Workshop Unlocking Solar Thermochemical Potential: Leveraging CSP Experience for Solar Thermochemistry

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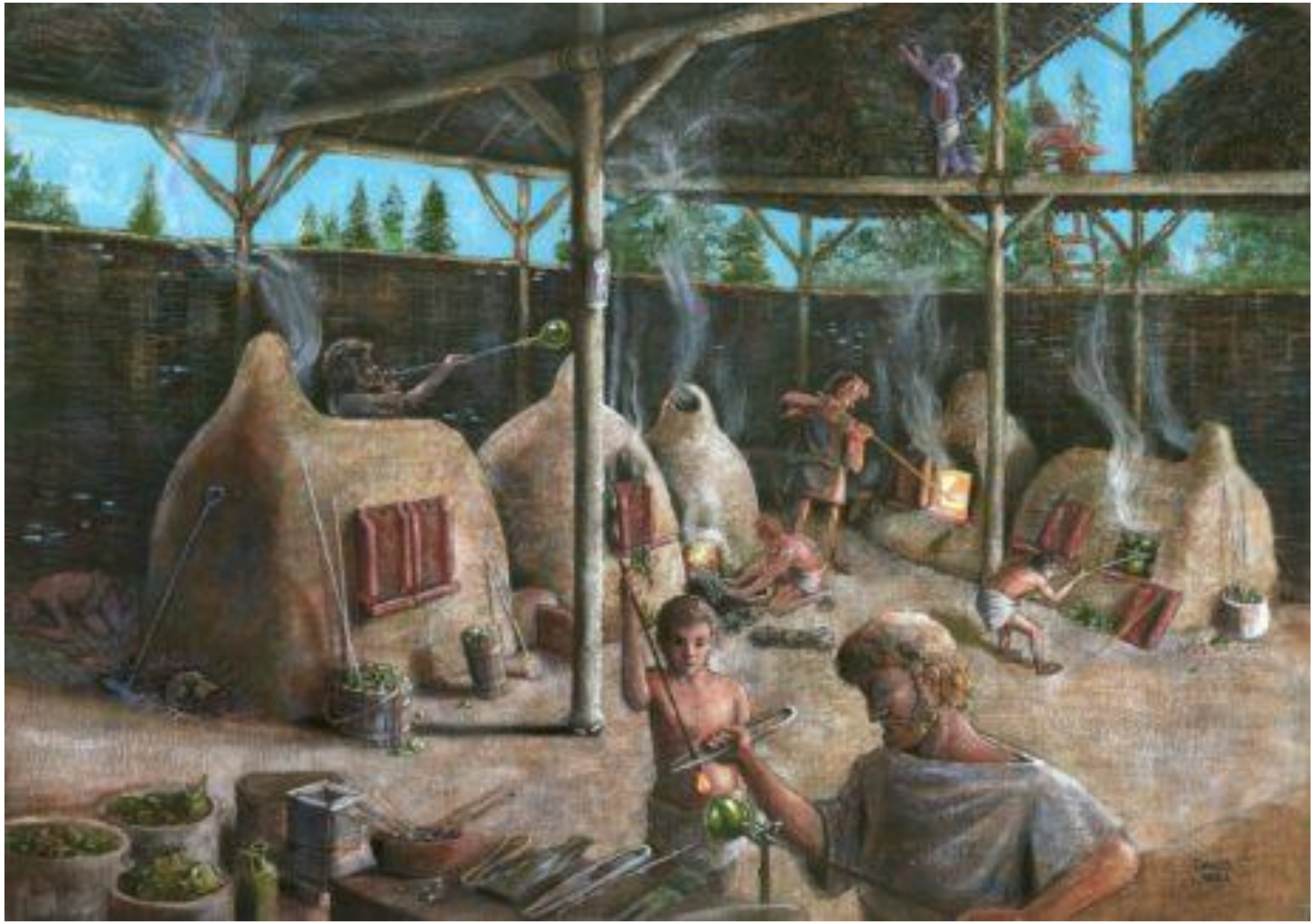
Pioneers of High Temperature Thermochemical Engineering—Glass Makers



Basic Tools for High Temperature Thermochemistry

- A high temperature furnace
- A reactor to contain reactants (crucible)
  Soda Lime Glass: SiO_2 (sand), Na_2CO_3 (soda ash), $CaCO_3$ (limestone)
- Energy to drive phase change and endothermic reactions (often involving metal oxides)
  $SiO_{2,solid} \rightarrow SiO_{2,liquid}$ $(+\Delta h)$
  $CaCO_3 \rightarrow CaO + CO_2$ $(+\Delta h)$
  $Na_2CO_3 \rightarrow Na_2O + CO_2$ $(+\Delta h)$

One Minute Primer on Thermochemistry

Given Reaction: $\upsilon_A A(\alpha) + \upsilon_B B(\beta) \rightarrow \upsilon_C C(\alpha) + \upsilon_D D(\beta)$ A,B,C,D are components; α,β are phases

Duhem Theorem: equilibrium states of a closed system whose initial mass is known, determined by two independent intrinsic variables, typically temperature and pressure for thermochemical systems

Change in system Gibbs free energy:

$$\Delta G_r(T) = (\upsilon_C \Delta G^\circ_{f(C)} + \upsilon_D \Delta G^\circ_{f(D)})_{products} - (\upsilon_A \Delta G^\circ_{f(A)} + \upsilon_B \Delta G^\circ_{f(B)})_{reactants}$$

$\Delta G^\circ_{f(A)}$ Free energy of formation

Affinity of reaction: $\Delta G_r < 0$ in order for reaction to proceed in the forward direction

Consider reaction: $CaCO_3 \rightarrow CaO + CO_2$ (Δh=+178 KJ/mol -- Endothermic) (**Ideally reversible reaction**)
$CaO + CO_2 \rightarrow CaCO_3$ (Δh=-178 KJ/mol – Exothermic)

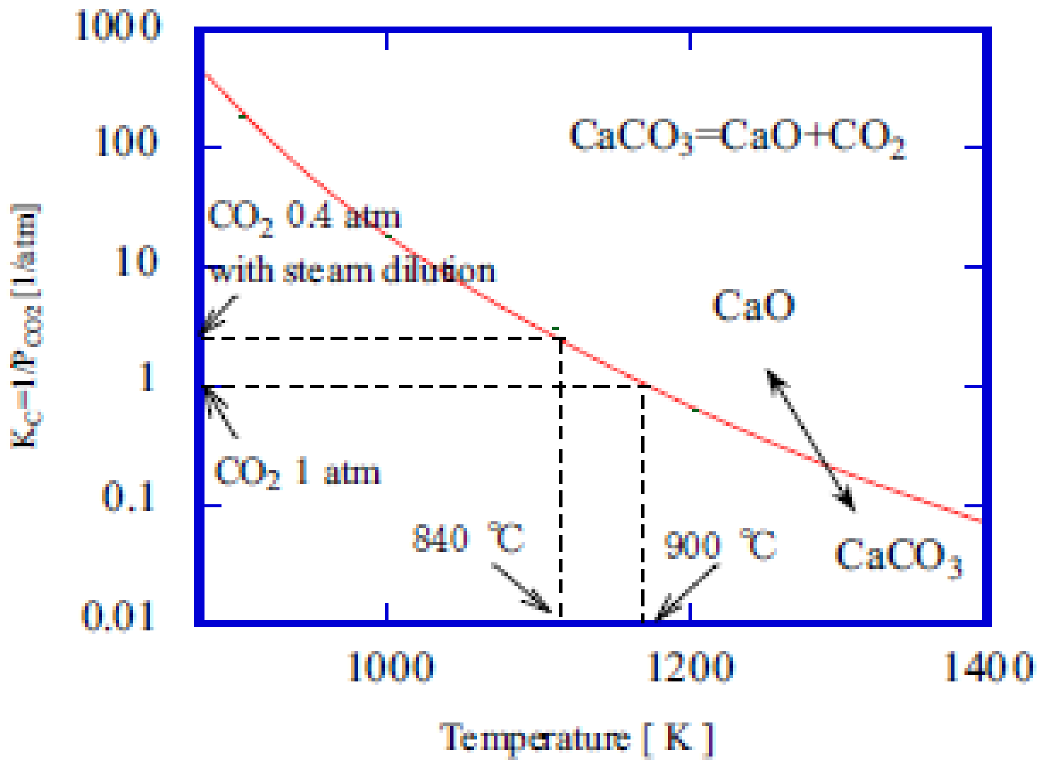


Figure 2 Reaction equilibrium constant for $CaCO_3$ decomposition.

