THE Zn/ZnO REDOX-CYCLE
FOR THE
CHEMICAL STORAGE OF SOLAR ENERGY

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZÜRICH

for the degree of
DOCTOR OF TECHNICAL SCIENCE

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Nomenclature

C = Solar concentration
DTA = Differential Thermal Analysis
EDX = Energy dispersive X-ray spectroscopy
ΔH = Enthalpy change (kW)
ΔG = Gibbs free enthalpy change (kJ/mol)
GC = Gas chromatograph
Fpeak = Peak solar flux intensity (kW/m²)
I = Normal beam insolation (kW/m²)
MS = Mass spectrometer
p = Pressure (mbar)
Qaperture = Incoming solar power intercepted by Aperture (kW)
Qreactor.net = Net power absorbed by the solar reactor (kW)
Qsolar = Total solar power coming from the concentrator (kW)
SEM = Scanning Electron Microscopy
TEM = Transmission Electron Microscopy
Treactor = Nominal cavity-receiver temperature (K)
TGA = Thermogravimetric analysis
r aperture = Radius of reactor aperture (m)
or = Optimum radius of reactor aperture for maximum ηabsorption (m)
α, ε = Apparent absorptance and emittance of the solar cavity-receiver
ηabsorption = Solar energy absorption efficiency
XPS = X-ray photoelectron spectroscopy
XRD = X-ray powder diffraction
μ = Radial standard deviation of Gaussian flux distribution (m)
σ = Stefan-Boltzmann constant (5.6705×10⁻⁸ Wm⁻²K⁻⁴)
0. Einleitung

Chemische Speicherung von Sonnenenergie

Die einzige uns bekannte erneuerbare Energiequelle ist die Sonne. Auch die fossilen Energieträger, die heutzutage den Großteil des Weltenergiebedarfs abdecken, sind das Produkt einer Sonnenenergieumformung in chemisches Potential. Sie sind jedoch umweltschädlich, wenn man sie verbrennt und nicht erneuerbar.

Die Sonne entspricht einem schwarzen Strahler mit einer Oberflächentemperatur von 5800 K. Die bei uns auf der Erde einfallende Strahlung ist stark verdünnt und nicht kontinuierlich. Im Mittel beträgt sie je nach Region ca. 1 kW/m². Die Strahlungsenergie, die im Verlauf eines Jahres die Erdoberfläche erreicht, ist jedoch mehr als genug um den Weltenergiebedarf zu decken. Vorausgesetzt, es ist möglich Sonnenenergie mit einem Umwandlungswirkungsgrad von 20% in eine speicherbare und transportierbare Form zu bringen, bräuchte man nur eine Fläche von 490 km² (siehe Abbildung 1) für die Bereitstellung sämtlicher benötigter Energie.

Abbildung 1: Sonneneinstrahlung auf der Erdoberfläche pro Jahr [Krieth & Krieger 1978]
Konzentriert man die Einstrahlung, so kann sie eingesetzt werden, um die Wärmeenergie für endotherme Umsetzungen bereitzustellen und somit wie bei der Photosynthese Sonnenenergie in chemisches Potential umzusetzen. So kann sie in Form von neuen Solarenergieträgern anschliessend von den sonnigen und spärlich besiedelten Gebieten des Sonnengürtels der Erde zu den industrialisierten und dicht bevölkerten Zentren mit hohem Energiebedarf transportiert werden.


Abbildung 2: Wirkungsgrad η eines solarthermischen Konverters als Funktion der Absorbertemperatur $T_A$ und des Konzentrationsfaktors $C$ bei Direkeinstrahlung von 1 kW/m$^2$.

Abbildung 3: Der neue Solarkonzentrator am PSI

Durch das Einfangen und Konzentrieren des Sonnenlichts in Solarkonzentrator-Anlagen (s. Abbildung 3) gelingt es, Hochtemperatur-Prozesswärme (oberhalb 2000°C) und Hochfluss-Solarstrahlung (mehr als 5000 kW/m²) zu erzeugen, um thermochemische Prozesse im Hinblick auf die Produktion von solaren Brennstoffen anzutreiben.


Konventionell wird Zink durch karbothermische oder elektrolytische Reduktion von Zinkoxid gewonnen. Es handelt sich dabei um energieintensive Prozesse, die bei
hohen Temperaturen ablaufen und grosse Mengen an Treibhausgasen in die Atmosphäre freisetzen (s. Kapitel 7). Diese Emissionen können signifikant reduziert werden, wenn konzentrierte Solarstrahlung als Energiequelle für die Hochtemperatur-Prozesswärme benutzt wird. Auf diese Weise kann Sonnenstrahlung in sonnenreichen Wüstengegenden durch thermochemische Transformation effizient in speicherbare und transportable Brennstoffe umgewandelt werden (s. Kapitel 1).


Es kann auch ein indirekter Weg eingeschlagen werden, der die karbothermische Reduktion von Metalloxiden verfolgt, jedoch fossile Energieträger (wie z.B. Kohle oder Erdgas) lediglich als Reduktionsmittel einsetzt und zur Bereitstellung der Prozesswärme konzentrierte Solarstrahlung nutzt [Steinfeld, Brack et al 1998], [Berman & Epstein]. Der Vorteil dieser Reaktionen liegt in den moderaten Prozesstemperaturen, wodurch die Anforderungen an die Prozesstechnologie wesentlich vereinfacht werden (siehe Kapitel 6). Durch diese Kombination einer konventionellen Technologie mit einer neuen können Brennstoffe mit einem durch Sonnenenergie angehobenen Energiegehalt hergestellt werden.

Neben ihrem Einsatz als chemische Sonnenenergiespeicher können diese Produkte auch als ökologisch sauberer hergestellte industrielle Erzeugnisse schneller ihren Einzug in die kommerzielle Anwendung finden, als Produkte aus reinen Solarprozessen. Ein solcher Energiemix, der auf fossilen Energieanlagen basierenden bestehender Technologien und der Sonnenenergie beruht, sollte eine Zwischenstufe auf dem Weg in das
zukünftige solarchemische Zeitalter darstellen, und Brücken zwischen heutigen und zukünftigen Energiewirtschaften bauen (s. Kapitel 2).


und den Zinkoxidpartikeln, welche entlang der heißen Reaktorwand bewegt werden. Somit wird die Energie effizient an die Reaktanden übertragen. Die ZnO Partikel werden in diesem Reaktortyp optimal vom Gasstrom umspült, wodurch ein sofortiger Produktabtransport gewährleistet wird, welcher zu höheren Dissoziationsraten führt (siehe Kapitel 2).


Die im Rahmen dieser Dissertation durchgeführten Solarexperimente, haben gezeigt, dass konzentrierte Sonnenenergie eingesetzt werden kann, um Zink aus Zinkoxid darzustellen. Dabei werden die Produkte durch die Kondensation von Zink während des einen Abkühlens getrennt. Setzt man Methan als Reduktionsmittel hinzu, so kann die Reduktion von ZnO bei niedrigeren Temperaturen erfolgen und die Reoxidation des kondensierenden Zinks wird durch das Produktgasgemisch von CO und H\textsubscript{2} unterdrückt.

Um ein besseres Verständnis der Reaktion und den Einfluss sämtlicher Prozessparameter zu bekommen, wurden im Rahmen dieser Doktorarbeit zusätzliche Studien im Labor (s. Kapitel 3 und 4) und in einem Batch-Solarreaktor in der 2 kW Solaranlage am IMP-CNRS in Odeillo, Frankreich durchgeführt (s. Kapitel 5).
1. CO₂ Abatement by Producing New Solar Energy Carriers - Product Formation in High Temperature Solar Chemistry

The potential of solar energy utilisation may be illustrated by comparing the anthropogenic annual world energy consumption of approximately $10^{14}$ kWh with the nearly $10^{18}$ kWh solar radiation reaching annually the Earth's atmosphere. The main energy carriers, however, are fossil fuels, which are the products of solar radiation converted into chemical potential by photosynthesis. They are taken irreplaceably from the Earth’s crust and return as CO₂ and other polluting substances into the environment. To provide carbon-free renewable energy carriers we consider simple and environmentally clean ways for a conversion of concentrated solar radiation into chemical potential. Specialy we investigate the thermal decomposition of zinc oxide and iron oxide to produce new solar energy carriers, that can be stored and transported over long distances. Figure 4 represents a closed cycle for producing hydrogen from water using the ZnO/Zn or Fe₂O₃/FeO redox systems [Nakamura 1977], [Bilgen, Ducarroir et al. 1977], [Tofighi & Sibieude 1984].
Figure 4: Schematic representation of a two-step thermochemical water-splitting cycle using the ZnO/Zn or the Fe$_3$O$_4$/FeO redox system. In the first endothermic solar step at temperatures around 2300 K, the metal oxide is thermally decomposed into a metal or a lower-valence metal oxide and oxygen. Concentrated solar radiation is the source of the required high-temperature process heat. In the second exothermic step, the metal reacts with water to produce hydrogen; the resulting metal oxide is then recycled back to the first step. The net reaction is: $\text{H}_2\text{O} = \text{H}_2 + 0.5 \text{O}_2$; hydrogen and oxygen are produced in different steps, eliminating the need for high temperature gas separation.

For comparison, Table 1 indicates the specific electricity output of two representative solar fuels and two representative fossil fuels.

<table>
<thead>
<tr>
<th>fuel</th>
<th>products</th>
<th>electric work output</th>
</tr>
</thead>
<tbody>
<tr>
<td>coal (anthracite)</td>
<td>$\text{CO}_2$, $\text{H}_2\text{O}$, $\text{SO}_x$, $\text{NO}_x$, solid and liquid by products</td>
<td>$\ast\ast 2.5 \text{kWh} / \text{kg}$</td>
</tr>
<tr>
<td>oil</td>
<td>$\text{CO}_2$, $\text{H}_2\text{O}$, $\text{SO}_x$, $\text{NO}_x$, solid and liquid by products</td>
<td>$\ast\ast\ast 3.7 \text{kWh} / \text{kg}$</td>
</tr>
<tr>
<td>hydrogen</td>
<td>$\text{H}_2\text{O}$</td>
<td>$\ast 33.2 \text{kWh} / \text{kg}$</td>
</tr>
<tr>
<td>zinc</td>
<td>$\text{ZnO}$</td>
<td>$\ast\ast 1.1 \text{kWh} / \text{kg}$</td>
</tr>
</tbody>
</table>

Table 1: Old and New Chemical Solar Energy Carriers

Assumptions:
- $\ast$ efficiency of $\text{H}_2\text{O}_2$ fuel cell = 83% [Abbleby & Foulkes 1998]
- $\ast\ast$ efficiency of Znair battery = 79% [Haas 1998]
- $\ast\ast\ast$ efficiency of coal power plant = 28% [Frischknecht, Hofstetter et al. 1997]
- $\ast\ast\ast\ast$ efficiency of turbine and electric generator = 31%
The solar facilities at PSI allow to test processes that store solar energy at high temperatures. Concentrated solar radiation can supply process heat at temperatures of 2500 K in specially designed solar reactors. Through these reactors, the reactants flow in a continuous mode absorbing the solar energy and leaving it in an energetically higher state. We use inorganic solid reactants (oxides and carbonates), which can melt or evaporate when they enter the reaction zone, and they decompose at high temperatures to form at least one gaseous product. The phase of the products affects the kinetics of the reverse reaction. Table 2 classifies three types of endothermic processes $AB(s) \rightarrow A + B(g)$ according to the product phases and, for each type, shows an example of a chemical reaction and its reverse reaction characteristics.

<table>
<thead>
<tr>
<th>AB(s) $\rightarrow$ A + B(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
</tr>
<tr>
<td>A is solid,</td>
</tr>
<tr>
<td>B is an unreactive gas</td>
</tr>
<tr>
<td>Example *:</td>
</tr>
<tr>
<td>A = CaO(s), B = CO$_2$</td>
</tr>
<tr>
<td>reverse reaction is slow;</td>
</tr>
<tr>
<td>process can be conducted</td>
</tr>
<tr>
<td>in the presence of air;</td>
</tr>
<tr>
<td>recovery of sensible heat</td>
</tr>
<tr>
<td>is possible.</td>
</tr>
<tr>
<td>Type 2</td>
</tr>
<tr>
<td>A is liquid,</td>
</tr>
<tr>
<td>B is a reactive gas</td>
</tr>
<tr>
<td>Example :</td>
</tr>
<tr>
<td>A = FeO(l), B = O$_2$</td>
</tr>
<tr>
<td>reverse reaction is fast;</td>
</tr>
<tr>
<td>in-situ separation and</td>
</tr>
<tr>
<td>recovery of sensible heat</td>
</tr>
<tr>
<td>is required.</td>
</tr>
<tr>
<td>Type 3</td>
</tr>
<tr>
<td>A is gaseous,</td>
</tr>
<tr>
<td>B is a reactive gas</td>
</tr>
<tr>
<td>Example :</td>
</tr>
<tr>
<td>A = Zn(g), B = O$_2$</td>
</tr>
<tr>
<td>reverse reaction is</td>
</tr>
<tr>
<td>heterogeneous; quenching</td>
</tr>
<tr>
<td>in the absence of nucleation</td>
</tr>
<tr>
<td>sites is required.</td>
</tr>
</tbody>
</table>

**Table 2 : High Temperature Solar Chemistry Reactions**

* The solar limestone decomposition (Example Nr. 1) is not a solar fuel production process. But CO$_2$ mitigation potential by using solar energy for the calcination process instead of burning fossil fuels, can be as high as 20%. This reaction was effected at PSI solar furnace using a cyclone-type reactor [Steinfeld, Imhof, et al. 1992].

The decomposition of iron oxide and zinc oxide proceeds endothermically at elevated temperatures, according to

$$\text{Fe}_3\text{O}_4(s) \rightarrow 3 \text{FeO(l)} + \text{O}_2$$ \hspace{1cm} (I)

$$\text{ZnO(s)} \rightarrow \text{Zn(g)} + \text{O}_2$$ \hspace{1cm} (II)
If we assume that the reactants are fed at 300 K and complete conversion is obtained at 2300 K, the enthalpies of the reaction are $\Delta H_1 = 784 \text{ kJ/mole}$ and $\Delta H_2 = 557 \text{ kJ/mol}$ for the reactions (I) and (II), respectively.

The theoretical maximum solar energy conversion efficiency were calculated for both reactions (I) and (II) a second-law analysis was conducted [Steinfeld 1995], [Steinfeld & Palumbo 1997].

At high temperatures, in the focus of the solar reactor, the thermal decomposition takes place because the reaction equilibrium is shifted towards the products. $\Delta G$ of the reaction is negative at high T. However, during the cooling of the products to ambient temperatures, a back reaction can occur, because $\Delta G$ becomes positive. We can avoid the product reoxidation by hindering the kinetics of the back reaction or by in situ separation of the products. At ambient temperatures the products are thermodynamically unstable, but kinetically stabilised. Solid state chemistry reactions are usually slow at room temperature, because of the very low diffusion coefficient of ions in the solid. After supplying the activation energy, the exothermic back reaction takes place and one can make use of the released energy.

A comparison with plant photosynthesis may be illustrative at this point. The conversion of $\text{CO}_2$ and $\text{H}_2\text{O}$ into hydrocarbons by photosynthesis can be seen as a concentration of Carbon atoms which requires energy. The products are metastable substances with a higher energetic value than the reactants. The solar energy stored in the C-C-bonds can be released when the activation energy is supplied, and when they are oxidised to yield $\text{H}_2\text{O}$ and $\text{CO}_2$.

**Dissociation of magnetite**

Iron oxides can be treated like iron dissolved in an oxygen solution. The reduction is a concentration of iron and the oxidation is a dissolution. At high temperatures magnetite particles are melting and oxygen desorbs from the surface of the droplets (see Figure 5) while iron ions move to the inner part of the reducing phase. If the cooling process is faster than the back reaction, as during a fast quenching we can ‘freeze-in’ a high temperature species, such as wüstit. 
Figure 5: Part of the defect structure of wüüstite and the inverse spinel structure of magnetite

In the phase diagram (Figure 6) we see that wüüstite is not stable at temperatures below 840 K. It disproportionates to iron and magnetite. In solar thermal reduction experiments of magnetite, the metastable phase is stabilised at room temperature by quenching procedures [Ehrensberger 1996]. The wüüstite phases produced by solar magnetite reduction are in a metastable phase; as such they are storable for years. The ion diffusion in the solid is very slow at room temperature [Weidenkaff, Nüesch, et al. 1997].

Figure 6: The iron-oxygen phase diagram in the range of wüüstite

Dissociation of zinc oxide

The ZnO decomposition reaction was performed using a vortex-flow reactor [Steinfeld, Brack, et al. 1998]. ZnO dissociates at high temperatures to zinc vapour and oxygen which both evolve from a shrinking particle. During the cooling down, when the gases leave the hot zone of the reactor, zinc begins to condense and can recombine with oxygen to form solid ZnO. For this reoxidation phenomena, a nucleation site is neces-
sary because latent energy of this very exothermic process has to be released. The growth of zinc can take place on the surface of incompletely reacted zinc oxide, on the surface of cool reactor walls or on the surface of a water cooled condenser. Zinc, even if it is used as a galvanising metal against corrosion, is metastable at room temperature. Like aluminium and other non-noble metals, zinc is inert to oxygen at room temperature because of the formation of a ‘protecting skin’ (thin metal oxide layer on its surface) preventing the particle from bulk oxidation. The transport of ions through this very dense solid layer is very slow.

The influence of the deposition rate, the material and the temperature of nucleation sites, the oxygen partial pressure and the flow rate on the condensation and crystallisation of zinc is still subject of research. The condensation and crystallisation of zinc in the presence of oxygen was studied by thermochromatography [Weidenkaff, Steinfield, et al. 1999]. By analysing the morphology of the condensed phase with electron microscopy we found that zinc grows in form of spheres at temperatures above the zinc melting point, as a result of the deposition of liquid Zn followed by crystallisation (and oxidation depending on O₂ dilution). At temperatures lower than the melting point of zinc, we observe the growth of crystals, as a result of the desublimation of Zn. SEM pictures of different reoxidated Zn particles show the formation of ZnO needles on the surface of zinc particles due to a low zinc- and a high oxygen partial pressure at the end of every experiment.

