectly heated from the top (beam down (Yogev, Kribus et al, 1998)) by radiation from a separation wall, whose upper side is subject to direct concentrated solar irradiation (figure 2). In batch tests the bed shrinks due to the chemical reaction and the reactor is basically empty after operation. First tests of the two-cavity concept with ZnO-C-mixture were performed with a solar reactor that had been previously developed and used in another project aiming at the solar processing of Electric Arc Furnace Dust ("EAF-dust") together with a solid reactant like activated charcoal or car shredder residues (Schaffner, Meier et. al., 2003).

Partner	**Location/ Country**	**Main tasks** (partners are active in further tasks)
CNRS-IMP	Odeillo/ France	Thermal and energetic diagnostics, administrative coordination
PSI	Villigen/ Switzerland	Solar reactor design, buildup, test, scientific coordination Infrastructure: Solar furnace
ETHZ	Zurich/ Switzerland	Solar reactor modeling. Infrastructure: solar simulator
WIS	Rehovot/ Israel	Balance of plant for pilot Infrastructure: solar testing at the 1MW beam down solar facility
ScanArc	Hofors/ Sweden	Zn-condensation from offgas
ZOXY	Oberderdingen/ Germany	Adaptation of mechanically rechargeable Zn-air fuel cell technology Treatment of spent cell products prior to reuse in solar plant

Table 1: The SOLZINC Consortium: two industrial partners (ScanArc, ZOXY) and four research institutes.

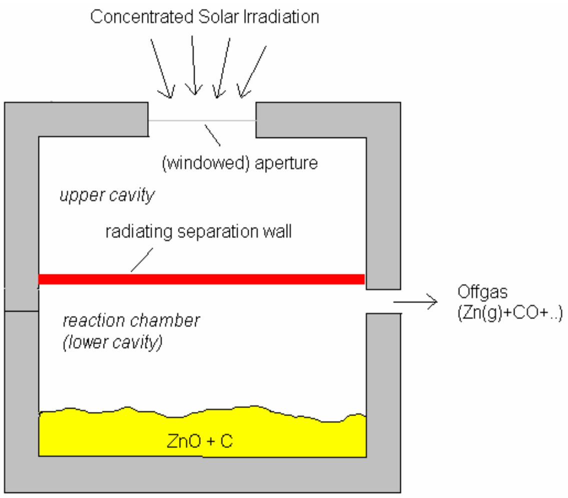

Figure 2: Schematics of two cavity reactor concept

For SOLZINC, this reactor has been modified/improved in several steps. It allows performing batch tests as well as continuous tests with feeding (Wieckert, Palumbo and Frommherz, 2002). Based on the respective test results a new batch reactor was build, tested and further improved. This process was supported by simplified modeling approaches (Wieckert, Palumbo and Frommherz, 2002; Wieckert, Meier and Steinfeld, 2003). Major features of the new reactor in comparison to the first one include a flat separation wall between the two chambers, an increased offgas duct and the concentration on batch operation only. Fig.3 shows a sketch of the latest version of the small scale reactor, Fig.4 a respective photo.

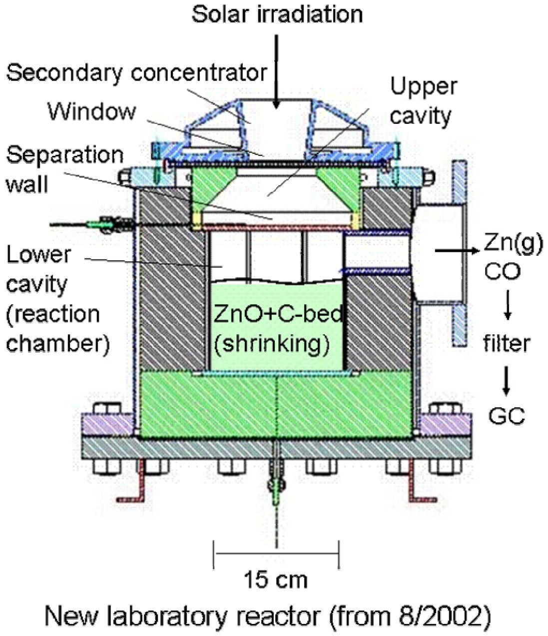

Figure 3: Sketch of the batch laboratory reactor.