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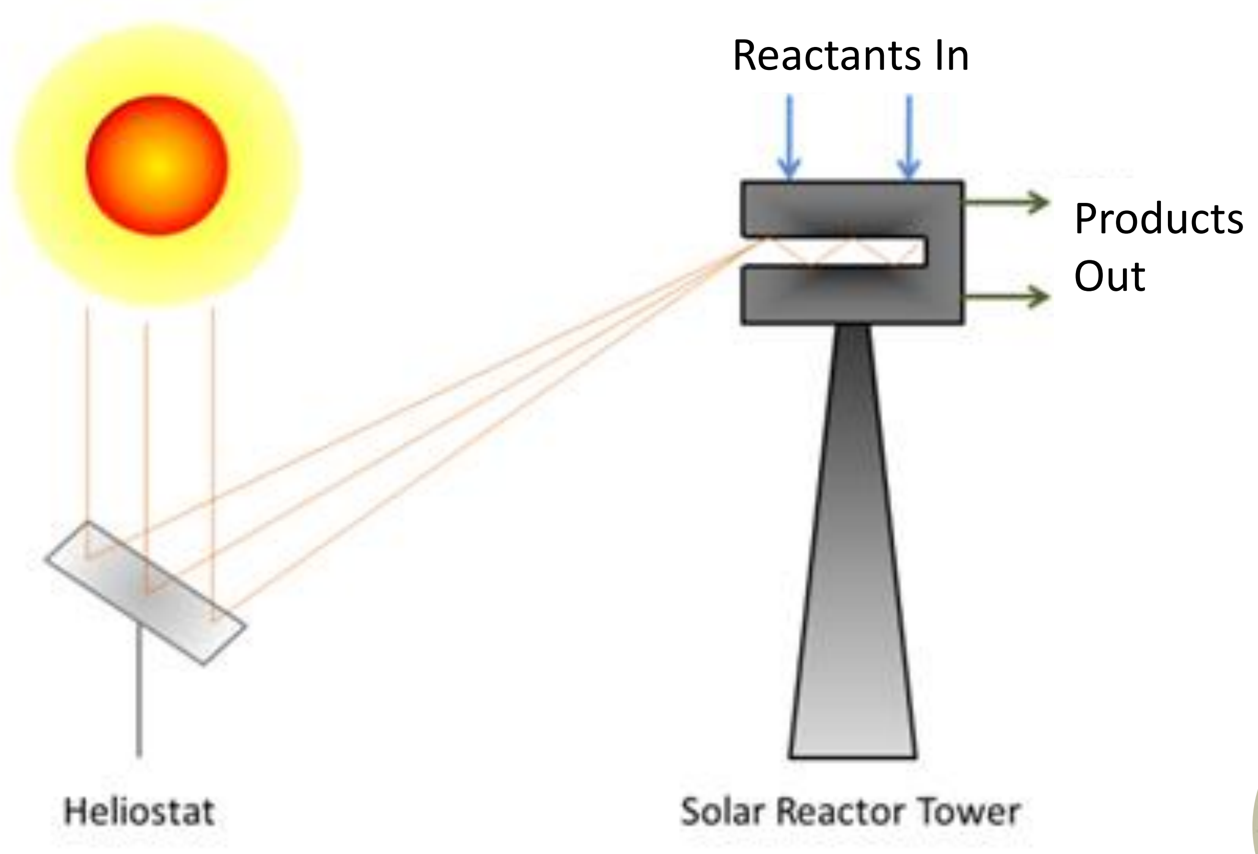
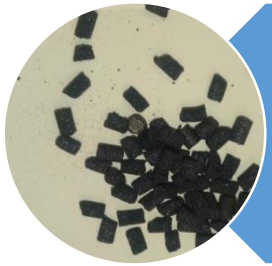
The Capture and Utilization of Solar Energy to Synthesize Carbon Neutral Fuel



Gas

Liquid



Solid

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Basic Chemistries for Solar Fuel Synthesis

Two-step water and CO_2 splitting to H_2/CO (syngas)

Reduction: $CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$ $T_{reactor}$ ~ 1450 °C

Oxidation: $Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2$ $T_{reactor}$ ~ 1100 °C

Some Materials studied in the solar thermochemistry community

$ZnO \rightarrow Zn + \frac{1}{2} O_2$	Zinc oxide (volatile)
$ZnO \rightarrow Zn + \frac{1}{2} O_2$	Magnetite (solid state)
$CoFe_2O_4 \rightarrow CoO + 2FeO + \frac{1}{2} O_2$	Cobalt Ferrite (solid state)
$CoFe_2O_4 \rightarrow CoO + 2FeO + \frac{1}{2} O_2$	Ceria (solid state)
$ABO_3 \rightarrow ABO_{3-\delta} + \frac{\delta}{2} O_2$ (e.g., $Sr_x La_{1-x} Mn_y Al_{1-y} O_3$)	Perovskite (solid state)
$MgFe_2O_4 + \varepsilon MgO \rightarrow (1+\varepsilon)MgO + xFeO + (2-x)FeO_{1.5} + \frac{x}{4} O_2$	Magnesioferrite (solid state)

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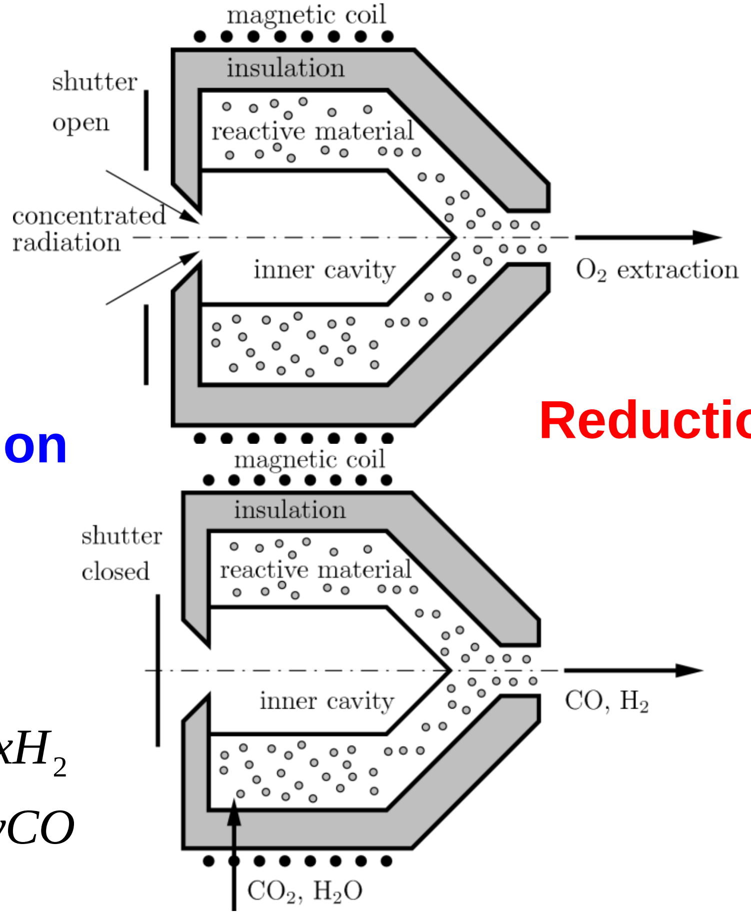
Basic Concept of Cyclical Redox Reactions Used for Solar Fuel Synthesis

