Solar Carbothermic Reduction of ZnO in a Two-Cavity Reactor: Laboratory Experiments for a Reactor Scale-Up

Solar energy can be stored chemically by using concentrated solar irradiation as an energy source for carbothermic ZnO reduction. The produced Zn might be used for the production of electricity in Zn-air fuel cells or of H_2 by splitting water. In either case the product is again ZnO which can be reprocessed in the solar process step. This innovative concept will be scaled up to 300 kW solar input power within the so-called SOLZINC-project. In this paper we report on experimental results obtained with a two cavity reactor operated at solar power inputs of 3-8 kW in a solar furnace. The objective was to generate input data which are necessary for designing the scaled up reactor, such as the effect of process temperature ($1100-1300^{\circ}C$) and carrier gas (N_2 and CO) on the overall reaction rate. Furthermore, construction materials were tested and a variety of carbonaceous materials were screened for their use as reducing agents by means of thermogravimetric measurements. As a result, beech charcoal was chosen as the standard reducing agent. [DOI: 10.1115/1.2147585]

Keywords: solar, zinc, ZnO, carbothermal, chemistry, reactor, hydrogen, fuel, SOLZINC

Introduction

Production of Zn from ZnO in a thermochemical process using concentrated solar radiation as an energy source is a possibility for chemical storage of solar energy. The Zn can also be transported to the location where it is needed. The energy stored chemically in the Zn can be used in two ways of great interest:

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(1) If electricity is needed the Zn could be fed into a zinc-air fuel cell:

$$2Zn + O_2 \rightarrow 2ZnO + electricity \tag{1}$$

These cells operate with KOH as an electrolyte [1].

(2) Alternatively high purity H_2 can be produced by reacting the Zn with water:

$$Zn + H_2O \rightarrow ZnO + H_2 \tag{2}$$

In both routes the chemical product is ZnO which can be recycled to the solar process. For the purely thermal dissociation of ZnO temperatures above about 1800°C are required [2–4]. This implies great challenges in the design of the solar reactor. For example, the high temperature restricts the variety of materials which can be used for its construction. High flux concentration ratios are needed to reduce reradiation losses which are very large at such high temperatures. Furthermore it is difficult to avoid the reoxidation of Zn in the quenching step of Zn-O₂ mixtures [5–8].

Thus the use of carbonaceous materials as reducing agents for lowering the operation temperature of the solar step to a range of 1300-1800 K was investigated. Examples for such carbonaceous reducing agents are gases such as methane as in the SYNMET process [9–13] or solid materials such as coke, biomass, or coal [13–17]. In these processes some CO₂ is released, but compared to conventional fossil fuel based production of Zn, where C is not only used as a reducing agent but also for supplying process heat, the CO₂ emissions are reduced by about a factor of 5 in solar driven carbothermic processes (less than 1 mol $CO_2/mol Zn$ compared to about 4.5 mol C/mol Zn in the conventional Imperial Smelting Process [18]). When biomass is used as a carbon source the net CO_2 emission could be zero.

For a solid carbon source the overall reaction can be represented approximately by:

$$ZnO + C \rightarrow Zn + CO$$
 (3)

The reaction is highly endothermic ($\Delta H_{1500 \text{ K}}$ =350.1 kJ/mol) and proceeds to completion at temperatures above 1220 K. For achieving reasonable rates of reaction it is suggested to operate at temperatures above 1500 K [16].

The effective ZnO reduction is dominated by the gas-solid reaction

$$ZnO + CO \rightarrow Zn + CO_2$$
 (4)

with the CO being formed from C via

$$CO_2 + C \rightarrow 2CO$$
 (5)

[16,19,20].

The CO in the offgas can be used for feeding a gas motor or for production of H_2 by the water-gas shift reaction

$$\rm CO + H_2O \rightarrow \rm CO_2 + H_2 \tag{6}$$

In earlier papers we described some prototype reactors which have been successfully used for solar carbothermic ZnO reduction according to reaction (3) [14,20,21].

