Running Chemical Reactions at Ultra-High Temperatures for Solar Energy Storage

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Potential and Challenges

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Solar Technology Laboratory (STL)

our mission is
to develop the science and technology
that is required for transforming, at an industrial scale,
solar energy into chemical fuels
with a thermochemical process
that effects this conversion more competitively
than any other solar-to-fuel process

concentrate — store — transport

Outline

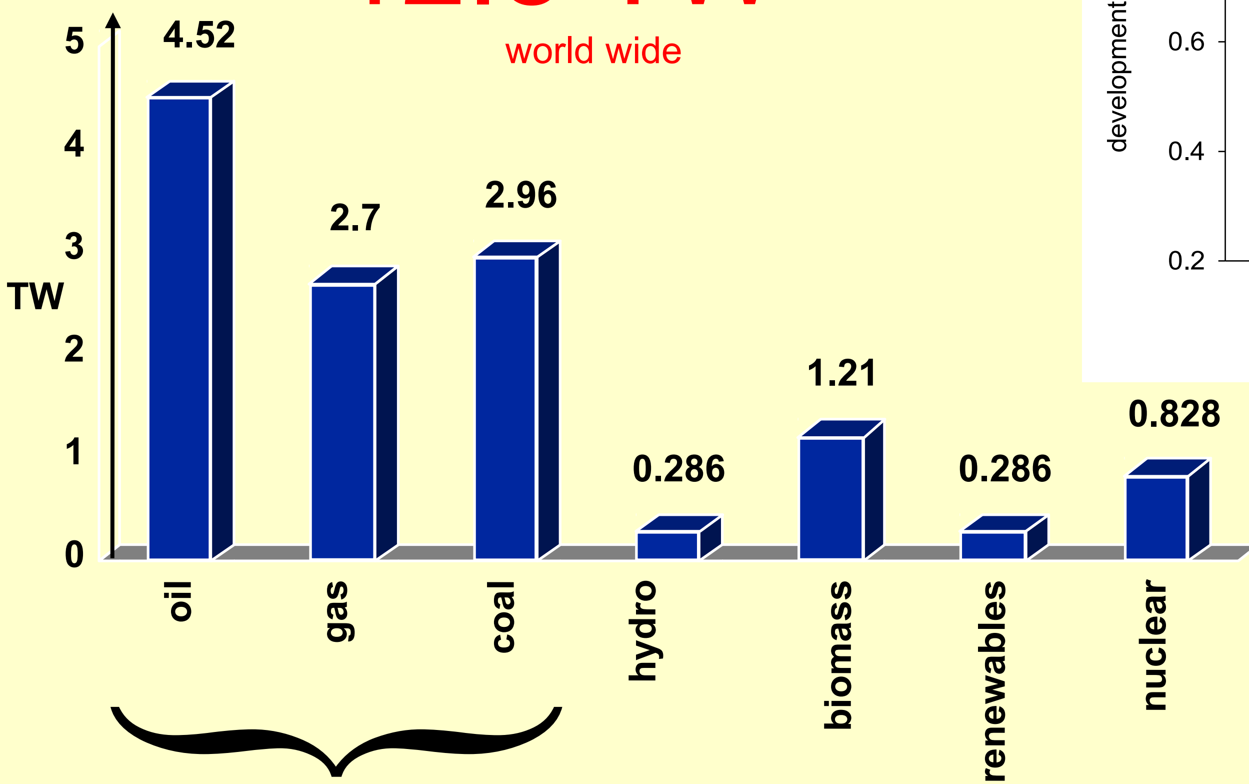
- general motivation: solar fuels
- concentrated solar radiation
  - concepts
- thermochemical cycles
  - basics
  - energetics / efficiencies
- instrumentation: solar furnace / solar simulator

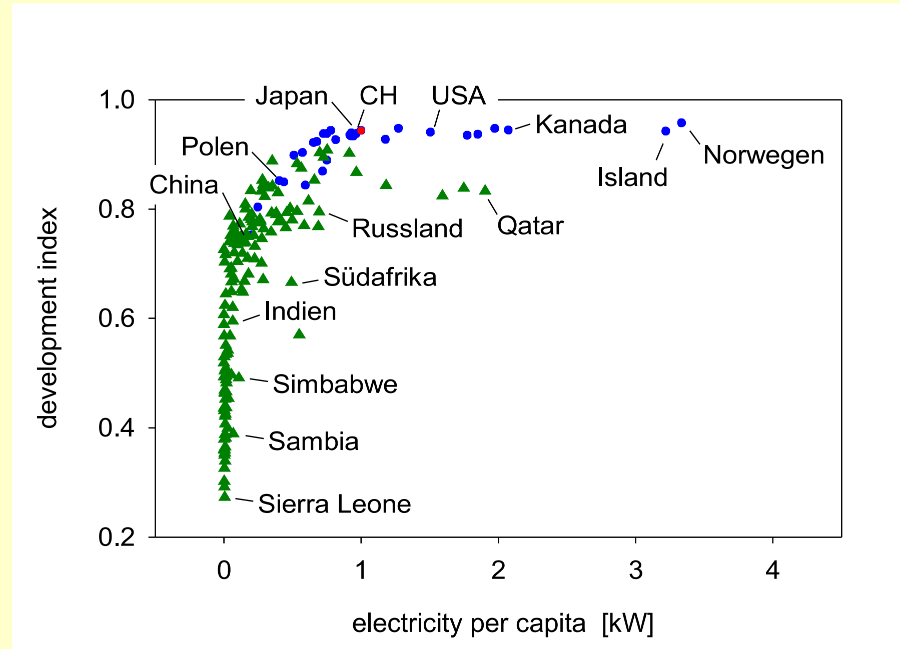
- example: Zn / ZnO cycle
  - carbon free
  - carbothermic

Electricity Consumption

12.8 TW

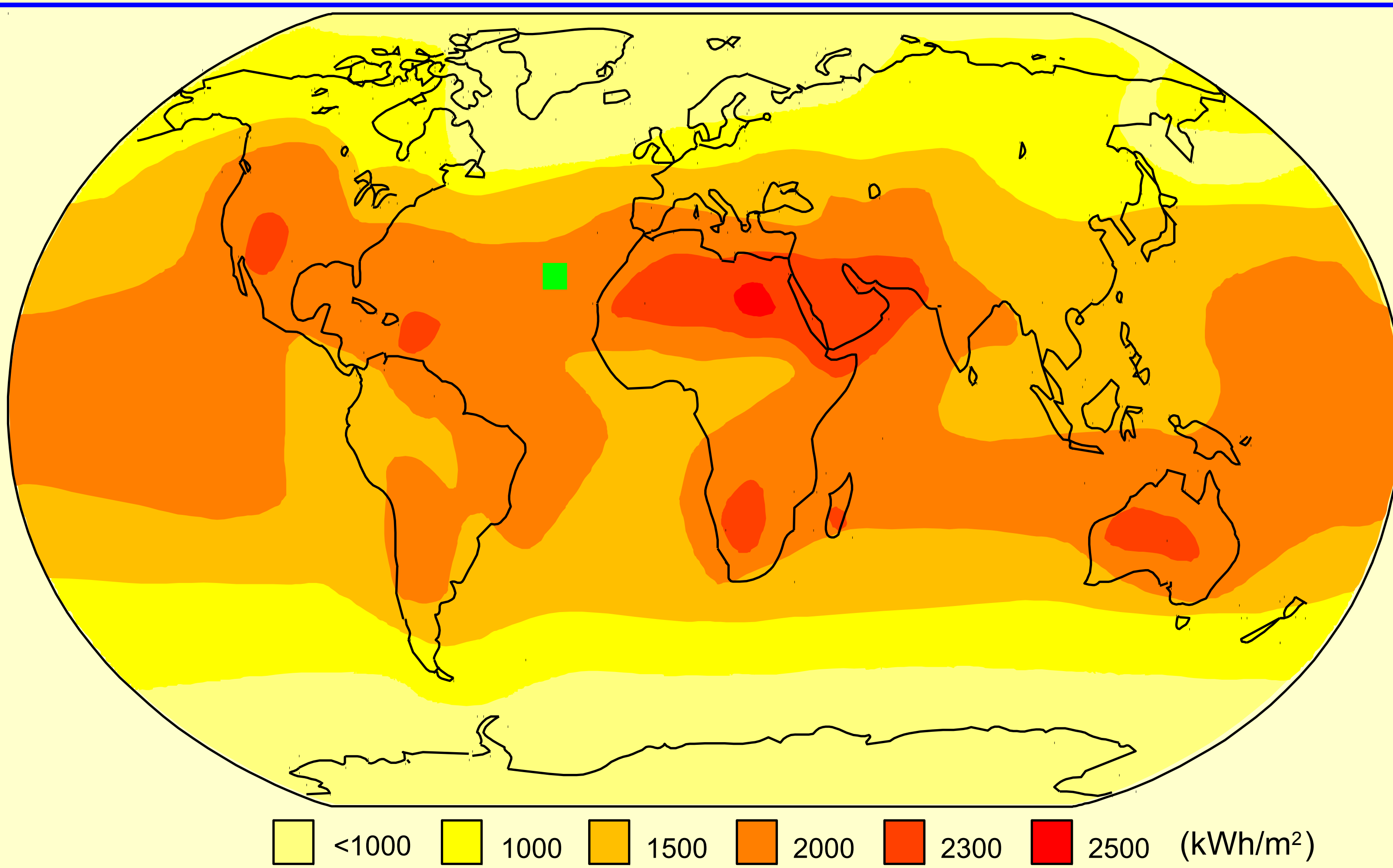
world wide





to be replaced

Solar Radiation



- annual energy consumption = 150‘000 TWh
- annual solar input = 2300 kWh/m^2
- energetic efficiency (solar to electricity) = 20%
- land use factor = 25%

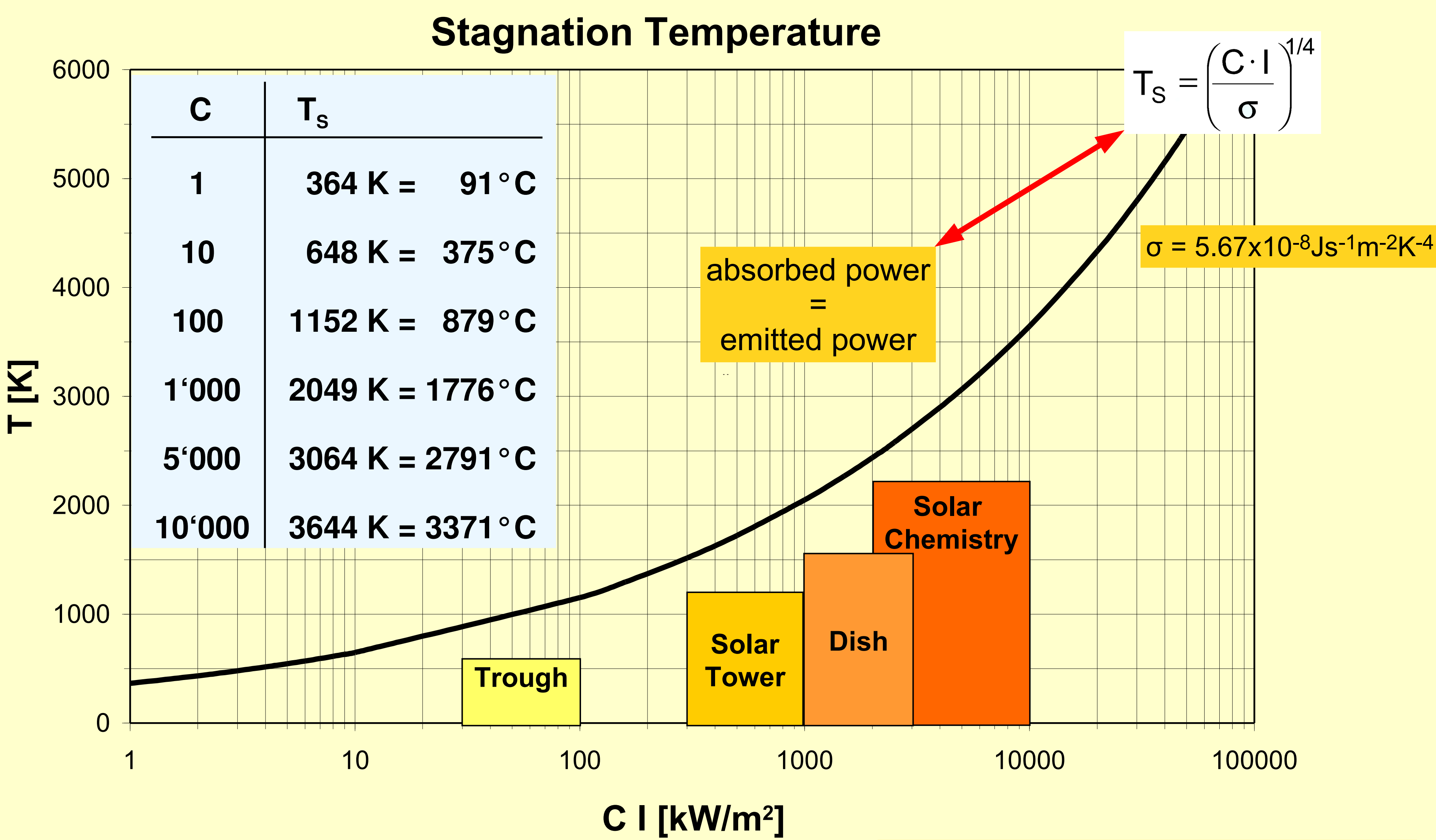
area used:
ca. 1000 km x 1000 km

Concentrated Solar Radiation: High Temperatures

Stagnation Temperature

C	T_S
1	364 K = 91 °C
10	648 K = 375 °C
100	1152 K = 879 °C
1'000	2049 K = 1776 °C
5'000	3064 K = 2791 °C
10'000	3644 K = 3371 °C

