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

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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 CO₂-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 H₂-O₂ 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 1750°C (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 °C, but at the expense of releasing CO₂. Nevertheless, compared to the conventional fossil-fuel-based production of Zn, the solar-driven carbothermic processes can reduce CO₂ emissions by a factor of 5. If biomass is used as a reducing agent, the process has basically zero net CO₂ 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:

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \]  \hspace{1cm} (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 CO₂-emissions.

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \]  \hspace{1cm} (1)

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 (Yoge, 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).

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

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

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

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.

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.

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/m²/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%.

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, CO₂, H₂ and N₂. ScanArc performs laboratory tests to realize a respective direct Zn-dust production from the “Solzinc-offgas”. Very fine Zn-dust (around 1µm) 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 °C 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.

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