Two-Step Cyclical Metal Oxide Reactions

$$MO_{ox} \xrightarrow{heat} MO_{red} + \frac{x}{2} O_2$$

Reduction



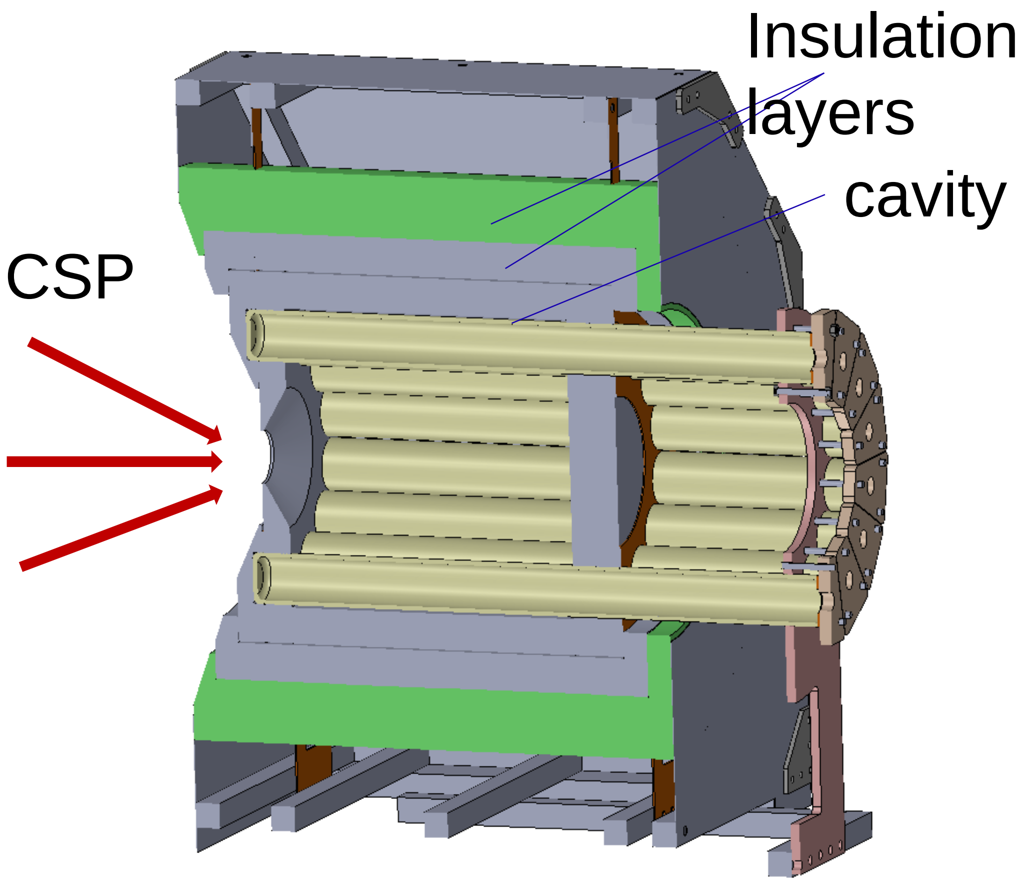
Oxidation

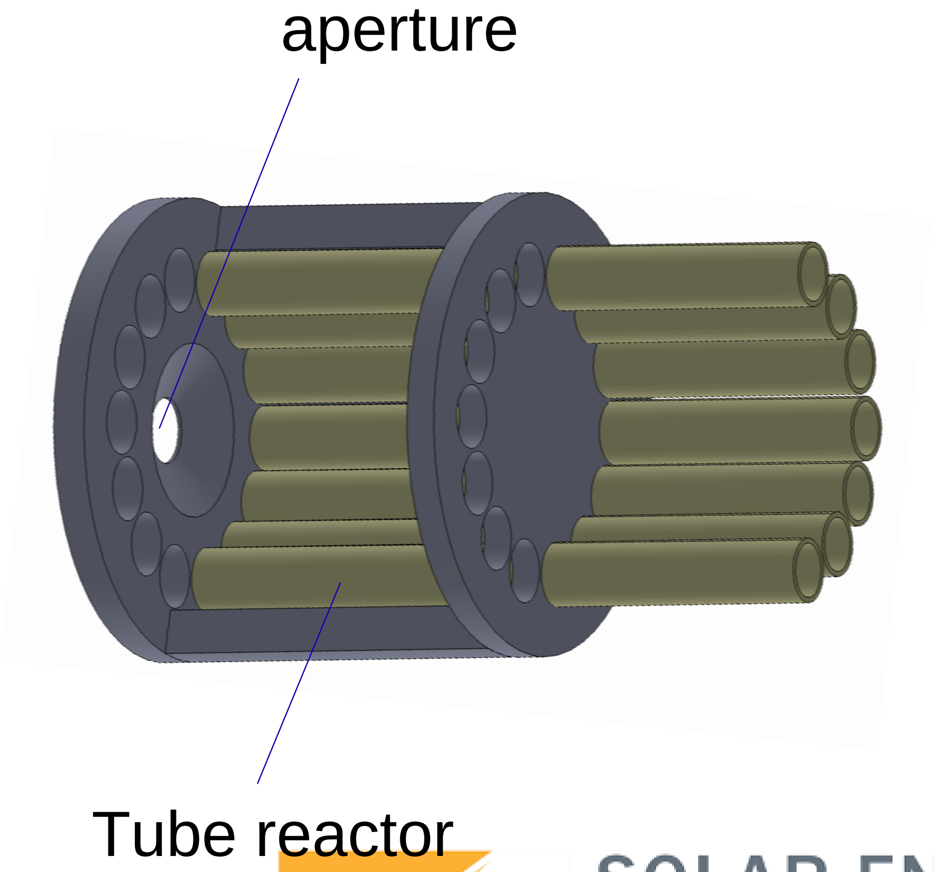
$$MO_{red} + xH_2O \rightarrow MO_{ox} + xH_2$$