$$T_S = \left(\frac{C \cdot I}{\sigma}\right)^{1/4}$$



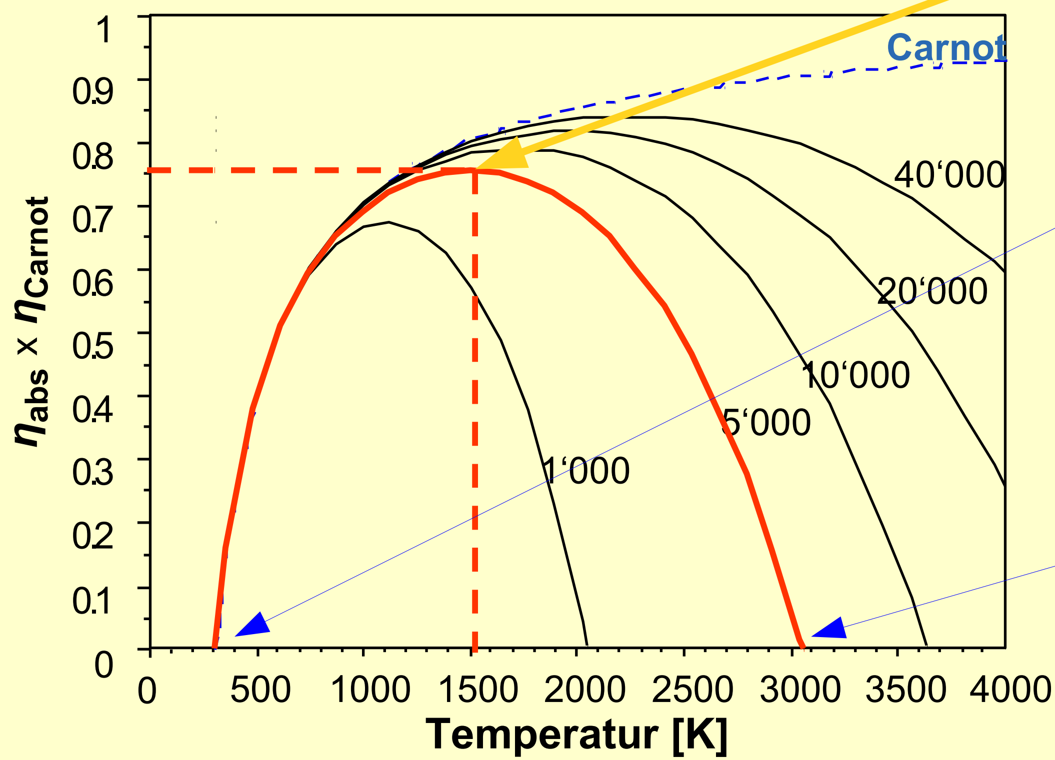
$\sigma = 5.67 \times 10^{-8} Js^{-1}m^{-2}K^{-4}$

irradiation: I = 1 kW/m² (1 Sun) C = 1

Concentrated Solar Radiation:

High Efficiency

$$\eta_{\max} = \eta_{\rm abs}\,\eta_{\rm Carnot} = \left(1 - \frac{\sigma T^4}{CI}\right)\left(1 - \frac{T_{\rm L}}{T}\right)$$



peak efficiency
(maximum power point)

T = 1500K, C = 5000
η_{max} = 0.75

$$\eta_{\rm Carnot} = 1 - \frac{T_{\rm L}}{T}$$

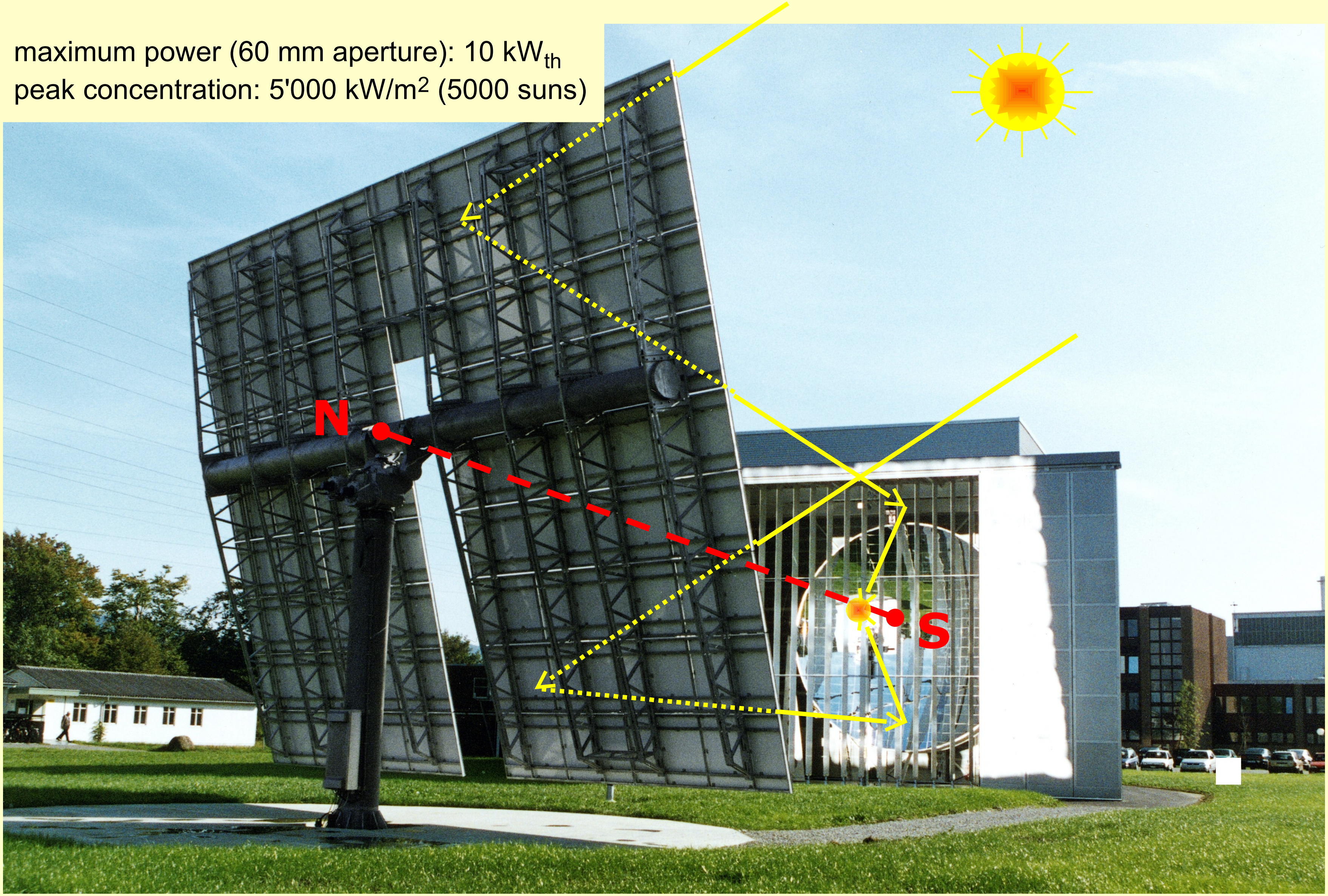
$$\eta_{\rm abs} = \frac{P_{\rm abs} - P_{\rm rerad}}{Q_{\rm solar}}$$

$$\eta_{\rm abs} = 1 - \frac{\sigma T^4}{CI}$$

Instrumentation:

Solar Furnace

maximum power (60 mm aperture): 10 kW_{th}
peak concentration: 5'000 kW/m^2 (5000 suns)



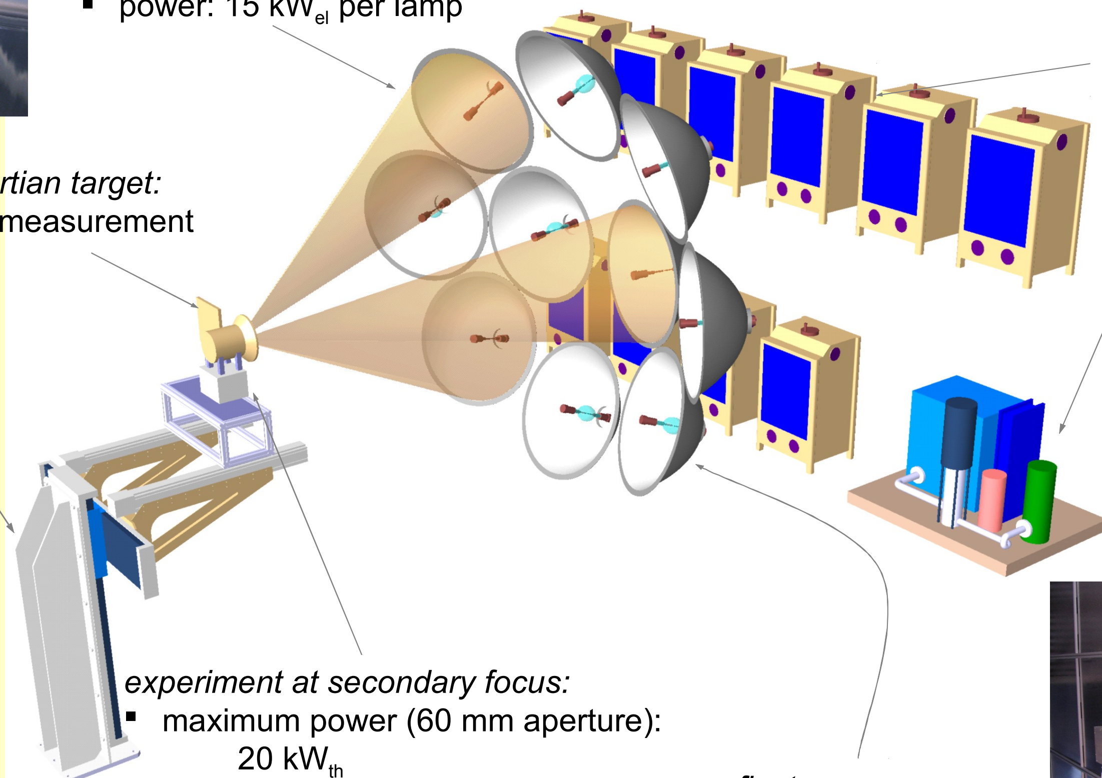
Instrumentation: Solar Simulator

lamps:
- 10 Xe-arc lamps (water-cooled)
- power: 15 kW_{el} per lamp

feeds:
- 10 rectifiers
- air and water cooling unit

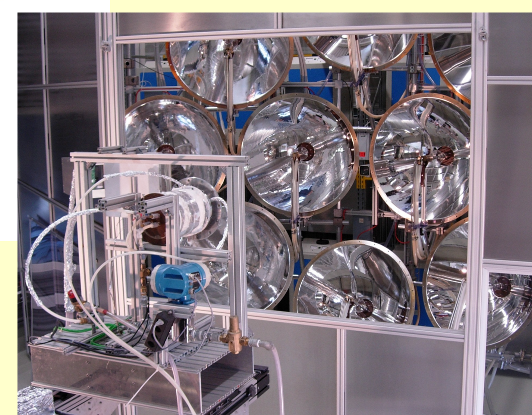
Lambertian target:
- flux measurement

plattform:
- 3-axis stage
- maximum: 500 kg



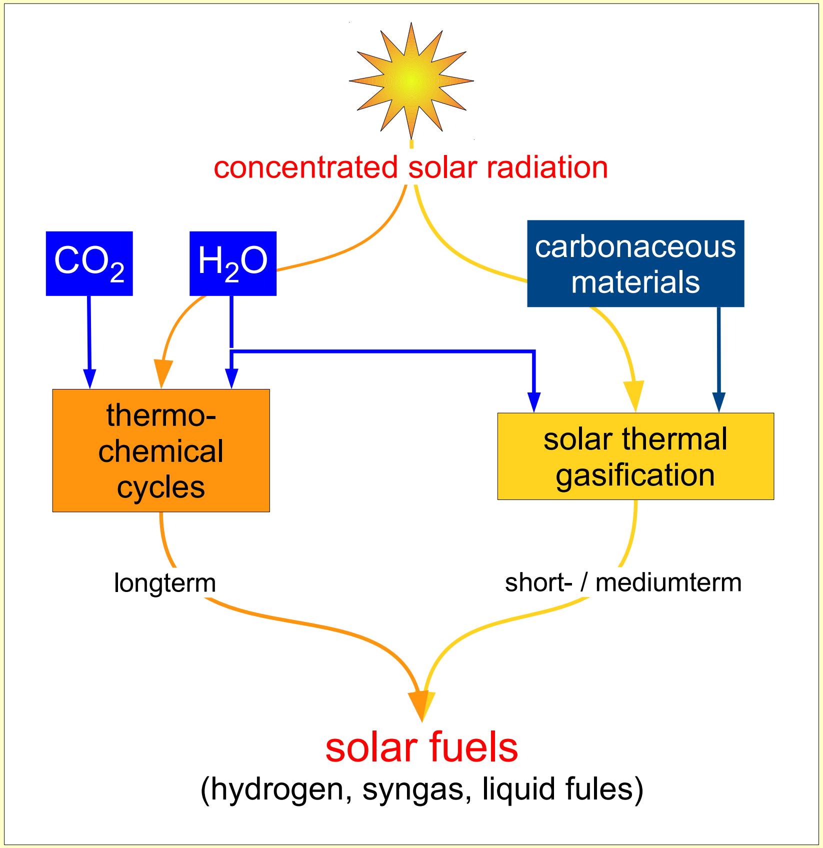
experiment at secondary focus:
- maximum power (60 mm aperture): 20 kW_{th}
- peak concentration: > 10’000 kW/m^2 (suns)

