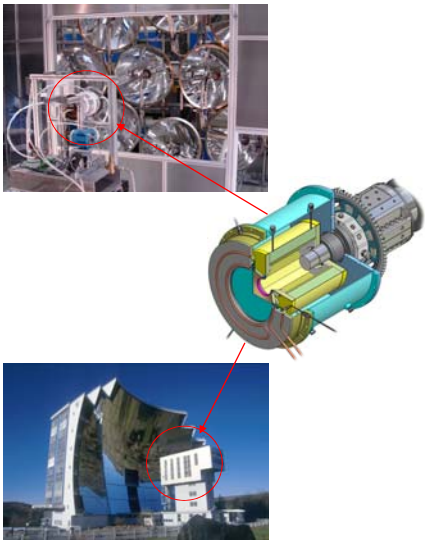
SFERA Winter School
ETH Zurich, March 24-25, 2011

The Zn-based Thermochemical Cycle for Splitting H_2O and CO_2

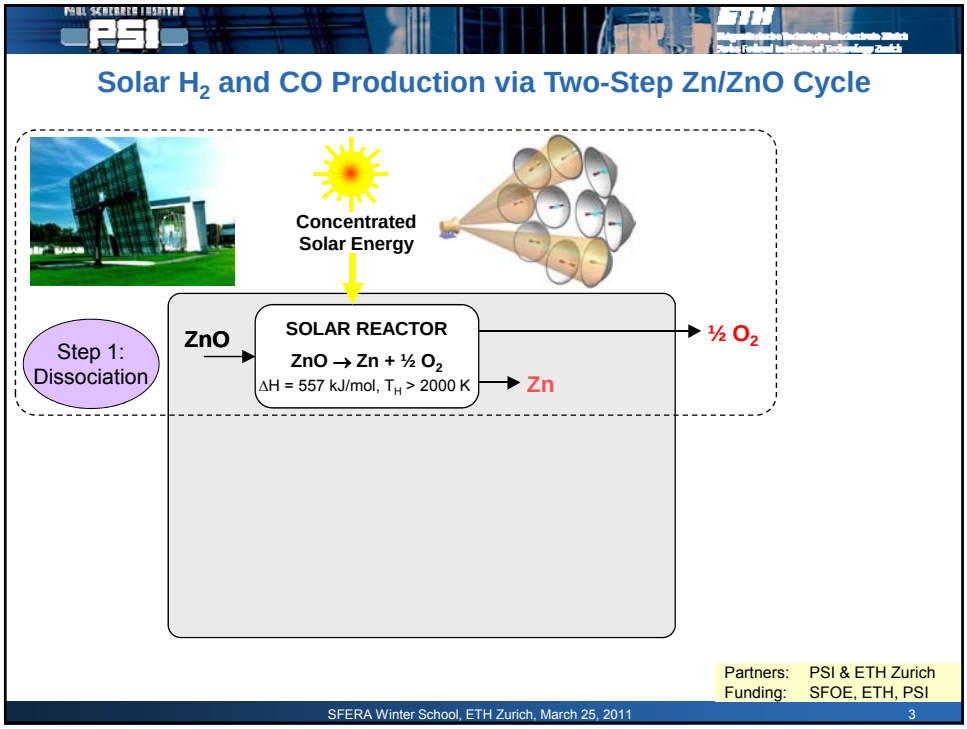
Anton Meier

Solar Technology Laboratory, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Outline



- Zn/ZnO Thermochemical Cycle
- Second-Law Analysis
- Solar Reactor Technology
  - PSI's Rotary Reactor
  - Challenges and Solutions
- Heat Transfer Modeling
  - 10 kW → 100 kW → 1000 kW
- Experimental Validation
  - 10 kW Reactor Prototype
- Scale-up Reactor Design
  - 100 kW Pilot Plant
- Life Cycle Analysis
- Economics
- Conclusions & Outlook


