# Weizmann Institute of Science

Solar Research Facilities Unit

## *ALUMINA CARBOREDUCTION AND ZINC OXIDE THERMAL SPLITTING IN VACUUM*

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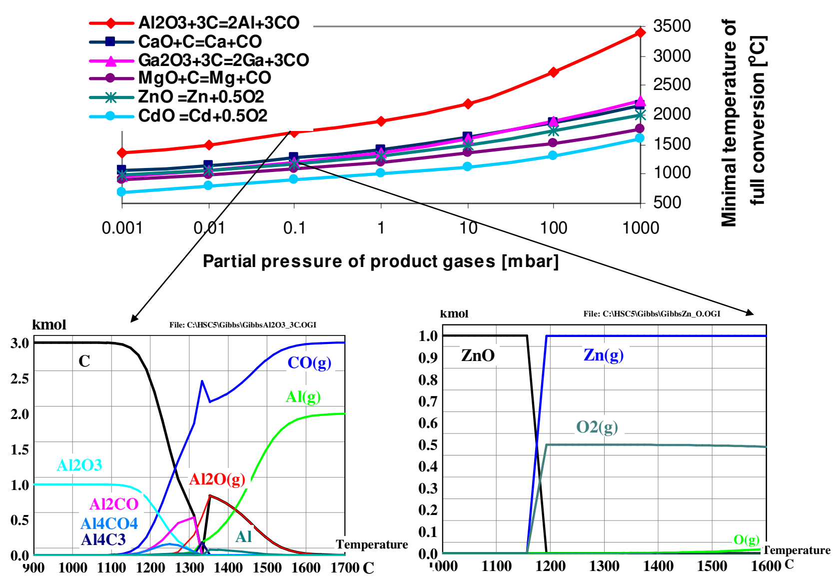
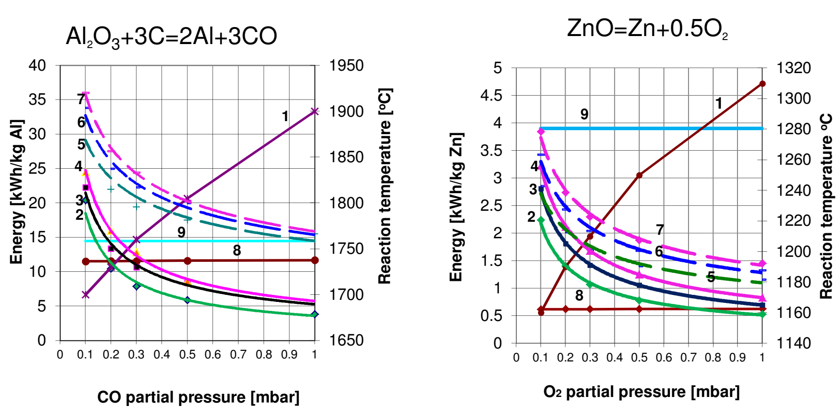
# Thermodynamics principles



# Merits and challenges

- Feasible operating temperature of the solar reactor;
- Energy consumption for pumping;
- Fast preheating to avoid volatile by-products formation in forward reactions with complicated chemistry;
- Avoiding reoxidation and by-products formation in the reverse reactions.

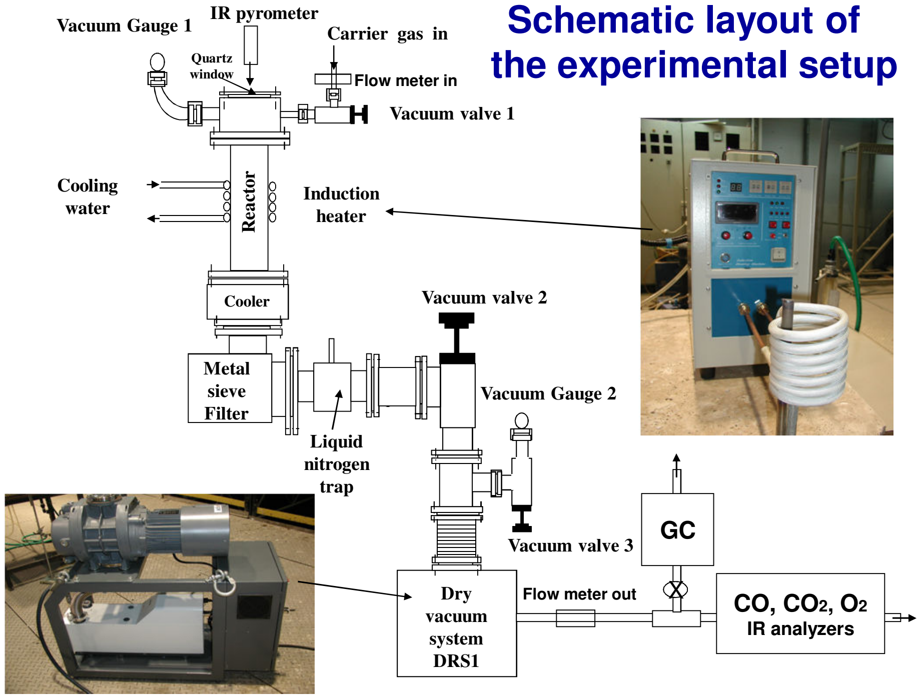
## Energy consumption in vacuum pumping per 1 kg metal product