If the product formation takes place in reducing atmosphere such as in the ‘SynMet process’ ZnO + CH₄ → Zn + 2H₂ + CO [Steinfeld, Brack, et al. 1998], reoxidation is unlikely. The products obtained from the hot reactor walls near the outlet (700°C > T > 400°C) show the formation of dendritic structures. Products formed at lower temperatures (T < 200°C) show a different morphology of spheres.

1.2. Summary and Conclusions

The described high temperature thermochemical processes are well-suited for the storage of solar energy and therefore for the substitution of fossil fuels and the abatement of CO₂. The mechanisms of the corresponding processes are characterised in terms of reversible heterogeneous solid state reactions.
The gas desorption from reactants, the adsorption and the transport of ions through particles plays an important role in high temperature solar processes for energy storage. The surface of the product, exposed to air, should be small to prevent product particles from recombination.

The results are decisive for the selection of the required engineering systems. If these solar processes can be realised in an industrial scale in the sunbelt of the Earth, we can imagine a future energy system that is CO$_2$ neutral and that can provide enough storable and transportable energy to cover the world energy demand.
2. Solar Thermal Production of Zinc: Program Strategy and Status of Research

Zinc is a versatile metal: besides being a widely used commodity in the galvanising and chemical industries, it is also a compact and safe-to-handle solid fuel that finds applications in Zn/air fuel cells and batteries. Zinc can also be reacted with water and form hydrogen that can be further processed for heat and electricity generation. The chemical product from these power generation processes is zinc oxide, which in turn needs to be reduced to zinc and recycled. However, the current industrial production of zinc carries severe environmental consequences. The commercial production techniques by electrolytic and smelting furnaces are characterised by their high energy consumption and their concomitant environmental pollution: the zinc world production amounts to about 7 million tonnes per year and discharges annually approximately 66 million tonnes of CO$_2$ to the atmosphere [Steinfeld 1997]. These emissions are derived mostly from the combustion of fossil fuels and could be substantially reduced by using instead concentrated solar radiation as the energy source of high-temperature process heat.

The thermochemical path for producing zinc using solar energy is further justified by thermodynamic arguments: the energy conversion efficiency can exceed 50% [Palumbo, Steinfeld, et al. 1998], [Steinfeld, Larson, et al. 1996]. High efficiencies directly translates to lower solar collection area and associated costs of the heliostat field, which amount to 25-30% of the capital cost for the entire solar chemical plant [Steinfeld & Spiewag 1998]. Under these assumptions, a recent economic assessment for a large-scale chemical plant indicates that the solar thermal production of zinc might be competitive with other renewable technologies (e.g. solar electricity plus electrolysis of ZnO), and, under proper conditions, be competitive even with conventional fossil-fuel-based processes at current fossil fuel prices plant [Steinfeld & Spiewag 1998].

* The contents of this chapter have been published in J. Phys. IV by A. Weidenkaff, M. Brack, S. Möller, R. Palumbo, A. Steinfeld
High-Temperature Solar Technology
Paul Scherrer Institute, CH-5232 Villigen PSL, Switzerland
Solar-made zinc offers the possibility of storing and transporting solar energy. Our ultimate objective is to develop a technically and economically viable technology for a solar thermal process that can produce zinc as a transportable chemical fuel.

2.1. Strategy

The strategy for reaching our long-term objective involves research on two paths, as illustrated in Figure 7 [Steinfeld 1996]:

1) the direct path via the direct solar thermal splitting of ZnO, represented by:

\[ \text{ZnO} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \quad (1) \]

2) the indirect path via the solar carbothermal and CH₄-thermal reduction of ZnO, represented by:

\[ \text{ZnO} + \text{C(gr)} \rightarrow \text{Zn} + \text{CO} \quad (2) \]

and \[ \text{ZnO} + \text{CH}_4 \rightarrow \text{Zn} + 2\text{H}_2 + \text{CO} \quad (3) \]

Figure 7: Strategy for the substitution of fossil fuels with solar fuels (zinc and hydrogen) involves research on two paths: a direct path via the solar thermal splitting of ZnO and an indirect path via the solar carbothermal/CH₄-thermal reduction of ZnO.

Reaction (1) proceeds at elevated temperatures (above about 2000 K) using solar process heat [Palumbo, Lédé, et al. 1998]. Such high-temperature reaction requires the
The development of a completely novel process engineering technology and will take time before such technology will be ready for large-scale commercialisation. It is clear that one should start developing now if one wishes to be ready in 30 years and avoid expensive and riddled-with-mistakes crash programs. This path requires supporting a continuous program of research, development, and demonstration. An overview of this research program are given in Ref. [Palumbo 1998].

Reactions (2) and (3) make use of fossil fuels exclusively as chemical reducing agents (such as C(gr) from coal or CH₄ from natural gas (NG)). Process heat is supplied by solar energy and not by the combustion of fossil fuels. The products of reactions (2) and (3) are cleaner fuels with a solar-upgraded energetic value because the solar input increases their energy content above the value of the fossil fuel. In the presence of a reducing agent, such as C(gr) and CH₄, the uptake of oxygen by the formation of CO brings about the thermal reduction of ZnO to Zn at much lower temperatures, above about 1300 K [Murray, Steinfeld, et al. 1995], [Steinfeld, Frei, et al. 1995]. Thus, reactions (2) and (3) require more moderate and presently, more technically-feasible temperatures. They use a combination of novel and conventional process technologies. Traditional materials and reactor concepts are thus possible for the mixed fuel/solar energy technology. With this path we hope to reduce the lead time for transferring important solar technology to industry. This route is an important intermediate solution toward a sustainable energy supply.

Pursuing R&D in both the direct and indirect path is a recommended strategy. The direct path helps define the "point of the compass" and brings us to the ultimate goal of substituting fossil for solar fuels. The indirect path helps create a link between today's fossil-fuel-based technology and tomorrow's solar chemical technology, and build bridges between present and future energy economies. The transition from fossil to solar fuels can occur smoothly with the help of processes that mix fossil fuels and solar energy.

2.2. Chemical Thermodynamics And Kinetics

The chemical thermodynamics and kinetics of reactions (1) to (3) have been reported in previous publications [Palumbo, Lédé, et al. 1998], [Steinfeld, Larson, et al.
For reaction (1), the equilibrium mole fractions of Zn(g) and O\textsubscript{2} are 0.67 and 0.33, respectively, in the temperature range 1700-2400 K [Palumbo, Lédé, et al. 1998]. The reaction enthalpy is $\Delta H_{298K} = 478$ kJ/mol. The decomposition rate of ZnO(s) was measured by thermogravimetry in a N\textsubscript{2} atmosphere; the apparent activation energy obtained was 312 kJ/mol, which is similar to a value cited in [Hirschwald & Stolze 1972]. The products gases need to be quenched to avoid re-oxidation; the efficiency of the quench is sensitive to the dilution ratio and surface temperature on which the products are quenched. A 2\textsuperscript{nd} law analysis of the ZnO decomposition/quench process indicates a maximum energy conversion efficiency of 55\%. The condensation of Zn(g) in the presence of O\textsubscript{2} was studied by fractional crystallisation in a temperature-gradient tube furnace. The oxidation of Zn is a heterogeneous process and, in the absence of nucleation sites, Zn(g) and O\textsubscript{2} can coexist in a meta-stable state [Weidenkaff, Steinfeld, et al. 1999].

For reaction (2), the enthalpy change is $\Delta H_{298K} = 365$ kJ/mol, and the equilibrium mole fractions of Zn(g) and CO are 0.5 at temperatures above 1200 K. For reaction (3), the enthalpy change is $\Delta H_{298K} = 440$ kJ/mol, and the chemical equilibrium composition of the system ZnO+CH\textsubscript{4} at 1250 K and 1 bar consists of a single gas phase containing Zn (vapour) and a 2:1 mixture of H\textsubscript{2} and CO [Steinfeld, Larson, et al. 1996], [Steinfeld, Frei, et al. 1995]. Assuming that chemical equilibrium is obtained in a black-body solar reactor operated at 1250 K and 1 atm, and with a solar power-flux concentration of 2000, closed-cycle efficiencies vary between 40 and 65\%, depending on the recovery of the product sensible heat [Steinfeld, Larson, et al. 1996]. The apparent activation energy obtained by thermogravimetric measurements on ZnO powder was 146 kJ/mol [Steinfeld, Frei, et al. 1995]. The reaction mechanism was found to be controlled by gas film diffusion in the Stokes regime. Energy and mass balances indicate that the use of solar process heat for reaction (3) upgrades the calorific value of the initial reactants by 39\% and, when compared to the traditional carbothermic reduction of ZnO, has the potential of reducing CO\textsubscript{2} emissions by up to 78\% [Steinfeld & Spiewag 1998].
Reactions (1) to (3) were effected at the solar furnaces of PSI (Switzerland), University of Minnesota (USA), Weizmann Institute (Israel), and CNRS (France) [Palumbo, Lédé et al. 1998], [Murray, Steinfeld et al. 1995], [Steinfeld, Frei, et al. 1995], [Möller 1996]. [Bilgen. Ducarroir, et al. 1977], [Epstein, Ehrensberger, et al. 1997], [Boutin 1996]. These solar experiments were exploratory in nature and their aim was to gain insights and acquire experience with the reduction of ZnO using high-temperature solar energy. Based on these previous studies and on the constraints that the chemistry places on the engineering design of solar chemical reactors, we have proceeded with the development of solar reactors that can operate continuously and have the potential of being scaleable for large-scale industrial applications. This work is now in progress. An example of a solar reactor for reducing Zn with CH₄ is shown next.

2.3. Solar Chemical Reactor Technology

Solar Reactor Design

A solar chemical reactor for performing reaction (3) was designed and a 5-kW prototype reactor was fabricated and tested. The design methodology and construction details have been previously described [Steinfeld, Brack, et al. 1998]. It consists of an insulated cylindrical cavity made of heat-resistant steel (m.p. 1670 K) that contains a windowed aperture to let in concentrated solar energy. Particles of ZnO, conveyed in a flow of NG, are continuously injected into the reactor's cavity via a tangential inlet port located at the back of the cavity. The gas-particle stream forms a vortex flow that progresses towards the front along a helical path. The chemical products, zinc vapour and syngas, continuously exit the cavity via a tangential outlet port located at the front of the cavity, behind the aperture. The quartz window is actively cooled and kept clear of particles by means of an auxiliary gas flow that is injected at the window and aperture planes. With this arrangement, the particles of ZnO are directly exposed to the high-flux irradiation. Such concept provides efficient radiation heat transfer directly to the reaction site, by-passing the limitations imposed by indirect heat transport via heat exchangers. Energy absorbed by the reactants is used to raise their temperature to above 1200 K, and to drive the simultaneous reduction of ZnO and reforming of NG.
Solar Experimental Results

Solar experimentation was conducted at the PSI's high-flux solar furnaces\(^1\). The 1997 experimental campaign was conducted at the smaller solar furnace which is capable of delivering peak flux concentrations of up to 3000 suns (1 sun = 1 kW/m\(^2\)). The 1998 experimental campaign was conducted at the new solar furnace which delivers peak solar concentration exceeding 5000 suns. The experimental set-up and results from the test campaign performed in 1997 were already presented in Ref. [Steinfeld, Brack, et al.]. In this section we present recent results obtained during the test campaign of spring 98.

ZnO powder (mean particle size of 0.4 \(\mu\)m) was fed at a rate of 4.8 gr/min. Main inlet gas flow rate, for various concentrations of CH\(_4\) in Ar, was varied in the 5-20 l\(\text{m}^3\)/min\(^1\) range. The auxiliary flow for the window protection was in the 20-40 l\(\text{m}^3\)/min range. The loading ratio of particles to gas was kept below the stoichiometric ratio (as given by equation (3) to avoid plugging and to protect the window from particle deposition. During a typical experiment, the reactor was solar-heated to the desired temperature under a flow of Ar and then isothermally subjected to the reacting flow. Maximum reactor wall temperatures, under approximate steady-state conditions, ranged between 1000-1600 K. The particles of ZnO were forced to the walls by the centrifugal force and were efficiently heated by contact with the hot walls and by direct absorption. Zinc vapour exiting the reactor was condensed in a Pyrex water-cooled tubular condenser.

The chemical conversion of ZnO to Zn obtained is shown in Table 3; the maximum reactor wall temperature, the CH\(_4\) concentration of the inlet gas, the main inlet mass flow rate and its inlet temperature are also indicated. As expected, best results were obtained at higher temperatures, higher CH\(_4\) concentrations, and when the reactants were pre-heated. The main differences between the 1997 and 1998 test campaigns are the inlet mass flow rate and the ZnO-feeding. As the inlet flow decreases, the residence time of the reactants at the hot reaction zone increases, leading to much higher zinc yields and approaching complete conversion. An additional consequence of reduc-

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\(^1\) Technical information on PSI's solar facilities may be obtained at www1.psi.ch/www_f5_hn/Solar/solar_home.html.
ing the inlet flow is that large ZnO particles which often result from agglomeration of poorly dispersed small particles are not conveyed and deposit on the reactor's cavity. These sediments eventually react and the product gases are finally transported out of the reactor. In contrast, when using 15-20 l/min, even large agglomerations of ZnO particles are conveyed and eventually leave the reactor before achieving complete reduction.

Zinc vapour exits the reactor in a reducing atmosphere of H₂, CO, and unreacted CH₄. Zinc is separated from the gas phase by condensation on the cold surface of the condenser. Zinc lost by re-oxidation during condensation is negligible. The implications of this simple observation are remarkable when one contemplates the conventional carbothermic smelting process, wherein coke serves as both reducing agent and primary energy source. There, coke is supplied in much excess of what is needed for reducing ZnO (about 4-6 times more), because it is burned internally to supply for the process heat [Graf 1996]. Thus, zinc vapour is produced together with CO₂, and as the gases are cooled and zinc condenses, it can react immediately with CO₂. Industrially, the re-oxidation of zinc by CO₂ is avoided by using lead-spray condensers, in which a shower of 400 tons of molten lead are needed to separate 1 ton of zinc from the gas phase [Graf 1996]. The proposed solar process eliminates the need for Pb condensers.

Several solar runs were conducted without CH₄, in which reaction (1) was tested using 100% Ar or N₂ in the carrier gas. The results of these runs are also shown in Table 3 (see for “0” in the “%CH₄-Ar” column). In the absence of a reducing agent, ZnO(s) dissociates to Zn(g) and O₂ and some portion of the zinc is subjected to re-oxidation during condensation. Higher zinc yields are obtained when using higher dilution of inert gas, but at the expense of reducing the energy efficiency. By studying the morphology of the solid products using scanning electron microscopy it is possible to distinguish between ZnO-particles formed by zinc re-oxidation and ZnO-particles from unreacted reactants [Weidenkaff, Steinfeld, et al. 1999]. For the runs of 1998 without CH₄, all of the ZnO collected in the condenser derived from the re-oxidation of zinc.

\[ \text{ZnO} + 2 \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O} + \text{CO} \]

† In means liters at normal conditions; mass flow rates are calculated at 273 K and 1 atm.
<table>
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Table 3: Results from the solar experimental campaigns of 1997 and 1998. Indicated are: maximum wall temperature ($T_{\text{max}}$), methane concentration in the inlet gas, main inlet mass flow rate and inlet temperature, and zinc yield obtained.

* 100% Ar in main and auxiliary flows; total 45 l/min
** 100% N₂ in main and auxiliary flows; total 45 l/min

Chemical conversion (or zinc yield) is defined as the amount of zinc produced in the solar furnace divided by the maximum amount of zinc that would have been recovered if the reaction had gone to completion. Representative product samples are taken from the material collected in the condenser and are analysed by X-ray diffraction and by measuring the volume of hydrogen evolved when reacted with HCl. The accuracy of such technique is ±7%. 


2.4. Summary and Conclusions

We have described our program strategy for developing a technically and economically viable technology for a solar thermal process that can produce zinc as a transportable chemical fuel. The program involves research on two paths: a direct path via the solar thermal splitting of ZnO in the absence of fossil fuels, and an indirect path via the solar carbothermal/CH₄-thermal reduction of ZnO, with fossil fuels (coke or NG) as chemical reducing agents. Both paths make use of concentrated solar energy for high-temperature process heat. The direct path requires elevated temperatures and the development of a novel solar process technology, while the indirect path requires more moderate temperatures and uses a combination of solar and conventional energy technologies. The transition from fossil fuels to solar fuels can occur smoothly with the help of processes that mix both fossil fuels and solar energy.

The use of NG as reducing agent combines in a single process the reforming of CH₄ to produce syngas and the reduction of ZnO to produce Zn. The advantages of the combined solar process are: the calorific value of the initial reactants can be upgraded by 39%; CO₂ emissions can be reduced by up to 78%, as compared to the emissions from the traditional smelting process; maximum energy conversion efficiencies exceed 50%; high-purity zinc can be separated without the need for Pb condensers. An economic assessment for a 50,000 tonnes/yr chemical plant, 30 to 51 MW solar input, indicates that the cost of solar zinc ranges between 89 to 133 S/tonnes (excluding the cost of ZnO feed and credit for pollution abatement), and thus might be competitive with conventional fossil-fuel-based processes at current fuel prices [Steinfeld & Spiewag 1998].

We have presented the results of solar tests using a gas-particle vortex flow confined to a solar cavity-receiver that is exposed to concentrated solar irradiation. Tests were conducted from 1000 to 1600 K and yielded high-purity zinc. The vortex flow configuration was proven to be an efficient reactor concept for the transfer of heat to gas flows laden with particles, such as the case of NG laden with ZnO particles. The technical feasibility of large-scale solar reactors and heat recovery techniques needs demonstration.
3. **Thermogravimetric Analysis of the ZnO/Zn Water-splitting Cycle**

Hydrogen is an attractive clean fuel when produced from water and the energy required to produce it is obtained from a renewable source, e.g., solar energy. Concentrated solar energy can supply process heat for driving endothermic processes at high temperatures. Water can be directly split using solar process heat via direct thermal dissociation at above 2500 K [Fletcher & Moen 1977], [Kogan 1998], [Bilgen, Ducarroir, et al. 1977]; however, the gaseous products need to be separated at high temperatures for avoiding recombination or otherwise obtaining an explosive mixture. The separation step can be by-passed with the help of thermochemical cycles in which hydrogen and oxygen are derived in different steps. Multi-step thermochemical cycles (more than two) allow also the use of more moderate operating upper temperatures, but their overall energy conversion efficiency is limited by irreversibilities associated with heat transfer and product separation [Bamberger 1978].