reflectors:
- ellipsoidal reflectors
- coated Al layer



Solar Fuels

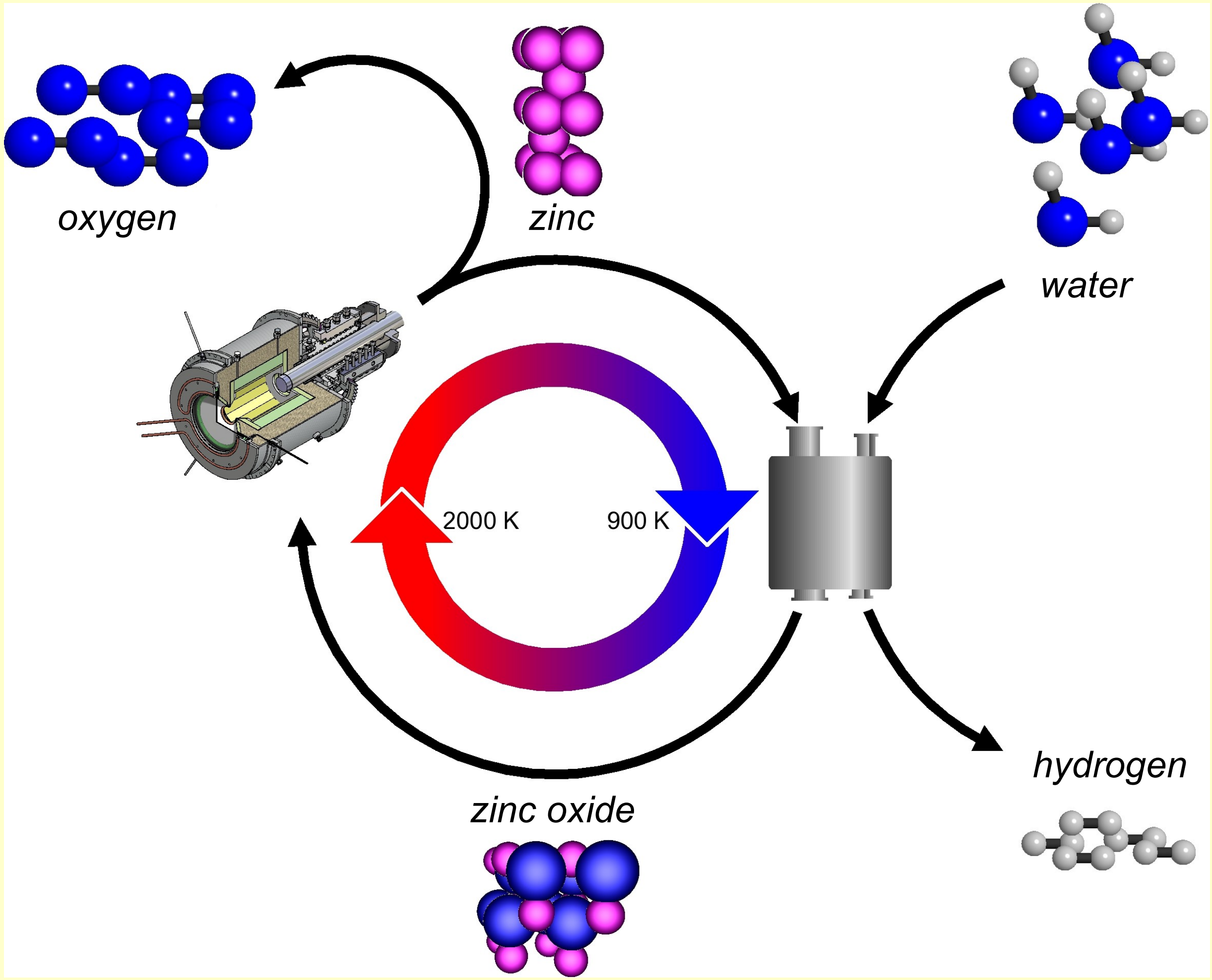
- Zn / ZnO cycle
  - hydrogen
  - syngas
- ceria cycle
  - syngas



- gasification of biomas
  $C + H_2O \rightarrow H_2 + CO$
- gasification of carbonaceous waste
  $C + H_2O \rightarrow H_2 + CO$
- cracking of hydrocarbons
  $C_xH_y \rightarrow C + H_2$
- steam reforming
  $CH_4 + H_2O \rightarrow CO + 3H_2$
  $(CO + H_2O \rightarrow CO_2 + H_2)$

Thermochemical Cycles:

Hydrogen from Water in Two Steps



metal:	base metals	(oxide is more stable than water)
	noble metals	(low reduction temperature of oxide)

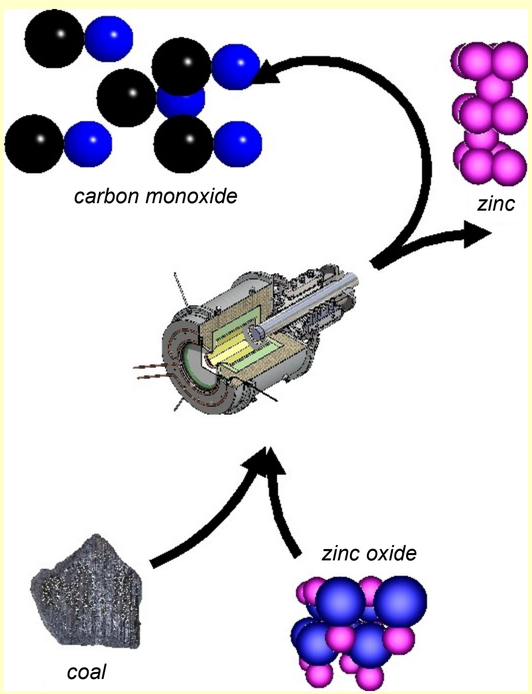
other candidates
Fe / Ce / Sn

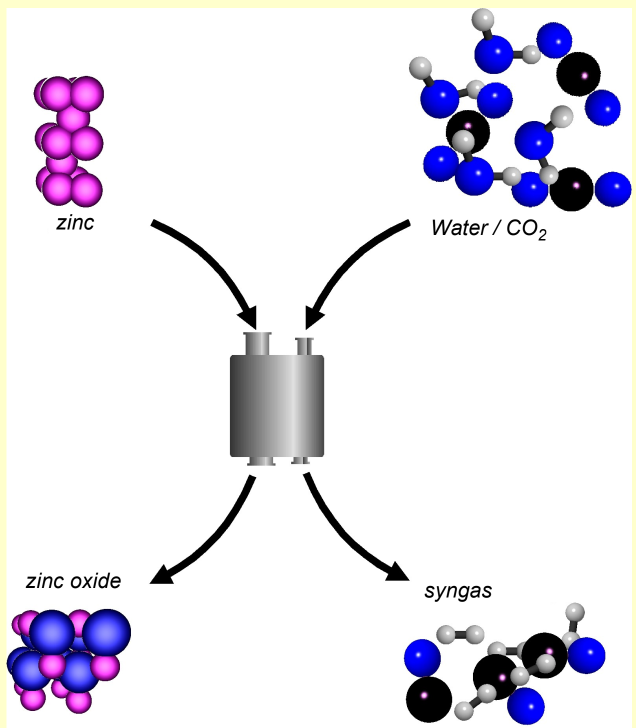
Thermochemical Cycles: Variations

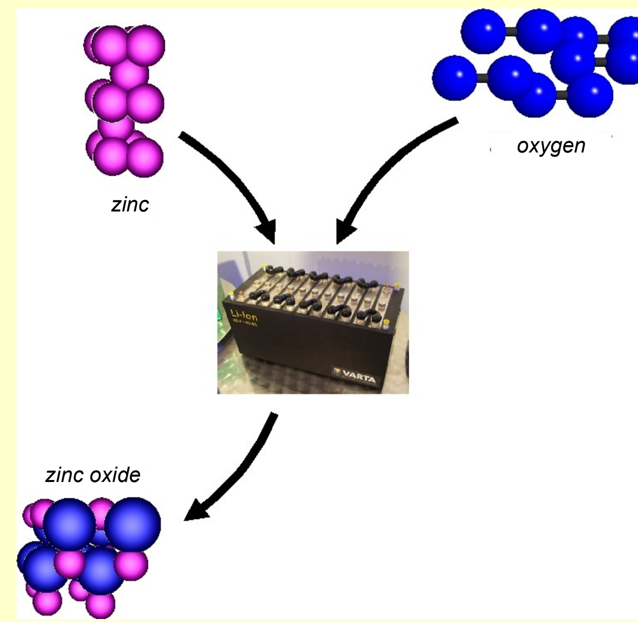
carbothermal
- (only) solar process heat
+ lower temperatur
+- syngas

syngas direct
+ "one pot" reaction
+ simple / cheap

zinc / air battery
- electricity
- transport (Zn / ZnO)

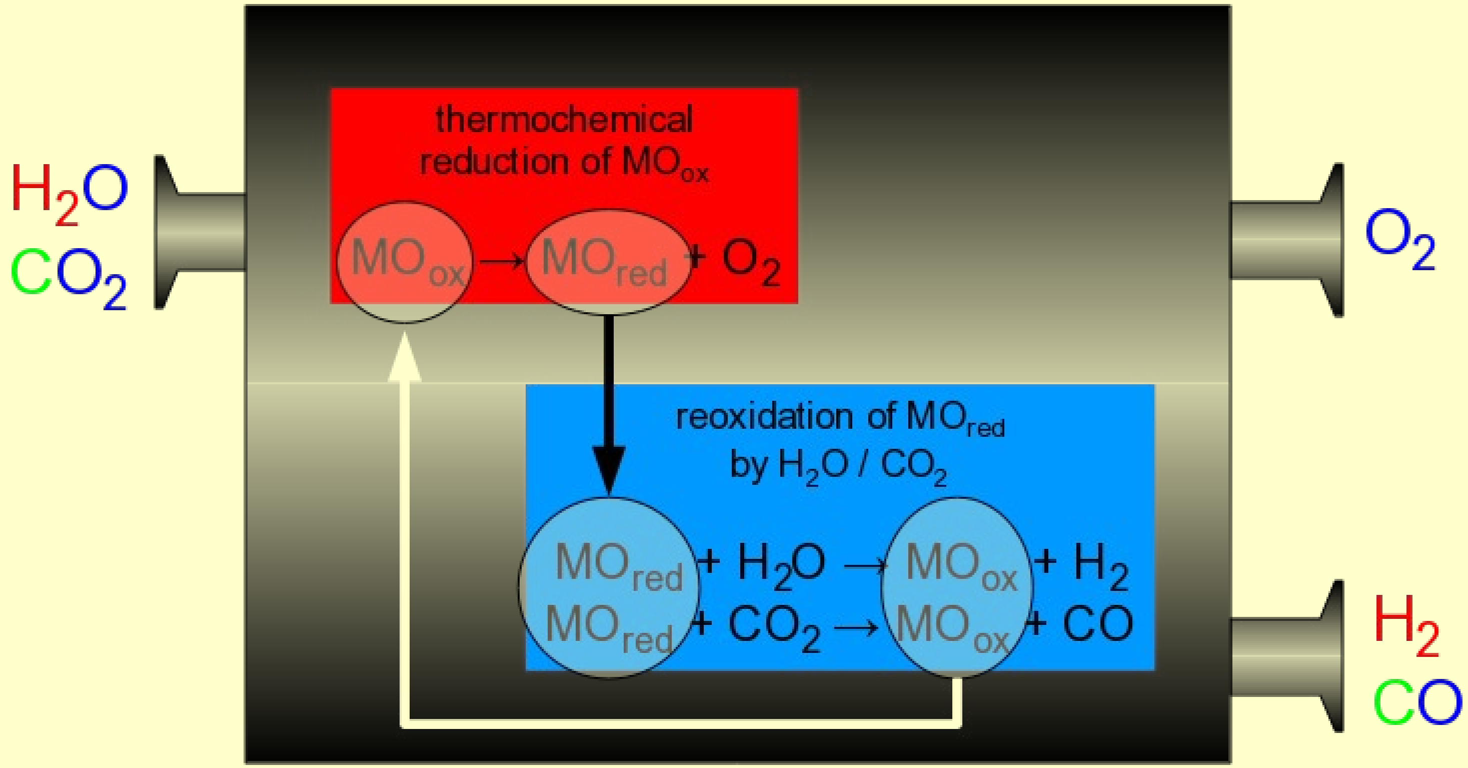






Thermochemical Cycles:

