

EXPERIMENTAL INVESTIGATION OF THE SOLAR CARBOTHERMIC REDUCTION OF ZnO USING A TWO-CAVITY SOLAR REACTOR

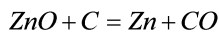
U. Frommherz, T. Osinga (ETH Zürich), A. Steinfeld (ETHZ and PSI), C. Wieckert

Zinc production by solar carbothermic reduction of ZnO offers a CO₂ emission reduction by a factor of 5 vis-à-vis the conventional fossil-fuel-based electrolytic or Imperial Smelting processes. Zinc can serve as a fuel in Zn-air fuel cells or can be further reacted with H₂O to form high-purity H₂. In either case, the product ZnO can be solar-recycled to Zn. We report on experimental results obtained with a 5 kW solar chemical reactor prototype that features two cavities in series, with the inner one functioning as the solar absorber and the outer one as the reaction chamber. Tests were conducted at PSI's Solar Furnace and ETH's High-Flux Solar Simulator to investigate the effect of process temperature (range 1350-1600 K) and reducing agent type (beech charcoal, activated charcoal, petcoke) on the reactor's performance and on the chemical conversion. In a typical 40-min solar experiment at 1500 K, 500 g of a 1:0.8 stoichiometric ZnO-C mixture were processed into Zn(g), CO, and CO₂. Thermal efficiencies of up to 20% were achieved.

1 INTRODUCTION

Compared to the purely solar dissociation of ZnO, the use of carbonaceous materials as reducing agents allows for a significant reduction in the process temperature. It also lowers the recombination risk of the produced Zn(g). The solar carbothermic reduction of ZnO has been experimentally demonstrated using C(s) [1] and CH₄ [2] as reducing agents. Zinc itself is an attractive solid fuel in mechanically rechargeable Zn-air fuel cells for electricity generation. The cyclic process from solar energy to electricity via solar-processed Zn-air fuel cells is being investigated within the EU-project SOLZINC [3]. We report on batch tests performed on the solar carbothermic reduction of ZnO with solid carbon at a 5-10 kW power scale, in view of a technology up-scaling to be performed within SOLZINC.

The overall process reaction can be represented by:



This reaction has a negative ΔG above 1230 K and proceeds endothermically ($\Delta H_{1500\text{K}} = 350.1 \text{ kJ/mol}$) at reasonable rates at above 1500 K. In the solar-driven process, a maximum of 1 mol C/mol ZnO is required, as compared to about 5 mol C/mol Zn in the traditional pyrometallurgical production.

2 THE SOLAR REACTOR

Figure 1 shows the solar reactor configuration. It features two cavities in series, with the inner one functioning as the solar absorber and the outer one as the reaction chamber. The inner cavity is made of graphite and contains a windowed aperture to let in concentrated solar radiation. A secondary concentrator (entrance diameter = 80 mm, exit diameter = 65 mm) is implemented at the reactor's aperture. The outer cavity (150 mm-inner diameter) is well insulated and contains the ZnO-carbon mixture that is subjected to irradiation by the 8 mm-thick graphite absorber separating the two cavities. With this arrangement, the inner cavity protects the window against particles and condensable gases coming from the reaction chamber

and further serves as a thermal shock absorber, reducing sudden thermal loads on the ceramic materials of construction. Generic design guidelines for such a two-cavity reactor concept are described in [4].

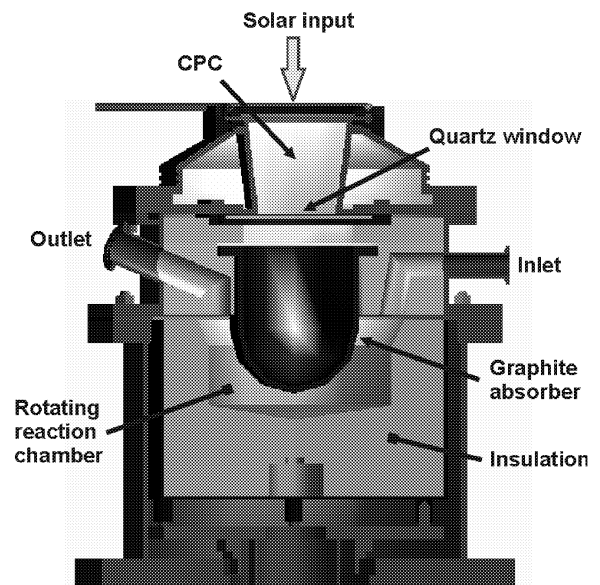


Fig. 1: Sketch of the two cavity solar reactor. It allows for batch tests and for continuous feed operation.