Two-step thermochemical cycles based on metal oxides offer the potential of achieving high conversion efficiencies while eliminating the need for high-temperature H₂/O₂ separation. Several metal oxide redox systems have been examined and experimentally demonstrated using solar energy [Steinfeld, Kuhn, et al. 1996]. In previous papers [Palumbo, Léde 1998], [Weidenkaff, Brack, et al. 1999], [Weidenkaff, Steinfeld, et al. 1999] we reported on a two-step water splitting thermochemical cycle that has the potential of achieving energy conversion efficiencies exceeding 50%. This cycle, schematically shown in Figure 8, is based on the thermal dissociation of ZnO into its elements according to reaction (4), followed by the exothermic hydrolysis of zinc according to reaction (5).

\[
\text{ZnO} \quad \xrightleftharpoons{} \quad \text{Zn(g)} + 0.5 \text{O}_2 \tag{4}
\]

\[
\text{Zn} + \text{H}_2\text{O} \quad \xrightleftharpoons{} \quad \text{ZnO} + \text{H}_2 \tag{5}
\]

---

*The contents of this chapter have been submitted to be published in Thermochimica Acta by A. Weidenkaff, A. Reiler, A. Wokaun, and A. Steinfeld.*

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Reaction (4) proceeds endothermically ($\Delta H^\circ = 478 \text{ kJ/mol}$) and the temperature for which the equilibrium constant equals 1 is 2350 K [Barin 1993]. The products, zinc vapour and oxygen, need eventually to be separated to avoid recombination. Thermochromatographic experiments conducted in a temperature-gradient furnace have shown that zinc vapour and oxygen can coexist in a meta-stable state in the absence of nucleation sites [Weidenkaff, Steinfeld, et al. 1999]. Reaction (4) was also demonstrated in solar furnace experiments [Weidenkaff, Reller, et al. 1999], [Bilgen, Ducarroir, et al. 1977], [Möller 1997]. It was observed that the Zn yield is strongly dependent on the dilution ratio of the gaseous zinc, defined as the mass flow rate of inert gas divided by the mass flow rate of zinc vapour.

The chemical reaction kinetics of both reaction steps place important initial constraints on the process engineering. In this paper we investigate the influence of temperature, oxygen partial pressure, inert gas flow rate, particle size, and chemical impurities on the ZnO dissociation (reaction (4)), and of temperature and chemical impurities on the zinc hydrolysis (reaction (5)). We further discussed the implications on the reactor design.

![Figure 8: Schematic representation of a two-step water splitting thermochemical cycle based on the ZnO/Zn redox system. It consists of an endothermic, high-temperature, solar step in which ZnO is reduced to metallic zinc, followed by an exothermic hydrolysis step for the production of solar hydrogen.](image)
3.1. Experimental

Thermogravimetric measurements were conducted using a Netzsch TASC-419 thermobalance. The experimental set-up is schematically depicted in Fig. 2. The furnace consisted of an electrically heated Al₂O₃ tube, 3 cm-diameter, which contained a water cooled quartz "cold-finger" condenser for trapping Zn vapour. ZnO powder samples (Fluka Nr. 96479); mean particle size of 1 μm; specific surface area, measured by Brunauer Emmett Teller method (B.E.T.), of 2 m²/g) were loaded on an alumina flat holder and placed in the thermobalance. Samples were heated at a rate of 50 degrees/min up to the desired temperature in the range 1273-1823 K, and finally held at isothermal conditions until complete dissociation. Evolved gases were measured on-line by mass spectrometry (MS) and gas chromatography (GC) at the gas outlet of the reactor. The following experimental parameters were varied: N₂ gas flow rate (0-200 ml/min), oxygen concentration in N₂ (500 ppm-20%), furnace temperature (1273-1973 K). Zinc yield of the solid products collected in the condenser was determined by X-ray powder diffraction and by measuring the volume of hydrogen evolved when reacted with HCl. The accuracy of such technique is ± 6% [Widmer & Estermann 1997].

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* Lₐ means liters at normal conditions; mass flow rates are calculated at 273K and 1 bar.
Figure 9: Thermogravimetric experimental set-up for conducting the thermal dissociation of ZnO. ZnO is heated in an alumina crucible. The weight loss is measured on-line. A water-cooled condenser is used for trapping Zn vapour.

A similar thermobalance was used for studying the hydrolysis of zinc. Zinc, either commercially purchased or product from the solar dissociation of ZnO, was placed in an Al₂O₃ crucible, heated to the desired temperature under a N₂ flow, and finally subjected to a 50 ml/min flow of steam-containing N₂ (pH₂O=30 mbar). The released heat due to the exothermic hydrolysis reaction and zinc melting was recorded by differential thermal analysis (DTA). Outlet gases were analysed by a mass spectrometer.

3.2. Experimental Results

ZnO dissociation experiments

Figure 10 shows the weight loss and furnace temperature as a function of time during the thermal dissociation of ZnO, using a 100 ml/min N₂ flow. The reaction already occurs at 1500 K and reaches reasonable rates at temperatures above about 1700 K. The removal of the gaseous products by the N₂ stream leads to non equilibrium conditions that favour further dissociation. The temperature dependency of the dissociation rate may be expressed by the Arrhenius law: $k = k_0 \exp(-E_a/RT)$, where $k$ is the rate constant, $k_0$ is the frequency factor (which may also be temperature dependent, but its
The variation of the dissociation rate with temperature is also shown in Figure 11. Plotted are the results of TG experiments in which samples were heated to 1273, 1573, 1673, 1723, 1773, and 1823 K, and finally held at isothermal conditions and under a flow of 100 mll/min N₂ until complete dissociation.
Figure 11: Variation of the reaction rate with temperature. Samples of ZnO were heated at a rate of 50 degrees/min up to the desired temperature in the range 1273-1823 K, and finally held at isothermal conditions until complete dissociation.

When ZnO crystals are heated to temperatures above about 673 K, oxygen desorbs from the surface, resulting in an increase of excess zinc in the crystal lattice [Duck & Nelson 1974]. In experiments conducted in a solar furnace [Weidenkaff, Relier, et al. 1999], in which samples of ZnO were directly exposed to the high-flux solar irradiation, we observed colour changes from white to yellow, red, and dark red, due to excess zinc on interstitial sites [Sleight & Wang 1997]. Figure 3 shows a ZnO crystal that has been solar heated in air to above 1500 K and finally underwent fast cooling. X ray photoelectron spectroscopy (XPS) analysis revealed excess zinc atoms on its surface as a result of oxygen evolution during heating.
Figure 12: Photo of a red ZnO crystal (3 cm diameter) with excess zinc in its lattice, obtained by solar heating in air, followed by fast cooling.

Figure 13 shows the rate of the reaction, expressed in weight loss percent per minute, as a function of the initial batch of ZnO. The reaction rate decreases monotonically as the ZnO amount increases, probably as a result of the impeded transport of product gases away from the ZnO surface. For example, we observed that a bulk of 200 mg dissociates four times slower than a bulk of 30 mg.

Figure 13: Variation of the reaction rate (at 1723 K) with the initial sample batch of ZnO.

During the heating of ZnO, the evolution of H2O and CO2 was detected at temperatures between 473-673 K. ZnO is known to chemisorb H2O and CO2 from the atmosphere and form an amorphous surface product with an approximate composition
Zn$_5$(OH)$_6$(CO$_3$)$_2$ [Ostwald, Mattmann, et al. 1972]. This layer is decomposed during heating under an inert gas flow or vacuum. This partial decomposition leads to a porous structure of the ZnO, with a B.E.T. of 6 m$^2$/g. We also observed that ZnO from different sources have different dissociation rates because the different processes used for ZnO production left various surface impurities; primarily CO$_2$ and H$_2$O [Bolis, Fubini, et al. 1998]. Figure 14 shows the weight loss as a function of time for commercial ZnO (Fluka No. 96479) and for ZnO obtained from the hydrolysis of solar zinc (i.e., zinc produced by ZnO dissociation in solar experiments). The latter sample dissociates at a faster rate, which may be due to the surface impurities that it contains.

![Graph showing weight loss as a function of time for commercial ZnO and ZnO from the hydrolysis of solar zinc.](image)

*Figure 14: Comparison of the ZnO dissociation for commercial ZnO (Fluka No. 96479) and for ZnO obtained from the hydrolysis of solar zinc (i.e., zinc produced by ZnO dissociation in solar experiments).*

The ZnO dissociation was also effected under various flows of inert gas and various concentrations of oxygen in the inert gas. Figure 15 shows the dissociation rate at 1723 K, as a function of N$_2$ mass flow rate. As expected, the reaction proceeded also in
a stationary system, but its rate increases with increasing N₂ gas flow rate as a result of improved transport of gaseous products.

![Graph of reaction rate vs. N₂ flow rate]

Figure 15: Variation of the reaction rate with N₂ gas flow rate at 1723 K. Reactor volume is 318 ml.

Figure 16 shows the variation of the reaction rate with O₂ concentration in N₂, at 1773 K. As expected the reaction rate decreases with oxygen concentration because the presence of oxygen shifts the chemical equilibrium to the left. The reaction proceeds about 10 times faster in inert gas than in air.

![Graph of reaction rate vs. % oxygen in nitrogen]

Figure 16: Variation of the reaction rate with O₂ concentration in N₂ at 1773 K and 100 ml/min gas flow rate.
In the presence of oxygen, zinc and oxygen recombine to form long whiskers of dendritic structure on the surface of the ZnO sample, as shown in Figure 17. Thus, the TG curves obtained are the result of overlapping the weight lost during ZnO dissociation and the weight gained during the formation of ZnO. It is however difficult to discriminate between both reactions because they occur simultaneously.

![Image of ZnO sample](image)

*Figure 17: Photo of the ZnO sample after an interrupted dissociation experiment in air.*

**Results of the Zn hydrolysis**

Figure 18 shows the results of DTA experiments on the zinc hydrolysis (zinc from Merck No. 108789 with mean particle size of 10 μm) and water. Plotted are the furnace temperature and the weight gain as a function of time. Also indicated is when heat is absorbed during melting of zinc (m.p. 692 K) and when heat is released during the exothermic hydrolysis of zinc [Bazan 1999].

Once zinc melts (m.p. 693 K), the reaction rate increases significantly. However, the reaction rate was found to be only weakly dependent on the water partial pressure, as observed in experiments conducted in the range 30-60 mbar.
Figure 18: DTA of the hydrolysis of zinc

Figure 19 shows the weight gain as a function of time for two types of zinc: commercial zinc (Merck, purity = 99%) and solar zinc obtained by the dissociation of ZnO in a solar furnace and Figure 20 the reaction rate for various temperatures. Similar to the oxidation of Zn(l) with O2 or CO/CO2 gas mixtures [Guppy, Wickens, et al. 1972], the oxidation of Zn(l) with water depends strongly on the presence of impurities. Zinc produced in solar experiments contains finely dispersed ZnO impurities [Weidenkaff, Reller, et al. 1999]; the particle size ranges between 1 and 1.5 μm and its specific surface area is 30 m²/g. The impurities serve as nucleation sites for further oxidation and function as a „ZnO-matrix“ in the reactant. With both samples, the reaction does not achieve completion: the product of experiments with commercial (pure) zinc consisted of black, hard, dense, and sintered material with a zinc content of more than 50%, while the products of experiments with solar zinc consisted of a grey, fine, porous, and voluminous material with zinc content of less than 10%.
Figure 19: Comparison of the extent of conversion during the water splitting of commercial and solar zinc.

Figure 20: Water splitting reaction in TGA with 40 mg zinc at 350°C, 400, 420, 470, and 500°C, 10.8 mm surface, nitrogen-flow = 50 ml/min.

Under the given TG experimental conditions, in which molten zinc in a ceramic crucible is reacted with steam, a ZnO(s) layer is formed and floats on top of the melt, preventing further reaction. The thickness and density of this layer varies depending on
the impurities and the amount of hydroxyl groups. Complete reaction can be obtained by removing the ZnO layer, by mixing, or by evolving zinc vapour at higher temperatures.

3.3. Summary and Conclusions

We have conducted a set of thermogravimetric experiments to study the effect of various operating conditions on the two reaction steps of a thermochemical water-splitting cycle: the ZnO dissociation and the Zn hydrolysis. As expected, the dissociation rate increased with temperature and mass flow rate of an inert gas, and decreased with oxygen concentration in the inert gas. Reaction rates were also faster for samples containing surface impurities. The hydrolysis reaction proceeded faster for molten zinc, but a layer of ZnO prevented reaching completion. Solar zinc containing small amounts of finely dispersed ZnO reacts faster and more completely with water to hydrogen and ZnO, as compared to commercial zinc samples.

The results of this study place important implications on the reactor and process design. For example, the dissociation reactor will have to be closed to air and operated at temperatures above 1823 K for obtaining an acceptable reaction rate. A flow of inert gas that sweeps the gaseous products will favour dissociation, but it will negatively affect the energy conversion efficiency. Although impurities seem to have a positive effect in both reaction steps, their influence in the cycling capabilities of the process needs to be further investigated. The hydrolysis reactor will have to be operated at above the melting point of zinc and will require good mixing between zinc and water to prevent the formation of a ZnO layer.
4. **Condensation and Crystallisation of Zinc in the Presence of Oxygen**

Two-step water splitting cycles using metal-oxides are considered for the solar production of hydrogen ([Relier, Maurer, et al. 1988] and literature cited therein). Using the Zn-ZnO redox pair is a possibility for it. As energy source concentrated sunlight provides high-temperature process heat for endothermic reactions. In this way, solar radiation can be directly converted into chemical potentials, e.g. when zinc oxide is thermochemically dissociated into zinc and oxygen (1st step). The solar energy stored in the condensed zinc phase can be used to split water (2nd step).

The decomposition of zinc oxide to zinc and oxygen is an attractive process for the storage of solar energy. Both products are evolved from the surface of a shrinking ZnO particle into the gaseous state. Thus, in contrast to other metal oxides reduction processes, the kinetics are not limited by the diffusion of ions through a condensed phase (see e.g. Fe-O-cycle [Weidenkaff, Nüesch, et al. 1997]).

Zn_{1+x}O (x ≤ 70 ppm) is a non-stoichiometric compound with excess zinc on interstitial sites, distorting the ideal wurtzite structure. Excess zinc is the result of the higher rate of oxygen vaporisation as compared to the rate of diffusion of zinc interstitials [Neumann 1981]. Due to further oxygen desorption from the solid, the heating of ZnO to temperatures above 573 K leads to an increasing amount of excess zinc and to a change of the colour from white to yellow.

Thermogravimetric (TGA) experiments have shown that the dissociation of ZnO to Zn(g) and oxygen is observed at about 1273 K (the evaporation point of zinc) at atmospheric pressure in a flow of inert gas [Weidenkaff, Wokaun, et al. 1999].

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The yield of zinc from the thermal decomposition of ZnO strongly depends on the ability to prevent reoxidation. The back reaction involves three different phases: oxygen and zinc vapour, condensed liquid zinc and solid ZnO.

This paper describes the study conducted on the oxidation of zinc vapour and condensed zinc by the evaporation and re-crystallisation of zinc in the presence of oxygen in the temperature range of $295 \, K < T < 1173 \, K$.

4.1. Experimental

The apparatus used for studying the condensation of zinc in the presence of oxygen is similar to the set-up for thermochromatographic studies in [Eichler, Zude, et al. 1992]. Supplementary to the solar experiments, this laboratory experimental set-up in this study allows us to investigate the influence of temperature, partial pressure and gas flow rate of the gases on the yield of zinc.

It consists of an electric furnace for the vaporisation of zinc followed by a temperature gradient tube furnace (see Figure 21). A well defined temperature gradient from the water cooled side to the hot zone is generated by winding a heating wire around a silver tube with increasing pitch. Small glass targets are placed beforehand inside the reactor along the condensation zone. A filter was placed at the outlet of the reactor to ensure that there are no aerosols formed during the experiments.
**Figure 21:** Scheme of the temperature gradient furnace set-up for the examination of zinc vapour reactivity. Zinc is vaporised in the evaporation furnace and the condensable products are deposited along the temperature gradient while non-condensable reactants are measured by gas chromatography.

The products, that deposited on glass targets, were examined by scanning electron microscopy (CamScan CS44) and X-ray diffractometry (Philips X’pert). The oxygen partial pressure at the end of the column was measured with a MTI P200 gas chromatograph.

At the beginning of each experiment, the furnaces are heated to the desired temperatures. Then a quartz tube reactor of 1 cm diameter was inserted into the Ag-tube. Nitrogen (in a range of 30 ml/min- 100 ml/min) was flown over 200 mg zinc (Merck purity >95%). Various flows of O₂ and N₂ are mixed with the zinc vapour in the carrier gas stream. The reacting gases (O₂ + Zn) and possibly the solid products are transported downstream by the carrier gas in the direction of decreasing temperature. Deposition starts where the temperature of the saturation partial pressure is reached. The position of condensation or desublimation depends upon the volatility of the compound. After approximately 20 min., the products are quenched with cold nitrogen while the reactor is withdrawn quickly from the furnace.

For isothermal zinc vapour oxidation experiments a tube furnace with a silica tube reactor of 3 cm diameter was used.
For solar experiments we used the SynMet solar reactor as described in [Steinfeld, Brack, et al. 1998] however in our experiments Argon was used as carrier gas instead of methane. In addition, solar thermal ZnO dissociation in air was conducted by direct irradiation of pressed ZnO.

The products were identified by X-Ray powder diffraction using a X’pert-MPD Philipps diffractometer with Cu Ka radiation. The zinc yield was determined by measuring the total volume of the evolving hydrogen when the Zn/ZnO mixture was completely dissolved in HCl (3.5%) [Widmer & Estermann 1997].

4.2. Results and Discussion

Thermoehromatography

Since the deposition temperature of a compound depends on its specific volatility, condensable gaseous substances can be separated by condensation in a temperature gradient tube. The experimental deposition temperatures were compared with calculated values (see Appendix) [Auer 1998].

The parameters that influencing the crystallisation in this experimental set-up are the condenser wall temperature (given by the temperature gradient), the reaction time, the amount of carrier gas, the oxygen partial pressure, and the zinc partial pressure. The zinc partial pressure can be controlled by changing the temperature of the evaporation furnace and by varying the amount of carrier gas for different experiments. The results of the experiments are summarised in Table 4.
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Table 4: Evaporation temperatures, gas flow rates, and deposition temperatures of thermochromatographic experiments

The deposition occurs axis-symmetrically around the reactor walls. An opaque white part was mostly found at temperatures between 913 K < T < 973 K, a first zinc mirror-like coating at around 853 K < T < 923 K, and a second mirror-like zinc coating at T < 693 K. The adsorptivity of zinc and zinc oxide on the reactor walls is low. Practically no influence of the gas flow rate on the deposition temperature was observed.