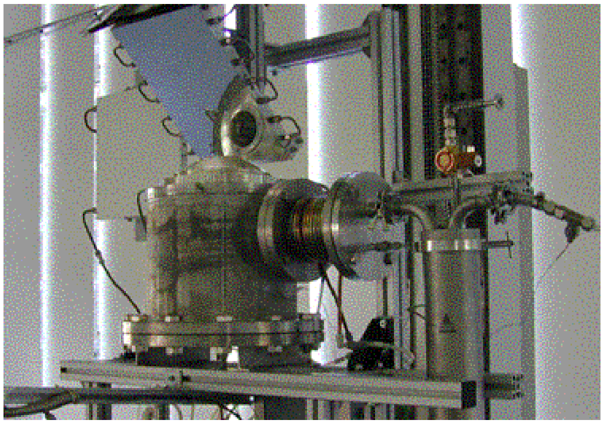

Figure 4: Photo of new solar batch reactor. Also shown on the photo are offgas duct and filter. On top is the 45° mirror that changes the horizontal beam in PSI´s solar furnace into the beam down radiation entering the reactor.

3.2 Solar Experimentation

PSI's solar furnace (Haueter, Seitz and Steinfeld, 1999) and ETH's High Flux Solar Simulator (Hirsch, v.Zedtwitz et al, 2003)) were used for about 25 solar runs with variants of the first reactor. In addition, up to now more some 20 experiments were performed with the new batch reactor at PSI. Typical duration of a single experiment was between 30 to 90 minutes (maximal 140 min) including typically 20-30 minutes for heating up and reaching approximate steady state conditions. The solar power input into the reactor ranges from 4 to 7.5 kW. Under quasi steady state conditions, the separation wall temperature reaches 1500-1750 K, and the reactant's temperature reaches 1350-1550 K. The reactants (ZnO powder and several types of reducing agents) were manually mixed. Figure 5 shows major readings of a typical experiment.

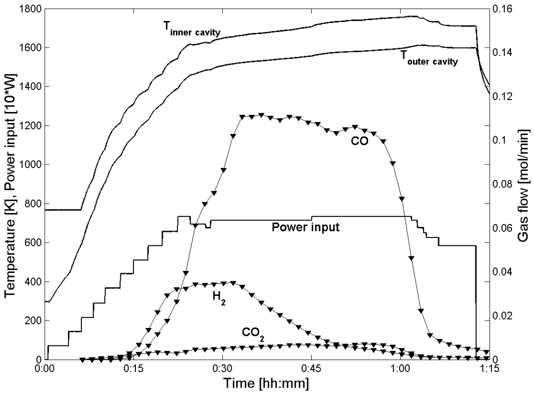

Figure 5: Solar power input, reactor temperature, and product gas flow rates during a representative batch run with 500 g of ZnO-C mixture (C:ZnO molar ratio = 0.8:1), using beech charcoal as reducing agent. CO is the main gaseous product and CO_2 represents 5-15% of the sum of CO+CO_2. H_2 originates mostly from the charcoal. Complete conversion was achieved after 35 min. of operation at above 1500 K.

Further experimental results of the tests with the first reactor are included in the publications (Wieckert, Palumbo and Frommherz, 2002; Osinga, Frommherz et al 2003). Details of the recent tests with the new batch reactor will be published separately. Below we just summarize some major overall findings concerning the process. The solar tests were also accompanied by tests in an electrically heated furnace at the Weizmann Institute, that was especially designed and build to study thermal properties of mixtures like ZnO-C. The results of these tests show that the mechanism of the reaction and its kinetics done under a large temperature gradient, typical in a real reactants bed, differ significantly from small samples under isothermal conditions, usually used for kinetic studies. The mechanism strongly depends on the nature, structure, size and relative amount of the carbon component in the mixture.

Operation mode: Tests with the first reactor clearly showed that for similar reaction chamber temperatures the effective Zn-production rate per surface area is similar for continuous feed operation and for batch operation (Wieckert, Palumbo and Frommherz, 2002). Since a solar heated continuous process has to be stopped once a day anyhow, it was decided to go for a comparatively much simpler batch process (concept: one batch per day).

Type of carbon source: Numerous different industrial materials proposed by major coal and coke suppliers were tested in reactivity tests using thermogravimetry first. Based on these results the majority of the solar experiments with the two-cavity reactor were performed using an industrial beech charcoal together with ZnO powder.

Temperature dependence: A strong increase of the overall reaction rate with temperature was found as seen in Figure 6 below: Increasing the temperature in the reaction chamber from 1400 K to 1550 K resulted in an increase of reaction rate per bed surface area by about a factor 3 to approximately 500 mol/m^2/h. The thermal efficiency (the fraction of the solar irradiation entering the solar reactor that is used for heating the reactants and for the endothermic chemical reaction) reached about 20%.