The quartz window is actively cooled by a N₂ flow injected at the aperture plane. This N₂ flows into the reaction chamber through small holes in the graphite absorber and sweeps out the product gases via a tangential outlet port located on the lateral wall. Reaction chamber walls, reactants, and gas outlet temperatures are measured with type-K thermocouples. The graphite absorber temperature is measured with a type-S thermocouple and with a solar-blind pyrometer. The reactor is typically operated with a constant underpressure of 5-10 mbar below ambient pressure. After exiting the reactor, the products flow first through a water-cooled Pyrex tube where part of the Zn condenses, and thereafter through a filter that collects the remaining solid products. The gas composition is monitored by gas chromatography (GC).

3 EXPERIMENTAL RESULTS

A set of 25 solar runs was carried out at PSI's Solar Furnace and at ETH's High-Flux Solar Simulator. Typical duration of a single experiment was between 30 and 75 minutes including 20 minutes for heating to the desired temperature and reaching approximate steady state conditions. Solar power input ranged from 4.5 to 7.5 kW. Under approximate steady state conditions, the graphite absorber's temperature ranged between 1500 and 1700 K, and the reactant's temperature ranged between 1350 and 1550 K. Figure 2 shows the solar power input, reactor temperatures, 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 gravel as reducing agent. CO is the main gaseous product. H₂ originates from the charcoal. Complete conversion was achieved after 35 minutes of operation at above 1500 K.

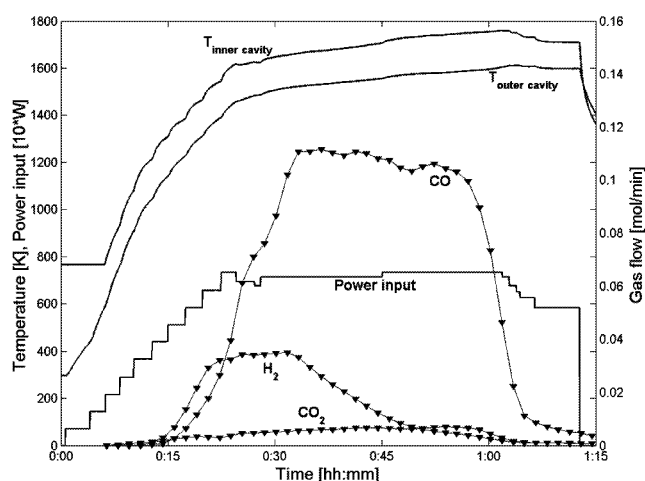


Fig. 2: Major parameter readings for typical batch test.

A representative continuous feed experiment can be found in [5]. The reaction rates obtained for batch and continuous feed runs were similar at the same reactor temperatures. The reaction rate is calculated from the sum of the O-moles measured by the GC ($\text{CO} + 2 \cdot \text{CO}_2$), taken as an indicator for the amount of ZnO reacted. The integrated amount of oxygen corresponds well with the material balance. Typically, 80% of the ZnO reduced was found in the off-gas system as basically pure metallic Zn. Figure 3 shows the measured reaction rates as a function of the reaction chamber's temperature for different carrier gas flows, reducing agents, and C:ZnO ratios. The strong temperature dependence indicates a chemical kinetics rate-controlling step. The majority of experiments were performed with beech charcoal gravel (from Chemviron) as reducing agent, resulting in similar reaction rates as those obtained when using activated carbon (Act. C). One test was performed with a much less reactive petroleum coke (from RAG Additive) resulting at a significantly lower Zn-production rate at the same temperature.

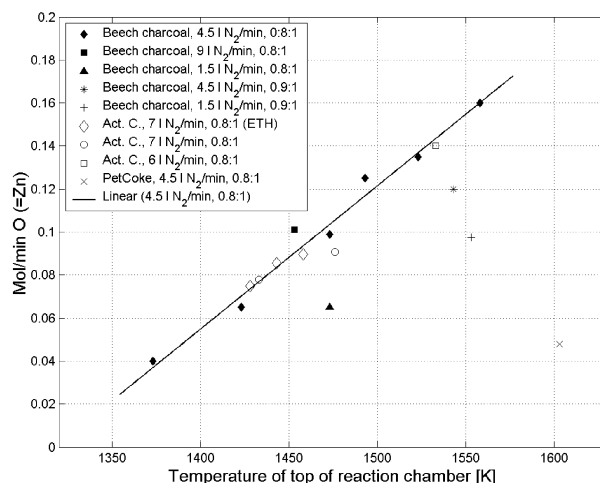


Fig. 3: Reaction rates vs. temperature for different carrier gas flows, carbon materials (beech charcoal, activated charcoal and petcoke) and C:ZnO ratios.

A significant portion of the incoming solar power is lost by conduction through the walls and by re-radiation through the aperture. The thermal efficiency, defined as the fraction of the solar power entering the reactor, that is used to heat up the reactants and to drive the endothermic process, reached 20% [5,6].

4 ACKNOWLEDGMENTS

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5 REFERENCES

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