In selective experimental runs we found zinc oxide needles on the surface of silica wool placed in the hot part of the reactor. Similarly long zinc oxide needles were formed on the surface of the oxidising gas inlet tube.

The Zn yield of the deposits depended on the oxygen partial pressure and varied in the range of 90% zinc yield (in 0.5% O₂) to 1% zinc yield (in 20% O₂).
When zinc was evaporated in a 30 ml/min flow of nitrogen, a well defined region consisting of a mirror-like deposit was found at the condensation temperature of 903 K. The transport of substances through a temperature gradient tube furnace is a dynamic process of alternating transport in the gas phase, deposition and re-volatilisation of the compounds. When the saturation partial pressure (depending on the partial pressure and the gas volume) is reached the main fraction deposited [Eichler, Zude, et al. 1992].

In an experiment under identical conditions, in which the zinc/nitrogen stream was seeded with 1% oxygen before entering the condenser tube, we found the same result as the one obtained in N₂ atmosphere. Oxygen was still measured at the outlet of the reactor (see Figure 22).

![Figure 22: Oxygen partial pressure measured on-line during experiment No. 6 at the end of the reactor by gaschromatography. (During insertion of the reactor into the pre-heated furnace the reactor and the GC capillary are open to air on the outlet side, so that in the first 2-3 min. of the experiment additional oxygen was measured.)](image)

The deposition temperature for zinc oxide is much higher than for zinc (see Figure 24). No deposition was found at T > 973 K, therefore no reaction takes place at these temperatures.
A small amount of an „opaque white coverage“ was found on most of the reactors at temperatures between $833 \text{ K} < T < 973 \text{ K}$ . Zinc begins to condensate in small amounts at $T < 1100 \text{ K}$ (see Appendix eq. A1), but the vapour pressure of zinc is still higher than 1 atmosphere. The deposit can react with oxygen to ZnO or with the silica reactor to form zinc silicate, but it might re-evaporate, condense again at lower temperatures and be transported like that as either the deposition temperature is reached or is oxidised to ZnO. More „opaque white coverage“ can be found when the amount of deposited zinc is low and the oxygen partial pressure is high.

At temperatures around $873 \text{ K}$, zinc in the gas stream is over-saturated and the main deposition takes place (see Figure 24). The X-ray diffraction pattern indicates that the yield of zinc is between 70-90%, depending on the oxygen pressure.

Figure 23: Zn vapour pressure over zinc at different temperatures
Figure 24: Photo of reactor after an experiment in diluted oxygen atmosphere: The deposition fields are divided in three mirrors surrounding the reactor walls: 973-853 K "opaque white" ZnO with the appearance of Zn droplets, 693-853 K with a grey zinc mirror (90% Zn) and 573-693 K with a glittering zinc mirror (90% Zn).

The amount of zinc vapour pressure in the gas stream depends on the temperature of the evaporation furnace (see Figure 23) and on the amount of carrier gas stream over the zinc. Modelling the amount of zinc evaporation under these special conditions is difficult, because the surface of the liquefied zinc can only be estimated. We measured, that a maximum of 20-30 mg zinc can be evaporated in this apparatus at 1173 K in 20 min. reaction time. The stoichiometric mass for totally oxidising this amount of evaporating zinc would be 0.5 ml / min of O_2 at normal conditions. By measuring the excess oxygen partial pressure during the experiment at the outlet of the reactor, we found, that most of the oxygen passed the zinc without reacting.

The experiments carried out in 10 ml/min O_2 flow lead to a white deposit at T < 973 K, while oxygen was still detected at the outlet. The X-ray diffraction pattern show that the condensed zinc phase is reoxidised to more than 95%. In contrast to the other experiments ZnO was also found in the filter at the outlet of the reactor.

A tube furnace (Heraeus RO 4/25) with a isothermal section was used to verify that at high temperatures no formation of zinc oxide takes place. The experiment was carried out in a 3 cm diameter tubular reactor. Zinc was evaporated and oxygen was mixed into the gas stream. No deposition was found on a 10 cm long region in which the temperature was 1273 K.

Morphology and crystal growth mechanisms

The morphology of the crystallised products depends, among other, on the nucleation conditions, the temperature, the O_2 partial pressure and the condenser material etc. The products were examined by X-ray diffraction and by scanning electron microscopy.
No deposit was found at temperatures above 973 K. At temperatures of 873 K < T < 973 K less than 1% of the total mass of deposit (the remained was mirror-like zinc deposit) was found in form of a white material which could not be removed mechanically from the reactor walls. In the temperatures range 693 K < T < 873 K we observed the formation of small spherical particles with growing prismatic facets to lower temperatures (see Figure 25a). The form of the deposit is similar as that described for the vapour-liquid-solid (VLS) growth of Cd crystals with Bi impurities [Hasiguti, Yumoto, et al. 1981]. Hexagonal prismatic Cd crystals grew with ‘hemispherical rounded tips’ observed by in-situ microscopy. The growth mechanism was found to be the VLS in contrast to vapour-solid (VS) growth, where the Cd vapour deposits directly on solid Cd and the morphology of the deposit changes to hexagonal prismatic crystals.

The surface of the condensate is rough, because of re-evaporation of some zinc and partial oxidation (see Figure 26a). At temperatures below 693 K (zinc melting point), the crystal growth is a result of de-sublimation. Atoms from the vapour phase are impinging directly on the formed Zn solid. The morphology of the deposit changes drastically (see Figure 25b) to crystals of hexagonal prismatic platelets (see Fig.6c), that grew in a 2-D growth mode layer by layer [Wang & Harris 1993].
Figure 25: Scanning electron micrograph of the deposit structures (a) droplets at $T > 693 \, K$, (b) boundary at $T = 693 \, K$ and (c) hexagonal prismatic crystals at $T < 693 \, K$. 
Depending on the experimental conditions, the deposits can be more or less reoxidised. The deposit from experiment number 12 shows a first stage of oxidation (see Figure 26b). On the surface of the particles the beginning of the formation of a hexagonal nucleus and zinc oxide needles at wrinkles of the particle was observed. In concentrated oxygen atmosphere most of the deposit is reacted to ZnO. The SEM pictures show long needles of ZnO (see Figure 26c).
Figure 26: (a) Scanning electron micrograph of the surface of a zinc droplet, (b) Scanning electron micrograph of 30% oxidised and (c) 90% oxidised zinc deposit.

Tetrapod shaped ZnO, like described by Iwanaga and co-workers [Iwanaga, Fujii, et al. 1994] can be formed if the zinc partial pressure is low and the oxygen partial pressure is high (see Figure 27).
Solar zinc

When ZnO is directly exposed to high-flux solar irradiation in air at temperatures around 1773 K, one can observe the evolution of a black smoke. The ZnO decomposes and in the residue of an incomplete thermal dissociation we found yellow, green and red ZnO crystals. The colour of ZnO depends on the amount of excess zinc [Sleight & Wang 1997].

The samples obtained from the condenser surface of the SynMet experiment [Steinfeld, Brack, et al. 1998] show variable morphologies, i.e. hexagonally shaped zinc crystallites and spherical zinc (see Figure 28).
Figure 28: Scanning electron micrograph of zinc obtained from solar thermal dissociation experiments. Part of the product is similar to the deposit on Fig.25a and part of it to Fig.25c.

4.3. Summary and Conclusions

High temperature chemistry driven by concentrated solar flux was investigated for the storage of solar energy in zinc as an option for the substitution of non-renewable energy systems. The dissociation of ZnO by means of solar energy has been demonstrated in the solar furnace in inert gas stream, methane and also in air.

To prevent the evolving zinc from reoxidation a quenching process is necessary. Experimental results have shown, that a high deposition rate (relatively big droplets) retards further oxidation, due to a smaller surface size. Furthermore the comparison of solar zinc samples have shown that the bigger the particle size of the product, the lower the reoxidation rate. The surface of the condensed zinc should be minimised. On the other hand we found that in a diluted atmosphere zinc vapour and oxygen can coexist, if the formation and growth of ZnO nuclei is suppressed.

These results show that the oxidation of zinc vapour in a diluted atmosphere is inhibited, as is the oxidation of solid zinc. Zinc at room temperature is kinetically stable
because of the formation of a thin, but very dense zinc oxide layer on the surface, which prevents bulk oxidation. The in-diffusion of vacancies or oxygen and/or the diffusion of zinc interstitials to the surface is too slow.

The temperature range in which zinc can easily be oxidised is, in its liquid state. The interpretation of the sample morphologies obtained in the temperature region of 873 K > T > 693 K reveals that the formation of zinc oxide needles begins at wrinkles and furrows. In the very beginning one can see the formation of hexagonal nuclei on the surface.

For the reoxidation reaction we should know, how much oxygen can be dissolved in liquid zinc before the saturation is reached and the ZnO solid is formed.

Oxidation stages of Zn and ZnO are of interest for the dissociation and for the reoxidation reaction.

4.4. Appendix

The theoretical deposition temperature depends upon the saturation partial pressure:

\[ T_D = \frac{-\Delta H^0_e}{R \ln \frac{nRT_0}{V_0^{\exp}P_0} - \Delta S^0_e} \]  

\( T_D \): deposition temperature  
\( \Delta H^0_e \): standard enthalpy of evaporation  
\( \Delta S^0_e \): standard entropy of evaporation  
\( n \): moles of zinc  
\( V_0 \): volume of gas at T_0 and P_0  
\( t_{\exp} \): duration of experiment  
\( T_0 \): standard temperature  
\( P_0 \): standard pressure  
\( R \): gas constant

For \( \Delta H_{800K} = 119360 \) J/mol, \( \Delta S_{800K} = 108.4 \) J/K mol, (Knacke et al, 1991), \( V_0 = 0.0001 \) m³/min, \( t_{\exp} = 20 \) min, \( n = 0.0003 \) mol, \( P_0 = 101325 \) Pa, \( R = 8,315 \) J/K mol, \( T_0 = 298 \) K, \( T_D \) calculates as approximately 1100 K.
5. **Experimental Investigations on the Crystallisation of Zinc by Direct Irradiation of Zinc Oxide in a Solar Furnace**

The thermal conversion of solar energy into chemical fuels "solar fuels" offers the possibility of efficiently storing and transporting solar energy. By concentrating the sunlight with the help of parabolic mirrors, we can provide high-temperature solar process heat for driving endothermic processes.

One possibility has been demonstrated by the solar thermal reduction of highly oxidised transition metal oxides. The corresponding products, i.e. metals or metal oxides can be used to split water for producing hydrogen as an environmentally neutral fuel. The identification of efficient and technically feasible thermochemical cycles requires detailed studies on both the reduction and re-oxidation step. Among the studied candidate systems functioning within an accessible temperature range, zinc oxide (ZnO) is most promising.

The reaction proceeds fast enough near 2000 K, yielding metallic zinc and oxygen. Zinc is a versatile metal: besides being a widely used commodity in the galvanising and chemical industries, it is also a compact and safe-to-handle solid fuel that finds applications in Zn/air fuel cells and batteries. Zinc can also be reacted with water and form hydrogen that can be further processed for heat and electricity generation [Bilgen, Ducarroir, et al. 1977]. Such a 2-step water-splitting cycle is represented by:

\[
\begin{align*}
\text{ZnO} & \quad \rightarrow \quad \text{Zn(g)} + 0.5 \text{O}_2 \\
\text{Zn} + \text{H}_2\text{O} & \quad \rightarrow \quad \text{ZnO} + \text{H}_2
\end{align*}
\]

(1st solar step, endothermic)

(2nd step, exothermic)

The chemical thermodynamics and kinetics of reactions (1) have been reported in previous publications [Palumbo, Lédé, et al. 1998], [Weidenkaff, Steinfeld, et al. 1999]. The most important results are briefly reviewed.

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*The contents of this chapter have been submitted to publish in* *Chemistry of Materials* *by*  
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The equilibrium mole fractions of Zn(g) and O\textsubscript{2} are 0.67 and 0.33, respectively, in the temperature range between 1700 K and 2400 K [Palumbo, Lédé, et al. 1998]. The reaction enthalpy is \( \Delta H_{298K} = 348 \text{ kJ/mole} \). The decomposition rate of ZnO(s) was measured by thermogravimetry in a N\textsubscript{2} atmosphere; the apparent activation energy obtained was 312 kJ/mole, which is similar to a value cited in [Hirschwald & Stolze 1972]. The product gases need to be quenched to avoid re-oxidation but the efficiency of the quench is sensitive to the dilution ratio of zinc and oxygen in the gas flow, and the temperature of the surface on which the products are quenched. The condensation of Zn(g) in the presence of O\textsubscript{2} was studied by fractional crystallisation in a temperature-gradient tube furnace. The oxidation of Zn is a heterogeneous process and, in the absence of nucleation sites, Zn(g) and O\textsubscript{2} can coexist in a meta-stable state. However, as soon as zinc condenses, re-oxidation can occur.

An understanding of the parameters that favour the formation of pure zinc is required. The present paper is concerned with the effect of the condensation conditions on the zinc yields during the solar thermal dissociation of ZnO (Figure 29).

**Figure 29: Parameters influencing the product formation during the solar production of zinc from zinc oxide.**

### 5.1. Experimental

The experiments were conducted in the 2 kW solar furnace in Odeillo, France (see Figure 30). The vertical axis solar concentrating system consists of a sun tracking heliostat and a 2m-diameter parabolic concentrator capable of reaching a peak energy concentration of 1600 W/cm\textsuperscript{2} [Ambriz, Ducarroir, et al. 1982].
Figure 30: The 2 kW solar furnace at IMP-CNRS, Odeillo. View from the heliostat to the parabolic reflector of 2m diameter.

The solar chemical reactor, scheme and photo are shown in Figure 31 and Figure 32, consists of a water-cooled copper sample holder enclosed by a Pyrex-dome positioned at the focus of the solar furnace. With this arrangement the reactants are directly illuminated by the high-flux solar radiation focused on a 8 mm diameter circular spot.
Figure 31: Schematic of experimental set-up for the solar thermal dissociation of ZnO.

Figure 32: Photo of experimental set-up.

The samples were prepared as 10 mm diameter pellets of pressed pure ZnO (Aldrich Nr. 14439), technical ZnO, and powder mixtures of ZnO with other inert metal oxides (e.g. 60-80% ZrO₂, Y₂O₃, or Er₂O₃).

Previous to each experiment, the Pyrex dome was evacuated and then filled with argon. The energy input was controlled by opening the shutter to different positions
(between 60-100%) or by varying the position of the sample holder in the solar furnace’s z-axis. The temperatures and heating rates achieved during irradiation were estimated by melting ceramic materials of high melting points. In detail: powder of Erbium oxide (Er₂O₃, melting point = 2400°C), Zirconium oxide (ZrO₂, m.p. = 2700°C) or Yttrium oxide (Y₂O₃, m.p. = 2430°C) [Stubican & Ray 1977]. The heating rates were typically in the range of 1000°C/sec.

The pellets were illuminated for various exposure time periods. The gaseous products, zinc and oxygen, evolved from the surface of the ZnO pellet and were transported by a flow of inert gas and by applying vacuum pressures downstream. The condensable products (Zn and ZnO) were collected simultaneously on 6 targets of 1 cm² each, located at the condenser (front side and laterally). The amount of dissociated ZnO was determined after the experiment. The following experimental parameters have been varied during the experiments: the pressure inside the Pyrex dome was varied from 10 mbar to atmospheric pressure by changing the capacity of the vacuum pump and the gas flow rates; the argon gas flow rate was varied from 0 to 5 l/min; the distance between the dissociating sample and the condenser was varied from 5 to 25 mm; the temperature of the condenser surface was varied between 6°C and 30°C; the sample illumination time (t_illum) was varied from 1 to 120 sec.

5.2. Results and Discussion

In order to elucidate the different stages and forms of nucleation, crystal growth, and re-oxidation, the condensed products collected from the targets were examined after each solar experiment by scanning electron microscopy (SEM) and by X-ray diffractometry (XRD). The zinc yield in the deposit defined as molar zinc fraction of Zn in ZnO has been determined semi-quantitatively (with an accuracy of ± 6 % [Widmer & Estermann 1997]. The influence of parameters such as gas flow rate, pressure, temperature and surface properties of the implemented nucleation sites on the product morphologies has been studied for several experiments. Table 5 lists 40 experiments conducted in the solar furnace and their operating conditions.
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Table 5: Conditions of ZnO dissociation experiments in the solar furnace: pressure inside the Pyrex dome, argon flow rate, time of pellet illumination, composition of the parent pellet, (ZnO = pure ZnO, teZnO = technical (impure) ZnO, mZrO\(_2\) = mixture with ZrO\(_2\)), distance of pellet to condenser, condenser surface temperature, zinc yield in product. (Only main experimental conditions are listed.)
The gas phase

In the solar furnace, the irradiation of ZnO pellets leads to the formation of gaseous zinc and oxygen. From literature it is known that gaseous ZnO only exists as highly activated species with an extremely short lifetime [Chertihin & Andrews 1997], [Liu, Gelinias, et al. 1994]. Thus, under the given experimental conditions, the existence of gaseous ZnO can be excluded. During the actual experiments, zinc vapour and oxygen evolving from the ZnO pellet are diluted by the argon flow until phase transitions occur, either through the condensation and/or desublimation of zinc or through the formation of solid zinc oxide by re-oxidation processes. As a consequence, the partial pressures of zinc and oxygen decrease while the amount of inert gas remains constant. The steady state partial pressure of gaseous zinc depends on the argon flow rate and the ZnO dissociation rate. During start-up and shut-down periods of the experiment, the composition of the gas phase is affected by transients due to heating/cooling and filling of the evacuated space inside the Pyrex dome.

Immediately after the shutter of the solar furnace system is opened and the ZnO pellet is irradiated, a vigorous reaction is observed. The formation of gaseous zinc and oxygen by the dissociative sublimation of ZnO leads to a pronounced increase of the local pressures: In several experiments, the pellets were even moved out of the focal position; these experiments had to be interrupted and could not be evaluated. The rate of the ZnO dissociation depends directly on the heating rate, which in turn depends on the solar irradiation, and the properties of the ZnO pellet, namely its absorptivity, size, density, and thickness. Due to the fact that the focal area is in the range of the dimensions of the pellets, these have to be moved along the z axis in order to adjust a constant irradiation diameter.