Solar H_2 and CO Production via Two-Step Zn/ZnO Cycle
Concentrated Solar Energy
Step 1: Dissociation
ZnO
SOLAR REACTOR
$ZnO \rightarrow Zn + ½ O_2$
ΔH = 557 kJ/mol, T_H > 2000 K
Zn
½ O_2
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
SFERA Winter School, ETH Zurich, March 25, 2011
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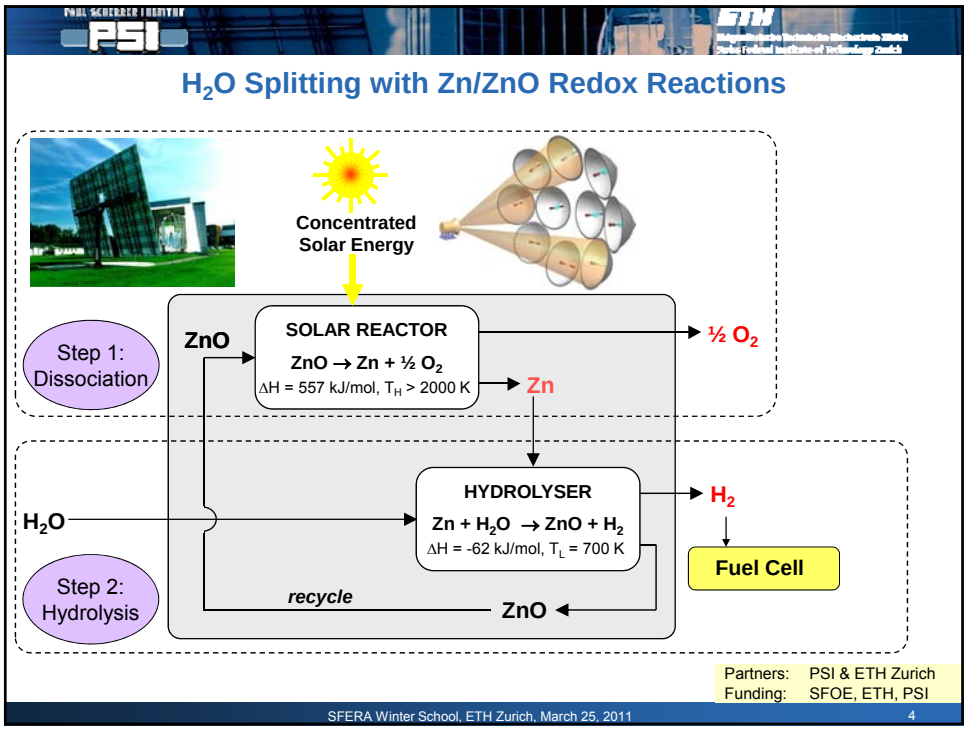
H_2O Splitting with Zn/ZnO Redox Reactions
Concentrated Solar Energy
Step 1: Dissociation
ZnO
SOLAR REACTOR
$ZnO \rightarrow Zn + ½ O_2$
ΔH = 557 kJ/mol, T_H > 2000 K
Zn
½ O_2
H_2O
HYDROLYSER
$Zn + H_2O \rightarrow ZnO + H_2$
ΔH = -62 kJ/mol, T_L = 700 K
H_2
Fuel Cell
Step 2: Hydrolysis
recycle
ZnO
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
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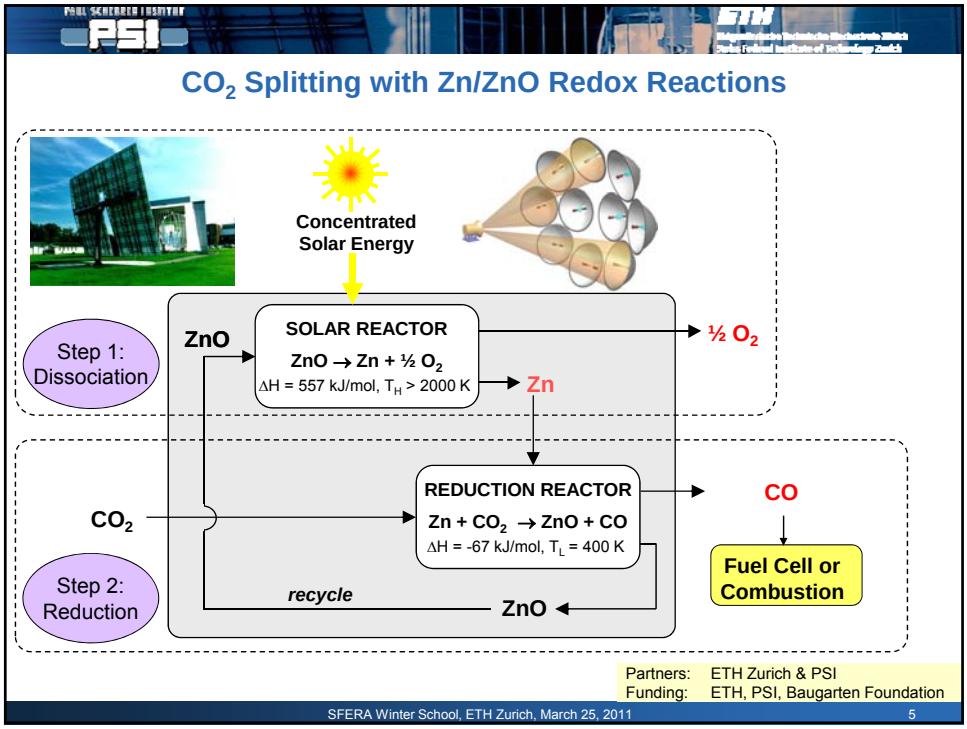
CO2 Splitting with Zn/ZnO Redox Reactions
Concentrated Solar Energy
Step 1: Dissociation
ZnO
SOLAR REACTOR
ZnO → Zn + ½ O2
ΔH = 557 kJ/mol, TH > 2000 K
½ O2
Zn
REDUCTION REACTOR
Zn + CO2 → ZnO + CO
ΔH = -67 kJ/mol, TL = 400 K
CO2
CO
Fuel Cell or Combustion
Step 2: Reduction
recycle
ZnO
Partners: ETH Zurich & PSI
Funding: ETH, PSI, Baugarten Foundation
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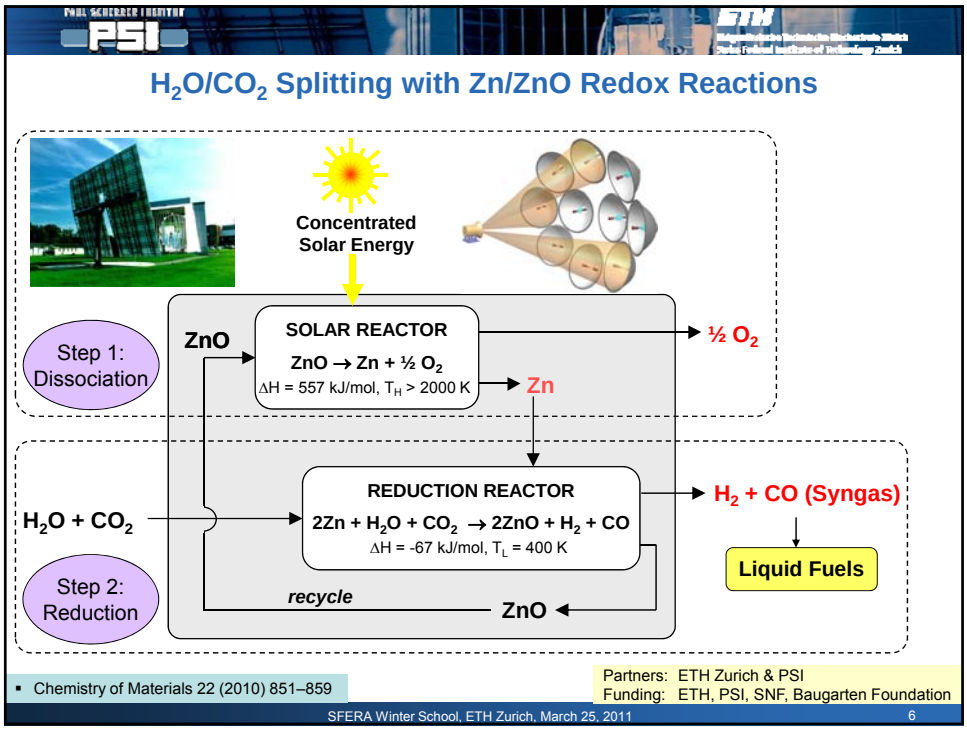
H2O/CO2 Splitting with Zn/ZnO Redox Reactions
Concentrated Solar Energy
Step 1: Dissociation
ZnO
SOLAR REACTOR
ZnO → Zn + ½ O2
ΔH = 557 kJ/mol, TH > 2000 K
½ O2
Zn
REDUCTION REACTOR
2Zn + H2O + CO2 → 2ZnO + H2 + CO
ΔH = -67 kJ/mol, TL = 400 K
H2O + CO2
H2 + CO (Syngas)
Liquid Fuels
Step 2: Reduction
recycle
ZnO
Chemistry of Materials 22 (2010) 851–859
Partners: ETH Zurich & PSI
Funding: ETH, PSI, SNF, Baugarten Foundation
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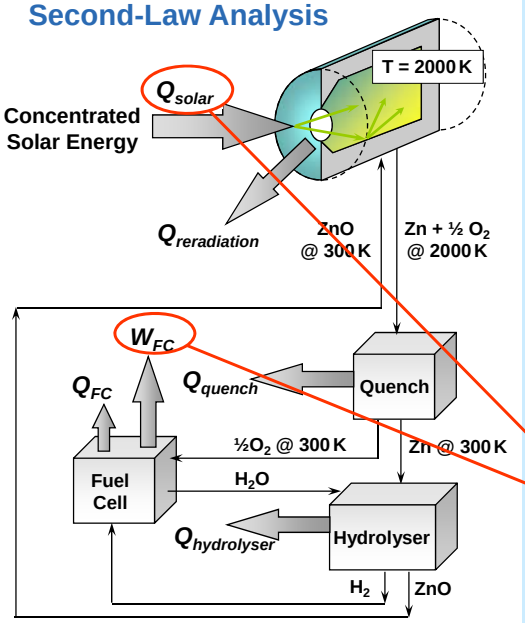
Second-Law Analysis



$\Delta H_{ZnO\ @\ 300K \rightarrow Zn+½O_2\ @\ 2000K} = 557$ kJ/mol

$$\eta_{absorption} = \frac{\Delta H_{rxn}}{Q_{solar}} = 1 - \frac{\sigma T^4}{I \cdot C} = 82\%$$

$Q_{solar} = 680$ kJ/mol

$Q_{rerad} = 123$ kJ/mol

$I = 1$ kW/m^2

$C = 5000$

$Q_{quench} = \Delta H_{Zn+½O_2\ @\ 2000K \rightarrow Zn+½O_2\ @\ 300K} = -209$ kJ/mol

$Q_{WS} = \Delta H_{Zn+H_2O \rightarrow ZnO+H_2} = -62$ kJ/mol

$W_{FC} = -\Delta G_{H_2+½O_2 \rightarrow H_2O\ @\ 300K} = 237$ kJ/mol

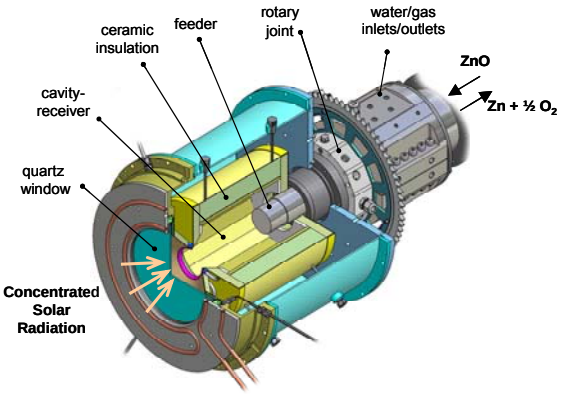
$Q_{FC} = (\Delta H - \Delta G) = -49$ kJ/mol

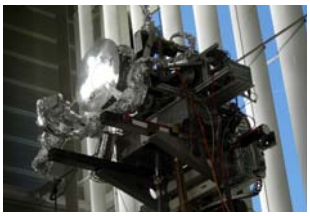
$$\eta_{exergy} = \frac{W_{FC}}{Q_{solar}} = 35\%\ (82\%)$$