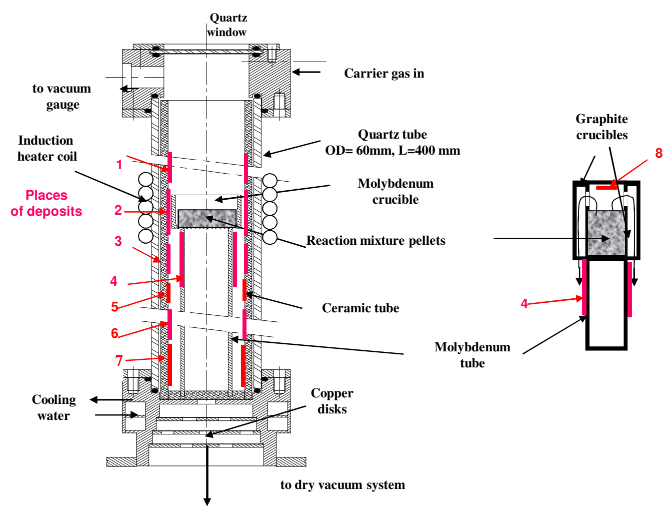

1 – reaction temperature [° C], 2 ,3,4– pumping energy; 5,6,7 –total energy; 8 – solar heat net; 9-energy consumption in electrolytic industrial process

2 ,5– 55.5 mol CO +0mol Ar / 7.65 mol O2+0mol Ar per hour;
3 ,6– 55.5 mol CO +55.5mol Ar / 7.65 mol O2+7.65mol Ar per hour;
4 ,7– 55.5 mol CO +100mol Ar / 7.65 mol O2+15.3mol Ar per hour;

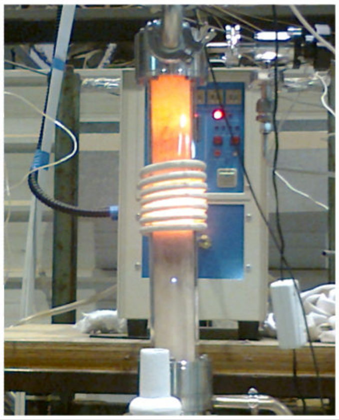
## Schematic layout of the experimental setup



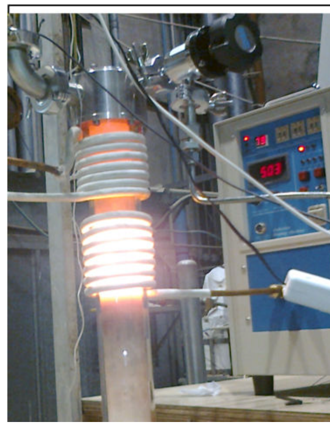

## Reactor design



# Reactor under test condition at about 1500°C



With molybdenum susceptor
(Test type *M*)



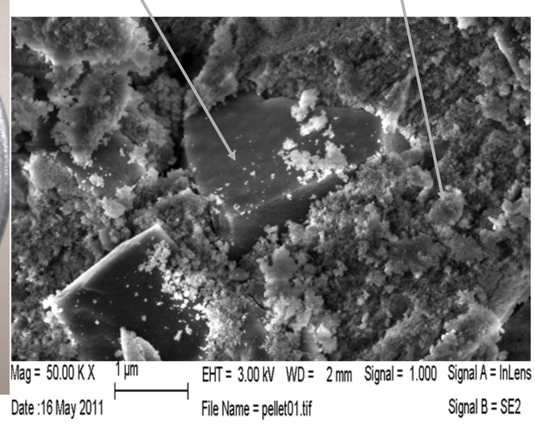
With graphite susceptor
(Test type *G*)