During the experiments, product deposition takes place on the surface of the Pyrex dome. This leads to a more or less pronounced decrease of the pellet illumination and, consequently, the dissociation rate of ZnO. During the first 30 seconds of illumination (at experimental pressures lower than 0.2 bar), the reaction rate is only slightly decreased by the mentioned product deposition leading to partial shading of the sample. Accordingly, longer periods of pellet illumination result in a remarkable decrease of the pellet temperature and the dissociation rate (see Figure 33).
Pre-sintering of the parent pellet and/or sintering effects during the solar experiments lower the dissociation rate. This result can be explained by a smaller reaction area from which gas desorption can take place. SEM images of partly dissociated ZnO pellets after the experiment show a rough surface with many concavities due to material ejection.

Pellets containing mixtures made up of ZnO and inert metal oxides such as alumina, silica, yttria, erbia, and zirconia were used in experiments # 12-16 and # 36-38. For these samples, we noticed a delayed beginning of the dissociation. The comparison between different ZnO/inert metal oxide ratios indicates however, that higher dissociation rates can be obtained. Evaluation of different experiments confirms an increase up to 20%. For example, the heating of a pellet made up of an initial compound mixture of 74 mole % ZnO in Y2O3 leads to the dissociation of 477 mg ZnO in 30 sec, whereas only 387 mg ZnO are dissociated in 30 sec starting from a pellet of pure ZnO.

The higher dissociation rates for the oxide mixtures is attributed to the higher rates of convection heat transfer through the melt in addition to the radiation absorption. For similar metal oxide melts, temperatures in the range of 2700°C have been registered [Bilgen, Ducarroir, et al. 1977]. This is far above the temperature for which ZnO(s) is stable, resulting in overheating of the material.
SEM images of the molten and re-solidified pellets reveal a highly textured surface (see Figure 34), suggesting that either the viscosity of the melt was low or the solidification rate was high.

![SEM image of highly textured surface](image)

*Figure 34: Scanning electron micrograph of highly textured surface of ZnO/ ZrO₂ pellet after 5 sec. Illumination period*

The pressure in the reactor and the inert gas flow rate determine the mass transport of the products and thus the local equilibrium on the ZnO surface.

In comparative experiments we investigated the influence of the argon flow rate on the product formation. Higher inert gas flows induce higher dissociation rates due to a faster product transport. For instance, in experiments #8 - #11 the dissociation rate of ZnO changes from 3.9 mg/sec when no argon flow is applied to 9.2 mg/sec for a 4.3 l/min argon flow. The resulting higher partial pressure of zinc is diluted by the higher amount of argon. The highest zinc yield is obtained for a gas flow rate of 2.9 l/min.

The pressure inside the Pyrex dome influences the ZnO dissociation rate and the zinc yield in the products. In experiments at lower pressure (p < 0.013 bar) up to 45 % more ZnO dissociates because of the faster removal of products from the ZnO surface.
The zinc yields at lower pressures are generally higher than at elevated pressure, as observed in experiment # 8 and # 5. The product obtained at 0.13 bar contains 59% Zn whereas the product obtained at 0.4 bar under the same conditions yields only 13% Zn.

In comparison with other experiments, more shading (caused by product deposition on the Pyrex dome) was observed at ambient pressure than at lower pressures. At elevated pressures the products are scattered into all directions, whereas at low pressures the products are transported directly to the condenser.

At ambient pressure it was observed that after the first second, a part of the product was already deposited on the surface of the Pyrex dome. The resulting shading effect leads to a pronounced decrease of the ZnO dissociation rate and consequently to the zinc deposition rate towards the end of comparatively long experiments. For short experiments, e.g. an experiment of 1 sec illumination time at ambient pressure, a zinc yield of 71% results. A possible explication for this remarkable difference in the zinc yield is that the experiments differ in the product deposition rate.

After the experiments, the residues of the parent pellets at ambient pressure and at 0.4 bar are covered with zinc oxide needles formed by the recombination of zinc and oxygen directly on the pellet surface. A higher yield of tetrapod like ZnO (T-ZnO) was observed at higher pressures (see following Chapter).

The condensed phase

Condensed product samples collected on the condenser surface were analysed by XRD. In all experiments metallic zinc was detected. Usually, yields in the range of 40 to 70 mole % zinc in zinc oxide were found. Exceptions were found for experiments conducted in air: A high excess of the oxygen partial pressure in the system results in a nearly complete product oxidation. This indicates the necessity of oxygen dilution or removal during the experiment.

The highest zinc yields were obtained from short experiments ($t_{illu} < 10$ sec) with very high dissociation rates ($\zeta > 100$ mg/sec). It was previously observed by [Bilgen, Ducarroi, et al. 1977] and confirmed by our experiments that the zinc yield in the condensed phase can be higher when zinc oxide is heated in a matrix of zirconia, yttria or
erbia. Morphological studies reveal relatively large zinc droplets and - in a subsequent step – finely dispersed ZnO (see Figure 35).

![Image](image.png)

*Figure 35: Scanning electron micrograph of condensed product from ZnO dissociation (exp #15): Typical product morphology shows relatively large zinc droplets and fine material.*

The amount of nucleation sites seems to vary from experiment to experiment. Products made up of many small particles and large dendritic intergrown crystallites (see Figure 36) are detected. In most cases both extremes are found on the same target.
Figure 36: Scanning electron micrograph of condensed product from water cooled target surface obtained in ZnO dissociation (exp #28). Small particles and large dendritic intergrown crystallites are found.

The growth mechanisms of zinc and zinc oxide suggested in this paper (see below) are based on detailed morphological products analysis. Scanning electron micrographs of the grown crystals reveal a very heterogeneous morphology. The particle size of the products is in the range of few nanometers to several micrometers in diameter. SEM images reveal a mixture of compact, coarse, droplet-like (see Figure 35), and filigran particles (see Fig. 37). The particle surface can be rough, topped with ZnO, or smooth.
Figure 37 a, b: Scanning electron micrograph of condensed product on water cooled target: fine material with tetrapod shaped ZnO (a) and tetrapod shaped ZnO with droplet like nuclei (b).

The formation of droplet-like particles found on the target surface (see Figure 34, Figure 37), suggests that the material was liquid before solidification and that either the condensation takes place before reaching the condenser surface (homogeneous nucleation) or "island growth" (heterogeneous nucleation) occurs.
This heterogeneous, but three-dimensional growth mode is known as Vollmer-Weber growth mode [Gilmer & Grabow 1987] and is observed, when the interfacial energy between the substrate and the deposit (adhesion) is lower than the energy between the atoms of the condensate (cohesion). In our experiments, the adhesion of the condensed phase on the target surface is very low, therefore both mechanisms are possible.

Samples taken from the front side of the condenser or from sites neighbouring the illumination spot, where the vapour temperature and the zinc vapour pressure are high, contain more deposit with bigger particles of up to 10 \( \mu \text{m} \) diameter. On the targets located laterally on the condenser, less product was deposited because most of the zinc vapour was already removed from the gas stream by condensation. These particles are fine (~100 nm), due to the high nucleation rate at a low growth rate. This can be explained by the lower mass transport of zinc. Similar observations were made previously for solar experiments [Steinfeld, Brack, et al. 1998].
The droplet-like particles are most probably condensed zinc, which is also supported by energy dispersive X-ray spectroscopy (EDX). Under the given conditions, zinc oxide cannot form a liquid phase during solidification.

Generally, ZnO can be found in the form of crystalline whiskers [Ataev, Kamilov, et al. 1997]. The whisker length depends on the process parameters and can vary from nanometers to attain several millimetres (see Figure 37).

The morphology of ZnO particles obtained in experiments with a very low zinc partial pressure or when most of the zinc is already condensed shows the characteristic tetrapod shape, so called T-ZnO, with platelets bridging between legs (see Figure 37). They resemble the morphology reported in [Kitano, Hamabe, et al. 1990] [Kitano, Hamabe, et al. 1991], and their growth mechanism on an inserted zinc nucleus is discussed in [Iwanaga & Shibata 1976], [Iwanaga, Yamaguchi, et al. 1978] [Kitano, Hamabe, et al. 1991], [Fujii, Iwanaga, et al 1993], [Fujii, Iwanaga, et al 1994] [Iwanaga, Fujii, et al. 1998]. Transmission electron microscopy of our T-ZnO particles show differences between the structural features of the centre and the leg crystals, similar to the samples obtained previously by [Fujii, Iwanaga, et al 1994]. The legs crystallise in a wurtzite structure with the c-axis parallel to the leg-axis. The nucleus has a different crystallographic structure than the leg crystals, but a detailed identification was not possible because of its small size (few nanometers). Such structural differences may be due to condensed zinc forming at the very initial stage of T-ZnO crystallisation.

Products found on hot parts of the apparatus (e.g. gas inlet, pellet surface) mostly contain high yields of zinc. SEM images of the pellet surface 1mm next to the illuminated spot show deposited zinc droplets and fine ZnO particles (see Figure 39). The zinc partial pressure directly over the pellet must have been relatively high, especially when the transport velocity and the dilution are low.
Figure 39: SEM image of the deposit on the pellet surface 1 mm next to the illuminated spot.

The partial pressure of oxygen, the deposition rate, and the gas temperature are not likely homogeneous throughout the Pyrex dome. The Pyrex itself is also not uniformly irradiated. We observed a black and adhesive layer, with a zinc content of more than 60%, formed at the top of the Pyrex dome (see Figure 40). The rest of the Pyrex surface was covered with a white material, not sticking to the surface, which consisted of fine ZnO needles.
This dramatic difference of product formation has also been observed previously in thermochromatographic studies [Weidenkaff, Steinfeld, et al. 1999].

**Processes during trajectory and deposition**

During the trajectory of the volatile species from the dissociation site (the illuminated spot) to the deposition site (the condenser surface or Pyrex surface), processes that are decisive to the product formation occur. The fundamental question is whether homogeneous or heterogeneous condensation processes decide upon the properties of the products. The observation of black smoke is a strong argument for the homogeneous nucleation of zinc in the initial stage of the trajectory. The droplet-like shape of condensed zinc corroborates this mechanism. If a heterogeneous condensation mechanism would occur, the different target surfaces and their temperatures would influence the product morphology. In our experiments, changing either the temperature (from 6 °C to 30 °C), the roughness, and type of the condenser (Cu, glass, or ZnO monocrystals), did not influence the product formation. Even varying the 'time of flight' by decreasing the distance from the dissociation site to the condenser (25 mm to 1 mm), did not result in a visible change in the product morphology or zinc yield (see experiment # 20 and # 21).
The temperature of the gas phase, measured 2 cm away from the illuminated spot, was 70°C during the experiment. Thus, the products are cooled down below the condensation temperature of zinc (~ 700°C) before reaching the condenser.

The driving force for a phase transformation is the difference of the chemical potential of the corresponding phases. A vapour-liquid transformation is driven by the chemical potential difference:

$$\Delta \mu = \mu_v(p, T) - \mu_l(p, T)$$  \hspace{1cm} (6)

where $\mu_v$ is the chemical potential of the vapour and $\mu_l$ the chemical potential of the liquid phase. Zinc agglomerates to form liquid zinc at a critical saturation of zinc vapour. The temperature dependence of the zinc partial pressure is given by the following equation [Knacke & Kubaschewski 1991]

$$\log p_{Zn} = -\frac{6163}{T} + 8.108$$  \hspace{1cm} (7)

The formation of nucleation sites depends on the temperature, the zinc partial pressure, and the total pressure. The process of the initial nucleation includes collision of atoms, ordered grouping of atoms in the gas phase, formation of clusters and aggregates, formation of critical nuclei and growth of these nuclei to a critical size. The hindrance of nucleus formation is due to the large specific surface area of the small droplets, which causes an increase of the vapour pressure on small aggregates.

The nuclei are formed at a critical supersaturation, achieved by cooling the zinc vapour (see equation (7)). But very small zinc droplets can re-evaporate completely instead of growing. Impurities and reactor walls can lower the surface tension and act as nucleation sites.

The number of nuclei appearing in a unit of volume in a period of time depends strongly on the critical supersaturation, corresponding to the growth zone temperature. A small number of nucleation sites and fast growth of the new phase lead to relatively large particles. We observed in thermochromatographic experiments [Weidenkaff, Steinfeld, et al. 1999], that a very high zinc vapour pressure leads to immediate and fast condensation at certain temperatures resulting in relatively large droplets. It also needs to be considered that zinc which is already deposited may re-evaporate once the surface temperature of the deposition site exceeds the zinc evaporation temperature.
When the nuclei achieve a critical size their further growth reduces the system energy (see equation (6)) so that the condensation proceeds very fast. The growth velocity depends on the velocity of zinc transport to the new phase boundary.

Compared to a solid surface a liquid surface is atomistically extremely rough and therefore a preferred site for deposition. At lower pressure the surface of the droplets is even more rough and larger than at ambient pressure [Yumoto, Yoshihiko, et al. 1998]. This kind of surface provides many sites for adsorption; furthermore, zinc grows fast on liquid zinc. At temperatures lower than the condensation temperature, zinc can be deposited in two ways: 1) as a liquid layer on the already condensed phase (classical condensation); 2) as a solid layer when the temperature is lower than the zinc melting point (desublimation) [Weidenkaff, Steinfeld, et al. 1999].

At temperatures lower than the melting point of zinc, a liquid-solid interface is formed and a vapour-liquid-solid (VLS) growth mode results [Hasiguti, Yumoto, et al. 1981].

Assuming that a homogeneous nucleation process is taking place in our experimental runs, the cooling rate of the liquid zinc depends on the size of the droplets/particles during their transport from the illuminated spot to the condenser surface. Latent heat of crystallisation is released in all directions. A fast cooling hinders the reverse, re-oxidation reaction. Best conditions to grow products with high zinc yield are observed when the growth of zinc is faster than the growth of zinc oxide.

The oxidation of solid zinc is very slow because a layer of oxide on the surface inhibits the oxidation of bulk zinc by forming a protective skin, due to the higher molecular volume of the oxide [Thomas 1957], [Guppy, Wickens, et al. 1972], [Zhang 1996]. The oxidation process is controlled by diffusion of zinc through the ZnO surface layer [Cope 1961].

ZnO whiskers are growing on wrinkles of the droplet surfaces. The latent heat of ZnO crystallisation is released through the substrate.

In order to lower the ZnO formation rate, the rate limiting factors need to be determined. Previous studies [Kitano, Hamabe, et al. 1993] assumed a re-oxidation mechanism based on the diffusion of metal from the centre of a particle through the
metal oxide layer to the surface, where the metal eventually reacts with oxygen to form a new metal oxide layer. This re-oxidation mechanism is not valid for the present chemical system because the source of zinc for the formation of ZnO is coming from the vapour phase.

5.3. Summary and Conclusions

We have conducted a set of experiments in a high flux solar furnace to study the formation of zinc by thermal dissociation of ZnO. The influence of the zinc vapour and oxygen dilution in inert gas during the experiment is complex. Experiments with low zinc vapour pressure (i.e. high dilution ratio) resulted in a slow growth of droplets and the formation of small particles with large specific surface areas which serve as nucleation sites and favour ZnO formation. Experiments with high zinc partial pressures (i.e. low dilution ratio) showed higher zinc content in the condensed phase than experiments with low zinc partial pressures, caused by faster growth of zinc and/or by the formation of larger particles with smaller specific surfaces areas. Evidently, the amount of nucleation sites should be kept low to inhibit the reverse reaction. Further complication arises from the need to separate oxygen from zinc vapour. The supersaturation of zinc vapour should preferably be high to obtain high deposition rates of zinc, whereas the oxygen should be diluted by the inert gas. The energy storage process results in the agglomeration of zinc atoms forming metal-metal-bond clusters [Weidenkaff, Steinfeld, et al. 1999].

The zinc oxide formation by re-oxidation of zinc was found to be of a heterogeneous nature, with homogeneously condensed zinc serving as the main nucleation sites. The morphology of ZnO particles obtained at low zinc partial pressures show the characteristic tetrapod shape, so called T-ZnO, with platelets bridging between legs. TEM measurements showed that the nucleus has a different crystallographic structure than the leg crystals due to condensed zinc forming at the very initial stage of T-ZnO crystallisation. The product inhomogeneity is thus caused by different growth and recombination mechanisms of zinc and zinc oxide.

Unique advantages of a solar furnace are extremely fast heating and cooling rates. Drawbacks are fluctuating power input and temperatures, and shading effects. Keeping
Isothermal conditions is particularly difficult for the ZnO/Zn/O₂ chemical system because of exothermic and endothermic processes occurring during ZnO dissociation, zinc re-oxidation, condensation and evaporation.

By pre-heating the carrier gas stream it should be possible to avoid the cooling of the products below the condensation temperature of zinc (~700°C) before reaching the condenser. The condensation conditions would be better defined.

Keeping a constant zinc partial pressure is also difficult because of the dynamic chemical equilibrium of the experiments.
6. A Solar Chemical Reactor for Co-Production of Zinc and Synthesis Gas

Zn is a widely used commodity in the galvanising, pharmaceutical, and food industries. It is also an attractive solid fuel. Its specific heat is 5320 kJ/kg. It may be used to generate electricity in a Zn/air battery or fuel cell. It may also be reacted with water to produce hydrogen that can be further used for heat and/or electricity generation. Industrially, Zn is extracted from ores in carbothermic and electrolytic processes. The production of Zn is characterised by high energy consumption (35-50 GJ/mt Zn) and high concomitant environmental pollution (3-12 mt CO₂/mt Zn). World production amounts to about 7 million mt/yr and annual discharges to the atmosphere approximate 66 million mt of CO₂. Carbon in the form of coke is the preferred reducing agent and also the primary source of process heat. When used exclusively as the reducing agent, the stoichiometric mass ratio of carbon consumed to Zn produced should be 0.09 [Steinfeld 1997]. Actually, commercial smelting furnaces use 0.8 mt of coke per mt of Zn while emitting vast amounts of contaminated nitrogen derived from the combustion of coke in air. These emissions could be substantially reduced if carbon (or other fossil fuels) were used exclusively as reducing agents and process heat were supplied by an alternative clean energy source, e.g., solar energy. Concentrated solar radiation can provide the process heat required to drive this kind of high-temperature endothermic processes 09 [Steinfeld 1997], [Steinfeld, Kuhn, et al. 1996].