Based on the results of these experiments at a 5-10 kW power level it was decided within the SOLZINC-project [21] to scale up this reactor concept to a pilot scale at a power level of about 300 kW. In this paper we report on further experiments at 5-10 kW scale with a reactor that was modified in view of the scheduled scale up. The objective was to get more insight into the process and identify the critical parameters for designing the pilot scale reactor. This includes the screening of different carbonaceous materials and studying the influence of the amount and composition of carrier gas flow as well as the temperature on the

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Fig. 1 Sketch of the laboratory solar reactor

process. A further important objective was the selection of industrially available materials for construction of the pilot scale reactor.

Experimental Equipment and Methods

The Solar Reactor. The reactor works in a beam down configuration [22] namely the concentrated sun light is entering the reactor at the top. It is a "two-cavity reactor" allowing for indirect heating of the reactants through a separation wall between the upper cavity accepting the concentrated irradiation and the lower cavity with the reactants. General design guidelines for two cavity reactors are provided in [23]. Based on the experiences with the earlier designs [14,21] we built a batch reactor with a flat separation wall as shown in Fig. 1. The upper cavity and thus the upper side of the separation wall is subjected to concentrated solar irradiation entering the reactor through a quartz window. The window is protected against condensable gases and particles by the separation wall and an additional inert gas flow. To increase the input solar flux density a secondary concentrator (entrance diameter =80 mm, exit diameter=65 mm) is mounted above the aperture. Furthermore a "45 deg mirror" is used for redirecting the horizontal beam of PSI's solar furnace into a vertical beam entering the secondary concentrator (compare Figs. 1 and 2). In the lower cavity a fixed bed of a ZnO-carbon mixture is heated indirectly from the top by radiation emitted by the lower side of the hot separation wall. Both cavities are thermally well insulated to reduce heat losses due to thermal conduction. The walls of the lower cavity are lined by SiC plates for reducing diffusion of zinc vapor into the insulation material. Due to the chemical reaction the fixed bed is shrinking and the gaseous products are leaving the reactor via an outlet pipe made of SiC.

Experimental Setup. The solar experiments were carried out at the high-flux solar furnace of the Paul Scherrer Institute. The characteristics of this solar concentrating facility, mainly consisting of a 120 m^2 flat heliostat on-axis with a 8.5 m diameter fixed parabolic concentrator, have been described in detail in an earlier publication [24].

A flow diagram of the experimental setup is shown in Fig. 2. During a solar run the quartz window is cooled and protected against condensable gases and/or particles by a gas flow (typically N_2) injected below the window. After passing the window the gas is flowing to the lower cavity through a pipe. There it acts as a carrier gas and leaves the reactor through the outlet together with the product gases of the reaction. Just after the outlet the gases flow through a water cooled condenser where the produced zinc condenses and is partially collected. Any remaining solid products are collected in a filter mounted after the condenser. Further downstream the noncondensed gaseous products are analyzed by gaschromatography (GC).

For investigating the influence of the atmosphere on reaction rate, in some experiments N₂ was partially substituted by CO. Typical carrier gas flow rates are $0.5-4 l_n/min$. The reactor is operated in batch mode. A typical initial weight of the well mixed reactants in the fixed bed is 500–750 g and the typical molar ratio between nonvolatile carbon C_{fix} and ZnO is 0.9:1.

The temperature of the lower cavity is measured by a type K thermocouple placed in the lower cavity at the inner SiC lining approximately 8 cm below the separation wall. As this is near the initial top layer of the fixed bed, this temperature represents the temperature of the top layer of the fixed bed. Another type K thermocouple measures the temperature at the bottom of the fixed bed. The separation wall temperature is measured by a type S thermocouple and a solar blind pyrometer.

The 45 deg redirecting mirror and the secondary concentrator including the window flange are cooled by water.