Solar Thermal Dissociation of ZnO

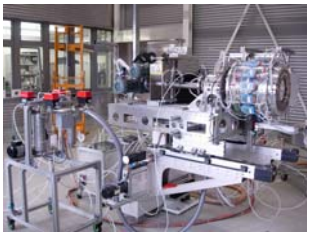
Solar reactor technology

- PSI's 10 kW solar reactor prototype
- Direct-irradiated rotary cavity reactor





Solar furnace, PSI, Switzerland

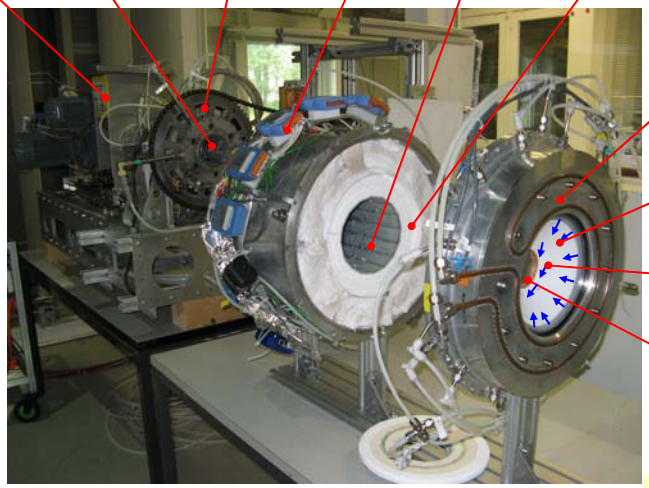


Solar simulator, PSI, Switzerland

- J. Solar Energy Eng. 130(2) (2008) 021009

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

10 kW Solar Reactor Prototype



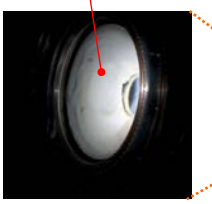
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

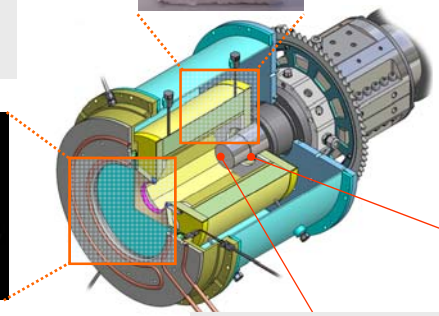
Solar Reactor Technology

Design challenges

Materials
- Lining of reactor walls
- Thermal insulation
- T > 2000 K
- Thermal shock resistant
- Chemically stable
- Mechanically stable

Window
- 2000-5000 kW/m^2
- Protection against deposition of condensing gases





Gas Separation
- Product gas separation [Zn(g) / O_2] at high temperatures > 1000 K
- Inert gas [Ar] separation and recycling

Conveying
- Particles [ZnO] feeding
- Products [Zn] removal

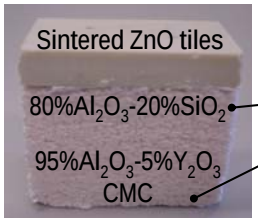
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

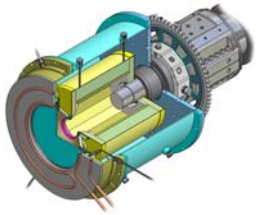
Solar Reactor Technology

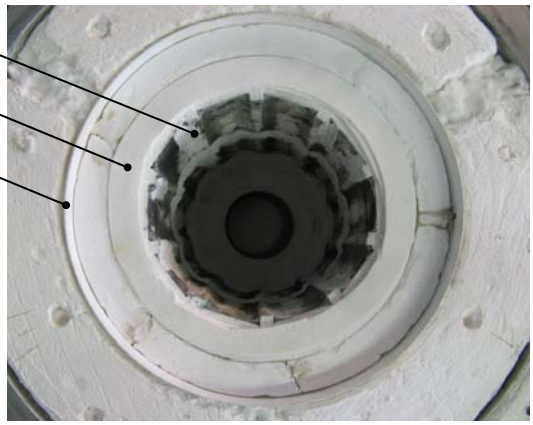
High-temperature cavity wall materials and insulation

Sintered ZnO tiles (3.7 mm thick)

Sintered Al_2O_3 tiles (7 mm thick)







- J. Solar Energy Eng. 130(2) (2008) 021009

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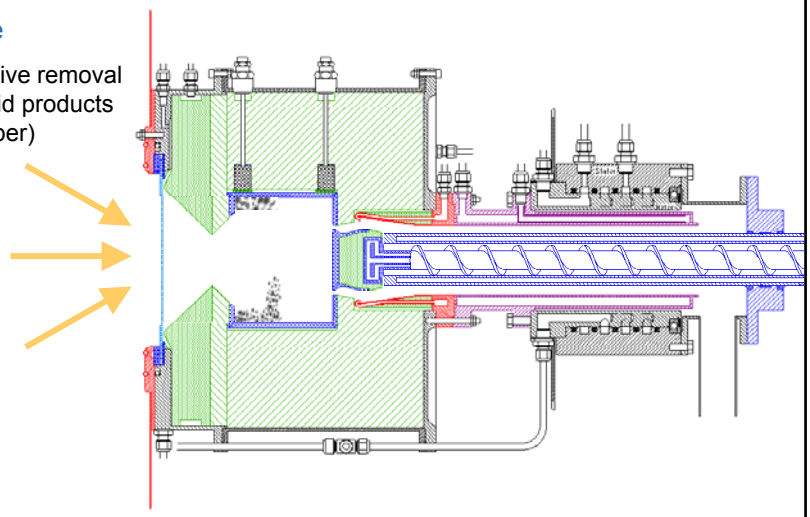
Solar Reactor Technology

ZnO feeding and product removal

Challenge

- Effective removal of solid products (scraper)



- J. Solar Energy Eng. 130(2) (2008) 021009

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Funding: SFOE, ETH, PSI

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Solar Reactor Technology

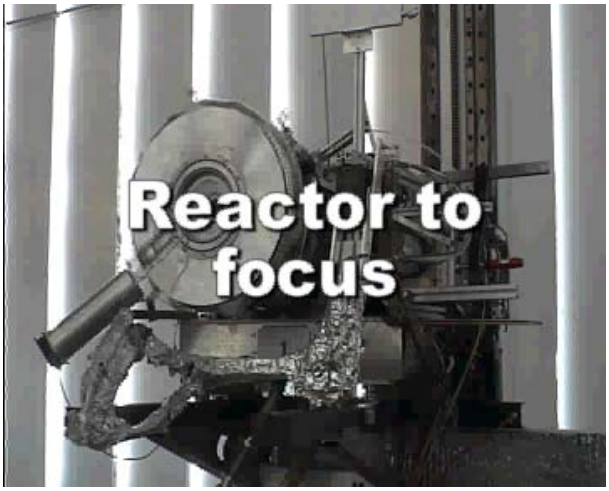
Typical experiment at PSI's solar furnace

Operating conditions

- Concentration: 3500 suns
- Temperature: >2000 K
- Power: 10 kW

Video

- Reactor to focus
- Flux map meas.
- Open shutter
- Reactor heat-up
- Feed cycle
- Pyrometer meas.

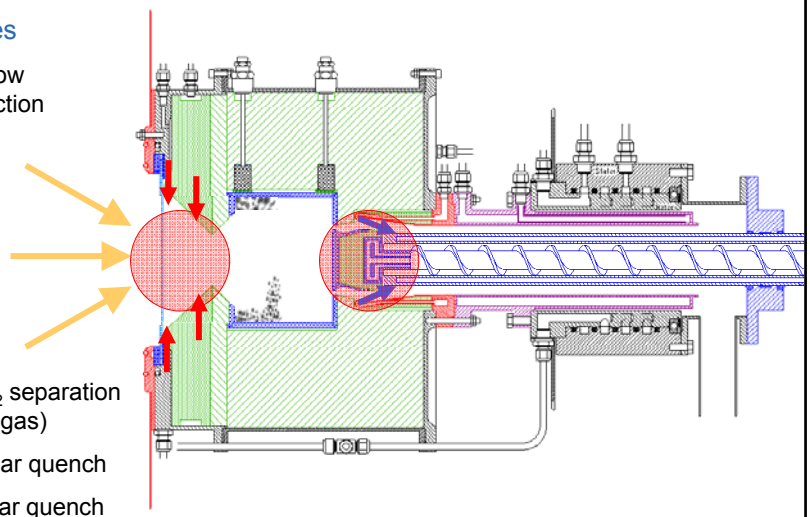


Solar Reactor Technology

Window protection and quench

Challenges

- Window protection



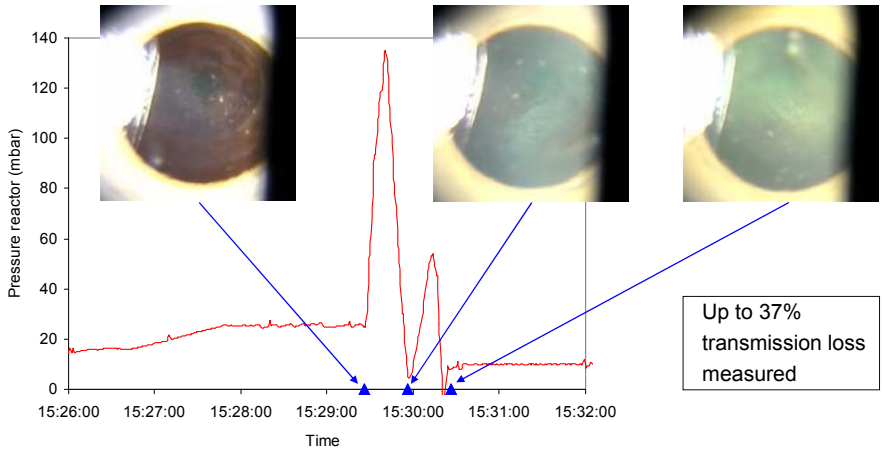
- Zn-O_2 separation (inert gas)
- Annular quench
- Tubular quench