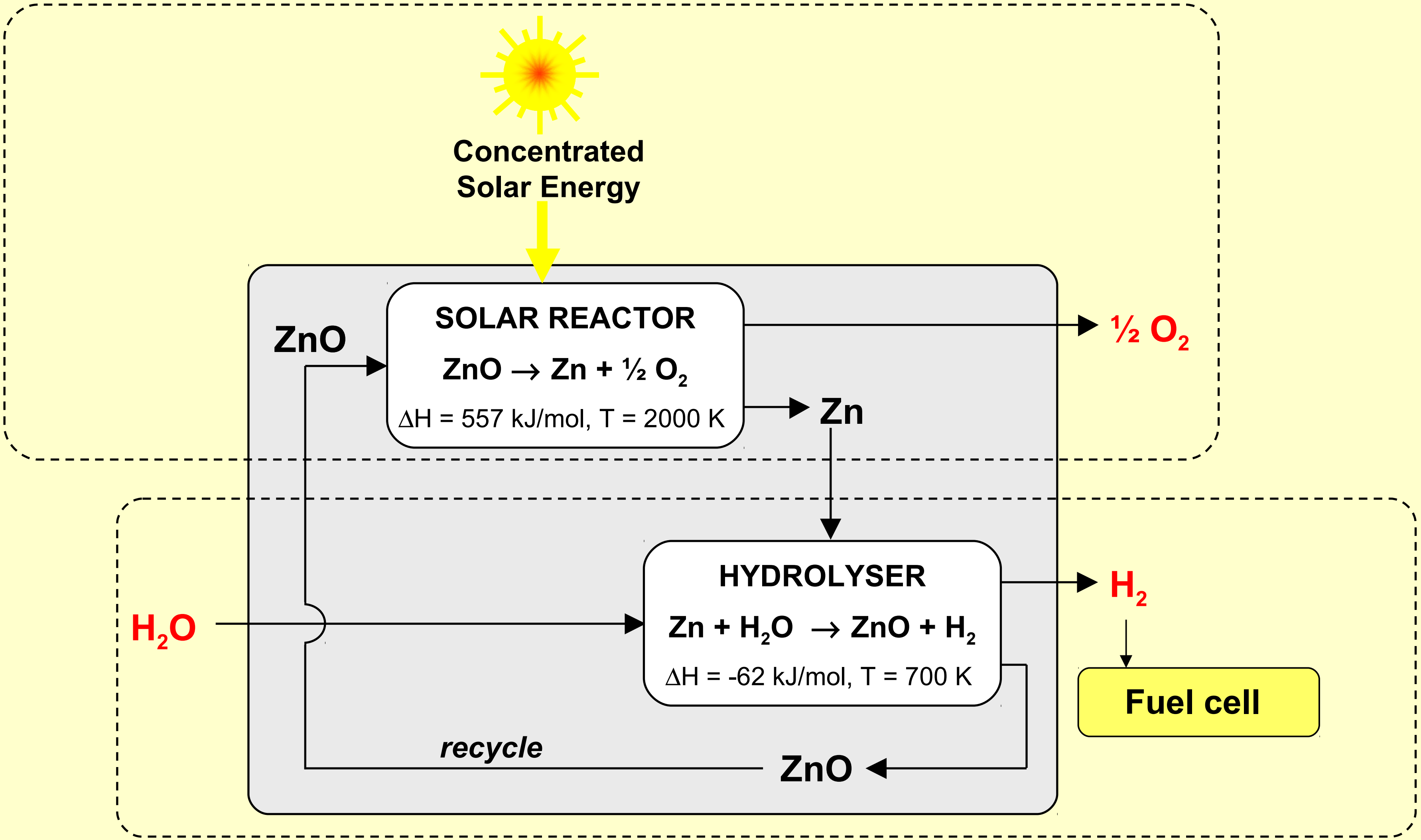
Black Box



water splitting reaction: $H_2O \rightarrow H_2 + ½O_2$

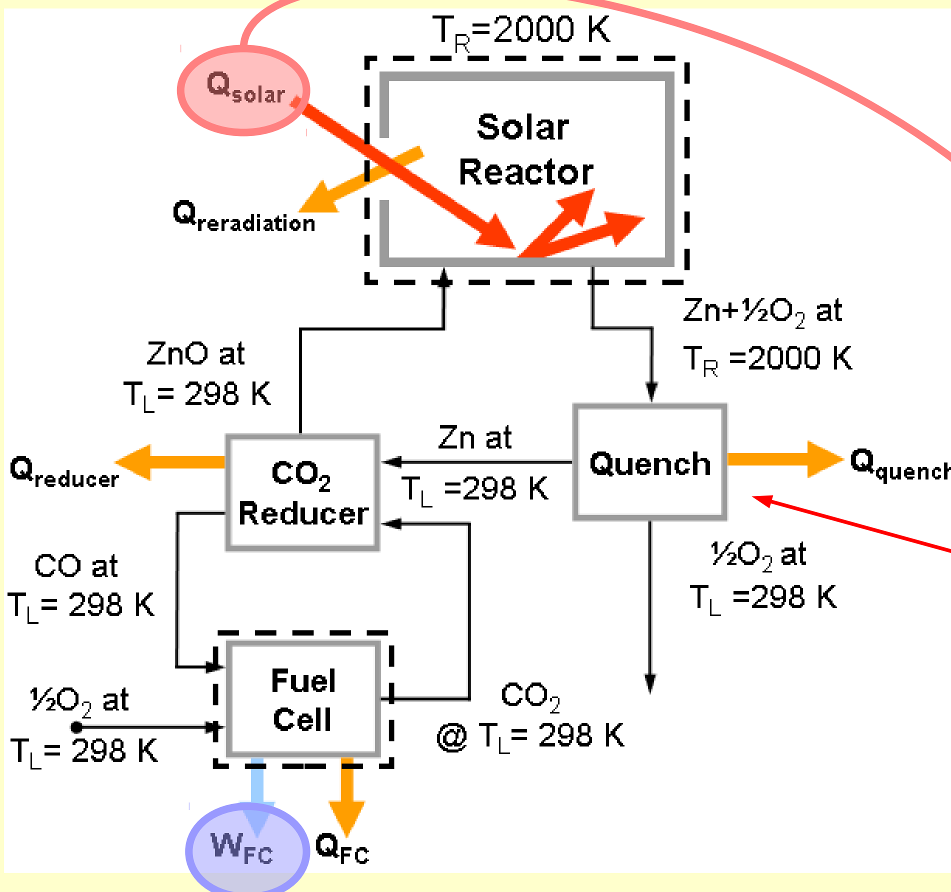
CO_2 reduction : $CO_2 \rightarrow CO + ½O_2$

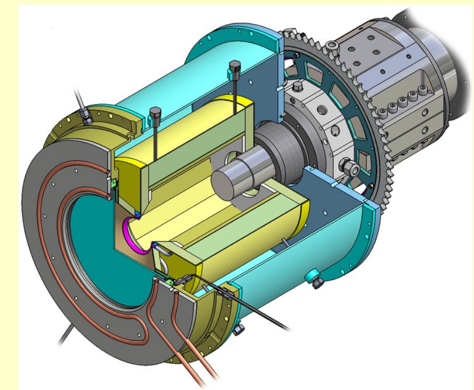
Energetics: $H_2O \rightarrow H_2$



Solar to Fuel Efficiency:

2nd Law Analysis



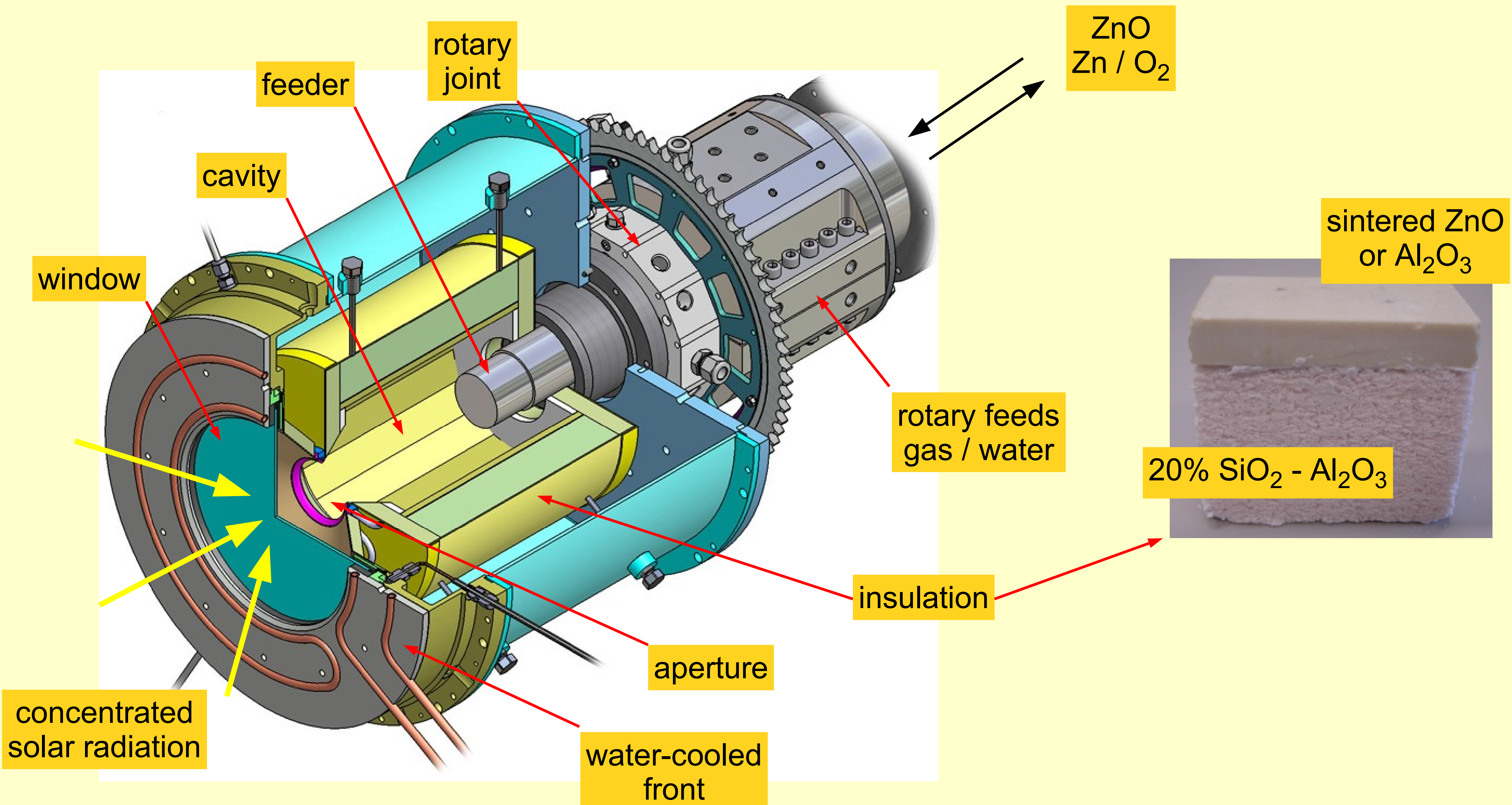


quenching with inert gas to separate $Zn_{(g)}$ / O_2 !

$$\eta_{solar\text{-}to\text{-}chemical} = \frac{W_{FC}}{Q_{solar}} = \begin{cases} 39\% \text{ ZnO/Zn-cycle} \\ 29\% \text{ Fe}_3\text{O}_4\text{/FeO-cycle} \end{cases}$$

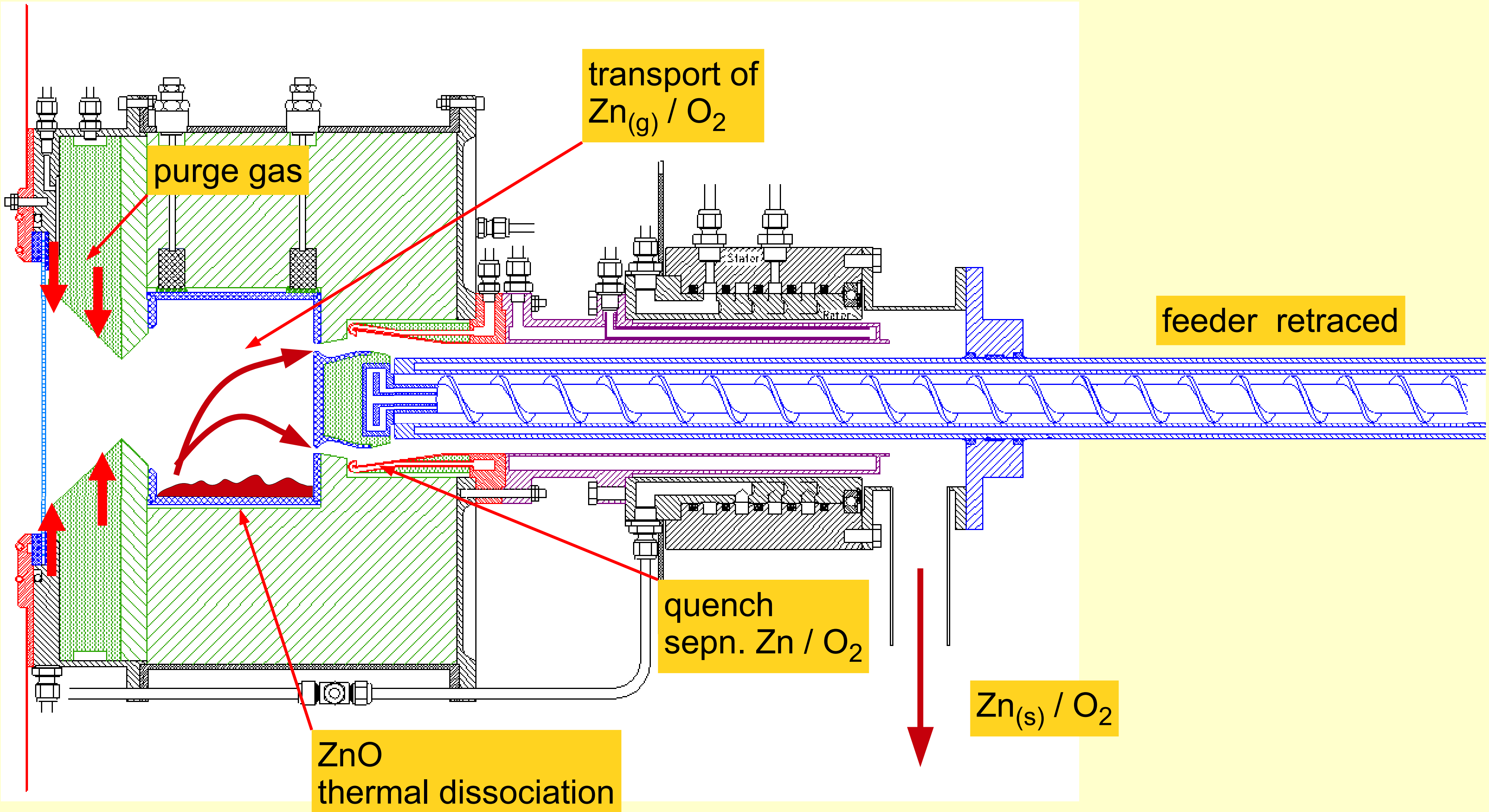
process efficiency will be lower: optical efficiency, support, ...