# Reactants pellets (Stoichiometric $Al_2O_3$+3C)

SEM image of a single pellet

Beech charcoal

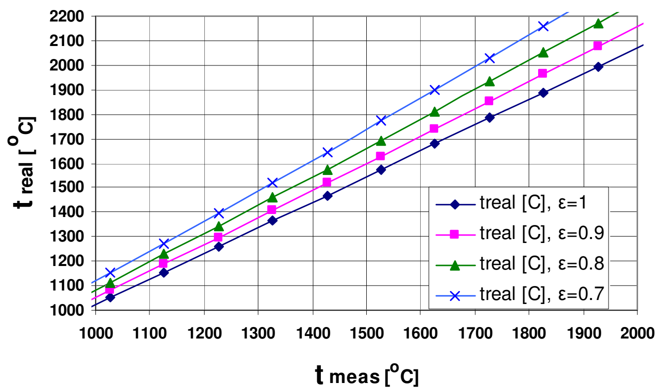
Alumina/nano



# Temperature measurement

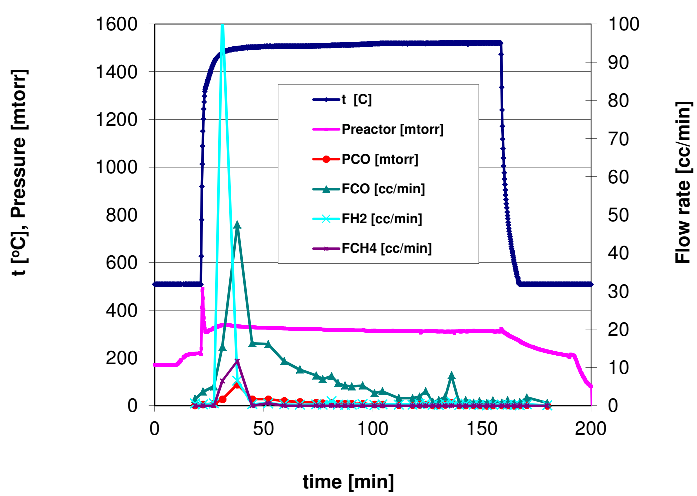
$$T_{real} = \frac{C_2}{\lambda \ln[k\varepsilon(e^{C_2/\lambda T_{meas}} - 1) + 1]}$$

**K=0.91 – quartz window attenuation factor; ε ≈0.98 – effective emissivity**

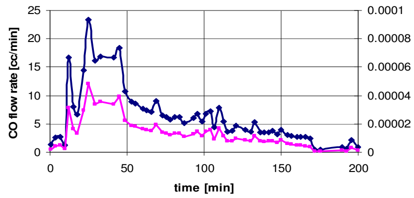



# Typical test parameters

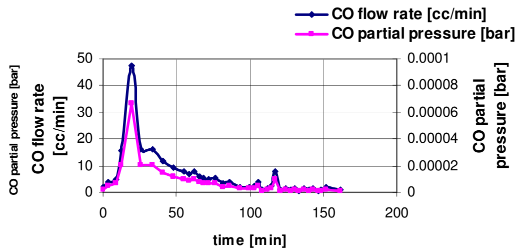
**(molybdenum susceptor with 2.7 g pellets as an example)**



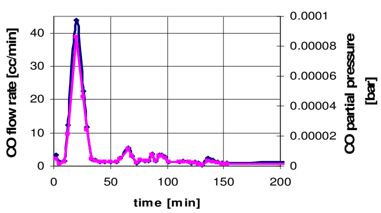
## CO flow rate and partial pressure for different test temperatures (alumina carboreduction)



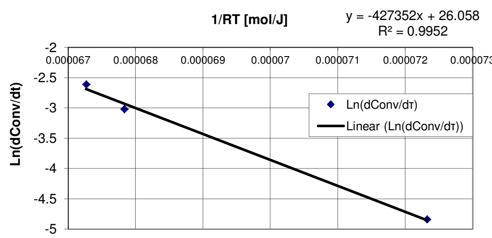

Test type *G*, 1390°C, 3.2 g mixture




Test type *M*, 1500°C, 2.7 g mixture




Test type *G*, 1515°C 2.1 g mixture




Logarithmic plot for the initial reaction rate

# Tests results

### Tests parameters

| Oxide | Test type | Reaction Tempera-ture [°C] | Carrier gas flow rate [cc/min] | Maximal total pressure (gauge 1) [bar] | Maximal $CO(O_2)$ average partial pressure [bar] | Oxides under reaction [mol/g] | Fix Carbon under reaction [mol/g] |
|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | *G* | 1515 | 107 | $7.32*10^{-4}$ | $8.57*10^{-5}$ | 0.0148/1.508 | 0.0444/0.533 |
| ZnO | *M* | 1490 | 106 | $7.07*10^{-4}$ | $3.48*10^{-6}$ | 0.108/8.79 | 0 |

### Total conversion estimation

| Oxide | Oxygen [g-atom] in oxide | Oxygen [g-atom] in output gases | Total Oxygen [g-atom] in deposits | Total Metal [g-[atom | Pure Metal [g-atom] in deposits | Conversion 3/2 | Conversion 6/5 | Balance (3+4)/2 |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| $Al_2O_3$ | 0.0444 | 0.0361 | 0.0032 | 0.0296 | 0.009 | 0.81 | 0.304 | 0.885 |
| ZnO | 0.108 | 0.0235 | 0.087 | 0.108 | 0.0533 | 0.217 | 0.494 | 1.023 |