The incoming solar power is calculated from measuring the solar flux distribution on a Lambertian target mounted horizontally next to the reactor and integrating it over the entrance of the secondary concentrator. This measurement is done before and af-



Fig. 2 Experimental setup in the solar furnace of PSI

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Table 1	Carbon sources	investigated for 2	ZnO reduction (data are mostly	/ based on infor	mation from	providers o	f the materials)

Name	Туре	Provider	Particle size	C _{fix} %	Volatiles %	Ash % $(T_{\rm fus, red})$	C _{tot} %	Test Solar
Activated	Activated	Fluka	powder	82.7	12.6	4.7	86.3	×
charcoal Beech charcoal	Charcoal Beech charcoal	Chemviron	<1 mm	83	<13	<4		×
gravel Beech charcoal	Beech charcoal	Chemviron	$<\!200~\mu{\rm m}$	83	<13	<4 (1415 C)		×
Ruhr-Brech-	Coke	Vögtlin-Meier	Crushed to	90.3	0.9	8.8		×
koks 20/30 Anthrazit	Coal	HG	<1 mm	89.8	5.6	4.6		
Starlight Anthrogit	Coal (Vietnam)	SSM-Coal		90.5	6	3.5		
Campana	Petcoke (Argentina)	SSM-Coal	powder	89.7	10	0.3 (1400 C)		
Kalzinat Braunkohlen- koks	Petcoke Coke from brown coal	RAG Additive RAG Additive	powder <5 mm, others	98 92–95	0.5 2–5	0.5 2.5–3.5 (1400 C)	95	××
Carbolux SK	Azetylen-	RAG Additive	0.2-1 mm	<99	0.45	0.3		
Flamm-Russ 101	Lamp black	Degussa	100 nm	99				
Guasare	Bitumious	SSM-coal	0-6 mm	54.5	37.5	8		×
Svea	coal Bitumious coal	SSM-coal	0-6 mm	60	30	(1470) 10 (1250)		
Statex N-121	Rubber black	Christ Chemie	15 nm (130 m2/g)	>99		(-200)		
Blair Athol	Coal	Outokumpu	(100	63.3	29.2	7.5	71.7	×

ter an experiment. The calculated input power is correlated to the solar irradiation, which is measured continuously during the whole experiment. Thus the incoming solar power on a vertical plane is known during the experiment. Due to reflection losses by the 45 deg mirror and the secondary concentrator and partial shadowing of the 45 deg mirror by the reactor only about 58% of this power are impinging on the window. In this way the effective solar input power of the solar reactor is determined.

Characterization of the Reactants. Before conducting the solar experiments, the input materials-ZnO and different carbon sources-have been tested in a Netzsch STA 409C thermogravimetric instrument (TG). The intention was a pre-screening of the carbon sources. The sample (typically 100 mg) is placed in a small crucible connected to a scale monitoring the weight of the crucible. The crucible itself is located in an electrically heated furnace, which can be heated with adjustable rates (typically 10 K/min) to 1400 °C. A gas flow (typical 25 ml_n/min of N₂) is flowing through the instrument. This setup allows for simple tests of important process properties, especially estimates for the reaction rates of the different ZnO-C mixtures. The tests are made to establish the dependence of the reaction rate on the temperature, the C-type, the ZnO-type, the gas atmosphere, etc. An important goal was the ranking of the carbon sources based on the interesting properties. The results were used for choosing the carbon sources for the solar experiments.

Experimental Results

Pre Screening of the Carbon Sources. The different industrial carbon sources proposed by major coal and coke suppliers included pet coke, anthracite coal, and beech charcoal which have been tested in our pre-screening experiments are listed in Table 1. Also listed are some major properties of these materials such as the mass fraction of volatiles, the mass fraction of the nonvolatile carbon $C_{\rm fix}$, the total mass fraction of carbon $C_{\rm tot}$, and the mass

fraction of ash.

ZnO as an industrial quality (Grillo 2011) as well as a pure quality (Fluka) were used. No significant influence of the ZnO type on the reaction rate was observed.