Using natural gas (NG) as reducing agent combines in a single process the reforming of methane to produce synthesis gas (syngas) and the reduction of ZnO to produce Zn (Ref. 09 [Steinfeld 1997] and literature cited therein). The overall reaction is

\[
\text{ZnO} + \text{CH}_4 \rightarrow \text{Zn} + 2\text{H}_2 + \text{CO}. \tag{8}
\]

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* The contents of this chapter have been published in *Energy, The International Journal* 1997 by A. Steinfeld, M. Brack, A. Meier, A. Weidenkaff, and D. Willemin
High-Temperature Solar Technology, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Assumptions: zinc production is 85% by electrolysis and 15% in the Imperial Smelting Furnace (ISF); total CO₂ emissions from electrolysis are estimated assuming 0.87 kg CO₂/kWhe for coal-fired electricity and energy consumption of 50 GJ/mt Zn produced [Hassmann & Kühne 1993];
This combined process has three positive features: (i) methane is reformed in the absence of catalysts and, with proper optimization, may be made to produce high-quality syngas with an H₂ to CO molar ratio of 2, which is especially suitable for methanol synthesis; (ii) the evolved gases are sufficiently valuable commodities to justify their collection, eliminating inherent gas emissions to the environment; (iii) performing of ZnO reduction and NG reforming in a single reactor improves energy efficiencies through concurrent high-temperature reactions. The co-production of Zn and syngas, as represented by reaction (8), avoids the chemically derived CO₂ emissions in the traditional carbothermic reduction of ZnO [Steinfeld 1997]. Furthermore, the use of solar energy upgrades the heating value of the initial reactants by 39%. Thus, using this process, solar radiation falling intermittently in the deserts of the earth's sunbelt can be stored as solar chemical fuels for transportation to the world's industrialised and populated centres.

The chemical thermodynamics and kinetics of reaction (8) have been reported in previous studies [Steinfeld, Frei, et al. 1995], [Steinfeld, Larson, et al. 1996]. The chemical equilibrium composition of the system ZnO + CH₄ at 1250 K and 1 atm consists of a single gas phase containing Zn (vapour) and a 2:1 molar mixture of H₂ and CO. By applying a shrinking-particle model, the reaction rate in a thermogravimeter reactor (flow of CH₄ over a packed bed of ZnO powder with mean particle size of 1.2 μm) was found to be controlled by gas film diffusion in the Stokes regime with an apparent activation energy of 146 kJ/mol [Steinfeld, Frei, et al. 1995]. The theoretical maximum overall efficiency for the conversion of solar energy into the Gibbs free energy of the products via reaction (8) has been assessed for an ideal, closed cyclic system that recycles all materials. Assuming a blackbody solar reactor operated at 1250 K, 1 atm, and with a solar power flux concentration of 2000 suns (1 sun = 1 kW/m²), maximum efficiencies vary between 40 and 65%, depending on the recovery of the sensible heat from the hot products [Steinfeld, Larson, et al. 1996], [Towhidi & Szekely 1983]. These previous studies on the thermodynamics and kinetics of the reaction define the constraints that the chemistry places on the engineering design of a solar chemical reactor.

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total CO₂ emissions from ISF assuming carbon consumption of 0.78 mt C/mt Zn produced [Kola 1985].
A novel solar reactor has been designed for conducting reaction (8). A small scale reactor prototype (for 5 kW solar input) has been fabricated and tested in a high-flux solar furnace. The present paper describes the reactor design methodology and presents the engineering aspects of its fabrication. Test results of the first solar measurement campaign are also presented and practical problems encountered during experimentation are discussed.

6.1. Reactor Engineering Design of SynMet †

SynMet is a solar chemical reactor designed specifically for the co-production of metallic Zn and syngas starting from ZnO and NG. It is shown schematically in Figure 4.1. It consists of an insulated cylindrical cavity (#1), that contains a circular, windowed, aperture (#2) to let in concentrated solar energy. Particles of ZnO, conveyed in a flow of NG, are continuously injected into the reactor's cavity via a tangential inlet port (#3) located at the back of the cavity. Inside the reactor's cavity, the gas-particle stream forms a vortex flow that progresses towards the front following a helical path. The chemical products, Zn vapour and syngas, continuously exit the cavity via a tangential outlet port (#4) located at the front of the cavity, behind the aperture. The window (#5) is actively cooled and kept clear of particles by means of an auxiliary flow of gas (#6) that is injected tangentially and radially at the window and aperture planes, respectively.

† this work was performed as a team work of the Solar Process Technology group at PSI
Figure 1: Schematic configuration of the SynMet solar chemical reactor for the coproduction of Zn and syngas. 1, cavity; 2, aperture; 3, inlet port for reactants; 4, outlet port for products; 5, window; 6, auxiliary gas flow. The particles of ZnO are directly exposed to high-flux irradiation, providing efficient heat transfer directly to the reaction site. Energy absorbed by the reactants is used to raise their temperatures to the range 1200-1600 K and to drive the simultaneous reduction of ZnO and reforming of NG. The chemical products exiting the reactor are Zn vapour and syngas.

Heat Transfer — With this arrangement, the ZnO particles are directly exposed to the high-flux irradiation. Such concept provides efficient radiation heat transfer to the reaction site where the energy is needed, by-passing the limitations imposed by indirect heat transport via heat exchangers. Some of the incoming irradiation undergoes multiple scattering among the particles and multiple reflections within the cavity walls, until it is absorbed by the particles and cavity walls. Other mechanisms of heat transfer to the reactants include infrared radiation by the hot particles and cavity walls, forced convection between the cavity walls and the gas stream, and conduction to ZnO particles that are swept across the hot reactor walls. Vortex (and cyclone) reactors have proven to be efficient devices for the transfer of heat to flows laden with particles [Szekely & Carr 1966]. Energy absorbed by the reactants is used to raise their temperature to above about 1200 K and to drive reaction (8).
**Reactor Geometry** — The reactor features a cavity-type receiver geometry. It is basically an insulated enclosure designed to effectively capture incident solar radiation entering through a small opening (the aperture). Because of multiple internal reflections, the fraction of the incoming energy absorbed by the cavity exceeds the surface absorptance of the inner walls. Such an effect, called the cavity effect, can be expressed by the apparent absorptance, defined as the fraction of energy flux emitted by a blackbody surface stretched across the cavity opening that is absorbed by the cavity walls. The apparent absorptance has been calculated for cylindrical, conical and spherical geometries having diffuse and specularly reflecting inner walls [Lin & Sparrow 1965], [Siegel & Howell 1992], [Steinfeld 1991]. The larger the ratio of cavity diameter or depth to aperture diameter, the closer the cavity-receiver approaches a blackbody absorber. For example, for a cylindrical cavity having the same relative dimensions as the SynMet (ratio of cavity diameter to aperture diameter = 1.7, ratio of cavity depth to aperture diameter = 2), the apparent absorptance is greater than 0.979 for surface absorptance greater than 0.5.

It is important to note that the apparent absorptance is calculated assuming a Lambertian directional distribution of the incident radiation. In reality, the power flux distribution will depend on the optics of the concentrator. It is also assumed that the medium inside the cavity does not participate in the radiation exchange, but, in reality, the reactants (especially the particles), absorb, emit and scatter radiation. Nevertheless, Monte-Carlo ray tracing simulations have shown that the apparent absorptance of a cavity-receiver is only weakly affected by the directional distribution of the incident power [Steinfeld 1991], [Steinfeld 1993]. As the incoming rays undergo multiple isotropic scattering among particles and multiple diffuse reflections within the inner walls, the apparent absorptance becomes less and less dependent on the direction of the incident rays.

**Reactor Sizing** — At temperatures above about 1000 K, the net power absorbed by the cavity-receiver is diminished mostly by radiative losses through the aperture. Thus, the aperture size is the most important dimension for determining the amount of power in and out. The solar energy absorption efficiency of a cavity-receiver $\eta_{absorption}$ accounts for this phenomenon. It is defined as the net rate at which energy is being ab-
sorbed divided by the solar power coming from the concentrator. For a perfectly insu-
lated cavity receiver (no convection or conduction heat losses), it is given by [Fletcher
& Moen 1977].

\[ \eta_{\text{absorption}} = \left( \alpha \frac{Q_{\text{aperture}}}{\varepsilon A_{\text{aperture}}} \sigma T^4 \right) / Q_{\text{solar}}. \] (9)

The first term in the numerator denotes the total power absorbed and the second
term denotes the re-radiation losses; their difference yields the net power absorbed by
the reactor. The incoming solar power is determined by the normal beam insulation, by
the collector area, and by taking into account for the optical imperfections of the collec-
tion system (e.g., reflectivity, specularity, tracking errors). The capability of the collec-
tion system to concentrate solar energy is often expressed in terms of its mean flux con-
centration ratio over an aperture, normalised with respect to the incident normal beam
insulation as follows:

\[ \tilde{C} = \frac{Q_{\text{aperture}}}{I A_{\text{aperture}}}. \] (10)

Solar concentration ratios of 1000 are technically feasible in large scale solar col-
lection facilities using present central-receiver and heliostat technology [Winter & Siz-
mann 1990]. They can be further increased by improving the optical precision of the
heliostat field or by using non-imaging secondary reflectors (e.g. compound parabolic
concentrators, often referred to as CPC [Welford & Winston 1998]. Higher \( \tilde{C} \) would
allow for smaller apertures to intercept the same amount of energy, thus reducing re-
radiation losses. Although larger apertures intercept more sunlight reflected from imper-
fect and imperfectly matched heliostats and concentrators, they also re-radiate more en-
ergy. Therefore, the optimum aperture size for maximum \( \eta_{\text{absorption}} \) results from a
compromise between maximising radiation capture and minimising re-radiation losses.
It is determined by solving [Steinfeld & Schubnell 1993]

\[ \frac{\partial \eta_{\text{absorption}}}{\partial r_{\text{aperture}}} = 0. \] (11)

For imaging solar concentrators, for which the incident flux-density distribution at
the focal plane is close to Gaussian (with maximum flux density \( F_{\text{peak}} \) and radial stan-
standard deviation $\mu$, and further assuming a blackbody cavity-receiver ($\alpha = \varepsilon = 1$), Equation (11) yields the optimum aperture radius

$$r_{\text{opt}} = \left[ -2\mu^2 \ln\left(\frac{\sigma T^4}{F_{\text{peak}}} \right) \right]^{0.5}. \quad (12)$$

Equation (12) serves to guide the determination of the aperture size for maximum efficiency. For example, for a reactor operating at 1400 K and for a solar flux input having the optical characteristics of PSI's solar furnace ($F_{\text{peak}} \approx 2500 \text{ kW/m}^2$ and $\mu \approx 2.5 \text{ cm}$, which are representative for 75% of full power load), the optimum aperture radius is 5.5 cm. An alternative approach is to determine the size of the aperture so that it intercepts a given incident solar power. Assuming again a Gaussian power flux distribution, the radius of the aperture becomes

$$r_{\text{aperture}} = \left[ -2\mu^2 \ln\left(1 - \frac{Q_{\text{aperture}}}{2\pi \mu^2 F_{\text{peak}}} \right) \right]^{0.5}. \quad (13)$$

For example, for a desired input power of 5 kW using PSI's solar furnace, the aperture diameter should be about 6 cm.

Given the total power input, the aperture size, and the operating temperature, one can estimate the power lost by re-radiation and the net power absorbed by the reactants. The mass flow rates of the reactants result from matching the net power absorbed with the enthalpy of the reaction,

$$Q_{\text{reactor,net}} = m \Delta H \bigg|_{\text{reactants}\rightarrow \text{products}}$$ \quad (14)

Table 6 shows the enthalpy change of the reaction as a function of the total pressure $p$; the reactants are 1 mol ZnO and 1 mol CH$_4$, fed at 298 K, and the products are in thermodynamic equilibrium at 1250 K and at 1350 K [Reynolds 1986].

<table>
<thead>
<tr>
<th>$T = 1250 \text{ K}$</th>
<th>$T = 1350 \text{ K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p = 1 \text{ atm}$</td>
<td>$p = 10 \text{ atm}$</td>
</tr>
<tr>
<td>$p = 3 \text{ atm}$</td>
<td>$p = 10 \text{ atm}$</td>
</tr>
<tr>
<td>$p = 5 \text{ atm}$</td>
<td></td>
</tr>
<tr>
<td>$\Delta H \text{ [kJ]}$</td>
<td></td>
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<tr>
<td>549</td>
<td>554</td>
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<td>545</td>
<td>541</td>
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<td></td>
<td>449</td>
</tr>
</tbody>
</table>

Table 6: Enthalpy change for ZnO + CH$_4$ @ 298K → products @ 1250K, 1350K.
Once the mass flow rates are determined, the dimensions of the cavity-receiver are estimated so that the residence time of the reactants inside the reactor chamber is sufficient for the complete reaction (or for a desired reaction extent), as imposed by the kinetics of the reaction. If the reactants are only partially reacted after one pass, they can eventually be recirculated back to the reactor until they are fully reacted.

**Flow Visualisation and Computational Fluid Dynamics (CFD)** — The reactor design evolved from an initial proposal as a result of flow-visualisation experiments and CFD simulations carried out in various geometries and flow configurations. Clear Plexiglas models were built for the purpose of visualising the flow patterns in cold conditions. The initial design had an axial outlet flow and did not perform satisfactorily because of particle sedimentation inside the cavity chamber as well as deposit of dust at the window and CPC. The sedimentation could be minimised to some acceptable levels by having instead tangential inlet and outlet ports at the cavity's back and front respectively, thus creating a stable vortex flow that is able to carry particles along a helical path, regardless of the orientation relative to gravity. In order to increase the residence time of particles inside the reactor chamber and to augment heat transfer between reactants and reactor walls, a spiral groove was machined to guide the particles into a tight helical path rather than the natural coarse helical path. Such a feature was applied with success in a vortex reactor for the ablative pyrolysis of biomass [Diebold & Scahill 1997]. A pitch of 3 cm for a reactor tube diameter of 10 cm was found to function properly for fine ZnO powder (0.5-2 μm particles) within a wide range of inlet velocities. The window and CPC were kept clear of particles with the help of auxiliary gas flows (not laden with particles) injected through tangential and radial ports located strategically at the window and aperture planes, respectively (see Figure 41).

CFD simulations were employed to calculate the velocity field and particle trajectories for different geometries and flow boundary conditions. The Navier-Stokes equations were solved by applying the hybrid differencing schemes and the k-ε turbulence model [Meier, Ganz, et al. 1996]. The motion of the particles in the gas flow was modelled using a discrete trajectory (Langrangian) approach. Optimization was accom-

† The CFD simulations are the work of A. Meier
plished for minimising the auxiliary flow while keeping the window and CPC clear of particles. Figure 42 shows the results of a 3-dimensional calculation of the isothermal gas flow. It is observed that, near the axis, the vortex flow moves in the positive direction (from left to right), primarily as a result of the auxiliary window flow, while close to the walls the vortex flow moves in the opposite direction (from right to left) as a result of the main gas/particle stream that progresses towards the front following a helical path. This helical path is illustrated by the particle trajectories in Figure 43. Larger (and heavier) particles follow a tighter spiral path, while the smaller (and lighter) particles follow closer the gas flow streamlines. For the given gas and particles mass flow rates, no particles escape through the aperture.

Figure 42: Wall boundaries and contour lines are shown for constant velocity (interval size 0.5 m/s) for the axial velocity component. Parameters: the main flow at the back inlet port = 27.8 l/min; the radial jet flow at the aperture = 13.9 l/min; the tangential flow at the window = 9.3 l/min; particle mass flow rate = 8.4 g/min. Positive values are for the direction from left to right.
Figure 43: Boundaries and particle trajectories projected on the vertical plane that contains the reactor axis. Parameters are the same as in Fig. 42. The full line refers to a particle diameter of 10.5 µm and the dotted line to 14.3 µm.

Fabrication of Reactor Prototype — A 5-kW prototype was fabricated and is shown in Figure 44. The cavity body is a 10-cm diameter, 20-cm length cylinder made of heat-resistant steel alloy (m.p.=1670 K). In front of the 6-cm aperture, the cavity receiver was equipped with a diverging conical aluminium funnel so that the window could be mounted 7 cm in front of the focal plane where the radiation intensity is about 10 times smaller and dust deposition is unlikely to occur. The window is a 24-cm diameter, 0.3-cm thick clear fused quartz disc. It has a nominal transmissivity of 0.94 in the 0.26-3.6 µm wavelength range, but its transmissivity drops to 0.20 in the 2.5-3.6 µm range. Thus, the quartz may absorb a substantial fraction of the infrared radiation emitted by the reactor in that range. Nevertheless, the physical and thermal properties of quartz should permit its continuous use up to 1300 K. The window is suspended in 3 o-rings that permit thermal expansion in any direction, and is mounted in a water-cooled copper ring that also serves as a shield for spilled radiation. In some of the experiments, we incorporated a water-cooled, diamond-machined aluminium CPC, which augmented the flux concentration by a factor of 2. Thus, for a given input power, the aperture size was reduced by half, and consequently, the re-radiation losses were reduced by half.
Figure 44: Photograph of the 5-kW solar reactor tested at the PSI solar furnace. The front face contains a 6-cm diameter aperture and a 24-cm diameter quartz window. The water-cooled target seen on the left is the Lambertian target used for measuring the solar power flux intensity optically. The water-cooled Pyrex condenser seen on the right is used for distillation of Zn vapour from the exiting gaseous products.

6.2. Solar Experimental Program

Experimentation was conducted at the PSI solar furnace\(^4\). The optical set-up is shown schematically in Figure 45. The solar furnace is a two-stage concentrating system consisting of a sun-tracking heliostat of 51.8-m² area, 100-m focal length, and a stationary parabolic dish of 5.7 m², 1.9-m focal length, delivering up to 15 kW with a peak concentration ratio of 3,500 suns (1 sun = 1 kW/m²). The power delivered to the reactor is controlled by a venetian blind-type shutter, located between the heliostat and the concentrator. Power flux intensities are measured optically by recording the image of the sun on an Al₂O₃-coated Lambertian target with a calibrated charge-coupled device (CCD) camera. The CCD camera is also used to monitor continuously the position of

\(^4\) Technical information on the PSI solar furnace may be obtained at
www1.psi.ch/www_f5_hn/Solar/solar_home.html
the reactor relative to the flux map, so that the regions of maximum flux intensity are intercepted.