$$MO_{red} + yCO_2 \rightarrow MO_{ox} + yCO$$

High Temperature Solar Thermochemical Reactor Concepts

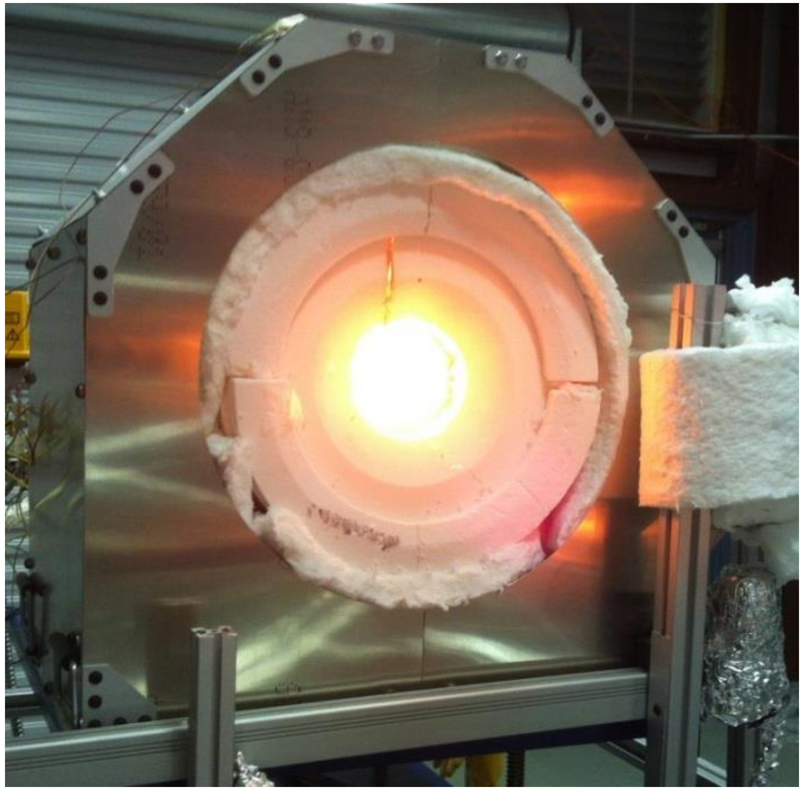
University of Florida Reactor



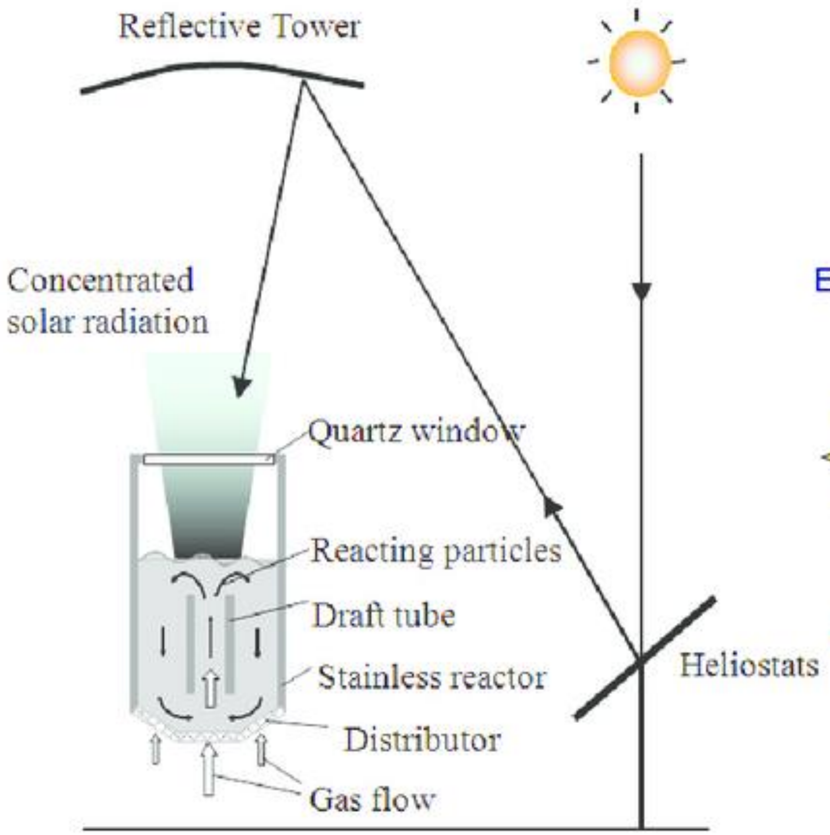


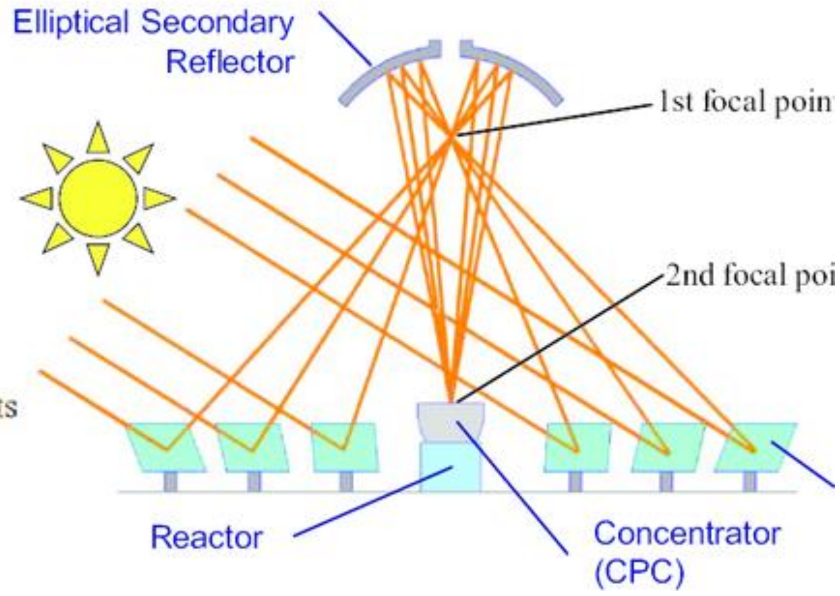
High Temperature Solar Thermochemical Reactor Concepts

University of Florida Solar Fuel Reactor in Operation



Niigata University Beam Down Fluidized Bed Reactor





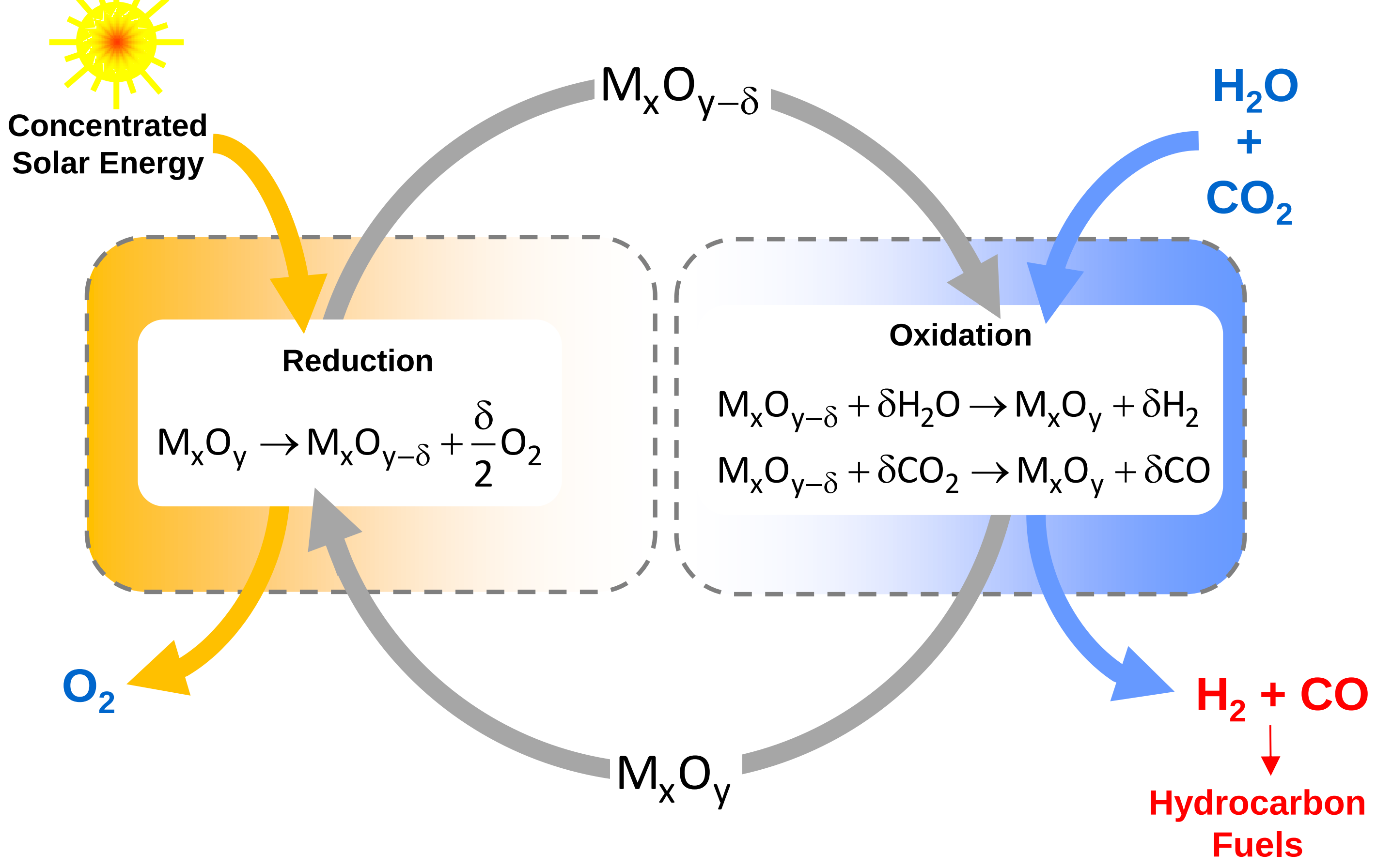
Aldo Steinfeld Professorship of Renewable Energy Carriers– ETH Zurich

ETH zürich

CO_2-neutral transportation fuels from sunlight and air

PREC

Scale up activity: 5 kW to 20 kW



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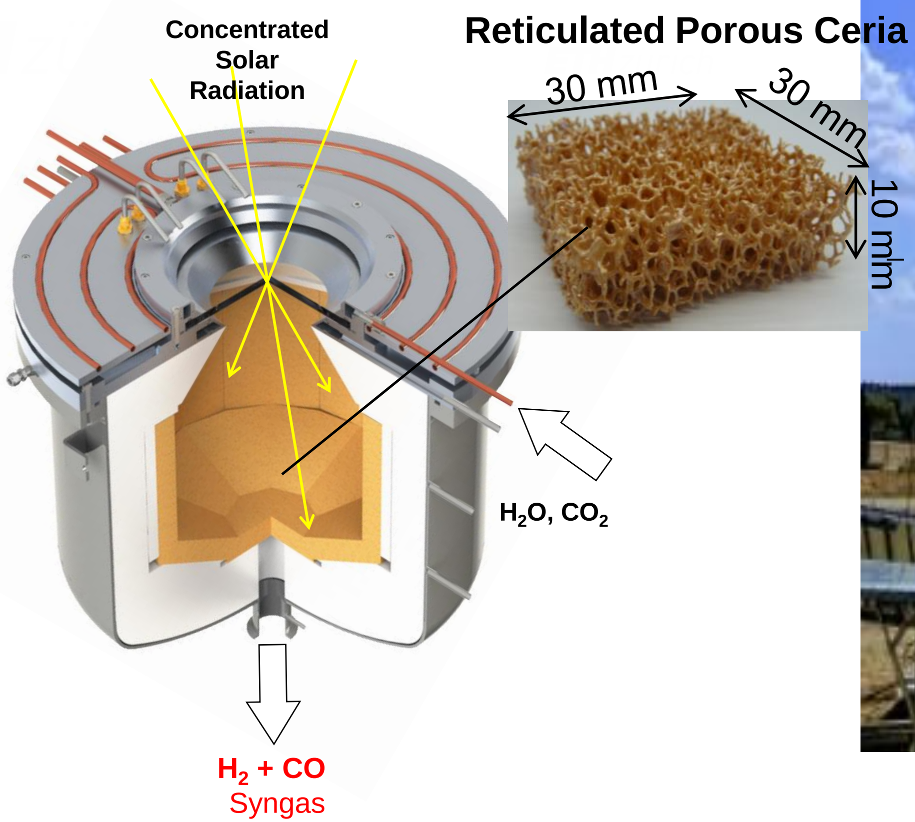
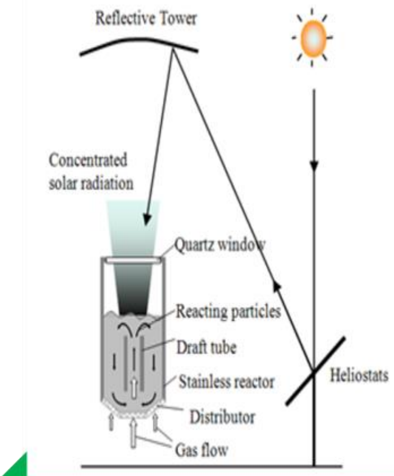
PREC