- J. Solar Energy Eng. 130(2) (2008) 021009

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

Solar Reactor Technology

Aerodynamic window protection



Up to 37% transmission loss measured

- Precipitation on the window due to pressure fluctuations (clogging of outlet)

100 kW Scaled-up Reactor

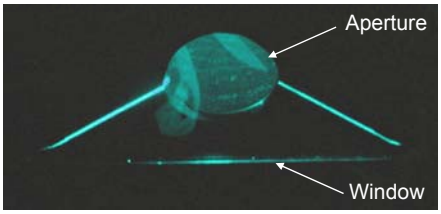
Window protection

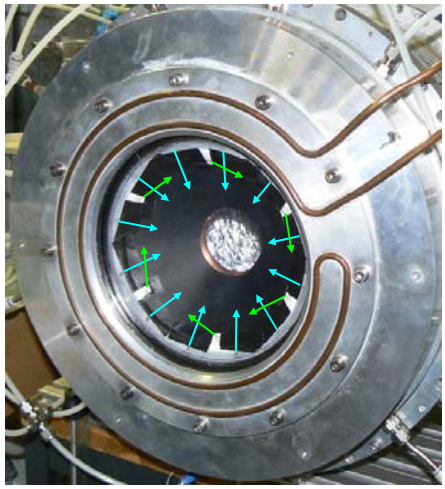
Challenge

- Avoid precipitation of condensable Zn(g) on window

Solution

- Aerodynamic window protection using inert gas (Ar) streams:
  - Radial / tangential flows
- Flow visualization & CFD

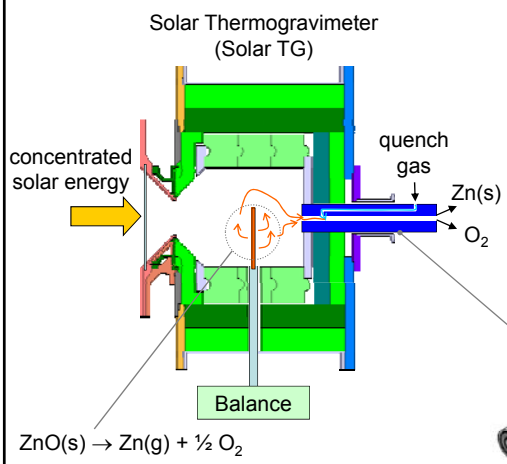


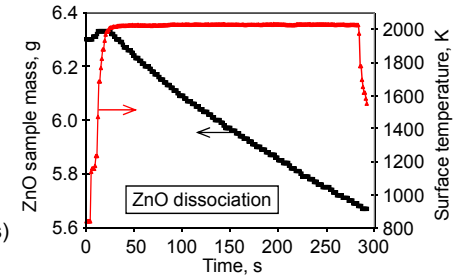


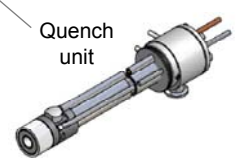
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

Solar Reactor Technology

Zn-O_2 separation







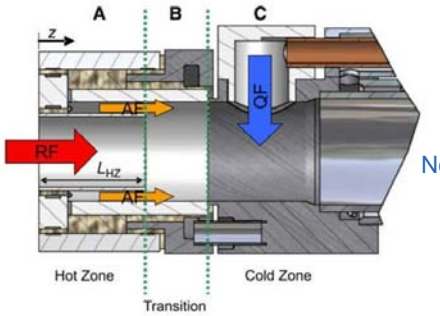
- J. Materials Science 43 (2008) 4729–4736

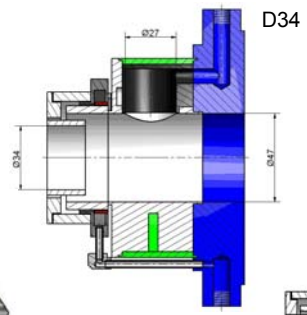
Solar Reactor Technology

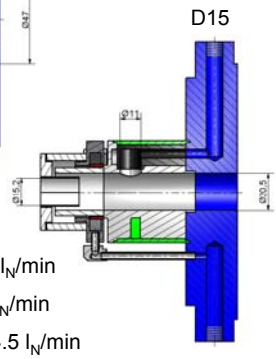
Zn-O_2 separation

Quench concept

- Solar TG :
  - Three zone approach
- Solar reactor:
  - Quench units D34 and D15







Nominal flows

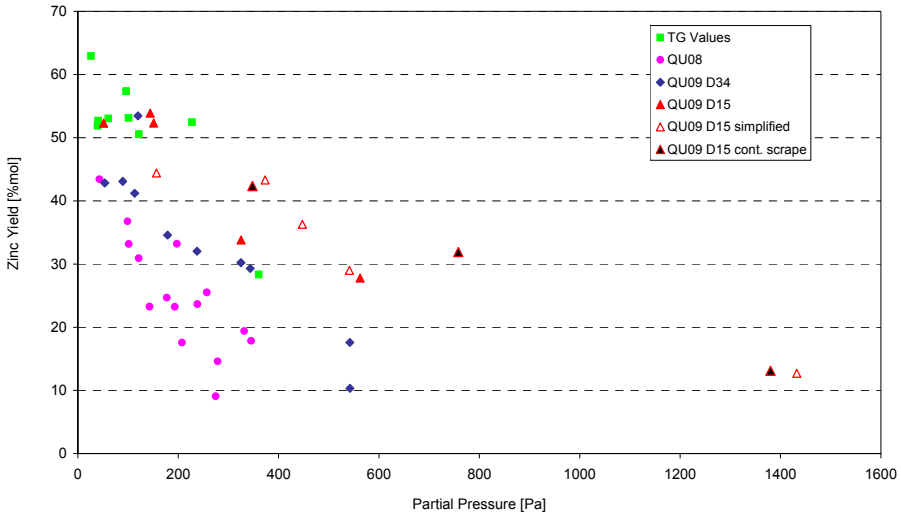
- RF (reacting flow): 7 l_N/min
- AF (annular flow): 7 l_N/min
- QF (quench flow): 24.5 l_N/min

- J. Materials Science 43 (2008) 4729–4736

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

Solar Experimental Results

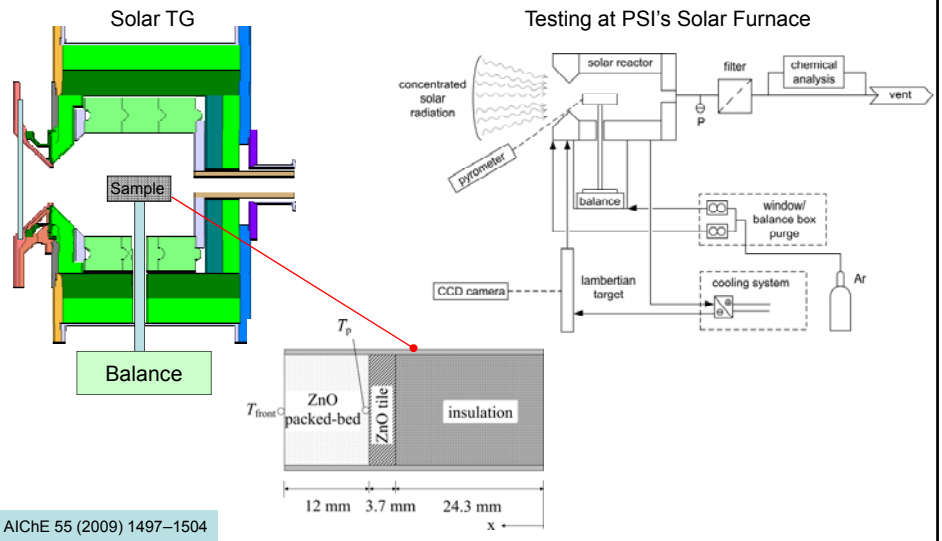
Quench units D34 and D15 compared to Solar TG