Figure 3 shows some selected typical results of the thermogravimetric measurements. The molar ratio between C_{fix} and ZnO is 0.8:1. Depicted is the mass change of the samples relative to the weight prior to the beginning of the heating as a function of temperature. The heating rate is 10 K/min for all experiments. All sample curves show a horizontal or slight decreasing region at low temperatures where the volatiles are evaporated prior to the main reaction of ZnO and C. This region is followed by a region where a steep decrease of mass occurs. This decrease is due to the reaction of ZnO and C. The products are gaseous and transported



Fig. 3 Results of TG experiments for screening of carbon materials (molar ratio C_{fix} : ZnO=0.8:1)

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Table 2 Composition of the ash of beech charcoal (main components)

Component	SiO ₂	CaO	MgO	Al_2O_3	FeO	Na ₂ O	K ₂ O	MnO	TiO ₂	SO ₃
%	20.0	44.8	14.4	2.4	2.2	0.9	4.4	3.0	1.3	3.5

away by the gas flow. Thus the measured weight is strongly decreasing. Once the weight is constant or slightly decreasing the main reaction has finished.

The earlier (lower temperature) the reaction occurs and the steeper the decrease in mass (fast reaction) the better is the suitability of the carbon source for the solar process.

For example, for beech charcoal the main reaction occurs in the range 950–1100°C, for Starlight 1000–1300°C, and for Campana and Kalzinat (petcoke) even higher temperatures are required for a similar reaction rate.

Other criteria for suitability of a carbon source for the process include:

— A low ash content;

- a high ash fusion temperature;

— industrial availability; and

- an acceptable market price.

Based on all these considerations beech charcoal was chosen as a standard material for most experiments. A few solar tests have been conducted with some other materials as indicated in Table 1. The difference between the temperature needed for achieving a specified reaction rate when using a low reactive carbon source and the temperature needed for achieving the same reaction rate when using the beech charcoal in TG analyses is similar to the one found in solar tests. For the petcoke "Kalzinat" in both, the solar test (Fig. 9 in [14]) and the TG experiment (Fig. 3), one needs about 200 K higher temperature for obtaining a reaction rate similar to beech charcoal. This shows, that simple TG tests can be used for screening and selection of carbon materials.

A systematic TG-test of all materials in Table 1 using stoichiometric mixtures C_{fix} :ZnO of 1:1 confirmed the choice of beech charcoal as the "standard" reductant [25].

Characterization of the Beech Charcoal. Beside the amount of C_{fix} and the fraction of volatiles as listed in Table 1, the composition and behavior of the ash during a solar run is an important criterion for the selection of the carbon source and for designing the solar process. The fusion temperature of the ash should be high enough for avoiding formation of a molten slag/glass phase during the process. Thus the ash of the beech charcoal was analyzed for its composition and its fusion temperature. Typical ash fraction of the beech charcoal is around 2.2 mass-percent. Composition of the ash was analyzed by atomic absorption spectrometry. The results are listed in Table 2.

The softening temperature of the ash is 1210° C and the fusion temperature is 1415° C, respectively. Both temperatures have been determined by high temperature microscopy according to DIN 51730. A cylindrical sample (diameter=3 mm, height=3 mm) is heated. During heating the shape of the sample is monitored by means of a microscope. When the shape of the sample begins to change the softening temperature is reached. Deformation of the sample is increasing until the sample is finally melting when reaching fusion temperature.

The behavior of a beech charcoal ash sample during heating can be seen in Fig. 4. The dark rectangle is the image of the sample (for observing the change of the shape a grid is superposed). At 1210° C deformation of shape starts and is increasing with increasing temperature. At 1415° C the sample is melted completely.

Solar Experiments. 27 experiments were performed with the solar reactor depicted in Fig. 1. The typical duration of an experiment was between 70 and 140 minutes (maximal 170 min) including typically about 30–55 min for heating up and reaching approximately steady state conditions. The investigated solar

power input range was 3.3-7.8 kW which resulted in lower cavity temperatures between 1080 and 1340° C and separation wall temperatures of $1190-1520^{\circ}$ C. The standard carbon source for the experiments was beech charcoal powder (<200 μ m), mixed in a molar ratio of C_{fix}:ZnO=0.9:1. The standard gas flow rate was 4 1_n /min N₂.