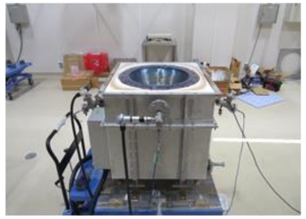
Solar Reactor Technology

5 kW → 50 kW



ARENA Thermochemical Hydrogen / CSIRO (AU), Niigata University, IAE (Japan)





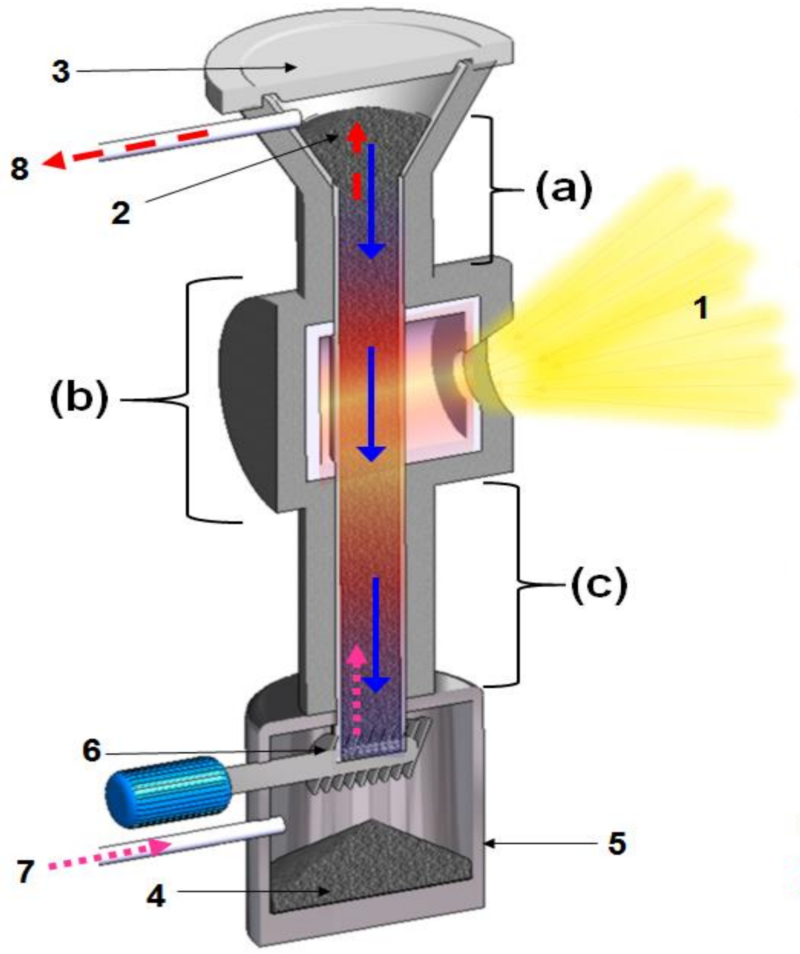
Demonstration at 100-kW$_{th}$ Miyazaki BD system, Japan

Pilot System

- Conversion of CSIRO 500-kW$_{th}$ Field 1 to beam down configuration
- Construction of NU's Fluidized bed system
- Total Budget AUD$ 4m
- 2018 - 2021

CSIRO Australian Government Australian Renewable Energy Agency ARENA 新潟大學 NIIGATA UNIVERSITY IAE 一般財団法人エネルギー総合工学研究所

Use Reduced Metal Oxide as a Solid State Solar Fuel (SoFuel)



1. Concentrated solar
2. Discharged(Oxidized) SoFuel
3. Discharged SoFuel feed hopper
4. Charged (Reduced)SoFuel
5. Charged SoFuel collection tank
6. SoFuel flow control mechanism
7. Oxygen depleted air in (from Sofuel combustor)
8. Oxygen enriched air out (to Sofuel combustor)

(a) Recuperation zone
(b) Reduction zone
(c) Quenching zone

Sofuel Flow
Oxygen depleted air
Oxygen enriched air

Advantages

●Fuel created through thermal reduction; no intermediate reaction – potentially high conversion efficiency (50%)

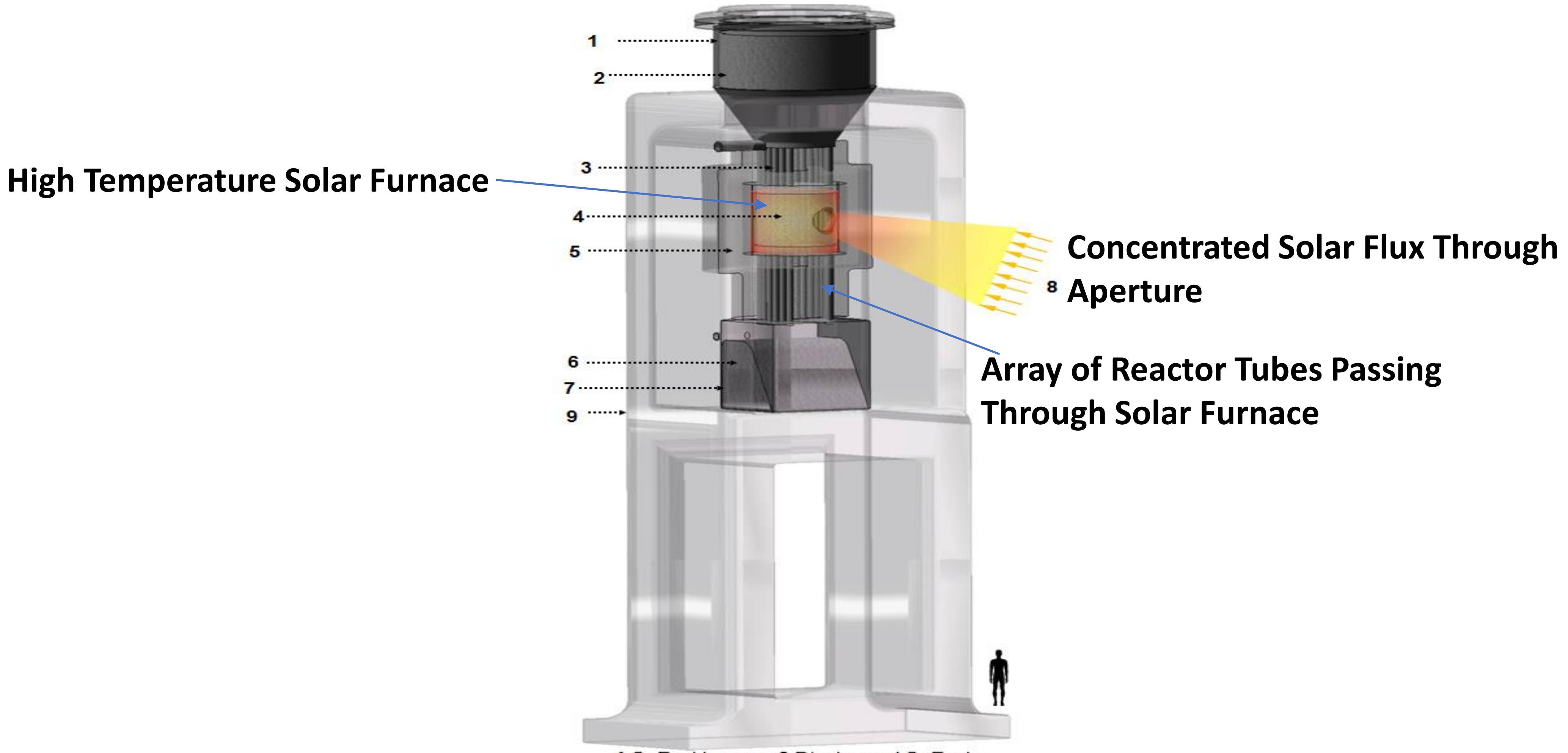
●Fuel synthesis is continuous; decouples solar field from power block

●Metal oxide is recyclable

●Fuel and gas in and out of the reactor is at low temperature; all handling is done at low temperature