- Zn yield > 50% (filter: > 60%)

Solar Reactor Modeling

Kinetic analysis of ZnO dissociation in a packed-bed

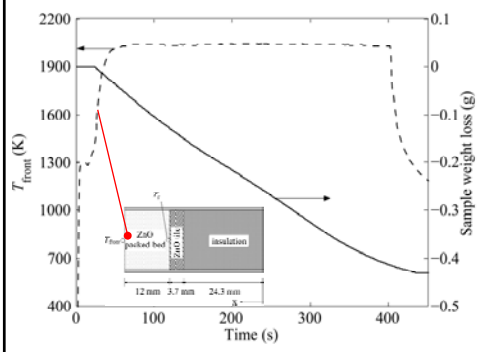


- AIChE 55 (2009) 1497–1504

Solar Reactor Modeling

Kinetic analysis of ZnO dissociation in a packed-bed

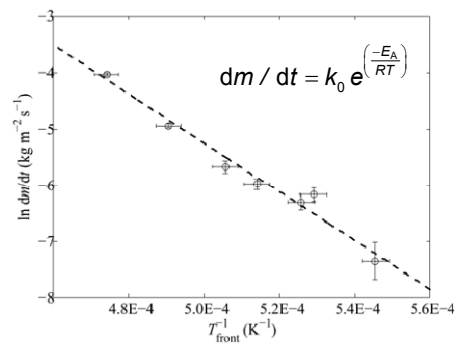
Surface temperature and weight loss vs. time



Arrhenius plot yielding

E_a = 361 kJ mol^{-1} and

$k_0 = 14.03 \cdot 10^6 \pm 2.73 \cdot 10^6$ kg m^{-2} s^{-1}

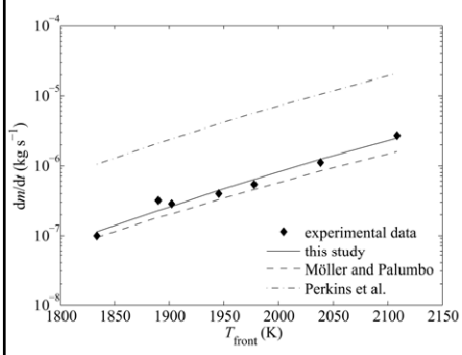


- AIChE 55 (2009) 1497–1504

Solar Reactor Modeling

Kinetic analysis of ZnO dissociation in a packed-bed

Comparison with theoretical results and with other studies



L'vov theory: $E_a = \frac{\Delta H_T^\circ}{a+b}$

$E_{a,th}$ = 356 kJ mol^{-1}, $E_{a,exp}$ = 361kJ mol^{-1}

$$k_0 = \frac{M_M D_M^{\frac{a}{a+b}} D_O^{\frac{b}{a+b}}}{zRT} \left(\frac{a}{\left(a^a b^b\right)^{\frac{1}{a+b}}} \right) e^{\frac{\Delta S_T^\circ}{R(a+b)}}$$

Combining with convection mass transfer:

$$z = f\left(\mathrm{Re}^{-1/2}, Sc, d\right)$$

$k_{0,th}$ = $5.99 \cdot 10^6$ kg m^{-2} s^{-1}

$k_{0,exp}$ = $14.03 \cdot 10^6$ kg m^{-2} s^{-1}

- AIChE 55 (2009) 1497–1504
- Chem. Eng. Sci. 62 (2007) 5952–5962
- Chem. Eng. Sci. 56 (2001) 4505–4515
- Thermoch. Acta 290 (1997) 239–251

Solar Reactor Modeling

Transient heat transfer model

- Numerical reactor model developed at PSI & ETH
- Transient model considering:
  - Radiative, conductive and convective heat transfer
  - Kinetics of ZnO dissociation occurring in a shrinking bed under an ablation regime

$$q^{'''}_{chemistry} = -r^{'''}\Delta H_r(T)$$

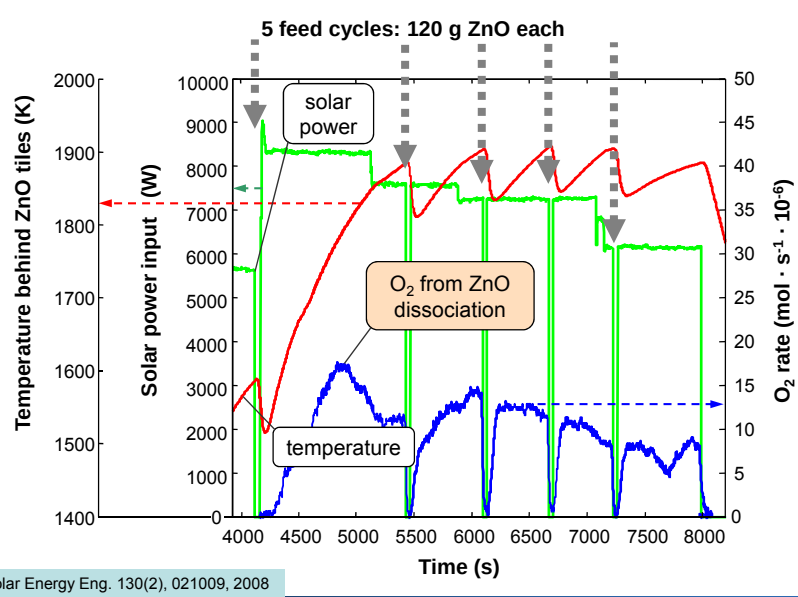
$$r^{'''} = k_0\, e^{\frac{-E_a}{RT}}$$

Radiative solar flux computed using an in-house Monte Carlo ray-tracing code (VeGaS).

Energy conservation	$\rho c_p \frac{\partial T}{\partial t} = \nabla(k_{eff}\nabla T) + q^{'''}_{chemistry}$
Boundary conditions	
cavity inner surfaces	$k_{eff}\nabla T \cdot \mathbf{n} = h_{in}(T - T_{gas}) + q^{''}_{radiative}$
outer surfaces	$k_{eff}\nabla T \cdot \mathbf{n} = h_{out}(T_{amb} - T) + \varepsilon\sigma(T^4_{amb} - T^4)$
Initial condition	$T(x,r,t=0) = T_0$

- Chem. Eng. J. 150 (2009) 502-508

Typical Experimental Run at PSI's High-Flux Solar Simulator



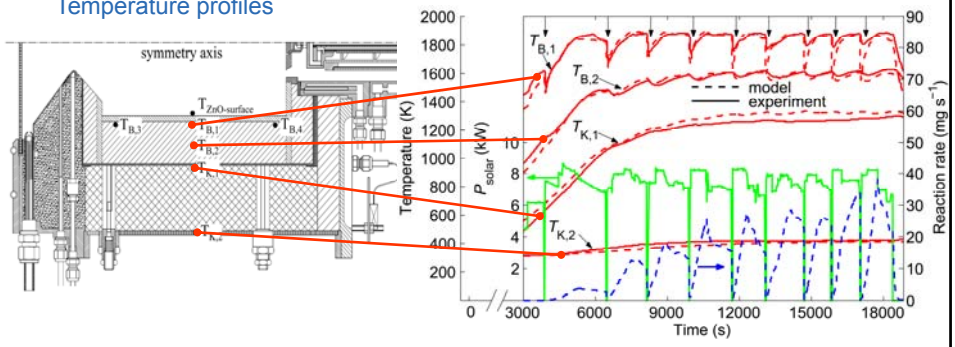
- J. Solar Energy Eng. 130(2), 021009, 2008

Solar Reactor Modeling

Experimental validation

Temperature profiles

9 feed cycles: 131 g ZnO each



Mass of ZnO dissociated

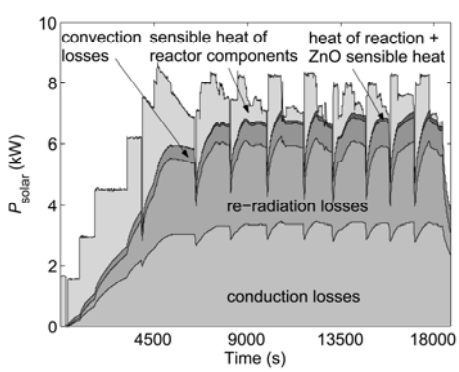
	ZnO dissociated (g)	
# feed-cycles	Measured	Calculated
3	68.5 ± 5.2	63.9
5	59.5 ± 6.8	54.0
7	148.4 ± 28.8	223.3
9	224.2 ± 49.5	197.1