Figure 5 shows the main readings of a typical experiment. The solar power input is stepwise increased up to 7.6 kW within the first 38 min. The temperature of the separation wall increases to 1480°C, those of the lower cavity reaches 1330°C. For lower cavity temperatures of 600°C and higher some H₂ is found in the off gas. This is caused by evaporating and cracking of the volatiles contained in the beech charcoal. As expected from the results of the thermogravimetric experiments, the reaction between carbon and ZnO starts at a lower cavity temperature of about 950°C as evident from the strong increase in the formation of CO and CO₂. 7 minutes later the upper cavity temperature reached its maximum of 1520°C accompanied with maxima of CO and CO₂ formation. Due to the low thermal conductivity of the ZnO-C mixture the temperature at the bottom of the fixed bed is still as low as 400°C in this period. The gas flow rate of CO reached 0.138 mol/min, that of CO₂ reached 0.013 mol/min, which is equivalent to a ZnO conversion rate of 13.3 g/min (this is followed by a slight decrease due to thin clouds reducing the solar input power). After 25 more minutes nearly all of the reactants mixture is reacted which results in a strong decrease of CO-CO₂ formation. Some minutes later the reaction terminates completely, the reaction chamber is empty and the temperature at the bottom of the fixed bed coincides with the temperature of the lower cavity.

The effective overall Zn-production rate, which is defined as the total amount of produced Zn per unit time and unit surface area of the fixed bed, strongly increases with temperature as shown in Fig. 6. Increasing the temperature in the lower cavity from 1100°C to 1250°C resulted in an increase of the effective overall reaction rate per bed surface area from 0.06 to $0.14 \text{ mol}/(\text{m}^2 \text{ s})$. Reducing the N_2 flow from







Fig. 5 Solar power input, product gas flow rates and reactor temperatures during a representative batch run of the reactor (500 g mixture of beach charcoal powder and ZnO with molar ratio C_{fix} : ZnO=0.9:1)

4 to $1.5 l_n/min$ did not result in significant changes in the effective reaction rate. As the process should be scaled up and the use of large amounts of N₂ is not desired at a pilot scale, for some experiments the N₂ in the gas flow was partially substituted by CO, as it would be available from the off gas (1 $l_n/min N_2$: 2.75 l_n/min CO and 0.25 $l_n/min N_2$: 0.5 l_n/min CO). No significant change in the overall Zn-production rate was found. Obviously the reaction rate is basically determined by the chemical processes in the upper layer of the ZnO–C bed and is only slightly influenced by the gas composition above it. This result implies the recycled off gas can be used instead of N₂ as the carrier gas in the pilot scale and in future industrial installations.

The importance of good mixing the reactants is indicated by the data points obtained from an experiment in which the reactants

have not been mixed but have been placed separately in the reaction chamber. In this experiment the Zn-production rate decreased by about a factor of 4 to 5.

Materials for the Separation Wall. One of the key points for designing a well working reactor is the material used for the separation wall. It has to withstand large temperature gradients in time and space, and it has to be resistant against the chemical atmosphere [Zn(g), CO, CO₂, H₂, H₂O, O₂, etc.]. Furthermore the material must withstand stresses induced by temperature cycles, and it should be commercially available in dimensions needed for a scaled up reactor. Table 3 gives a survey of the tested materials for application as the separation wall material. 170 mm diameter plates were used.