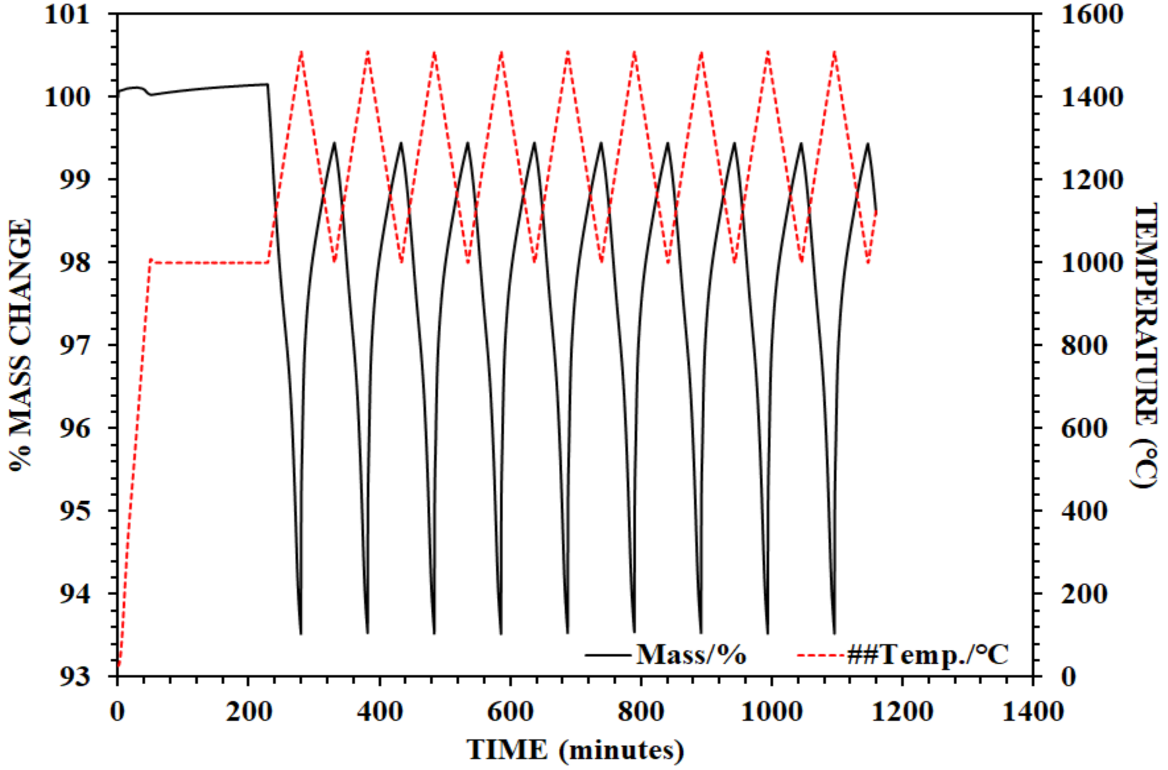
●Heat recuperation is built into the design

SoFuel Reactor Design is Highly Scalable



1.SoFuel hopper, **2.**Discharged SoFuel, **3.**Reactor tubes, **4.**Solar cavity receiver, **5.**Insulation, **6.**Charged SoFuel, **7.**Collection tank, **8.**Concentrated solar power, **9.**Solar tower

Mg-Mn-O is Excellent Candidate Solid Fuel Material



- Excellent reactive stability; no loss in reactivity over 100 cycles
- Energy density>1600 MJ/m^3 demonstrated
- Easily pelletized for ease of handling and fluidization

Magnesium Manganese Oxide Redox Material

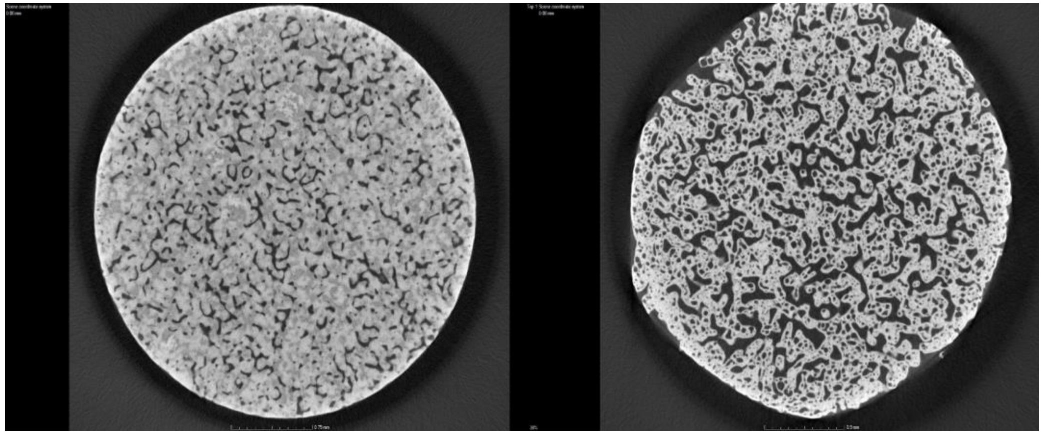
Cyclical stability independently demonstrated in TG, tube furnace, and bench reactor experiments
Material chemical thermodynamics and kinetics well developed and understood
Literally “dirt” cheap

2298 ± 88 MJ/m^3 **energy density** based on tube furnace experiments (**3 times SOA molten salt**)

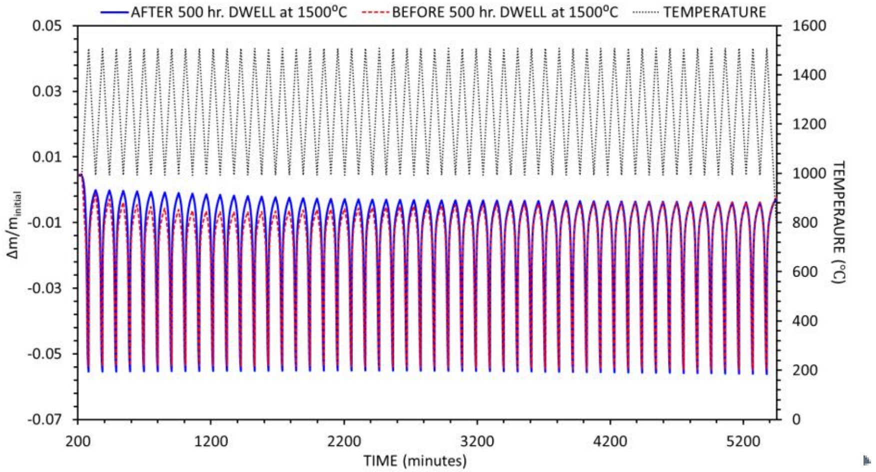
0% measurable loss in energy density over 100 cycles (50 c. - 500 h dwell @ 1500 °C - 50 c.)

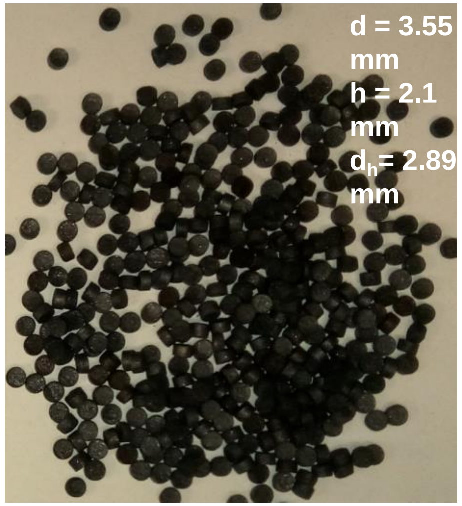
1000-1500 °C operating range for high efficiency heat-to-electricity conversion