Zn / ZnO Cycle: 10 kW Solar Reactor



Zn / ZnO Cycle: 10 kW Solar Reactor II

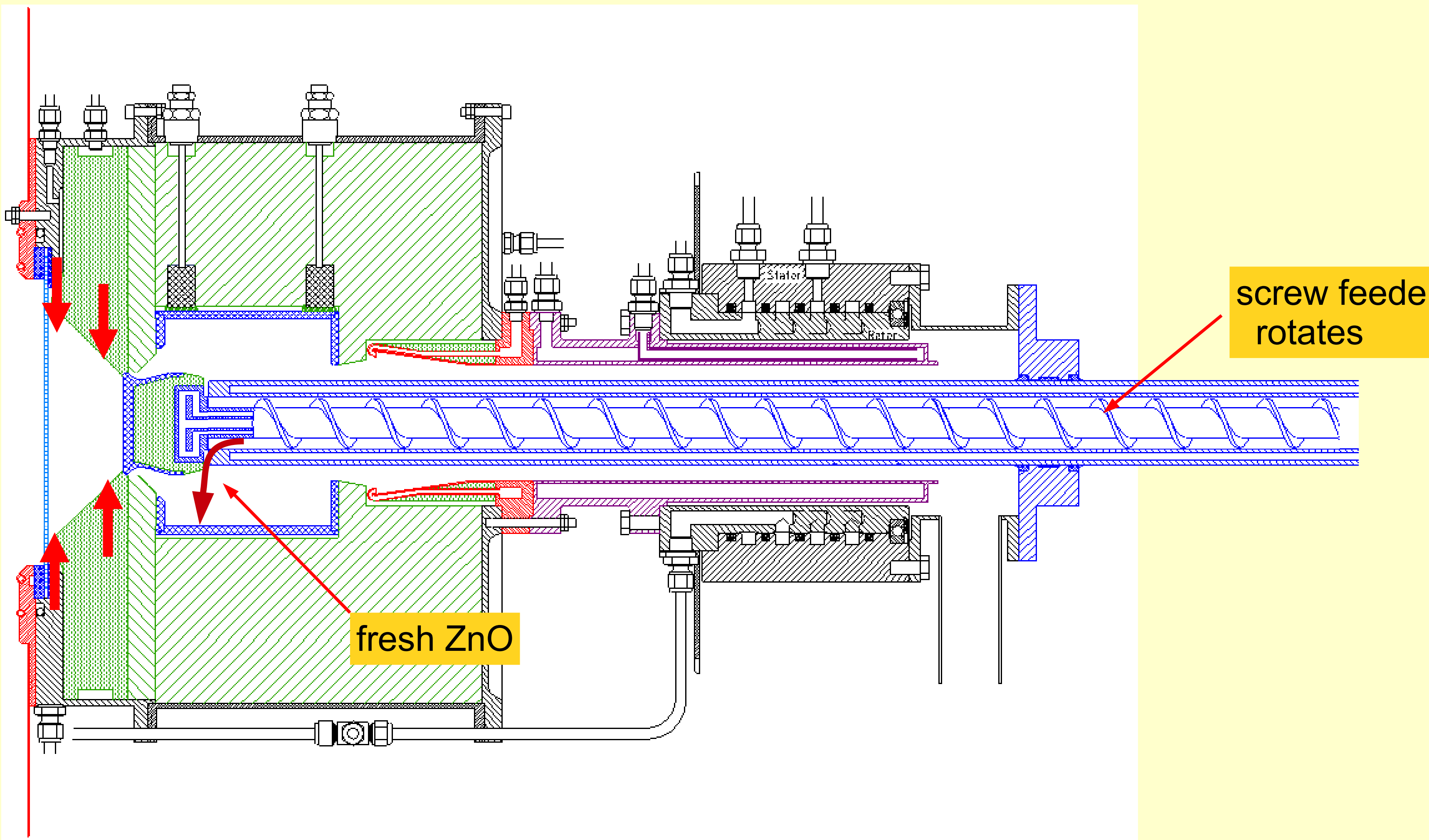
Thermal Dissociation



Zn / ZnO Cycle: 10 kW Solar Reactor

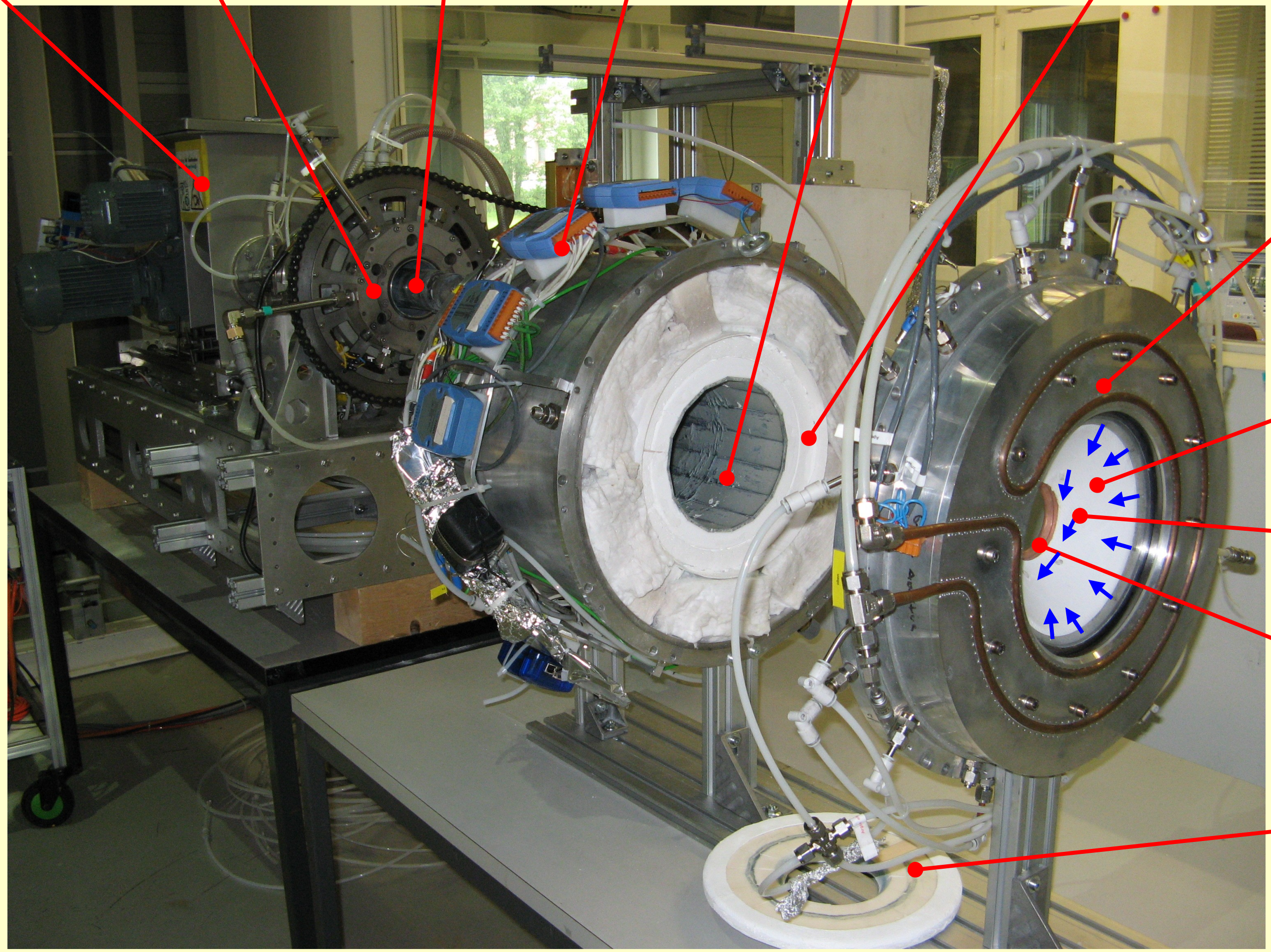
III

Feeding



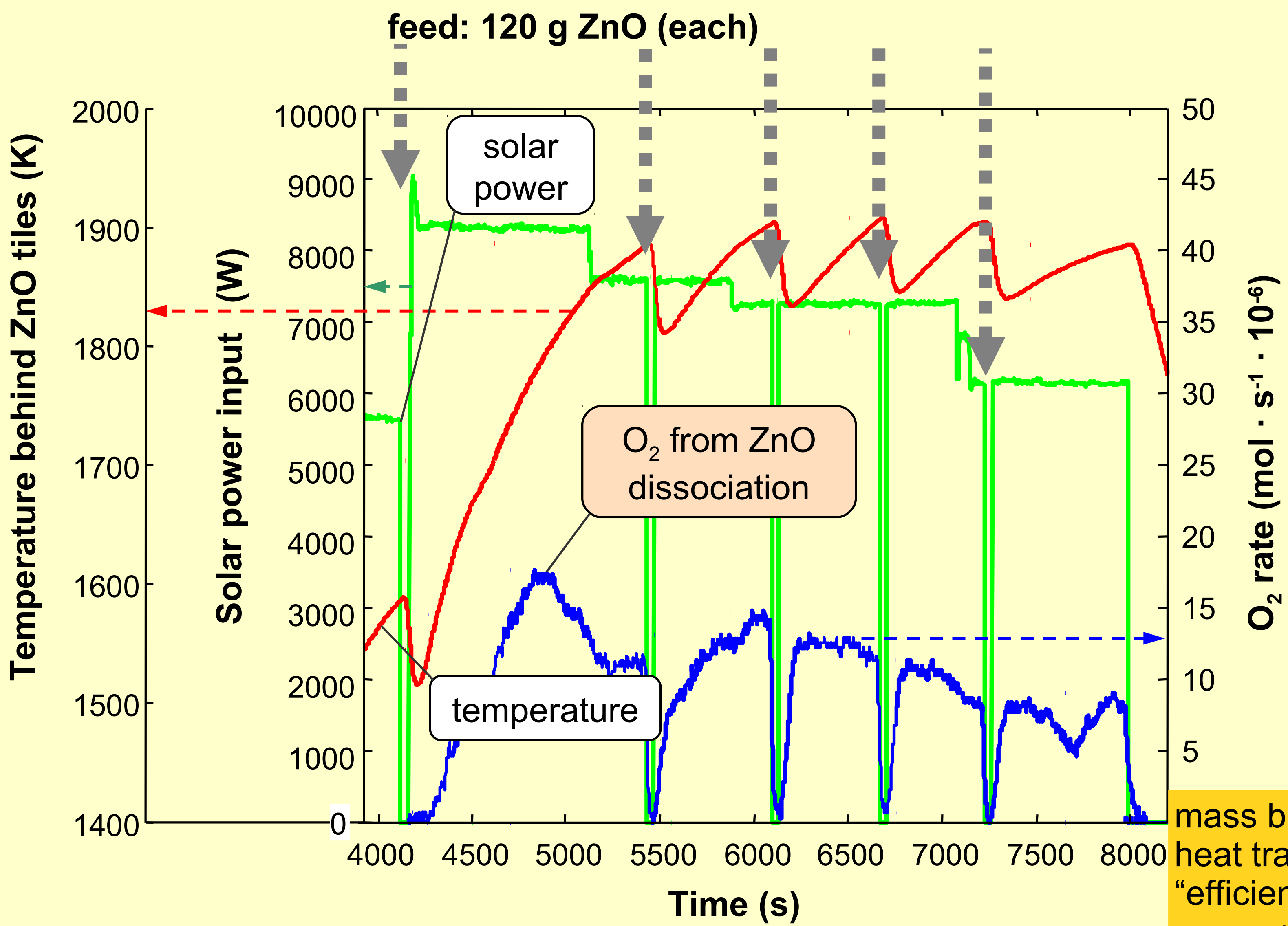
Zn / ZnO Cycle: 10 kW Solar Reactor

IV



Zn / ZnO Cycle: 10 kW Solar Reactor

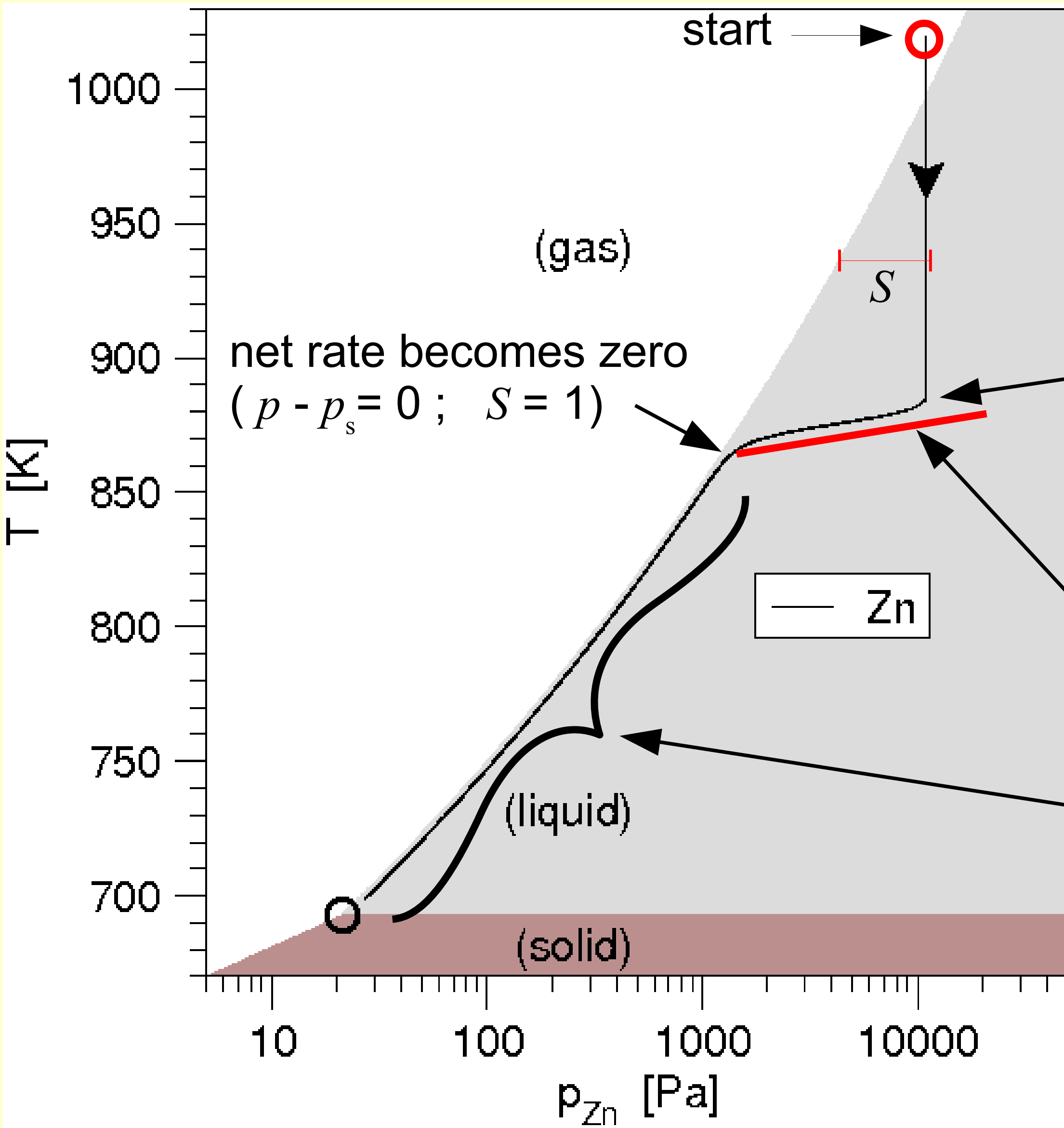
V



mass balances
heat transfer analysis
“efficiencies”
→ models

Quench: Pure Zinc

time



quench rate

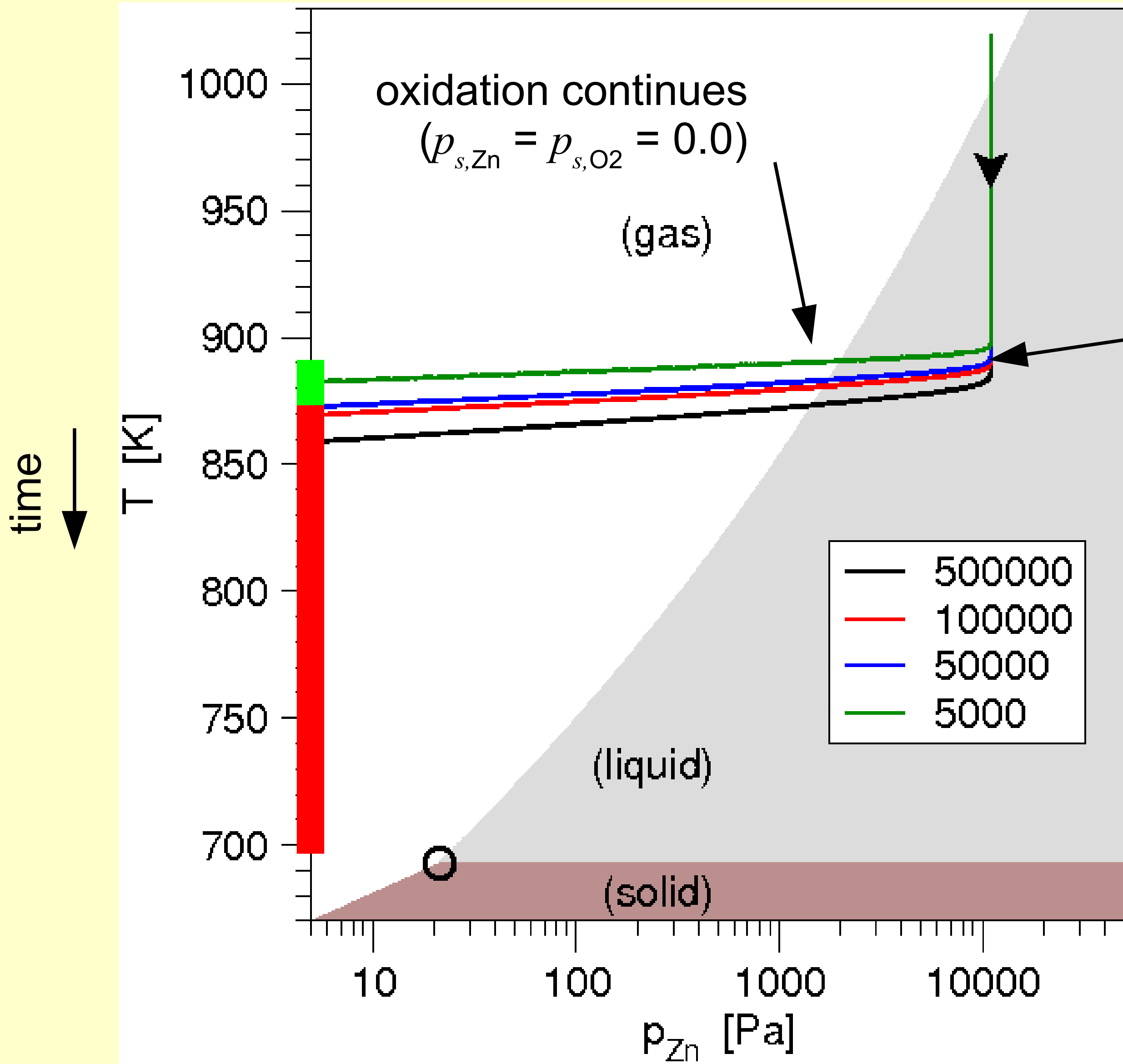
condensation rate

- nucleation sets in
- surface is made available
- condensation starts

condensation rate > quench rate
- small slope

system follows phase boundary

Quench: Zn / O_2 (Quench Rate) II