- Chem. Eng. J. 150 (2009) 502-508

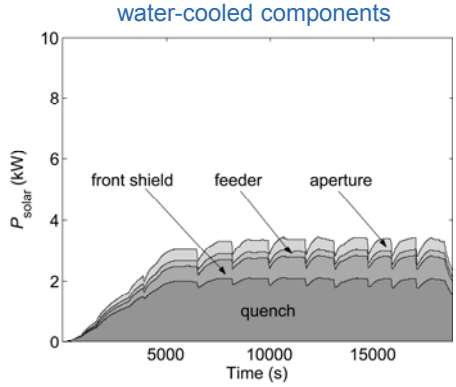
Solar Reactor Modeling

Energy balance

Global energy balance



Energy lost by conduction to water-cooled components



- Max. solar-to-chemical energy conversion efficiency: ~3%

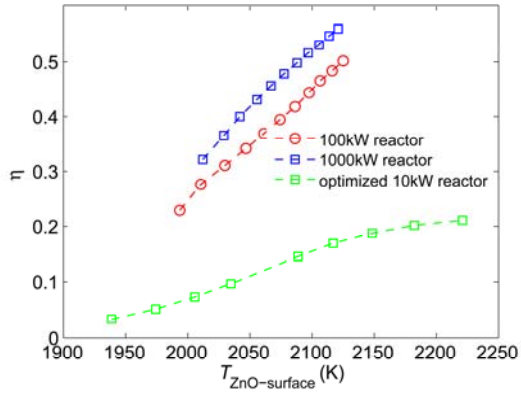
$$\eta = \int_{t=0}^{t=t_{end}} \frac{r(t)\left(H_r(T) + \int_{T_0}^{T} c_{p,\mathrm{ZnO}}\,\mathrm{d}T\right)}{P_{\mathrm{solar}}(t)}\,\mathrm{d}t$$

- Chem. Eng. J. 150 (2009) 502-508

Solar Reactor Modeling

Theoretical efficiency of 10 kW, 100 kW, and 1000 kW reactors

Solar-to-chemical efficiency vs. ZnO surface temperature

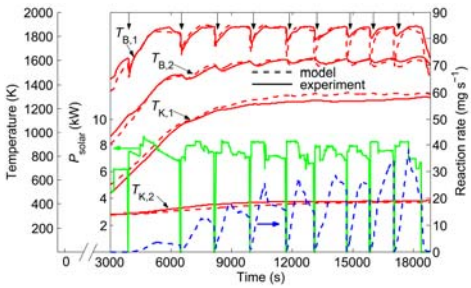


- Efficiency optimized by
  - minimizing water-cooled components
  - increasing ZnO surface temperature (→ materials issues)

Solar Thermal Dissociation of ZnO

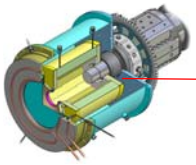
10 kW reactor prototype

- Solar thermal dissociation of ZnO demonstrated:
  - Experimental runs > 4 h; up to 9 semi-continuous feed cycles
  - Transient heat transfer model validated



Scale-up to 100 kW pilot plant

- Demonstration scheduled for June/July 2011:
  - Testing at 1 MW Solar Furnace, Odeillo, France



- J. Solar Energy Eng. 130(2), 021009, 2008
- Chemical Energy J. 150, 502-508, 2009

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

PROMES-CNRS Odeillo: 1 MW Solar Furnace (MWSF)

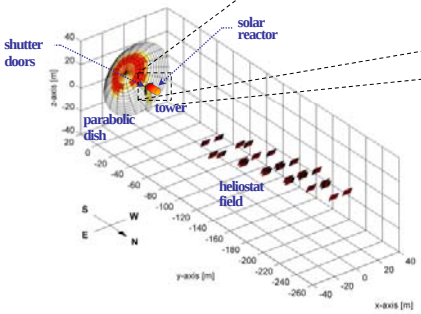
Heliostat field, parabolic concentrator, tower

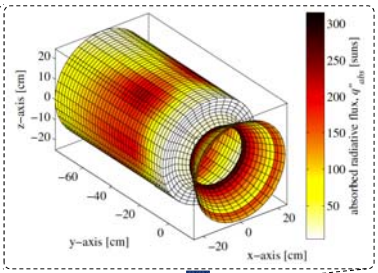
Elevation view of the Odeillo MWSF facility

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

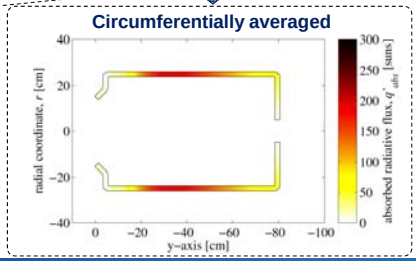
PROMES-CNRS Odeillo: 1 MW Solar Furnace (MWSF)

Monte Carlo (MC) ray tracing





Circumferentially averaged

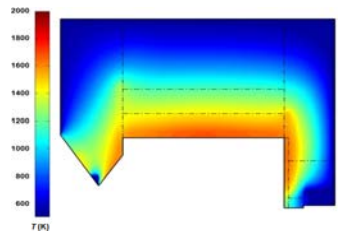


100 kW Scaled-up Reactor

Heat transfer model

- Reactor dimensions:

	100 kW	10 kW	
Cavity diameter	580	160	mm
Cavity length	750	230	mm
Reactor outlet diameter	110/37	80/15	mm
Al_2O_3 tiles thickness	12.7	7	mm
Outer shell diameter	1080	200	mm
Aperture diameter	190	60	mm
Window diameter	520	160	mm
Average concentration ratio	3500	3500	suns

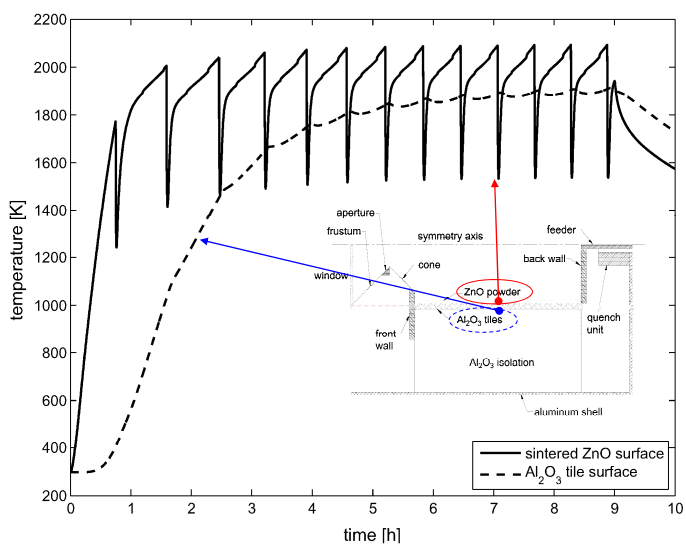


- Reactor modeled for two consecutive days of operation:
  - Power increased linearly over a 1-hr span
  - Nominal power kept constant for 8 hours
  - No incident power during 15 hours to simulate overnight condition

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

100 kW Scaled-up Reactor

Predicted temperatures: 1st day of operation



100 kW Scaled-up Reactor

Thermal performance predictions

- Assumptions (ideal case): 100% ZnO dissociation, 100% Zn yield

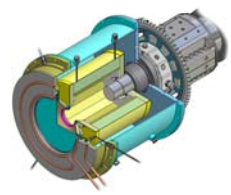
		Day 1	Day 2	
Reactor efficiency	$\eta_{reactor}$	23.1	23.6	%
Average reaction rate	r	27.4	29.7	kg h^{-1}
External incoming radiation				
Total incident power	Q_{solar}	232.8	232.8	kW
Passing through the aperture	$Q_{aperture}$	100.0	100.0	kW
Energy flows				
Chemical energy	$Q_{chemical}$	23.1	23.6	%
Reradiation losses	$Q_{reradiation}$	36.0	36.2	%
Cavity reradiation		*7.0*	*7.1*	%
External reradiation[a]		*26.3*	*26.4*	%
Window reradiation		*2.7*	*2.7*	%
Reflection losses	$Q_{reflection}$	25.6	25.6	%
Window reflections		*10.0*[b]	*10.0*[b]	%
Inner reflections[c]		*15.6*	*15.6*	%
Conduction losses	$Q_{conduction}$	11.6	11.6	%
Front shield		*2.8*	*2.8*	%
Aperture		*1.6*	*1.6*	%
Quench unit		*7.2*	*7.2*	%
Convection losses	$Q_{convection}$	2.5	2.9	%
Reactor sensible heat	$Q_{sensible}$	1.2	0.1	%