![Diagram of the PSI solar furnace](image)

**Figure 45:** Schematic of the PSI solar furnace (the dimensions are not to scale). It is a two-stage concentrating system consisting of a sun-tracking heliostat and a stationary parabolic dish delivering up to 15 kW with a peak concentration ratio of 3,500 suns.

The complete experimental reactor system, including the peripheral components and the measuring and control instrumentation, is shown schematically in Figure 46. ZnO particles are fed mechanically into the main gas stream by means of a spiral-type feeder, just before injection into the reactor. Gas mass flow rates and concentration of CH$_4$ in Ar are electronically controlled. Both gas and particles are injected at ambient temperature and at slightly above atmospheric pressure. If preferred, the main gas stream can be pre-heated electrically to simulate heat exchange with the exiting hot products. Reactor wall temperatures are measured with thermocouples type-K inserted in the wall and not exposed to the direct irradiation. Pressure inside the reactor is also electronically monitored and its value is limited by a pressure release safety valve. Reaction products exiting the reactor flow through a 1 m long water-cooled Pyrex con-
denser, where some portion of the Zn condenses. Downstream, a battery of filters collects the remaining particles, derived either from Zn condensation, Zn re-oxidation, or unreacted ZnO. The composition of the product gases is quantitatively analysed by gas chromatography. The nature of the solid products collected at the condenser and at the filters is analysed by X-ray powder diffraction. The amount of Zn produced is determined by reacting the solid products with HCl and measuring the volume of hydrogen evolved. The accuracy of such technique is ± 6%.

Figure 46: Flow sheet diagram of the complete experimental set-up. The reactor operates in a continuous mode; the reactant mass flow rates and inlet solar power are controlled.

Preliminary Solar Experimental Results — ZnO powder (Alfa No. 85113) with a mean particle size of 0.4 μm was fed at a rate of about 5 g/min. Inlet gas flow rate, for various concentrations of CH₄ in Ar, was in the 15-20 lₜ/min range; the auxiliary flow without particles was in the range of 20-30 lₜ/min. The loading ratio of particles to gas was kept below the stoichiometric ratio [as given by Equation (8)] to avoid plugging or

\(^{\dagger}\) lₜ means litres at normal conditions; mass flow rates are calculated at 273 K and 1 atm.
sedimentation, and to protect the window from particle deposition. Excess methane was between 5 and 25 times more than the stoichiometric amount. During a typical experiment, the reactor was solar-heated to the desired temperature under a flow of Ar or N₂ and then isothermally subjected to the reacting flow. The reactor was exposed to peak solar fluxes of about 2,000 suns; higher flux intensities were possible but were avoided to prevent overheating. Maximum reactor wall temperatures, under approximate steady-state conditions, ranged between 1000-1600 K and were measured typically at the centre top. As soon as particles were injected into the hot reactor, wall temperatures dropped by about 100-150 degrees, as a result of the endothermic reaction and of the shielding effect of the particles. The particles of ZnO were forced to the walls by the centrifugal force and were efficiently heated by contact with the hot walls (besides being heated by direct absorption, as described in the Heat Transfer section). Wall temperatures were not uniform; close to the aperture, where the main and cold auxiliary flows are mixed, temperatures were typically 100-250 degrees lower than those at the centre top. A more uniform temperature distribution may be obtained by pre-heating both flows. Temperatures were controlled indirectly by controlling the amount of incoming power flux with the furnace’s shutter. Zn vapour exiting the reactor was distilled in the water-cooled condenser.

The chemical conversion of ZnO to Zn obtained after a single pass of about 3 seconds is shown in Table 7; the maximum reactor wall temperature and the CH₄ concentration of the inlet gas are also indicated. As expected, best results were obtained at higher temperatures, higher CH₄ concentrations, and when the reactants were pre-heated. Conversions of over 50% were obtained when the maximum wall temperature exceeded 1300 K. Up to 90% Zn yield was obtained when the maximum wall temperature was 1600 K, however such high temperature approaches the maximum operating temperature of the materials of construction. Mean particle size of the Zn collected in the condenser was typically 2 μm; all particles were smaller than 10 μm. No carbon deposition was detected among the products. The conversion of methane to syngas was

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Chemical conversion (or zinc percentage yield) is defined as the amount of zinc produced in the solar furnace divided by the maximum amount of zinc that would have been recovered if the reaction had gone to completion.
incomplete because the reaction was effected with considerably excess methane. Complete conversion of ZnO and CH\textsubscript{4} may be achieved by increasing the operating temperature and the residence time, or by recirculating the unreacted effluents through the reactor. The use of methane-reforming catalysts, such as Ni, Rh, and others, will most probably result in higher rates of reaction, but their use would be subjected to the feasibility of recovering them from the products.

<table>
<thead>
<tr>
<th>T\textsubscript{max} [K]</th>
<th>% CH\textsubscript{4}-Ar</th>
<th>Zn yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>100%</td>
<td>0.9</td>
</tr>
<tr>
<td>1050</td>
<td>10%</td>
<td>7.5</td>
</tr>
<tr>
<td>1150</td>
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<tr>
<td>1175</td>
<td>22%</td>
<td>32.2</td>
</tr>
<tr>
<td>1200</td>
<td>10%</td>
<td>9.9</td>
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<tr>
<td>1200</td>
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</tr>
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<td>40.3</td>
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<tr>
<td>1250</td>
<td>10%</td>
<td>15.3</td>
</tr>
<tr>
<td>1250</td>
<td>100%</td>
<td>43.4</td>
</tr>
<tr>
<td>1260</td>
<td>10%</td>
<td>15.6</td>
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<td>54.6</td>
</tr>
<tr>
<td>1410</td>
<td>100%</td>
<td>78.0</td>
</tr>
<tr>
<td>1550</td>
<td>10%</td>
<td>85.0\textsuperscript{f}</td>
</tr>
<tr>
<td>1600</td>
<td>10%</td>
<td>90.0\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{f} The reactants were electrically preheated to 800 K.

Table 7: Maximum wall temperature, CH\textsubscript{4} concentration in the inlet gas, and Zn yield obtained in solar runs.

Scanning electron micrographs (S.E.M.) were obtained from the reactants and the products for the solar run using 10\% CH\textsubscript{4}-Ar and at a maximum wall temperature of 1280 K. Figure 47 shows ZnO powder used as reactant; particles underwent partial sintering while being dried for 2 hours at 873 K. Figure 48 shows the products collected at the water-cooled condenser where the average Zn yield obtained was 26.1\%. It is observed that Zn grew in plane layers, resulting from the condensation of Zn vapour when coming in contact with the cold surface. Figure 49 shows the products collected in the
form of aerosol at the filter downstream from the condenser, where the average Zn yield was 30%. The spherical particles of 1-4 μm resulted from the condensation of Zn vapour and contain more than 70% Zn (as determined by Energy Dispersive X-ray spectroscopy, EDX). The remaining particles are mostly unreacted ZnO that were carried away by the gas flow.
Figure 47: S.E.M. of the reactant ZnO powder (Alfa No. 85113) after drying for 2 hours at 873 K.

Figure 48: S.E.M. of products collected at the water-cooled condenser. Zn grew in plane layers as a result of the condensation of Zn vapour.
Figure 49: S.E.M. of products collected at the filter downstream from the condenser. The large spherical particles (of 1-4 μm) resulted from condensation and solidification of Zn vapour. The remaining particles are mostly unreacted ZnO.

Some observations about windows and CPCs — The window worked well during the course of the experiment. But, while trying to minimise the auxiliary flows, some Zn vapour would diffuse to the front, condense at the window, and decrease its transmissivity. Windowed reactors offer the advantage of direct irradiation of the reactants. However, windows that operate in the presence of severe atmospheres such as particles and condensing vapours require aerodynamic protecting flows. Unless such auxiliary flows serve also the function of reactants in gas-solid reactions, the energy conversion efficiency will be significantly decreased due to the energy requirement for separation and re-circulation processes. For example, for the ZnO + CH₄ reaction, methane should be used to protect the window. Another gas-solid reaction for which SynMet may find application is the solar gasification of carbonaceous materials (e.g., coal and biomass). For gasification processes using steam as the gasifying agent, it would be preferable to use steam for protecting the window. The same problem affects the implementation of CPCs in severe gas-solid reacting environments. Since the con-
centrated light exits the CPC with a view angle of 180°, the CPC exit should be positioned exactly at the aperture plane. In this critical zone, ZnO particles or Zn vapour may be deposited and cause deterioration of the CPC reflectivity. Similar to the window protection, the CPC can also be protected by having an auxiliary flow that prevents dust deposition but, unless such a flow acts as a reactant, it will affect the reactor efficiency significantly. The use of CPCs and windows in gas-particle environments should be further investigated.

6.3. Summary and Conclusions

We have presented the engineering design of a solar chemical reactor for conducting the simultaneous ZnO-reduction and CH₄-reforming. The vortex flow configuration was proven to be an efficient reactor concept for the transfer of heat to gas flows laden with particles and for conducting fast gas-solid thermochemical processes. First tests conducted in a solar furnace using a small scale reactor prototype yielded up to 90% chemical conversion to Zn in a single pass. Technical feasibility for the proposed solar process has been demonstrated. There is still room for improvement and optimization.

The use of high-temperature solar process heat for the co-production of zinc and synthesis gas offers the possibility of reducing greenhouse-gas and other pollutant emissions produced in conventional fossil-fuel-based processes. Furthermore, it provides an efficient conversion path of solar energy into storable and transportable chemical fuels.

Present market prices for Zn are about 1000 US$/mt. The cost of this valuable metal is directly tied to the cost of the energy required to produce it: assuming an energy consumption of 35-50 GJ/mt when produced electrolytically and a power cost of 0.05 US$/kWh, the cost of the energy represents between 40-70% of the value of Zn. The cost of solar producing Zn from ZnO would have to be compared with the economics of conventional fossil-fuel-based processes. Once the cost of energy will account for the environmental externalities from burning fossil fuels (e.g. depletion, CO₂ mitigation, and pollution abatement), solar energy will become a favourable competitive long term prospect.

Decreasing the use of fossil fuels as the prime energy source for any industrial process is a means to reducing that process's carbon dioxide emissions. Table 8 shows some industries that are major producers of CO₂ emissions. Yearly estimates of anthropogenic CO₂ production and the corresponding percentage contributed to the world’s total is presented for the iron, aluminium, zinc, and gas reforming industries [Steinfeld 1997]. The emission levels for these industries are high enough to warrant considering how to reduce their fossil fuel consumption.

<table>
<thead>
<tr>
<th>Source</th>
<th>Annual Production, kg</th>
<th>Annual CO₂ emission, kg</th>
<th>% World CO₂ emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc (Electrolysis &amp; Smelting)</td>
<td>$6 	imes 10^9$</td>
<td>$0.07 	imes 10^{12}$</td>
<td>0.3</td>
</tr>
<tr>
<td>Synthesis gas (Natural Gas Reforming)</td>
<td>$2 	imes 10^{11}$ m³</td>
<td>$0.30 	imes 10^{12}$</td>
<td>1.4</td>
</tr>
<tr>
<td>Iron (Blast Furnace)</td>
<td>$505 	imes 10^9$</td>
<td>$1.11 	imes 10^{12}$</td>
<td>5.4</td>
</tr>
<tr>
<td>Aluminium (Electrolysis)</td>
<td>$14 	imes 10^9$</td>
<td>$0.52 	imes 10^{12}$</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*Table 8. Annual World Production and corresponding CO₂ emissions for the production of iron, aluminium, zinc, and synthesis gas. (Table reproduced from reference [Steinfeld 1997]).*

It is self evident, however, that any process which decreases the use of fossil fuels as a prime energy source will be used by industry for CO₂ abatement only if the alternate energy source is cost effective vis-à-vis all of the other CO₂ reduction options. It appears to us that what defines cost effectiveness will be a function of a myriad of complex variables that include items like the technical state of the various CO₂ abatement technologies, the cost for fuels, the political climate, and the public's cognisance of the greenhouse issue. Furthermore, the importance of any one of these variables can change with

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*The contents of this chapter have been published in *Greenhouse gas emission control technologies*, Elsevier 1999 by Aldo Steinfeld, Anke Weidenkaff, and Robert Palumbo Laboratory for Energy and Process Technology Paul Scherrer Institute, CH-5232 Villigen-PSI On leave from Valparaiso university in Valparaiso IN, USA*
time; thus the best technical solution can change with time. In a situation like this one, it seems appropriate for the scientific and industrial communities to develop a variety of technological options for greenhouse gas abatement. With regard to the alternative prime energy sources options, one appears likely to be cost effective in the foreseeable future: various manifestations of solar energy.

In this paper, we demonstrate the potential of using solar energy to reduce CO₂ emissions in the extractive metallurgical industry. Using solar energy in this context means developing solar thermal processes that operate at temperatures in excess of 1200 K; one will see that the potential of this energy resource extends beyond that promised by solar space heaters, photovoltaic cells, and solar thermal to electricity systems. We start with thermodynamic arguments that illustrate why high temperature solar energy is well suited as a non fossil fuel energy option for this industry. To keep the arguments concrete in nature, we focus on zinc production but comment on their general application to the other industries. We present our latest experimental work with respect to a solar carbothermic process for producing Zn from ZnO, thereby illustrating the potential and the difficulties for developing the high temperature technology. We conclude with some general perspectives on solar energy utilisation.

### 7.1. A Thermodynamic Argument for Solar Energy

Although Zn is primarily found in the form of ZnS, the sulphide is roasted in industrial processes to give ZnO [Graf 1996]. It has been shown that solar energy is well suited for decomposing the oxide [Palumbo & Fletcher 1988], [Fletcher, Macdonald, et al. 1985], [Fletcher & Noring 1983]. For clarity, we again present the arguments.

The minimum amount of energy required to decompose the oxide into its elements is shown in Figure 50 as the ΔH₀ for the following reaction at various temperatures:

\[ \text{ZnO(s)} \rightarrow \text{Zn} + .5 \text{O}_2 \]

The ΔG₀ for this reaction is the minimum amount of energy in the form of electric work required if the elements evolved in their standard state for the specified temperature. Thus ΔH₀ - ΔG₀ of energy can be supplied as process heat. This figure demonstrates that the higher the temperature at which the reactants receive process heat the lower the amount of electric work that needs to be supplied to the process to produce the
metal. Because the sun is a 5800 K thermal energy source, it can be the process heat source for all of the temperatures shown in Figure 50.

![Figure 50: Energy Requirements for ZnO(s) → Zn + 0.5 O₂](image)

This figure (and those like this one for other oxide systems) show the full range of potential for solar energy as an alternate energy source in the metal extraction industry. Above 2300 K, there would be no need for electric work to drive the reaction, and there would be no CO₂ emissions from a Zn extraction process. At temperatures below 2300 K, solar electro-thermal processes can be used to produce the metal, but the amount of electric work required can be substantially reduced from that required by the current low temperature industrial electrolytic processes for producing Zn. Given the fact that electricity is supplied primarily by fossil fuels, lower electrical consumption for metal production would mean lower CO₂ emissions from the process.

Rather than supplying electric work to the process, one can also effect the chemical transformation substantially below 2300 K by supplying a carbon source. This type of reducing agent lowers the temperature at which one can drive the reaction with process heat. Consider for example the following reaction:

\[
\text{ZnO(s)} + \text{CH}_4 \rightarrow \text{products.}
\]
The chemical equilibrium composition of the products at 1250 K and 1 bar are Zn vapour and a 2:1 mixture of H₂ and CO. When the process heat for driving this reaction is supplied by solar energy, CO₂ emissions are lower by a factor of almost 10 than those from the current industrial carbon reduction process [Steinfeld, Brack, et al. 1998]. One has the added benefit in this process of producing synthesis gas, the starting material for many other industrially produced chemical products. It is also important to recognise that one has great latitude with the carbon source — consider for example coal, natural gas, or the multitude of forms of carbonaceous biomass materials.

Thermodynamics demonstrates that solar energy can supplement or replace fossil fuels to reduce CO₂ emissions. The question is, “Are there solar processes that can be cost-effective when compared to other CO₂ reduction technologies?” [Fletcher 1996]. In the more immediate future, it is our opinion that the most likely ones will be the solar carbothermic processes [Steinfeld & Spiewag 1998]. The chemistry is well known, and industrial carbothermic reduction processes have survived competition. Thus, research and development can be focused on interfacing the reaction to sunlight at temperatures in which we have a great deal of industrial experience [Fletcher 1996]. We discuss the status of our work with regard to a solar thermal ZnO/CH₄ process.

7.2. Theoretical Energy Balance for the ZnO/CH₄ Process

Figure 51 is a schematic illustrating the energy and material flow for an ideal process operating at 1250 K and 1 atm [Steinfeld, Larson, et al. 1996]. The energy calculations presumed that the solar receiver was a perfect black body cavity receiving concentrated radiation from a perfect optical system having a concentration ratio of 2000 suns. No allowance was made for frictional losses, for energy required to transport reactants and products, or for energy required to drive product separation equipment. Chemical equilibrium composition is presumed for a system pressure of 1 atm at each location within the process. Although each of these assumptions make for an ideal process, it is to be noted that the products exiting the solar receiver are quenched to room temperature. The quench, however, may not be required: the reverse reaction between Zn and synthesis gas may be slow enough that one can separate the products and recover their sensible energy, thereby making better use of the available solar energy. None-the-less it would likely be less complicated to build and to operate a quench process when com-
pared to one that used a heat exchanger that must transfer sensible energy from products to reactants.

In the case of the ideal quenching process, 38% of the solar energy entering the process converts to available chemical energy in the form of Zn(s) and syngas [Steinfeld, Larson, et al. 1996]. This result is significant when one recognises that the best conversion from solar energy to electricity is only about 20%, and if one were able to add a heat exchanger to the ZnO process, more than 60% of the solar energy could theoretically be transformed to available chemical energy [Steinfeld, Larson, et al. 1996]. Thus the process is attractive when one considers how well it uses solar energy.

Such a result can have positive consequences on whether or not the process can someday economically compete with other CO₂ abatement technologies. The single most expensive part of the solar process will be the heliostat field. It is currently estimated to represent between 30-40% of the plant’s capital cost [Steinfeld & Spiewag 1998]. Thus, solar processes that are simple and efficient like this one are most likely to be the most economical.