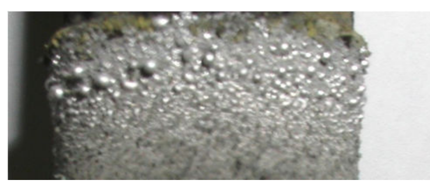
## XRD quantitative analysis of products deposits from different sites in the reactor

| Reac-tants | Sample place | Sample mass [g] | Al | $Al_2O_3$ | $Al_4C_3$ | $Al_4O_4C$ | C crystal. | Zn | ZnO | $Zn_2Mo_3O_8$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | [weight %] | | | | | | | |
| $Al_2O_3$ +3C 1515 °C | 3a* | 0.41 | 58.7 | 0 | 33.7 | 7.6 | 0 | - | - | - |
| | 3b | 0.07 | 2.9 | 0 | 6.8 | 90.3 | 0 | - | - | - |
| | 4 | 0.1 | 0 | 19.2 | 55.6 | 25.2 | 0 | - | - | - |
| | 8 | 0.015 | 0 | 0 | 2 | 0 | 98 | - | - | - |
| ZnO 1490 °C | 1+3 | 6.63 | - | - | - | - | - | 9.6 | 38.6 | 51.9 |
| | 5 | 0.3 | - | - | - | - | - | 35.5 | 52.4 | 12.1 |
| | 6a+6b | 1.15 | - | - | - | - | - | 84.5 | 15.5 | - |
| | 7 | 1.77 | - | - | - | - | - | 97.8 | 2.2 | - |

*a – outer layer; b –inner layer

## Powders and drops at different deposit sites

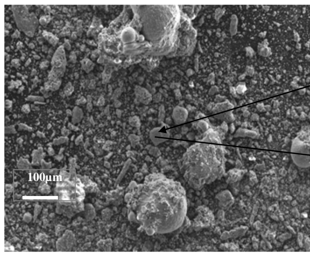
Place 3a, 58.7%Al, 69w% of all deposit
(test type *G* at 1515°C)

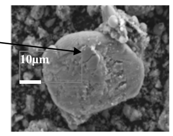


Place 4a, 100%Al, 18 w% of all deposit
(test type *G* at 1390°C)

Place 6a+7, 97.8%Zn, 30w% of all deposit
(test type *M* at 1490°C)

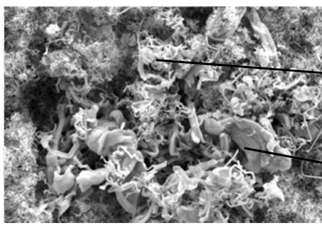
## Deposits morphology
## (SEM images with EDS data)




| Element | Weight% | Atomic% |
|---|---|---|
| O | 14.91 | 22.93 |
| Al | 82.95 | 75.67 |
| S | 0.53 | 0.41 |
| Ca | 1.61 | 0.99 |

**Sample 3a**
**with reduced aluminum**



| Element | Weight% | Atomic% |
|---|---|---|
| O | 3.74 | 13.70 |
| Zn | 96.26 | 86.30 |

| Element | Weight% | Atomic% |
|---|---|---|
| O | 1.52 | 5.92 |
| Zn | 98.48 | 94.08 |

**Sample 7**
**with reduced zinc**

# Summary and conclusions

- **First results of alumina carboreduction and zinc oxide thermal splitting in vacuum at temperatures up to 1800°C and total pressure less than 1 mbar are presented .**
- **At temperature higher than 1500°C and CO partial pressure of <0.1 mbar, the forward reactions is fully completed and the products of reaction in gas phase leave the crucibles. Solid by-product were not found there.**
- **Round form of aluminum particles indicates that the main mechanism of Al deposition is vapor condensation. Most aluminum vapor that condensates on the surface of the ceramic tube with high temperature still subject to reverse reaction with by-product formation. The achieved aluminum yield is about 60 weight% according to the XRD quantitative analysis and about 83 weight% according to the EDS analysis .**

## Summary and conclusions (contd.)

- Specific shape of almost fully reduced zinc discovered on the coldest lower part of the ceramic tube leads to the conclusion that the main mechanism of zinc vapor deposition is desublimation that happens in places with temperature suitable to avoid reoxidation.

- Solar reactor design has to guarantee drastic temperature drop at the interface between the reaction chamber and the quencher to ultimately avoid the reverse reaction.

- Investigation will be continued to make a compromise between maximal acceptable temperature and pressure as well as minimum use of carrier gas to decrease the electrical energy consumption in the pumping.