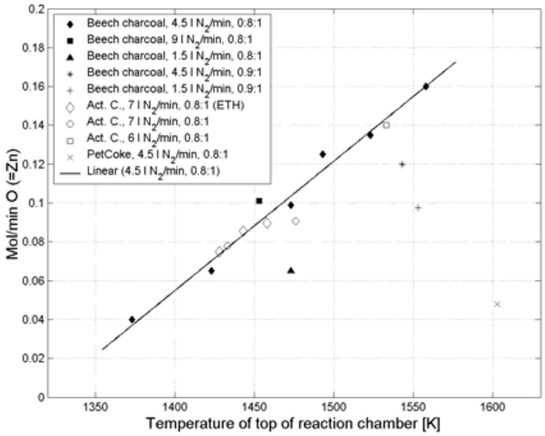

Figure 6: Reaction rates vs. temperature for different carrier gas flows, carbon materials (beech charcoal, activated charcoal and petcoke) and C:ZnO ratios established in the first reactor. The solid line refers to beech charcoal with 4.5 l N_2/min window flushing/carrier gas and a C:ZnO stoichiometry of 0.8:1.

C:ZnO stoichiometry: For the process it is important, that neither C nor ZnO accumulate over time, but that both are consumed in parallel. This excludes an overstoichiometric mixture (mol C:mol ZnO >1), since it results in an unreacted C-cover sheet. Tests have shown, that a stoichiometric mixture in the range (0.8 < C:ZnO < 0.9) results in a good performance and an offgas composition with a CO_2:CO ratio around 1:10 in line with steady state requirements.

3.3 Zinc condensation for the Zn-air fuel cells

For the mechanically rechargeable Zn-air fuel cells the condensed Zn should have a large surface area. One route to a respective Zn-powder goes over liquid Zn, as may be produced from the offgas in Lead-Zinc or in Zinc-splash or spray condensers and subsequent atomization (Lee, 1995). A much more direct process would be the production of Zn-dust directly from the offgas. Conventional Zn-dust production works via Zn-nucleation of evaporated Zn in nitrogen (Harzer Zinkoxyde, 2002). In SOLZINC we have a different gas composition including Zn, CO, CO_2, H_2 and N_2. ScanArc performs laboratory tests to realize a respective direct Zn-dust production from the "Solzinc-offgas". Very fine Zn-dust (around 1 μm) has been produced.

3.4 Zn-air fuel cell using Zn-powder and dusts

Zoxy has performed tests with different Zn-powders (100 μm) and dusts (1-10 μm). The first results show, that the performance of a chosen cell is similar for these fine Zn-dust and powders as for the Zn-sponge anodes used up to now, so that the chosen approach is promising.

4. CONCLUSIONS AND OUTLOOK

Overall it can be stated, that we have now generated the basic information required to realize the solar pilot plant, in terms of process know-how as well as in terms of design. The design of the pilot plant has been started.

The envisioned solar pilot reactor will look similar to the laboratory batch reactor shown in Figure 3, with an inner diameter of the reaction chamber of about 1.4 m. This allows a bed surface temperature close to 1200 ºC for an estimated production of 50 kg/h Zn, when the reaction rate values shown in Fig. 6 are assumed. The thermal efficiency is expected to be around 35-40 %. The height of the reaction chamber will be around 0.8 m, enough for introducing the material mixture for one day of solar processing. In the evening the solar reactor cools down. In the morning prior to start-up the lower part of the reaction chamber is disconnected. This bottom part is taken away for emptying in case residual materials are left and for refilling with a new batch for a one day operation. A batch for a full day is estimated to amount to 350-500 kg of ZnO-C-mixture.

Design and building of the solar reactor for the pilot plant will be mainly carried out by PSI. ScanArc will realize the corresponding Zn-condensation unit. The diagnostic instrumentation equipment will be provided by the CNRS group in Odeillo. The solar pilot plant will then be erected and tested in the existing beam down solar concentrating facility of the Weizmann Institute of Science (WIS), which is also in charge of the "balance of plant". Figure 7 shows the site for the pilot plant.

A Ph.-D. study is under way at ETH Zurich with the goal to describe the complex processes occurring in the solar reactor and especially in the ZnO-C fixed bed in the reaction chamber.

In addition, ZOXY will build and operate a 10 kW Zn-air cell module and will work on the other interface with the solar plant, namely, on the separation and reuse of KOH-electrolyte from the spent Zn-air fuel cell anodes.

In the last project year (2005) the results will be used to perform detailed design studies for a solar ZnO-reduction demonstration plant as well as for the complete solar to electricity cycle process. Eco-efficiency studies for different scenarios of technology implementation, such as electricity generation for peak demand, different consumer locations, etc will also be performed.