*Figure 51: Energy balance of the ZnO/CH₄ Process [Steinfeld & Spiewag 1998]*.
7.3. Initial Reactor Design for the ZnO/CH₄ Process *

It was for this reason that we decided to develop the process idea. The following is an abstracted version of the design details for a 5kW process reactor. A complete description of the design can be found in reference [Steinfeld, Brack, et al. 1998]. Here emphasis is placed on the design philosophy. In this regard, it is important to recognise that we wanted to develop a solar reactor that we could imagine as scaleable to an industrial level. But at the same time we wanted a reactor in which we could test how various design features and operating conditions would influence the reactor’s performance. In other words, the reactor is as much an industrial reactor concept as it is an experimental research tool. It consists of an insulated cylindrical cavity that contains a circular aperture closed by a quartz window. Concentrated solar energy enters the reactor through this aperture. At the back of the reactor, particles of ZnO are continuously injected and then conveyed in a continuous flow of CH₄ and Ar to the front of the reactor’s cavity. The gas-particle stream forms a vortex flow that progresses towards the front following a helical path. The chemical products, Zn vapour and syngas, continuously exit the cavity at a tangential outlet port just behind the aperture. The window is actively cooled and kept clear of particles by means of an auxiliary flow of CH₄ and Ar that is injected tangentially and radially at the window and aperture planes respectively.

The shell of the reactor is made from conventional alloy steel that enables the reactor to operate up to 1600 K. Emphasis was placed on using materials that have proven their worth in industrial settings. But it was essential that they were also capable of operating at elevated temperatures under the severe environment of concentrated solar energy. Namely, materials were chosen so that the reactor would operate continuously even after experiencing severe thermal shocks as a result of the transient nature of solar energy.

This concern with the transient nature of solar energy also contributed to the decision to introduce the particles into the reactor in the form of a particle cloud. ZnO particles are directly exposed to high-flux irradiation. In this manner, radiant energy is transferred directly to the reaction site where the energy is needed, avoiding excessive ther-

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* This work was performed by the solar technology group at PSI
mal inertia associated with indirect heat transport via heat exchangers. Thus the chemical reaction can be quickly restarted at the start of a day or after a cloud passes over the process plant. This feed condition also develops good convection heat transfer to the particles and transport gas due to the turbulent nature of the flow. Furthermore, the reactor operates continuously.

These features of continuous flow, good thermal response to transients, and being made from conventional materials are all features that contribute to making the reactor scaleable in nature. But they do not guarantee it. Our premise at the start of this article was that to be attractive to industry the solar process has to be cost effective when compared to all of the CO₂ abatement options. To reach this objective, we speculate that we need a reactor that converts radiant energy to available chemical energy with efficiencies like those quoted above. Thus the reactor was designed with the intention of eventually being able to experimentally establish its thermal performance.

A number of variables are important. First, it will be essential to keep the window free of particles with a minimum flow of CH₄. High flows will mean high convection heat losses at the surface of the window which in turn means solar energy that does not end up as chemical energy. An important experimental variable is thus the auxiliary gas flow rate. Secondly, it will be important to operate the reactor near the stoichiometric ZnO/CH₄ ratio without the presence of an inert gas. If one operates on either side of the stoichiometric ratio in a quench process, a portion of solar energy again is transformed into sensible energy that is dissipated to the environment. To evaluate the significance of this effect, the experimental program will need to establish how close one can obtain the particle cloud density that gives the stoichiometric ratio for ZnO /CH₄. Thirdly, the mass flow rate must be matched to the solar flux input such that one obtains high conversion efficiencies from ZnO to Zn at the desired operating temperature.

This third requirement needs some elaboration. The efficiency for which solar energy can be converted to available chemical energy is determined, in part, by the inter-relationship between the flux intensity of the solar furnace, the chemical kinetics of the reaction, and the method by which the reactants are fed to and extracted from the reactor [Palumbo, Lédé, et al. 1998]. If for example the heat flux is much higher than the rate of the chemical reaction for a given particle feed condition, a large portion of the solar en-
ergy goes into heating the particles rather than into effecting the chemical transformation [Palumbo, Lédé, et al. 1998]. This result, obviously, leads to low conversion efficiencies of radiant to chemical energy. Part of the experimental program will establish how well our reactor concept can match the chemical kinetics of the reaction to the flux intensity on the particles.

7.4. Some Experimental Results from the ZnO/CH$_4$ Process

We present an abstracted version of our results to date. Here reference [Weidenkaff, Brack, et al. 1999] can be consulted for more details. Our current experimental objectives are to demonstrate that the reactor can be run continuously and produce high Zn yields. (Future work will be directed at the other issues described above.)

ZnO powder with a mean particle size of 0.4 microns was fed at a rate of 4.6 and 8 g/min [Weidenkaff, Brack, et al. 1999]. The main inlet gas flow rate for various concentrations of CH$_4$ in Ar was varied from 5 to 20 STD l/min. The auxiliary flow for the window protection was in the range of 20-40 STD l/min. At this point in our work the loading ratio of particles to gas was kept below the stoichiometric ratio; from the main gas flow and the auxiliary flow, we had on average 3 moles of CH$_4$ per each mole of ZnO rather than the 1 to 1 stoichiometric ratio. During a typical experiment, the reactor wall temperature ranged from 1000 to 1600 K [Weidenkaff, Brack, et al. 1999]. The products exited the reactor through a Pyrex water-cooled tubular condenser. The Zn vapour condensed on the walls of the cold tube.

The details of the experimental results can be found in reference [Weidenkaff, Brack, et al. 1999]. Here it is sufficient to say that the chemical conversion of ZnO to Zn (the molar ratio of Zn recovered to the total moles of solid product recovered) reached over 95% when operating at temperatures above 1273 K and using the reducing gas, 10% CH$_4$ - 90% Ar. Furthermore, our results suggest that the Zn yield increases with temperature, residence time of the ZnO particles, and CH$_4$ concentration.

7.5. Perspectives

The ZnO/CH$_4$ process is one concept for how solar energy research addresses the greenhouse gas problem. At the start of this article, we presented a general argument for this role of solar energy. Let’s end by returning to a more global view.
Solar thermal chemical processes can potentially be used to produce a wide variety of chemical commodities that are currently important to society and come from processes that emit large quantities of CO₂. Further, examples include the production of cement found in reference [Steinfeld, Imhof, et al. 1992], carbides and nitrides of which reference [Murray, Steinfeld, et al. 1995] is an example, and metals other than just Zn of which reference [Steinfeld, Kuhn, et al. 1996] is an example. Each of these examples have characteristics that make them interesting candidates for solar thermal processing.

The cost of the product is strongly tied to the cost of energy. When this relationship exists, solar energy has a chance to compete with other energy resources for a role in the world economy. The moment the total cost for energy, the price for the fuel and the price for removing environmental threats from the fuel's utilisation, tips in favour of solar energy, it will be the desired energy resource for the product's production. Also, each of the above processes are or can be conducted at elevated temperatures, making them suitable from a thermodynamic point of view for concentrated solar energy: the high quality of solar energy opens up the possibility for effecting chemical reactions with the minimum quantity of a reducing agent or electricity. Furthermore, they are processes in which the chemistry is well understood; the technical challenge is to adapt the reaction to a solar input. Finally, the processes we discussed are ones where the raw materials are often located in the sunny regions of the world. For example, Australia is rich in sunlight, natural gas, and Zn minerals.

In each of these examples, we see a potential means by which solar energy can contribute to reducing greenhouse gas emissions. However, in each example given, there is some CO₂ released because these examples in some way utilise a carbon source. But as was pointed out in the introduction, solar energy processes can even eliminate the utilisation of carbon based fuels.

Furthermore, there is enough solar energy reaching the earth to supply the current world wide demand for energy. Of course the radiation reaching the earth is dilute, intermittent, and unequally distributed. But solar chemical processes that lead to the production of fuels can overcome these significant drawbacks. Consider for example a solar thermal decomposition process for directly splitting ZnO(s) to Zn. Thermodynamics requires that we operate at temperatures in excess of 2200 K and the Zn and O₂ would
need to be quenched to ambient temperature or the gases would need to be separated at elevated temperatures in an electrolytic step. We refer those who are interested in the latest progress in these areas to reference [Weidenkaff, Brack, et al. 1999]. In such a process, ZnO(s) is decomposed in a sunny region of the world. Then the Zn can be used to produced H₂ or it can itself be used as a fuel. When the fuels are utilised, the by-product is ZnO which would need to be recycled back to the solar furnace. The only energy input to the process is solar energy. Thus a car running on solar produced hydrogen or a Zn-air fuel cell, is running on solar energy, even if it happens to be rolling through Zurich during a rainy evening.

Whether research in high-temperature solar chemistry is forging the connections between old and new technology or developing the scientific and technological know-how for a radically new technology, the ultimate goal is the same—the development of the means by which we can be supplied by a clean, universal, sustainable energy resource.
8. Summary

The present work is concerned with the storage of concentrated solar energy in the form of the Gibbs free energy (chemical potential) of a high energy product or fuel. This concept is investigated by means of the Zn/ZnO water splitting cycle. It consists of an introduction and seven chapters that are based on scientific publications.

In the introduction, background and motivation for this thesis are described. The fundamental ideas of the two step Zn/ZnO cycle, which consists of an endothermic solar driven reaction in which ZnO is reduced to zinc, and an exothermic hydrolysis reaction, are presented.

In Chapter 1, the possibilities of high temperature solar chemistry to generate new solar energy carriers are discussed. They offer a simple and environmentally clean way to provide carbon-free renewable fuels. An estimate of the achievable CO₂ abatement is given. The mechanisms of the endothermic high temperature processes are characterised in terms of reversible heterogeneous reactions. The morphology of the particles, the adsorption and gas desorption from the reactants, and the transport of ions through particles are playing an important role in the energy storage process.

In Chapter 2, strategies for the solar production of zinc are discussed. The ultimate objective is to develop a technically and economically viable process that can produce “solar zinc”. The strategy for achieving this goal involves research on two different reduction possibilities: a direct path via the solar thermal splitting of ZnO, and an indirect path via the solar carbothermal and CH₄-thermal reduction of ZnO. Solar tests (see also Chapter 6) conducted at the PSI solar furnaces with a vortex-flow solar reactor for reducing ZnO with CH₄ yielded high chemical conversion to zinc.

Chapter 3 deals with mechanistic and kinetic investigation of the thermal ZnO dissociation process and the water splitting reaction. Thermogravimetric measurements are used to study the influence of parameters like oxygen partial pressure, gas flow rate, and temperature on the ZnO dissociation and the water splitting. It turned out that samples of ZnO with more surface impurities (Zn-hydroxide/-carbonate) react faster.
In high inert gas flows the dissociation proceeds faster due to an enhanced product transport which influences the local equilibrium on the particle surfaces. Excess oxygen in the carrier gas stream lowers the dissociation rate, because of its influence on the local equilibrium on one hand and the faster and direct re-oxidation on the reactant surface on the other hand. Oxidation experiments with several zinc samples show that water is a better oxidising agent than oxygen. The water splitting reaction proceeds faster when the reacting zinc is molten. Solar zinc, containing small amounts of ZnO impurities, reacts faster and more completely with water to yield hydrogen and ZnO than commercial zinc.

In Chapter 4, the condensation and crystallisation of zinc in the presence of oxygen is studied by fractional condensation and crystallisation experiments of zinc and zinc oxide in a temperature gradient furnace. Under the conditions of these experiments zinc vapour and oxygen can coexist if no ZnO nuclei are present. In the temperature range $420^\circ C < T < 600^\circ C$ spherical Zn particles are formed. At temperatures below $420^\circ C$ (zinc melting point), the crystal growth is a result of de-sublimation. The interpretation of the product morphologies obtained in the temperature region of $600^\circ C > T > 420^\circ C$ reveals that the formation of zinc oxide needles starts at wrinkles and furrows. In the very beginning formation of hexagonal nuclei on the surface is observed.

In Chapter 5, the solar zinc production in the dissociation-condensation chamber of the vertical 2 kW solar furnace in Odeillo is described. Concentrated solar irradiation was used to thermally dissociate ZnO. The zinc vapour condensation in the presence of oxygen under several conditions of dilution, temperature, pressure and irradiation was investigated. High zinc yields were obtained under conditions which favour supersaturation of zinc vapour and high deposition rates of zinc.

Chapter 6 is dedicated to the solar thermal dissociation of ZnO particles distributed in inert gas/methane mixtures. A novel solar chemical reactor ("SynMet" Reaktor) has been designed by a team of engineers of the Solar Process Technology group at PSI to perform the combined ZnO-reduction and CH₄-reforming process. A 5-kW reactor was constructed from scratch and tested in a high-flux solar furnace. This chapter contains results of solar experiments that were conducted by team-members of the Solar
Process Technology Group at PSI to which I belonged. The sections of the paper to which I have not contributed are footnoted and credited to the major contributors.

Chapter 7 demonstrates the substitution of high temperature solar thermal chemical technologies for various industrial processes driven by fossil fuels as a promising path for reducing CO₂ emission. Solar energy used in processes operating at temperatures near 1000°C can replace fossil fuels as the source of process heat to drive the carbothermic reduction of metal oxides. As the temperature of the solar process can be increased to near 2000°C, some metals can be produced directly from their oxides without a carbon source, thereby eliminating the production of CO₂.

The solar experiments outlined in this work were performed at PSI's solar furnaces and at IMP-CNRS's solar furnace in Odeillo.
9. Zusammenfassung

Die vorliegende Arbeit beschäftigt sich mit der chemischen Speicherung von konzentrierter Sonnenenergie in Form eines energetisch hochwertigen Produktes oder Brennstoffes. Dieses Konzept wird im Zn/ZnO Wasserspaltungszyklus erforscht. Sie besteht aus einer Einleitung und sieben Kapiteln, welche auf wissenschaftlichen Publikationen beruhen.

In der Einleitung werden Hintergrund und Motivation des zweistufigen Zn/ZnO Wasserspaltungszyklusses vorgestellt, welcher aus einer endothermen solar betriebenen Reaktion und einer exothermen Wasserspaltungsreaktion besteht, vorgestellt.


In Kapitel 2 werden Strategien zur solaren Produktion von Zink diskutiert. Das eigentliche Ziel ist eine technisch und ökonomisch realisierbarer Prozess für die Herstellung von „solarem Zink“. Um dieses Ziel zu erreichen werden zwei verschiedene verfolgt: der direkte Weg über die rein thermische Dissoziation von ZnO und der indirekte Weg über eine solare Reduktion mit Kohlenstoff oder Methan als Reduktionsmittel. Solarexperimente, (s. auch Kapitel 6) die in den Solaranlagen am PSI mit einem Partikelwolkenreaktor für die Reduktion von ZnO mit Methan durchgeführt wurden, führten zu hohen Umsatzraten.

Kapitel 3 behandelt mechanistische und kinetische Untersuchungen der thermischen ZnO Dissoziation und der Wasserspaltungsreaktion. Thermogravimetrische Messungen wurden durchgeführt, um die Einflüsse der Reaktionsparameter wie Sauerstoffpartialdruck, Gasflussgeschwindigkeit und Temperatur auf die ZnO Dissoziation und
die Wasserspaltungsreaktion zu bestimmen. Es zeigte sich, dass ZnO Proben mit Oberflächenverunreinigungen (Zinkhydroxid und Carbonat) schneller reagierten.

Mit hohen Gasflussgeschwindigkeiten verläuft die Dissoziation, dank besseren Abtransport der Produkte schneller. Dies beeinflusst das lokale Gleichgewicht an der Partikeloberfläche. Zusätzlicher Sauerstoff im Trägergasstrom verringert die Dissoziationsgeschwindigkeit wegen des Einflusses auf das lokale Gleichgewicht über dem ZnO einerseits und wegen der sofortigen Rückreaktion auf der Reaktandenoberfläche andererseits.

Oxidationsexperimente ergaben, dass Wasser ein besseres Oxidationsmittel ist als Sauerstoff. Die Wasserspaltungsreaktion verläuft schneller mit geschmolzenem Zink. Auf solarem Wege hergestelltes Zink, welches fein verteilte geringe Mengen von ZnO Verunreinigungen enthält, reagiert schneller und vollständiger zu Wasserstoff und ZnO, als kommerzielles Zink.

In Kapitel 4 wird über die Untersuchungen der Kondensation und Kristallisation von Zink in der Gegenwart von Sauerstoff im Temperaturgradientenofen berichtet. Sind keine ZnO-Keime vorhanden, so können Zinkgas und Sauerstoff koexistieren. Im Temperaturbereich $420^\circ C < T < 600^\circ C$ bilden sich kugelförmige Zinkpartikel. Bei Temperaturen unter $420^\circ C$ (Schmelzpunkt von Zink) ist das Kristallwachstum ein Resultat von Desublimationsprozessen. Die Interpretation der Produktmorphologie im Temperaturbereich von $600^\circ C < T > 420^\circ C$ ergibt, dass ZnO Nadeln an Falten und Unebenheiten zu wachsen beginnen. Im ganz frühem Stadium der Reoxidation kann man die Ausbildung von hexagonalen Keimen an der Zinkoberfläche erkennen.


Die Solarexperimente, die in dieser Arbeit beschrieben werden wurden entweder in den Solaranlagen des Paul Scherrer Institutes oder am IMP-CNRS in Odeillo ausgeführt.
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Dank

Ich danke allen, die zum Gelingen dieser Dissertation beigetragen haben, insbesondere: Alexander Wokaun, Armin Reller und Aldo Steinfeld, unter deren Leitung diese Arbeit in der Sektion Solarchemie am Paul Scherrer Institut entstand und die mir immer wieder hilfreiche Anregungen gegeben haben; vielen weiteren Kollegen am PSI, am CNRS und an der ETH, darunter Max Brack, Roland Brütsch, Stefan Eckhoff, Bernd Eichler, Alwin Frei, Hansi Frey, Thomas Lippert, Tony Meier, Bernhard Mischler, Christoph Müller, Robert Palumbo, Francois Sibieude, und Roland Wessiken, die mir eine grosse Hilfe beim Erstellen dieser Arbeit waren; Wilken Boie, der sich immer Zeit nahm für meine Computer Probleme und meiner Mutter, die sich Zeit nahm für die anderen Probleme; dem BFE (Bundesamt für Energie) und SolarPACES für die finanzielle Unterstützung.
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