increased quench rate results in increased nucleation super saturation and nucleation rate

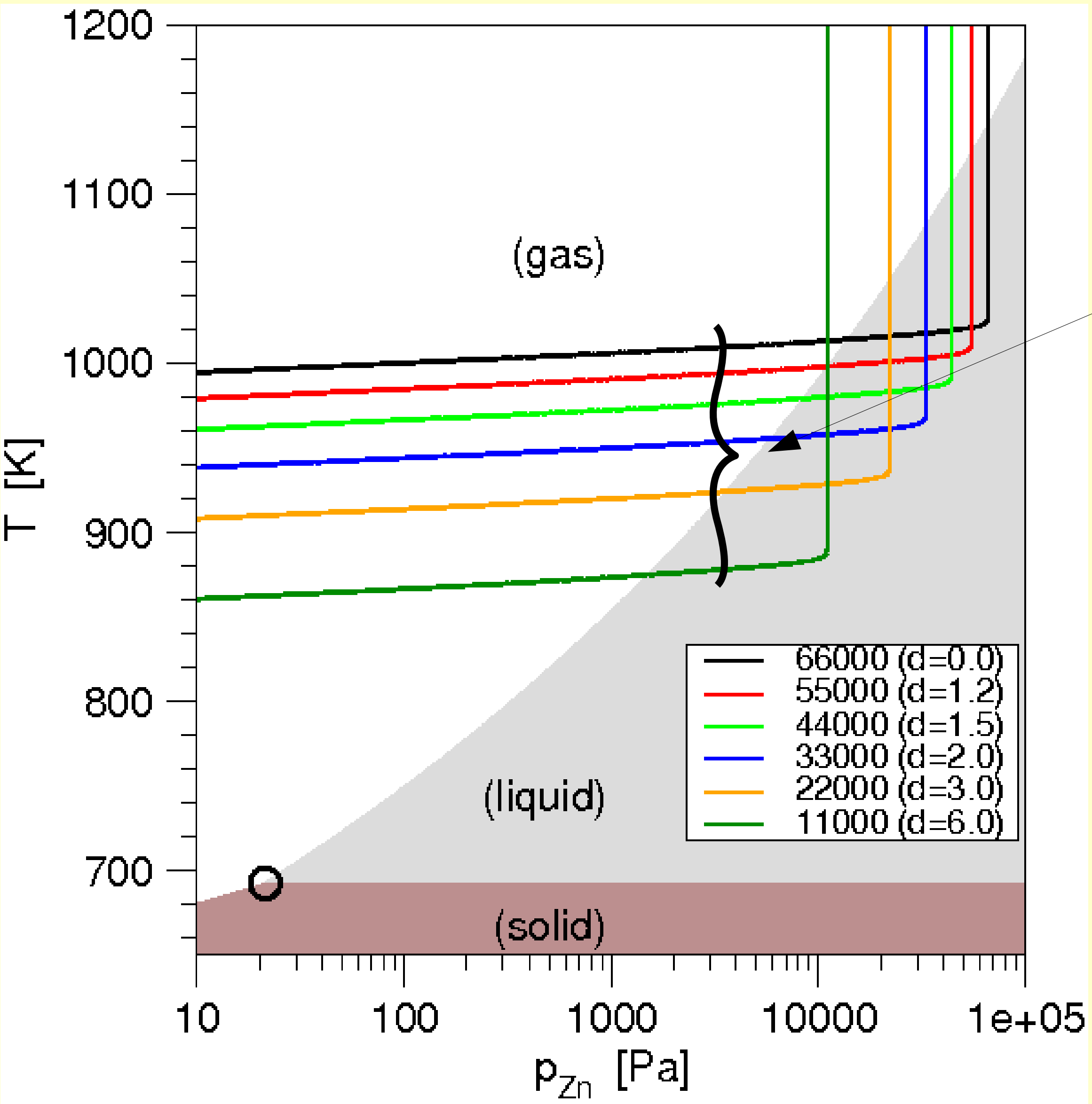
- ▶ more surface is created
- ▶ **all** surface reactions become faster (slopes do not vary a lot)

condensation and oxidation
evaporation and oxidation

(evaporation not included)

avoid leaving region Zn_{liquid} (or Zn_{solid})

Quench: Zn / O_2 (Initial Dilution) III

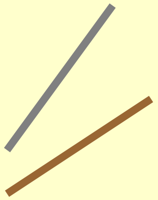


parallel curves

- same rates

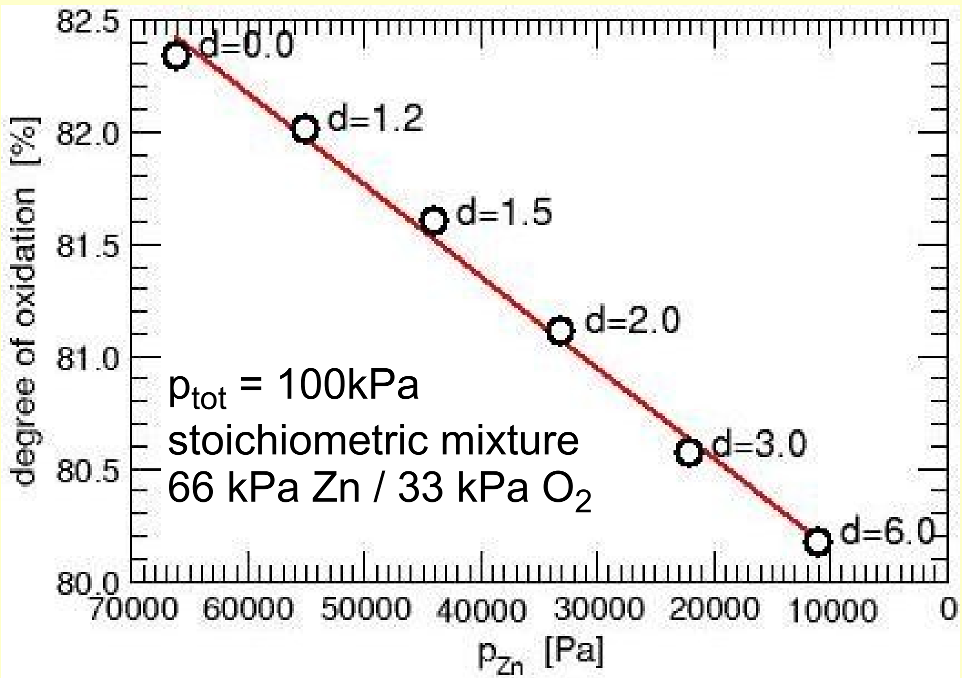
increased dilution delays nucleation

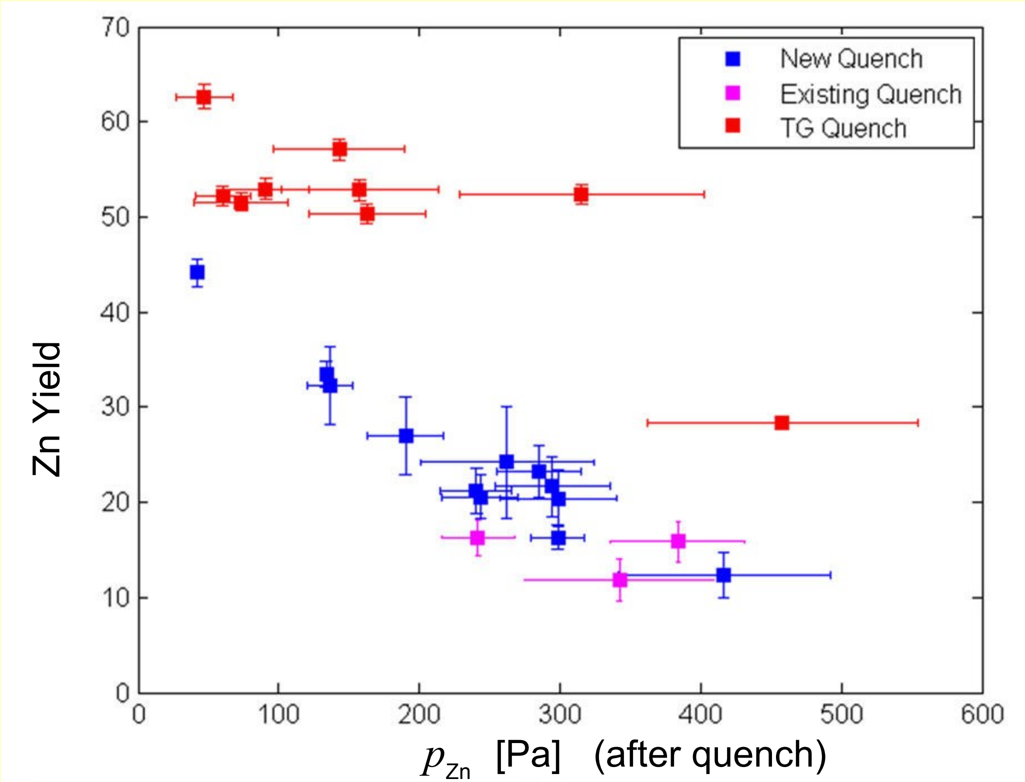
- reaction(s) occur at lower p_{Zn} and T
- smaller slope of vapor pressure curve at lower T
- system remains longer within liquid phase