[a] Emitted from front cone and aperture.
[b] Assumed. The actual value depends on the window deposits.
[c] Over 99% occurring at the frustum.

$$\eta_{reactor} = \frac{Q_{chemical}}{Q_{solar}} = \frac{r\left[\Delta H_r(T) + \int_{T_0}^{T} c_{p,ZnO}\, dT\right]}{Q_{solar}}$$

$Q_{chemical}$ = enthalpy of reaction + sensible heat

Q_{solar} = total radiative power incident on window's outer surface

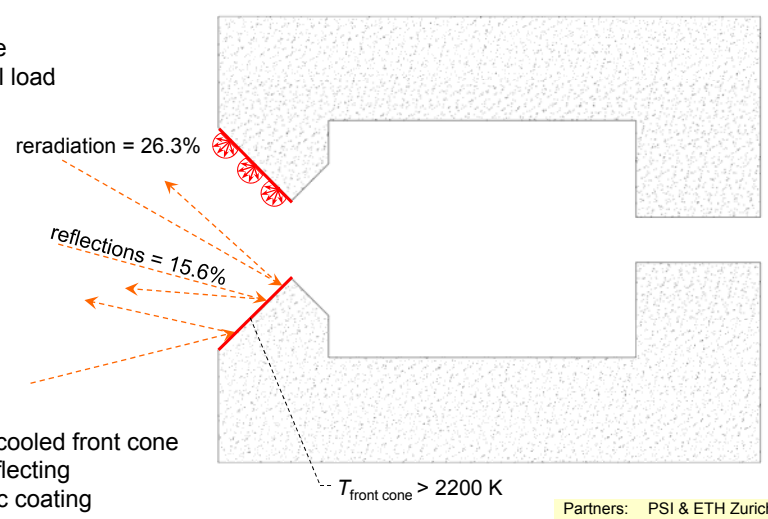


100 kW Scaled-up Reactor

Heat losses at front cone

Challenge

- Reduce thermal load



Solution

- Water-cooled front cone with reflecting ceramic coating

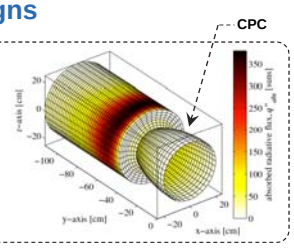
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

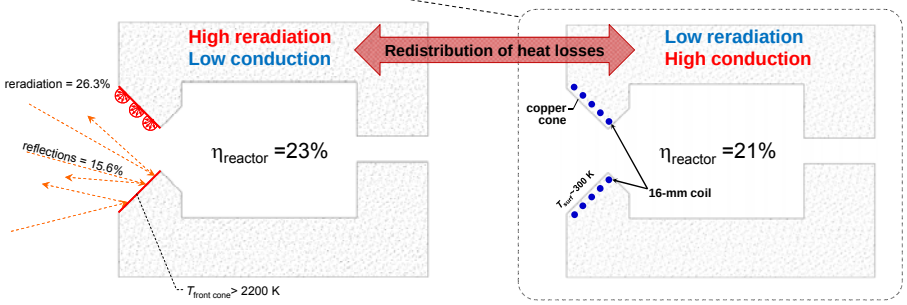
100 kW Scaled-up Reactor

Front cone: alternative designs

- Secondary concentrator: CPC (Compound Parabolic Concentrator)
  - Prevent Zn vapor from condensing on cold CPC surface
- Water-cooled front cone

ε = 0.1
D_o = 19 cm
D_i = 28 cm
L = 25.4 cm
Φ = 43 deg
C_{CPC} = 2.2

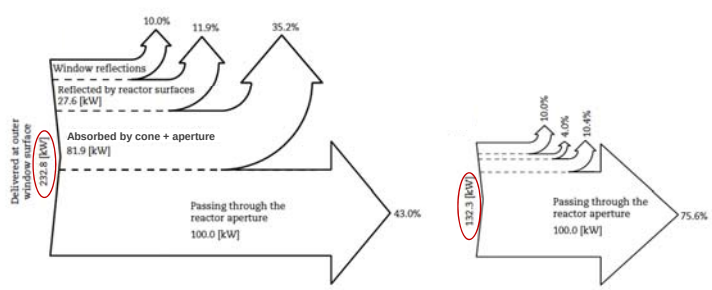




Baseline design | Water-cooled cone

100 kW Scaled-up Reactor

Compound Parabolic Concentrator (CPC)

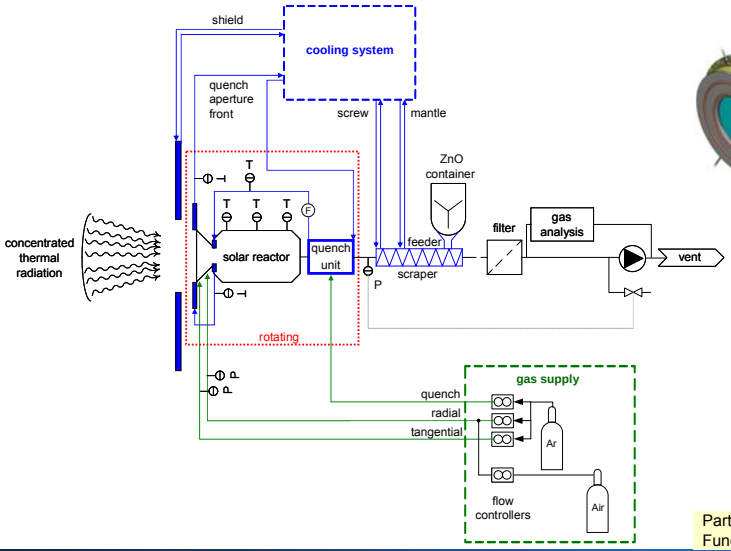


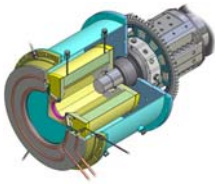
Without CPC | With CPC

- Radiation reflected and absorbed by front cone significantly reduced → $\eta_{reactor}$ = 38%
- Total input power, Q_{solar}, decreases by more than 40%
- Required number of heliostats reduces from 22 to 12 → **Investment cost reduced**

100 kW Scaled-up Reactor

Simplified process scheme

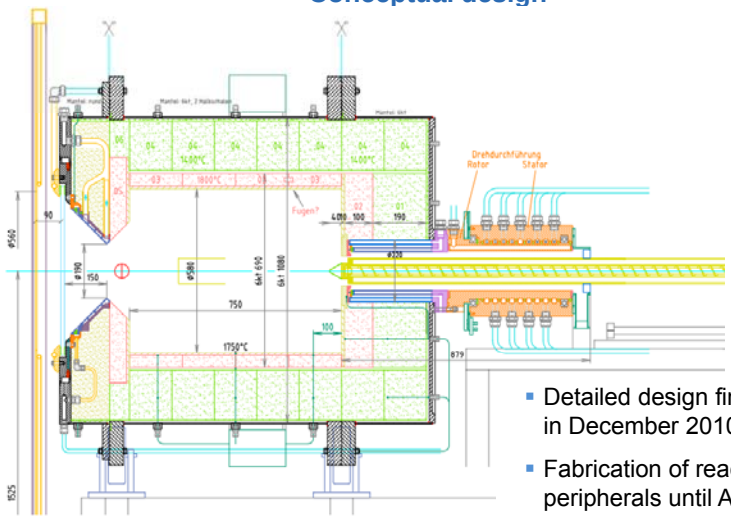




Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

100 kW Scaled-up Reactor

Conceptual design

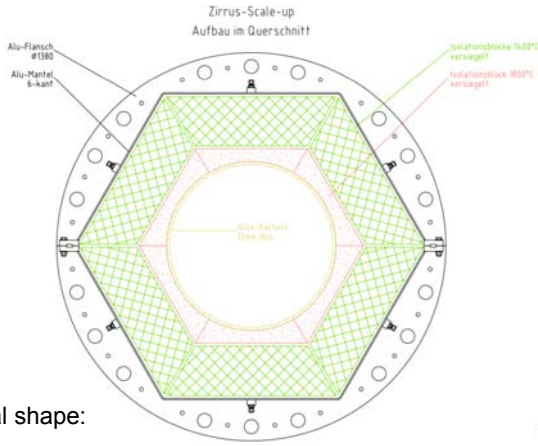


- Detailed design finalized in December 2010
- Fabrication of reactor and peripherals until April 2011