Fig. 6 Overall reaction rate as a function of temperature for different carrier gas flows (C_{fix}: ZnO=0.9:1)

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Table 3 Materials tested as separation wall material

No.	Type/Description	# of Tests	Problems occurred
1	Graphite	6	strong mass loss (oxidation)
2	SiC, nitride bonded	1	cracked
3	SiC, recrystallized	1	cracked
4	SiC, sintered	1	cracked
5	Long C fiber, coated with SiC	2	
6	Long C fiber, coated with SiC	5	
7	Short C fiber, infiltrated with Si, reacted to SiC	4	
8	Graphite with SiC layer	7	

All SiC materials (Nos. 2-4) failed due to cracks while heating up the reactor. We guess, that this problem could be overcome by intelligent segmentation of the plates, etc. This was not further investigated, since in the mean time we identified materials like Nos. 5-8, which appeared to be superior for this application. Pure graphite (No. 1) shows no mechanical problems but is significantly oxidized by CO₂ and H₂O present in the gas, as evident from the high mass loss occurring during the experiments (see Fig. 7). Most promising are the carbon-SiC composite materials as could be seen from Fig. 7. The weight of the separation wall made of material No. 7 increased slightly during the experiments which according to the manufacturer might be caused by the formation of some silicon nitride. On the other hand the samples made of materials Nos. 6 and 8 lost mass during the experiments but 40 times less than unprotected graphite. These losses are primarily located at the noncoated edges of the samples (the disks have been cut out of plates). Both materials are promising candidates for a scaled up reactor, more so, since coating of the edges is possible.

Efficiency. The energy required for heating the reactants and driving the chemical reaction $Q_{\text{reactants}}$ is given by the enthalpy difference between products *i* at T_i for which we use the lower cavity temperature T_{reactor} and educts *j* at T_j (ambient temperature).

$$Q_{\text{reactants}}(T_i, T_j) = \sum_i n_i \cdot H^0_{i, Ti} - \sum_j n_j \cdot H^0_{j, Tj}$$

with $i = CO, CO_2, Zn$, and $i = ZnO, C$ (7)

where H^0 is the enthalpy and *n* the amount of the respective species. The amounts of CO and CO₂ are measured by GC. The amounts of C and produced Zn are calculated from the amounts of CO and CO₂. This calculated amount of Zn fits to the amount which would be expected according to the mass balance of the ZnO in the fixed bed. However not all of the Zn was recovered in the condenser and the filter. This was caused by some joints where pipes (e.g., for gas outlet and for the thermocouples) intersect the



Fig. 7 Mass change of separation wall materials used in solar reactor tests

insulation material and the SiC lining. In these regions some Zn was diffusing into the insulation material and was also condensing at the inner side of the outer shell of the reactor. 50–95%, typically above 80% of the reacted Zn was recovered in the offgas system. Typically pure Zn was recovered, with negligible ZnO-content.

The energy amount Q_{N2} needed for heating the N₂ gas flow can be calculated as follows:

$$Q_{N_2} = n_{N_2} \int_{298 \text{ K}}^{T \text{reactor}} c_{p,N_2}(T) dT$$
(8)

where c_{p,N_2} is the specific heat capacity of N₂.

We evaluate the following three efficiencies:

(1) The thermal efficiency η_{thermal} describing the fraction of solar energy used for the process is defined as follows:

$$\eta_{\text{thermal}} = \frac{Q_{\text{reactants}}(T_{\text{reactor}}, 298 \text{ K}) + Q_{\text{N}_2}}{Q_{\text{solar}}}.$$
 (9)

(2) The energy storage efficiency η_{storage} characterizing the fraction of solar energy which is stored chemically at ambient temperature can be calculated by

$$\eta_{\text{storage}} = \frac{Q_{\text{reactants}}(298 \text{ K}, 298 \text{ K})}{Q_{\text{solar}}}.$$
 (10)

(3) The exergy efficiency η_{exergy} is defined as the fraction of solar energy which is converted into Gibbs free energy change of the reactants, i.e., the quantum of work which is maximal extractable by the process

$$_{\text{orgy}} = \frac{\sum_{i} n_{i} \cdot G_{i,298 \text{ K}}^{0} - \sum_{j} n_{j} \cdot G_{j,298 \text{ K}}^{0}}{Q_{\text{solar}}}$$
(11)

where G^0 is the Gibbs free energy of the appropriate species.