even more favorable: resublimation

Quench: Comparison Model ↔ Experiment

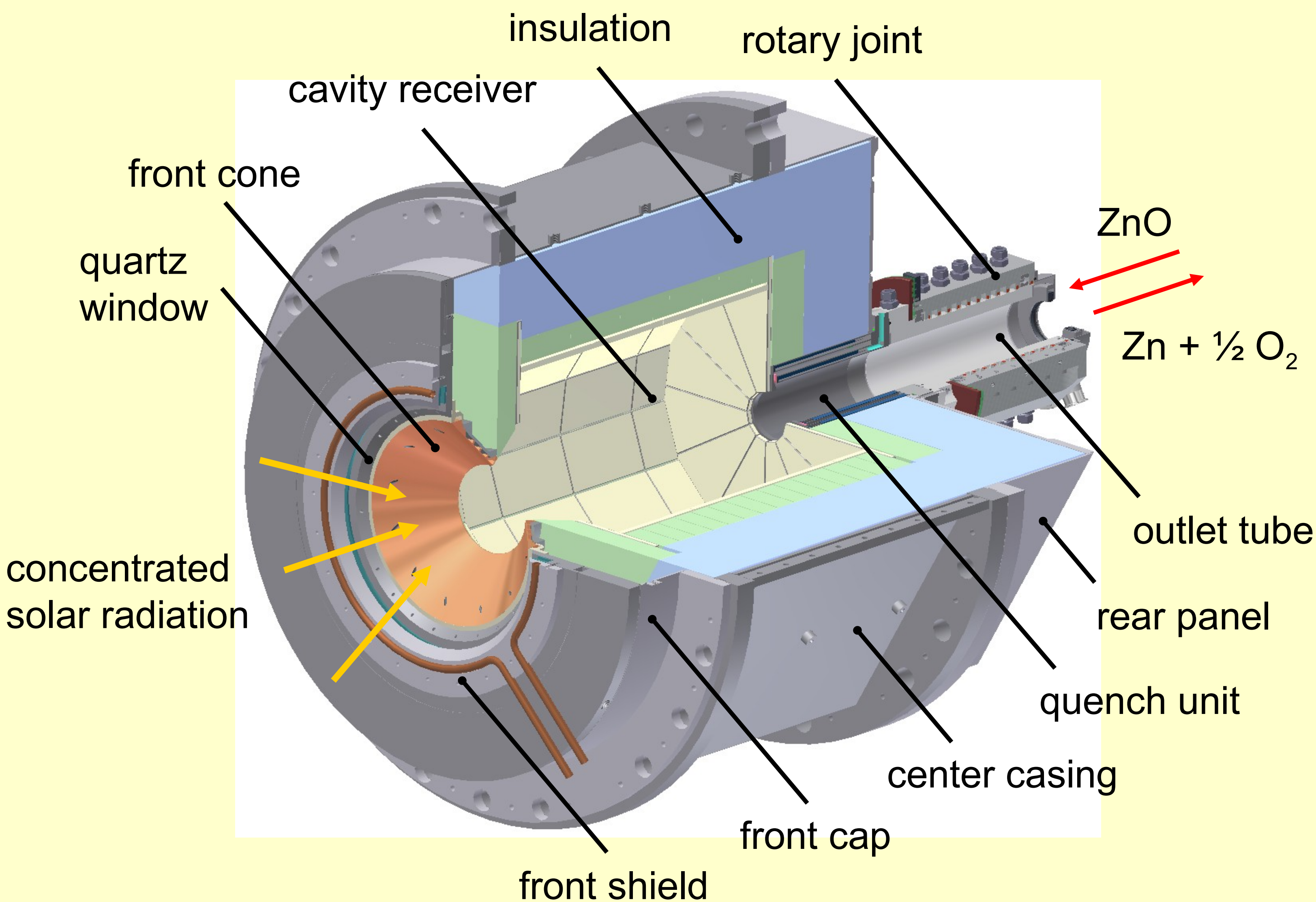




model ↔ experiment

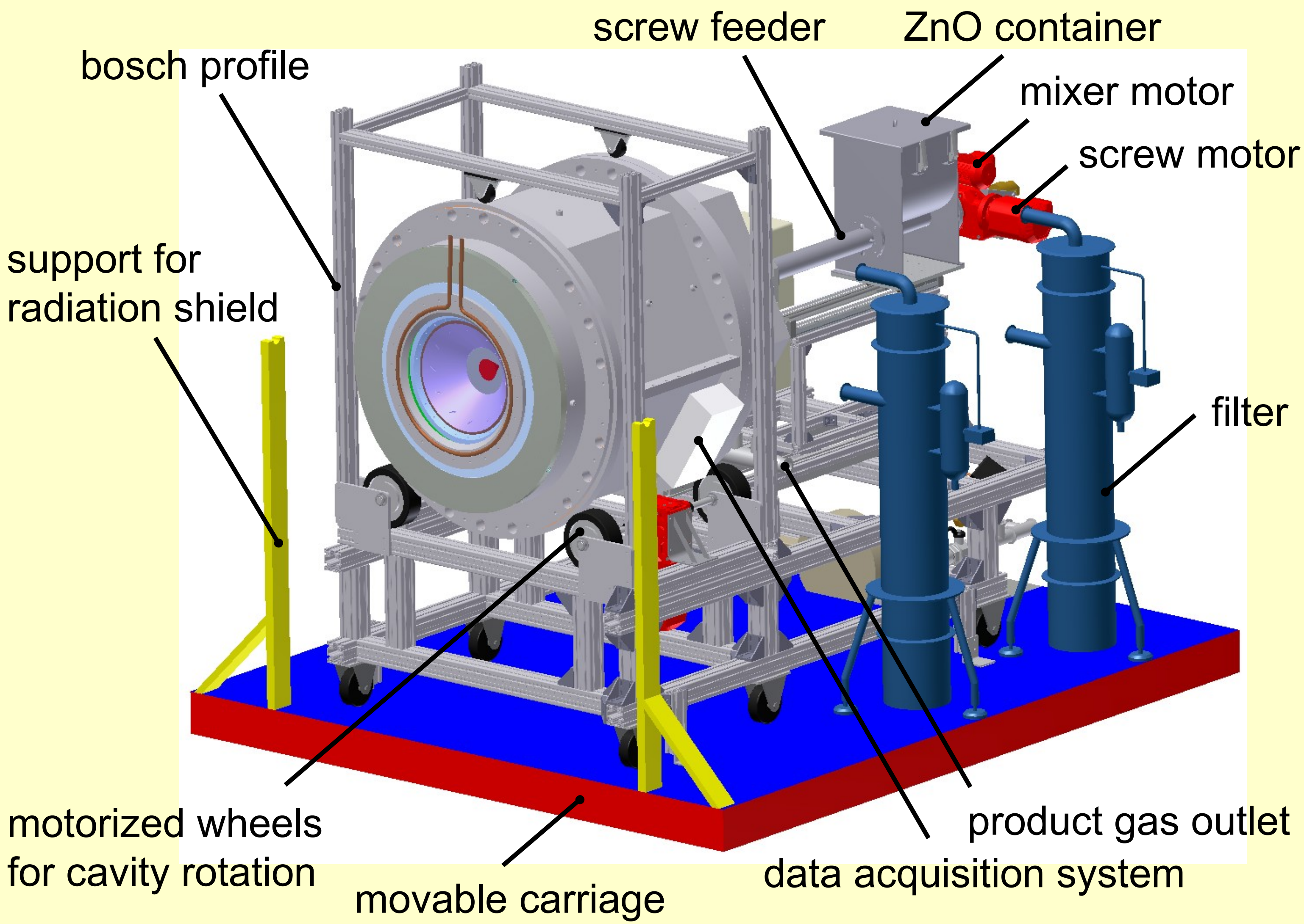
model explains experimental observations on a qualitative level
large amounts of inert gas to be recycled (solar process?)

Zn / ZnO Cycle: Scale Up to 100 kW



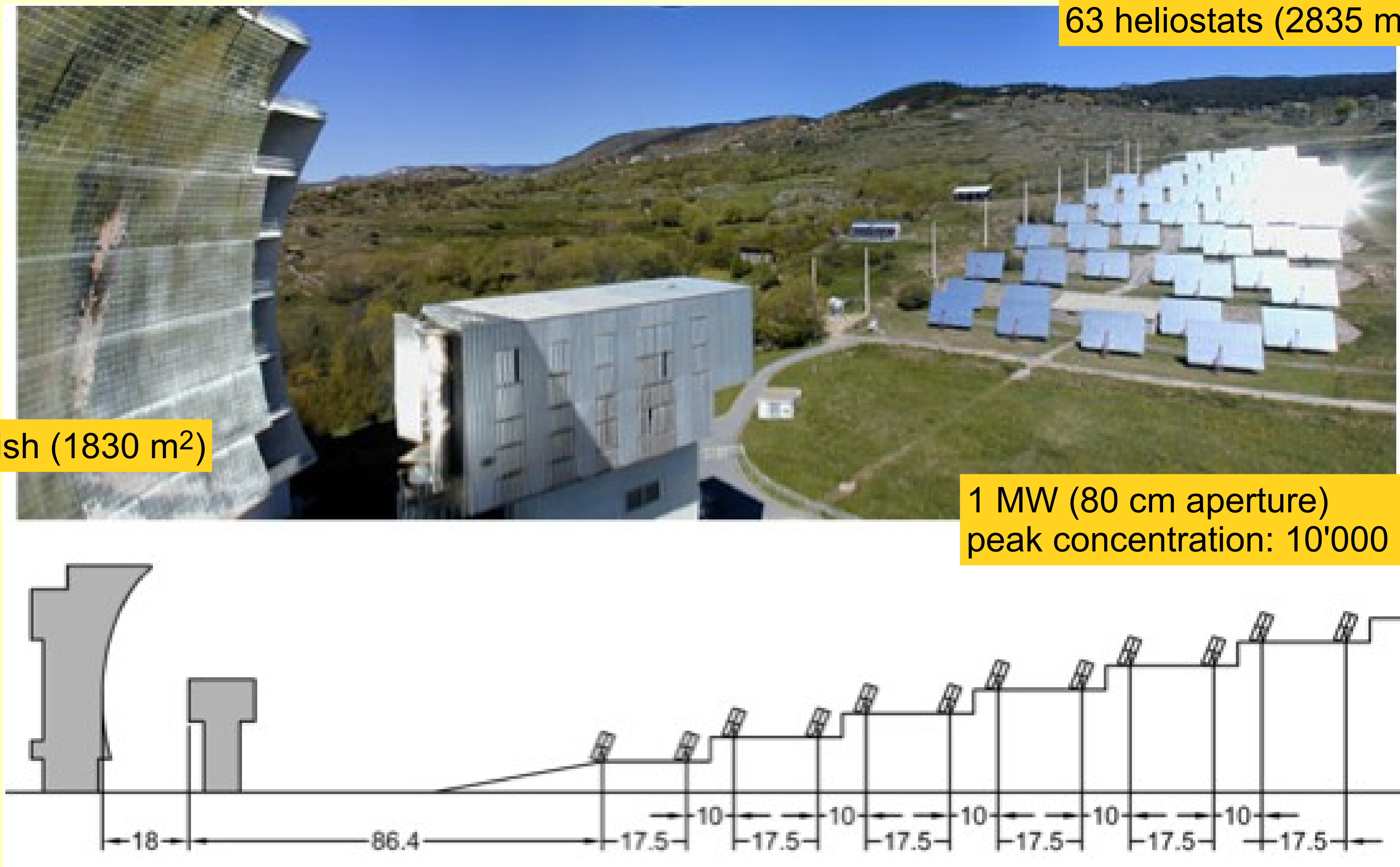
Zn / ZnO Cycle: Scale Up to 100 kW

II



Zn / ZnO Cycle: Scale Up to 100 kW

MWSF: PROMES-CNRS Font Romeu Odeillo



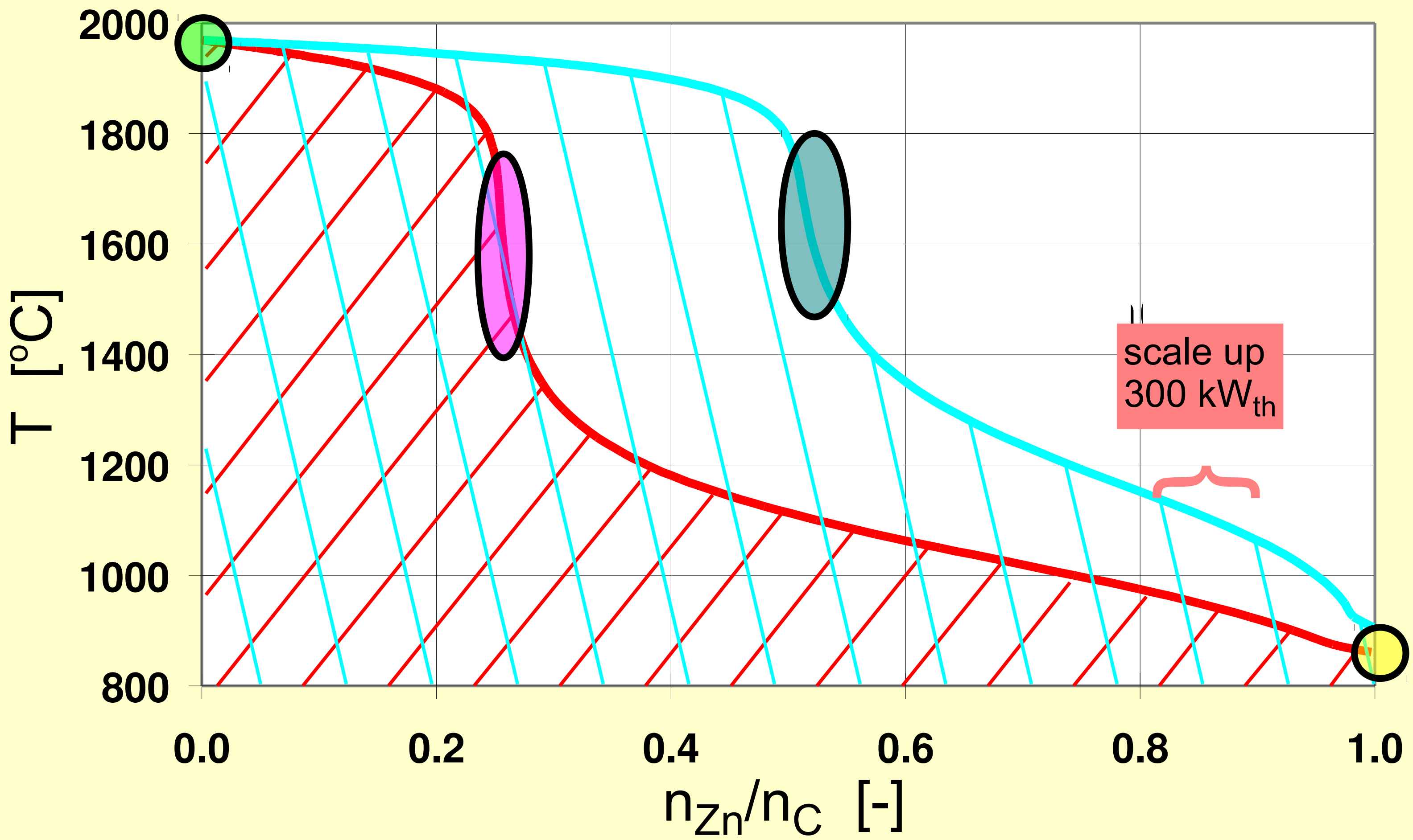
Zn / ZnO Cycle: Scale Up to 100 kW

no results yet:
- installation completed
- start up / initial testing under way
- experimenting starts soon