100% Recyclable



Fresh Cycled





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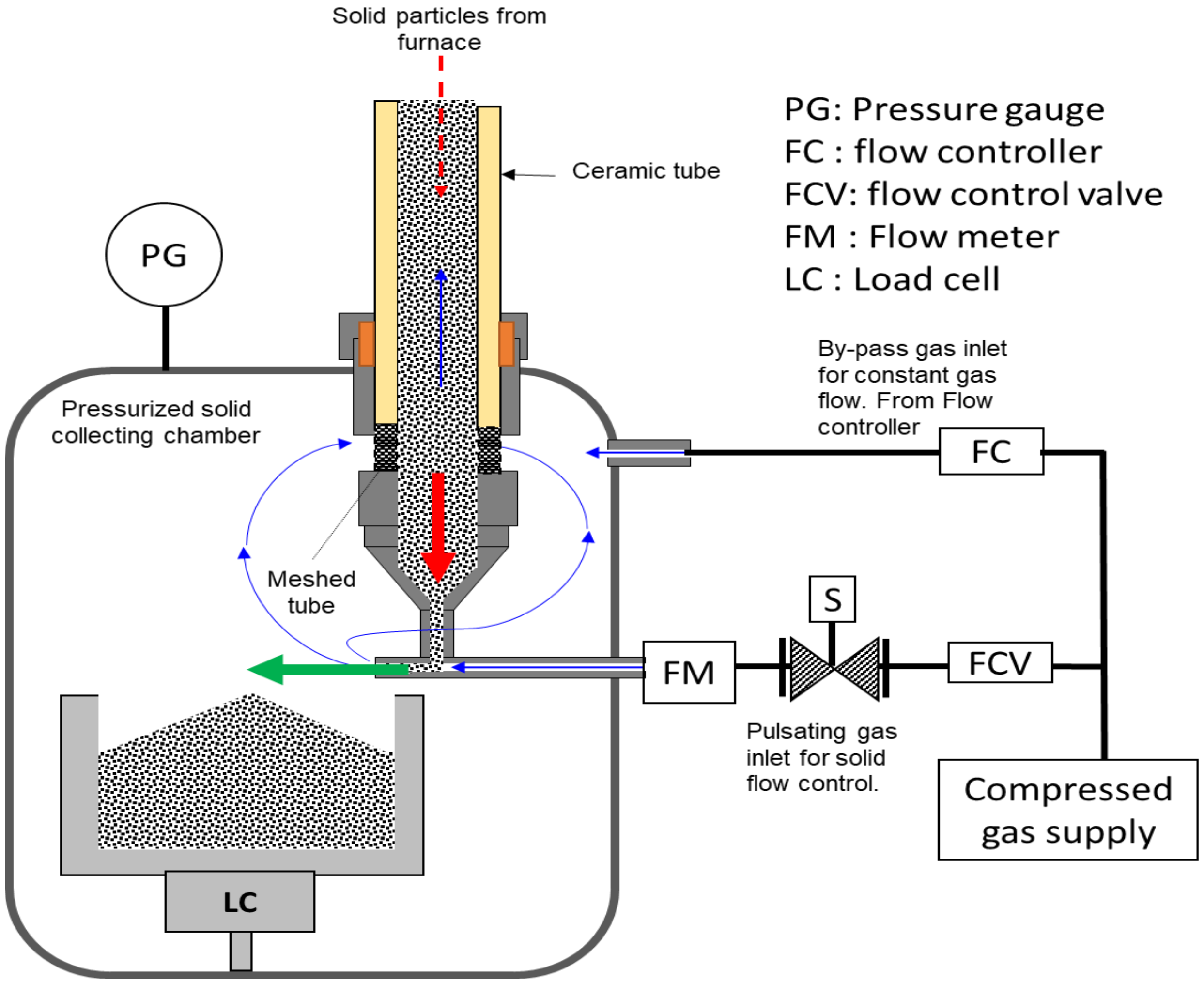
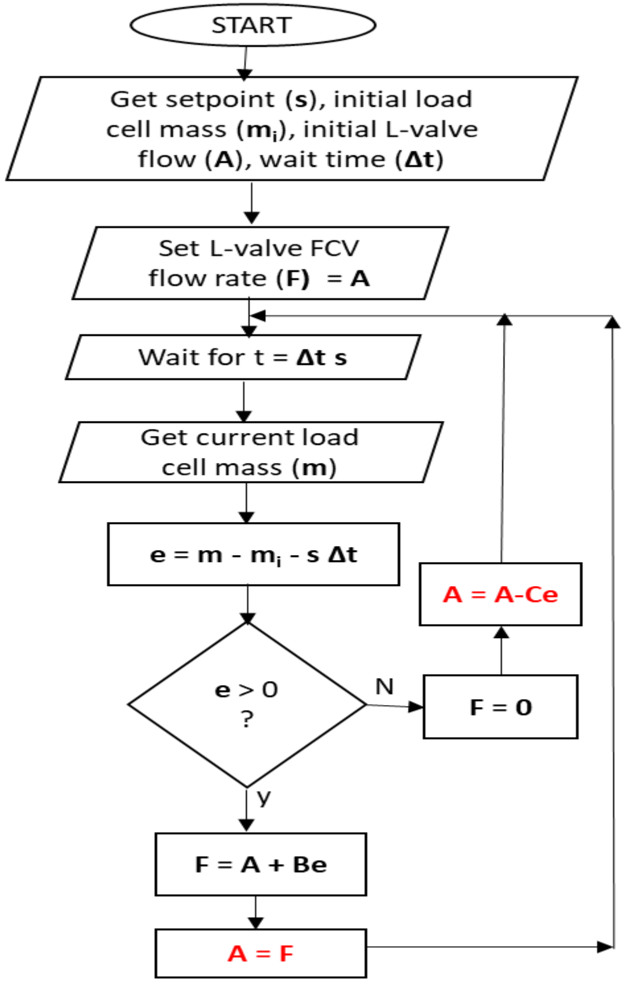
SoFuel Powder Bed Control



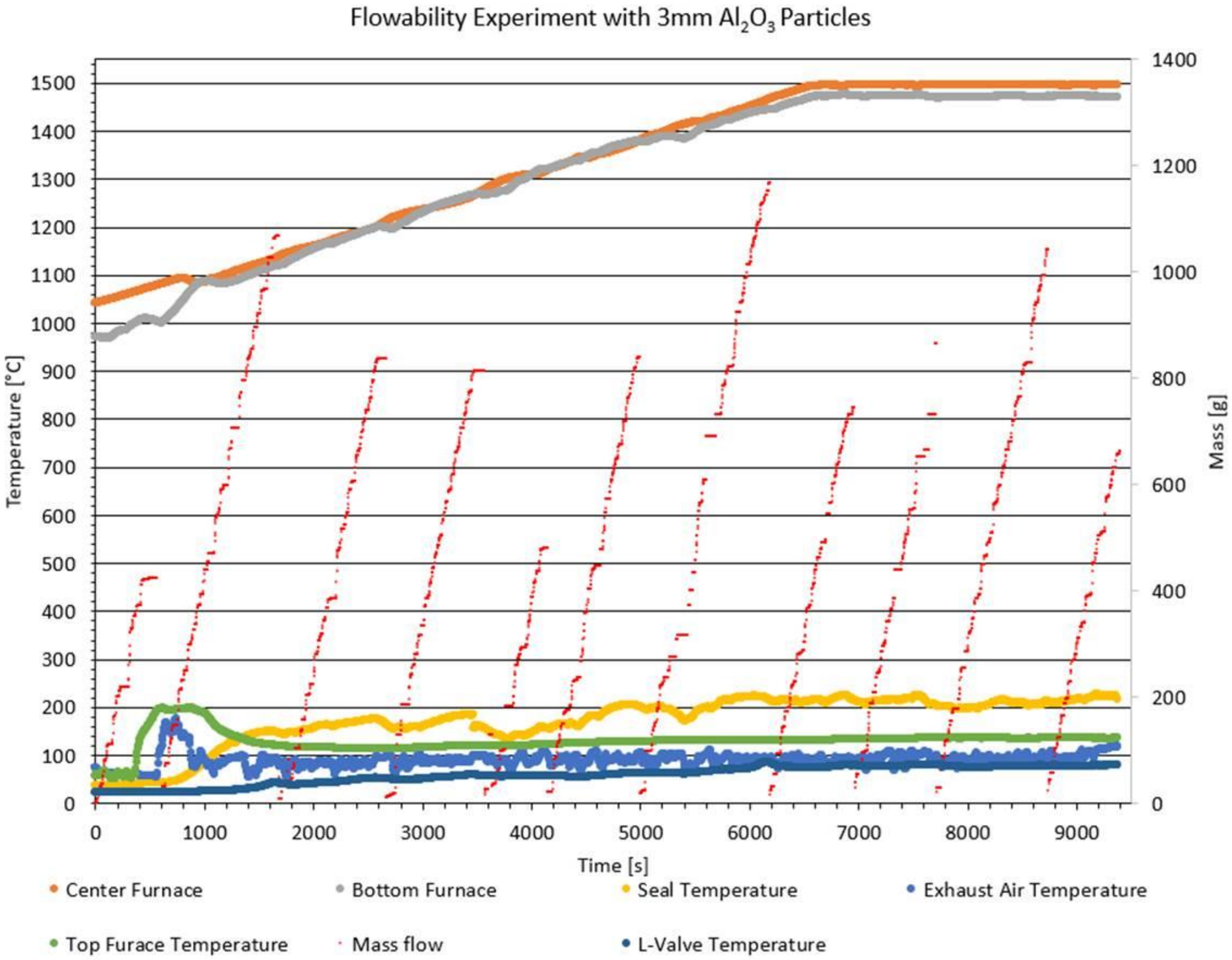


*A , B and C are system dependent parameters.

Fig. 3. Flow chart of the control logic for solid flow control using L-valve

Steady Powder Bed Flow at 1500°C !!