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

100 kW Scaled-up Reactor

High temperature materials



Reliable reactor materials
for applications at T > 2000 K

- Ceramic wall materials:
  - ZnO and Al_2O_3 tiles
  - Al_2O_3–SiO_2 insulation (1800°C / 1400°C)
- Cylindrical shape → hexagonal shape:
  - Mechanical stability for rotary motion

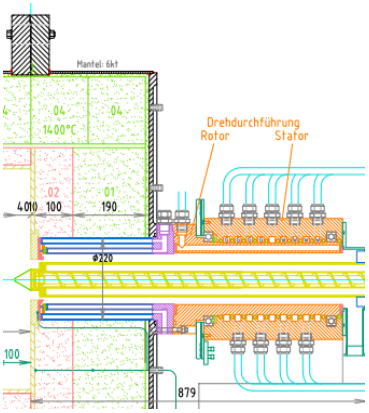
Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

100 kW Scaled-up Reactor

Zn-O_2 gas separation

Rapid quench

- Dilution with cold inert gas (Ar)
- High Zn yield → high dilution
- Future: Recycling of Ar for process economics



Reactor operating strategy

- Annular quench:
  Feeder remains at cavity exit (semi-continuous mode)
- Tubular quench (modular units):
  Feeder remains fully retracted (batch mode)

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

100 kW Scaled-up Reactor

Goals for 1st experimental campaign

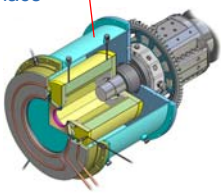
1st Priority: Reliable reactor operation at high temperatures

- Front cone heat removal
- Window protection
- High-temperature materials
- Particle feeding and removal

2nd Priority: Gas separation and efficiency

- Separation of Zn and O_2 by rapid quench
- Zn yield > 50%; $\eta_{reactor}$ > 5%

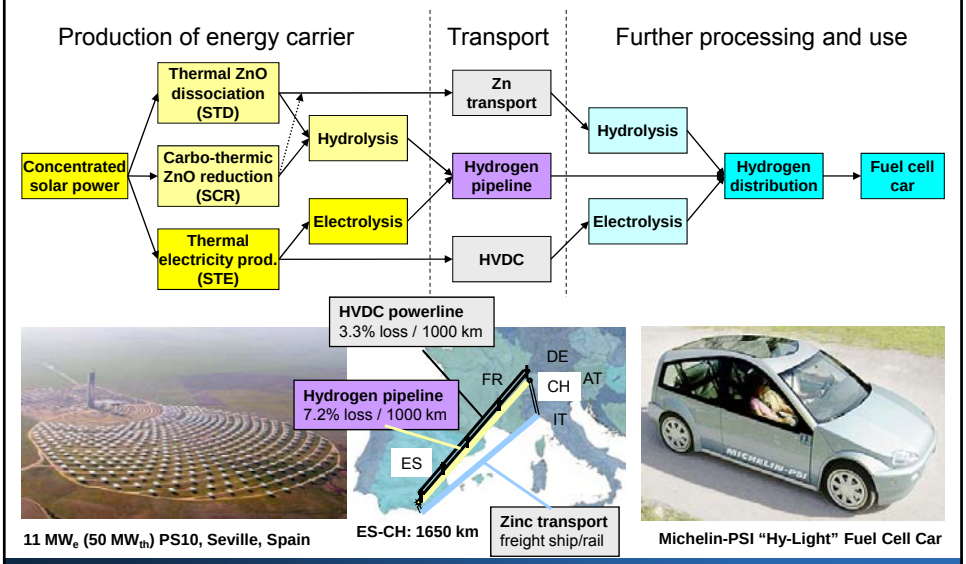
1 MW Solar Furnace
Odeillo, France



Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

Life Cycle Analysis (LCA)

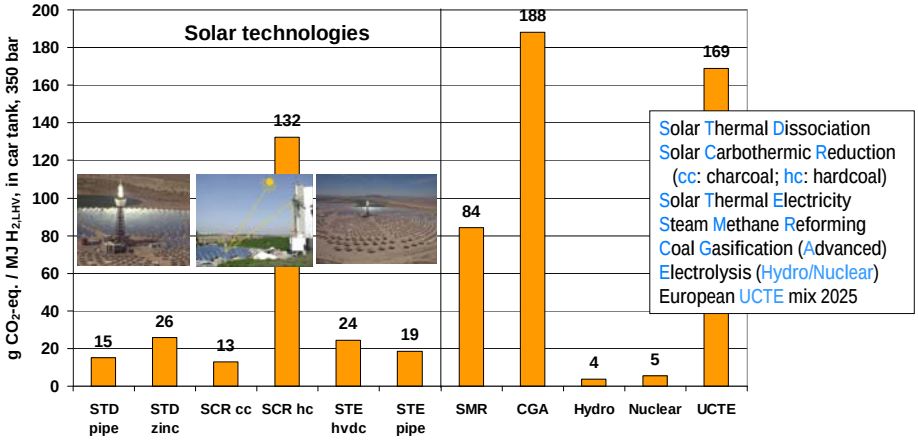
Well-to-wheel analysis for solar-produced H_2 used in a fuel cell car



Life Cycle Analysis (LCA)

Well-to-tank analysis for solar-produced H_2: GHG emissions

- Radiative forcing in g CO_2-equivalents (time horizon 100 years)



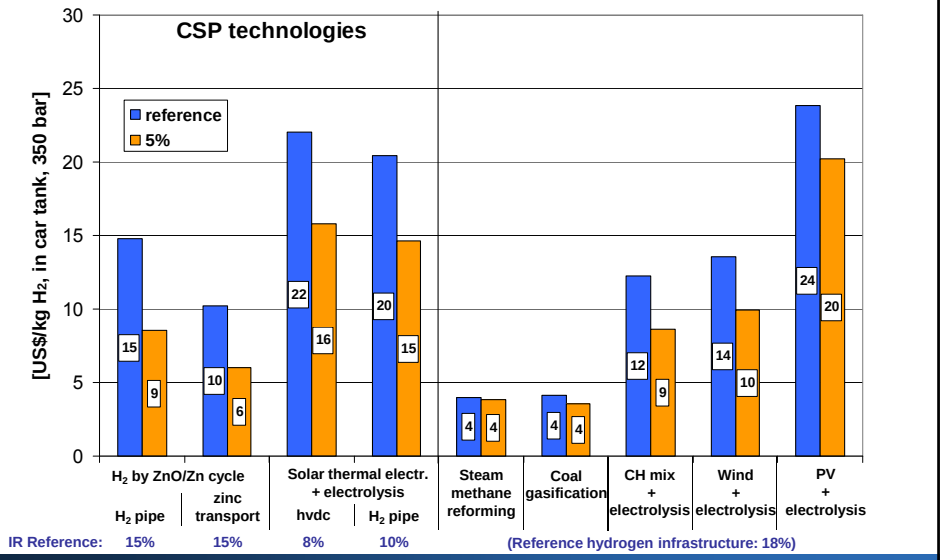
- J. Solar Energy Eng. 130 (2008) 011017

Partners: PSI & ETH Zurich
Funding: Baugarten Foundation, PSI

SFERA Winter School, ETH Zurich, March 25, 2011 43

Economic Analysis

H_2 supply costs in car tank: Variation of interest rate (IR)



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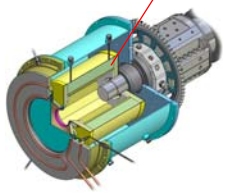
Conclusions & Outlook

Conclusions

- Zn-based thermochemical cycle for splitting H_2O and CO_2
- 1st step: Solar thermal dissociation of ZnO
- Solar reactor technology from prototype (10 kW) to pilot plant (100 kW)
- 2nd step: Reduction of CO_2 and H_2O with Zn → Lecture of P. Loutzenhiser



Outlook

- Pilot plant demonstrations 2011 & 2012
- Development of conceptual design for industrial solar Zn production plant based on CSP tower technology
- Analysis of system economics

Acknowledgements

Financial Support

- Swiss Federal Office of Energy (SFOE)
- Baugarten Foundation

Further Information

- http://solar.web.psi.ch
- http://www.pre.ethz.ch

Review Article

- P.G. Loutzenhiser, A. Meier, A. Steinfeld
  Review of the two-step H_2O/CO_2-splitting solar thermochemical cycle based on Zn/ZnO redox reactions
  Materials **3**, 4922-4938 (2010).
  http://www.mdpi.com/1996-1944/3/11/4922/