Carbothermic Reduction of ZnO

ZnO is stable in presence of CH_4 / C

$ZnO + CH_4 \rightarrow CO + 2H_2$
$ZnO + C \rightarrow Zn + CO$



carbon free

$ZnO \rightarrow Zn + ½O_2$

minimum carbon

$ZnO + ¼CH_4 \rightarrow Zn + ¼CO_2 + ½H_2O$

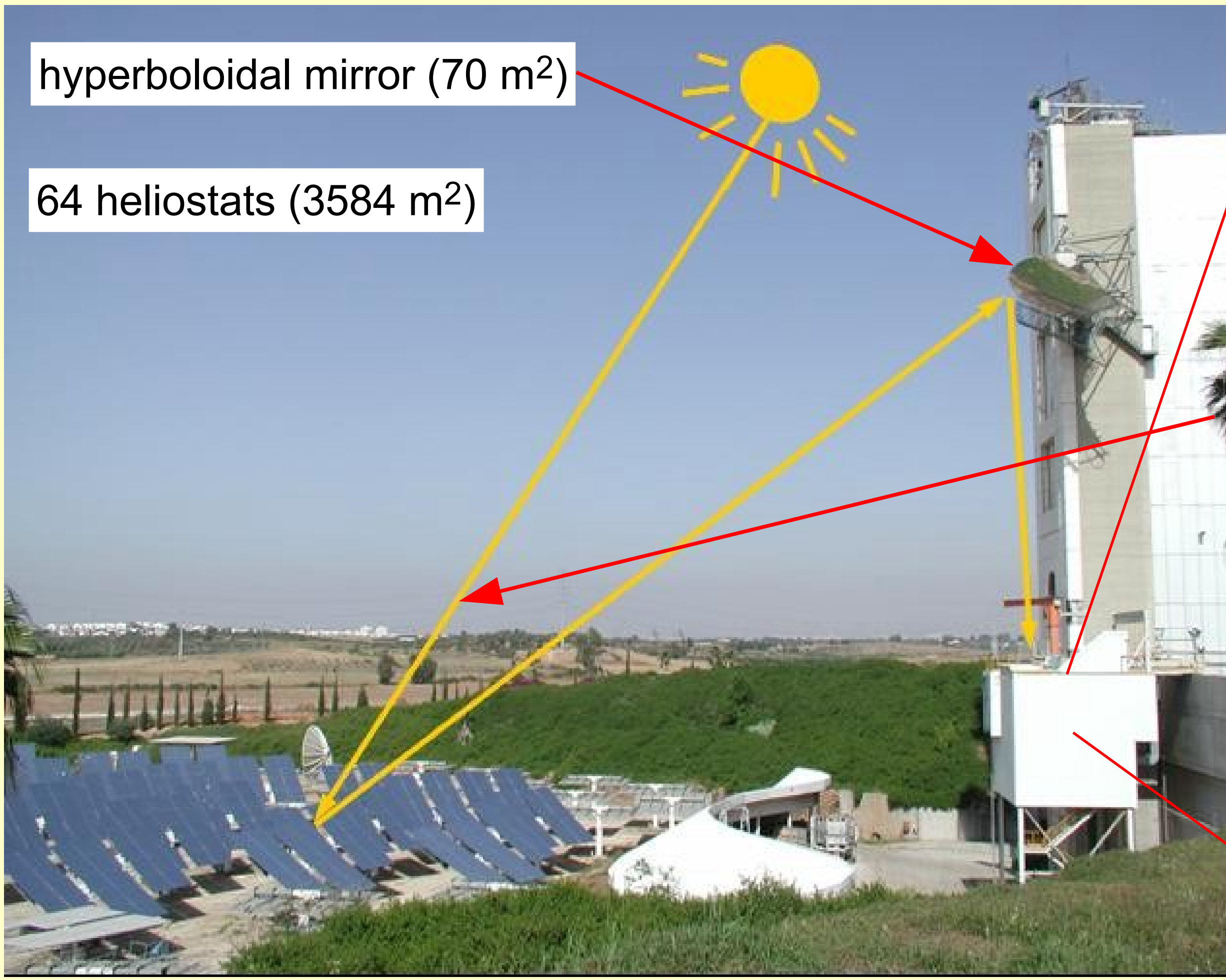
$ZnO + ½C \rightarrow Zn + CO_2$

ideal syngas

$ZnO + CH_4 \rightarrow Zn + CO + 2H_2$

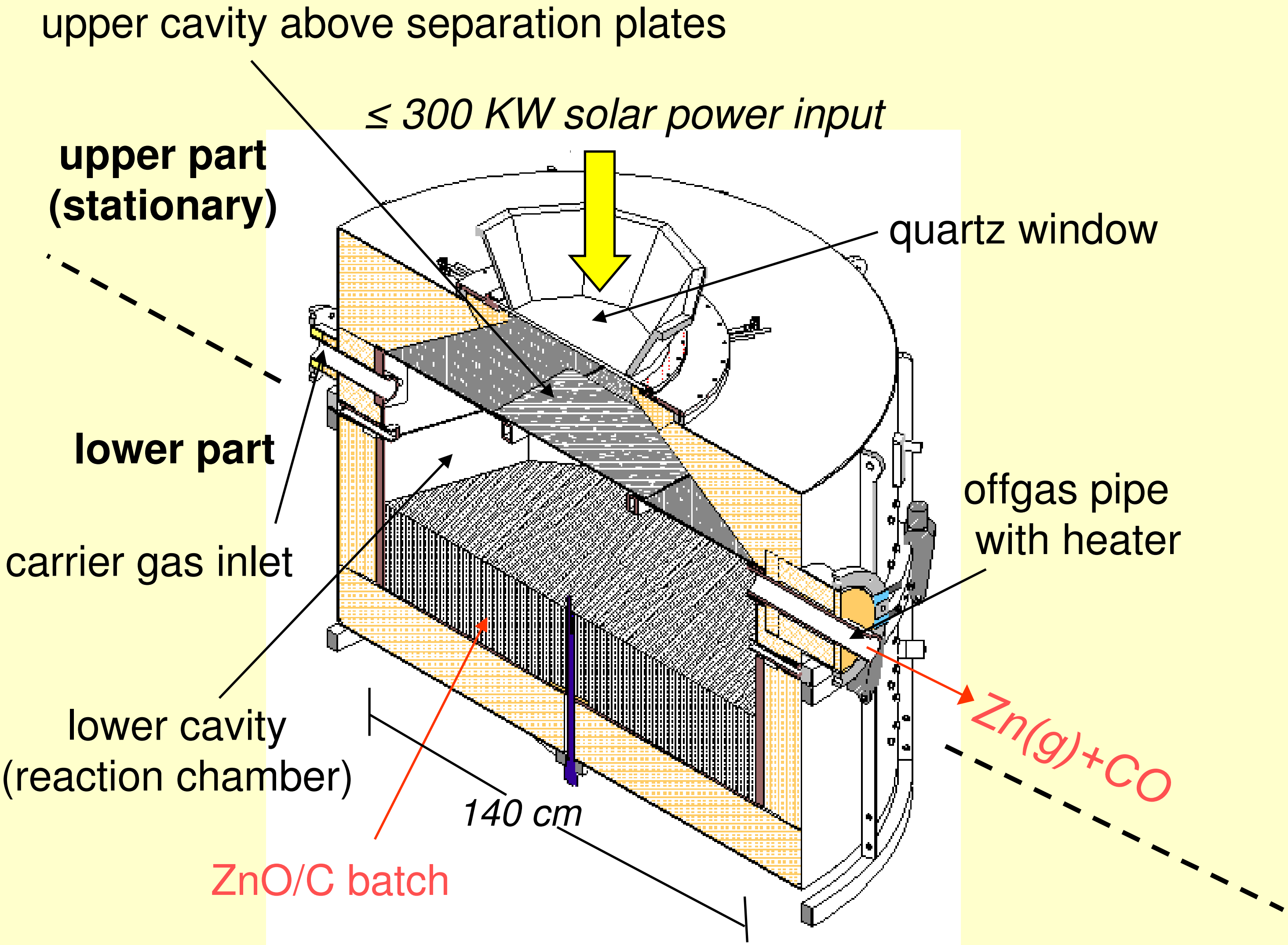
Carbothermic Reduction: Beam Down Concept

SRFU: Weizmann Institute of Science



aperture of experiment
0.5 MW (0.5 m aperture)
4000 suns

Carbothermic Reduction: 300 kW_{th} pilot reactor



principle:

- "2-cavity" reactor
- fixed bed of ZnO/C-mixture
- 1 batch per day

features:

$D_{rxn\text{-}chamber}$ = 1.4 m

H_{bed} ≤ 0.5 m

capacity ≤ 500 kg ZnO/C

lining: SiC plates

insulation: Al_2O_3-SiO_2

separation plates:
  graphite, SiC on graphite

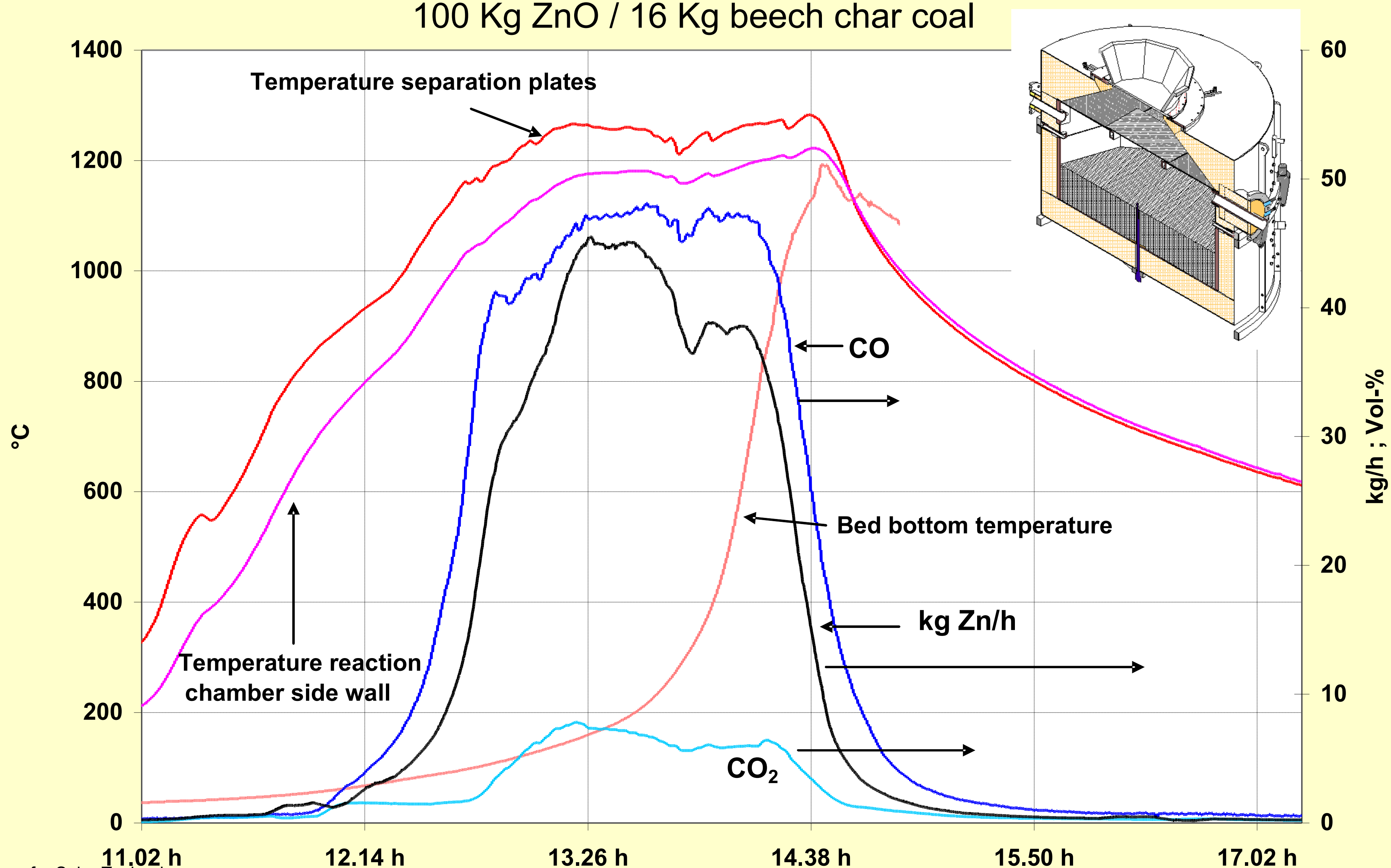
lower part easy to lift down
  for refilling

Carbothermic Reduction: 300 kW_{th} pilot plant II

Impressions

Carbothermic Reduction: 300 kW$_{th}$ pilot plant III

100 Kg ZnO / 16 Kg beech char coal



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(PSI / ETHZ)