 $\eta_{\rm exe}$

The needed thermochemical data have been obtained by fitting thermodynamic data extracted from Barin [26]. Table 4 gives a survey of the main experimental results and the resulting efficiencies of some selected experiments. Data shown in the table have been determined during near steady state conditions, i.e., after heating to the desired temperature of the lower cavity.

The thermal efficiency of the reactor under approximately steady state conditions during the solar runs is in the range 11%–20% (around 7% for the run with nonmixed ZnO and beech charcoal), the storage efficiency reached up to 10.3% and the exergy efficiency reached up to 7.9%, respectively.

These are promising results more so, since the reactor was not especially designed for reaching a high performance but for generating input for designing a scaled up reactor as described above. First rough estimations on the thermal efficiency of a scaled up reactor at a solar power input level of 200 kW result in values around 35–40% [27]. More details on this topic are addressed in separate publications [28–30].

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Table 4 Main experimental results of some selected experiments (ZnO mixed with beech charcoal)

Experiment	Ι	II	III	IV	V	
$T_{\text{lower cavity}} / ^{\circ} \text{C}$	1177	1118	1191	1175	1156	
carrier gas flow $N_2/1/min$	4	4	1	1	0.3	
carrier gas flow CO/1/min			2.75	2.75	0.5	
separation wall material	6	7	8	7	6	
$n_{\rm CO}/{\rm mol}$	1.14	0.69	1.27	1.06	0.97	
$n_{\rm CO2}/\rm{mol}$	0.11	0.05	0.14	0.07	0.05	
n_{7} /mol	1.36	0.79	1.54	1.19	1.07	
$\dot{n}_{Zn}/\text{mol}/(\text{m}^2 \text{ s})$	0.11	0.06	0.13	0.075	0.075	
$O_{\rm solar}/\rm kWh$	0.89	0.91	0.94	1.05	0.88	
$\frac{2}{n_{\text{thermal}}}/\%$	20.1	12.0	19.5	14.0	14.4	
$n_{\text{dense}}/\%$	9.6	5.6	10.3	7.3	7.9	
$\eta_{\rm energy}/\%$	7.4	4.3	7.9	5.6	6.0	

Conclusions and Outlook

In the present paper we investigate the influence of temperature, carbon source, and carrier gas flow composition on solar carbothermal reduction of ZnO. Furthermore tests for choosing the material for building the separation wall between the two cavities of indirectly heated solar reactors are reported. The generated basic information is used to perform the next step in the SOLZINC project-the design and manufacturing of the scaled up pilot solar reactor. The planned pilot reactor will look similar to the small scale laboratory reactor shown in Fig. 1. The inner diameter of the lower cavity will be approximately 1.4 m, the height 0.8 m, respectively. The height of the upper cavity will be about 0.3 m. The reactor will be tested in the existing beam down solar facility of the Weizmann Institute of Science. For this purpose the aperture of the upper cavity will be mounted directly underneath the existing secondary concentrator. Like the small scale reactor the pilot reactor will be operated in batch mode. Typically after cooling down over night the lower part of the reaction chamber will be disconnected in the morning for (re-) filling with the reactants for one day of solar processing. The plant is designed for about 50 kg/h of Zn-production from day batches of up to 450 kg ZnO-C-mixtures. More design details of the pilot plant are given in [28,30].

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Nomenclature

- c_{p,N_2} = specific heat capacity of N₂ (kJ mol⁻¹ K⁻¹)
- $G_{i,T}^0$ = Gibbs free energy of species *i* at temperature *T* (kJ/mol)
- $H_{i,T}^0$ = enthalpy of species *i* at temperature *T* (kJ/mol) n_i = amount of substance *i* (mol)
- $Q_{\rm N_2}$ = energy for heating N₂ (kJ)
- $Q_{\text{reactants}}$ = energy for heating and reacting reactants (kJ)
 - $Q_{\text{solar}} = \text{solar energy input to the reactor (kJ)}$ T = temperature (°C)

- $\eta_{\text{exergy}} = \text{exergy efficiency}$
- $\eta_{\text{storage}} = \text{storage efficiency}$
- η_{thermal} = thermal efficiency

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