Figure 7: View from the heliostat field to the solar tower at the Weizmann Institute of Science in Rehovot/Israel. Mounted on the right side of the tower is the hyperbolic beam down mirror, which reflects the concentrated solar light coming from the heliostats into a secondary concentrator (CPC) in the white building below. The Solzinc pilot plant will be installed underneath this CPC.

ACKNOWLEDMENTS

Funding by the European Community's Research Directorate (Contract ENK6-CT2001-00512) and by the Swiss Federal Office of Education and Science (BBW) is gratefully acknowledged. Parts of this work were performed at the Solar Furnace, Paul Scherrer Institut, Villigen, Switzerland.

REFERENCES

Adinberg R., Epstein M. (2002). Experimental study of solar reactors for carboreduction of ZnO *Proceedings of 11th SolarPaces Int. Symposium Zurich*.

Berman A., Epstein M. (2000). The kinetics of hydrogen in the oxidation of liquid zinc with water vapor. *Int. J. Hydrogen Energy* 25, 957-967.

Bilgen E., Ducarroir M., Foex M., Sibieude F. and Trombe F. (1977). Use of solar energy for direct and two-step water decomposition cycles. *Int. J. Hydrogen Energy* 2, 251-257.

Graf G. (1996). Zinc, in: *Ullmann's Encyclopedia of Industrial Chemistry.* VCH Verlagsgesellschaft Vol. A 28, 509-530.

Harzer Zinkoxyde (since about 2002) Website: http://www.harzer-zinkoxide.de/

Haueter P., Seitz T. and Steinfeld A. (1999). A New High-Flux Solar Furnace for High-Temperature Thermochemical Research. *Journal of Solar Energy Engineering*, 121, 77-80.

Hirsch D., v. Zedtwitz P., Osinga T., Kinamore J., Steinfeld A. (2003). A new 75 kW High-Flux Solar Simulator for high-temperature thermal and thermochemical research. *ASME - J. Solar Energy Engineering* 125, 117-120.

Iliev, Kaisheva A., Stoynov Z., Pauling H.J.(1997). Mechanically rechargeable zinc-air cells. *Battery-Recycling `97*, Noordwijk (Netherland) July 1-4, 1997.

Kräupl, S., Steinfeld, A. (2003), Operational Performance of a 5 kW Solar Chemical Reactor for the Co-Production of Zinc and Syngas. *ASME- Journal of Solar Energy Engineering* 125, 124-126.

Lee R. (1995). The role of ISP in the recovery of zinc and lead from secondary waste materials and wastes. *Waste Processing II*, Rao R.S. et al (eds), pp 127-138, CIM, Montreal, Quebec, Canada.

Möller S., Palumbo R. (2001). Solar thermal decomposition kinetics of ZnO in the temperature range of 1950-2400 K. *Chemical Engineering Science* 56, 4505-4515.

Osinga, T., Frommherz, U., Steinfeld, A. and Wieckert, C. (2003). Experimental Investigation of the Solar Carbothermic Reduction of ZnO using A Two-Cavity Solar Reactor, *Proc. ISEC 2003 Int. Solar Energy Conference*, Hawaii, March 2003, and *ASME - Journal of Solar Energy Engineering*, in press.

Schaffner B., Meier A., Wuillemin D., Hoffelner W., Steinfeld A.(2003). Recycling of hazardous solid waste using high-temperature solar process heat – II. Reactor design and experimentation. *Environmental Science and Technology* 37, 165-170.

Steinfeld A., Palumbo R. (2001). Solar thermochemical process technology. *Encyclopedia of Physical Science and Technology* 15, 237-256.

Wieckert, C., Epstein, M., Olalde, G., Palumbo, R., Pauling, H.J., Reichhardt, H.U., Robert, J.F., Santen, S., and Steinfeld, A. (2002). The SOLZINC-Project for Solar Carbothermic Production of Zn from ZnO, *Proc. 11th SolarPaces Int. Symposium Zurich*, pp. 239-245.

Wieckert C., Palumbo R. and Frommherz U. (2002). A two cavity reactor for solar chemical processes: Heat transfer model and application to carbothermic reduction of ZnO. *Proceedings of 11th SolarPaces Int. Symposium Zurich* and *Energy-the Int. Journal*, in press.

Wieckert C., Meier A., Steinfeld A. (2003). On Indirectly Irradiated Solar Receiver-High-Temperature Thermochemical Processes", *ASME - Journal of Solar Energy Engineering* 125, 120-123.

Yogev A., Kribus A., Epstein M., Kogan A. (1998). Solar „tower reflector" systems: a new approach for high-temperature solar plants. *Int. J. Hydrogen Energy* 23(4), 239-245.