1 g/s particle bed and gas flow



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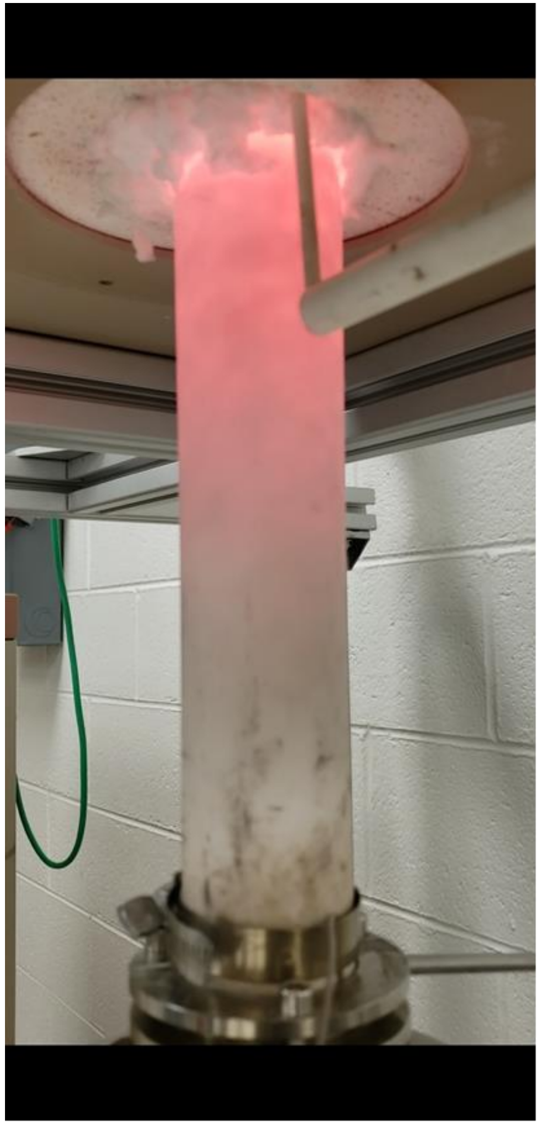
Countercurrent Flow Heat Recuperation Works!

Particle Bed Flow



Gas Flow

Bed velocity: 0.025 cm/s
Residence time: 20 min

Economics of Long Duration Storage

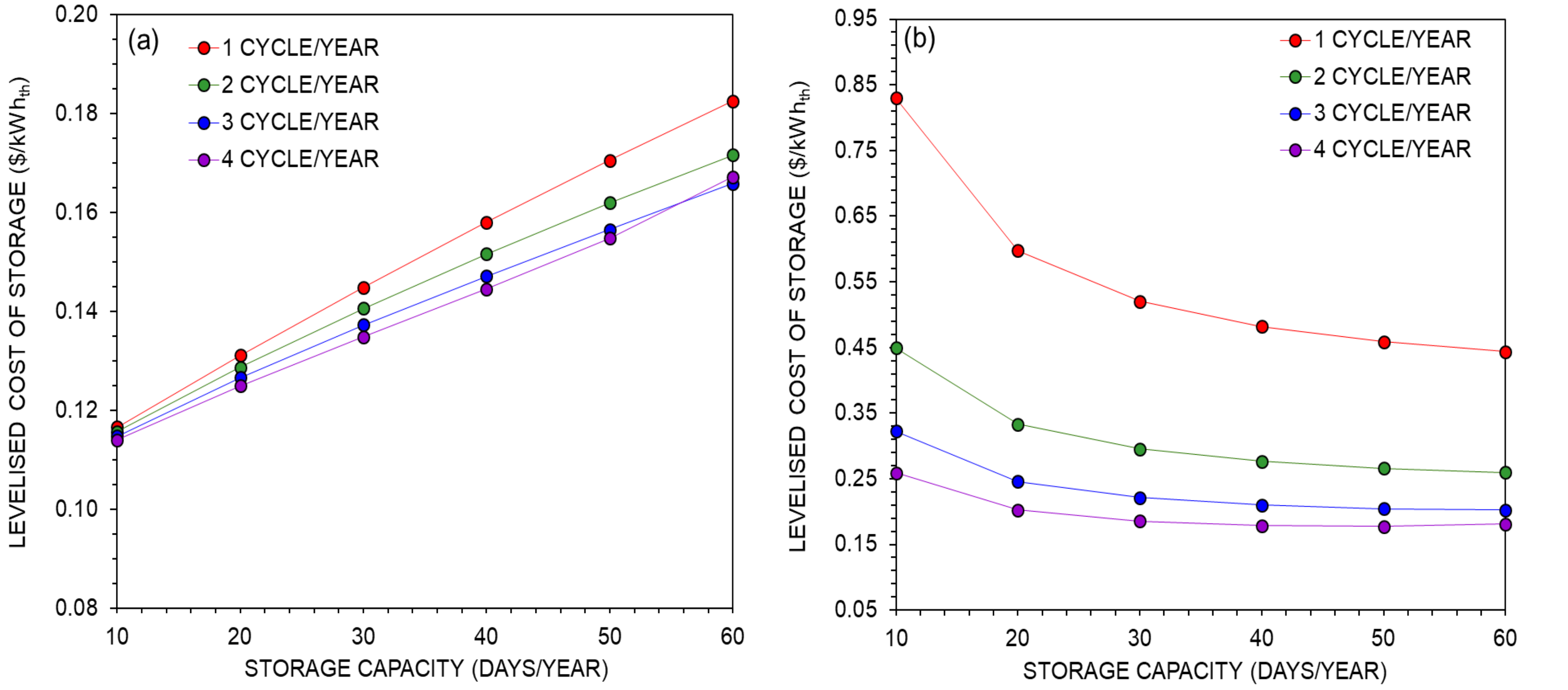


Figure Levelized cost of storage a) Seasonal storage with daily storage b) Seasonal storage without daily storage

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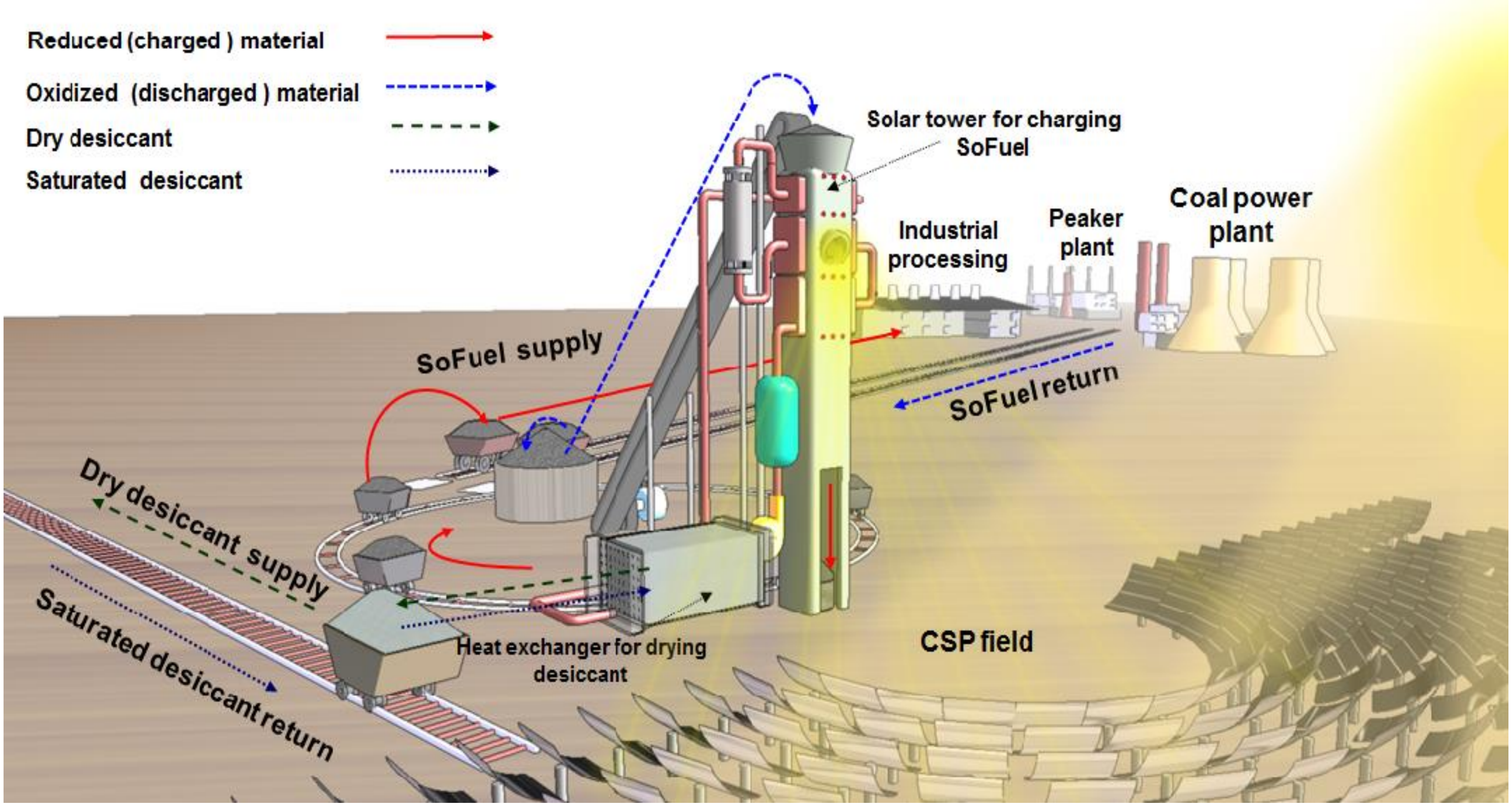
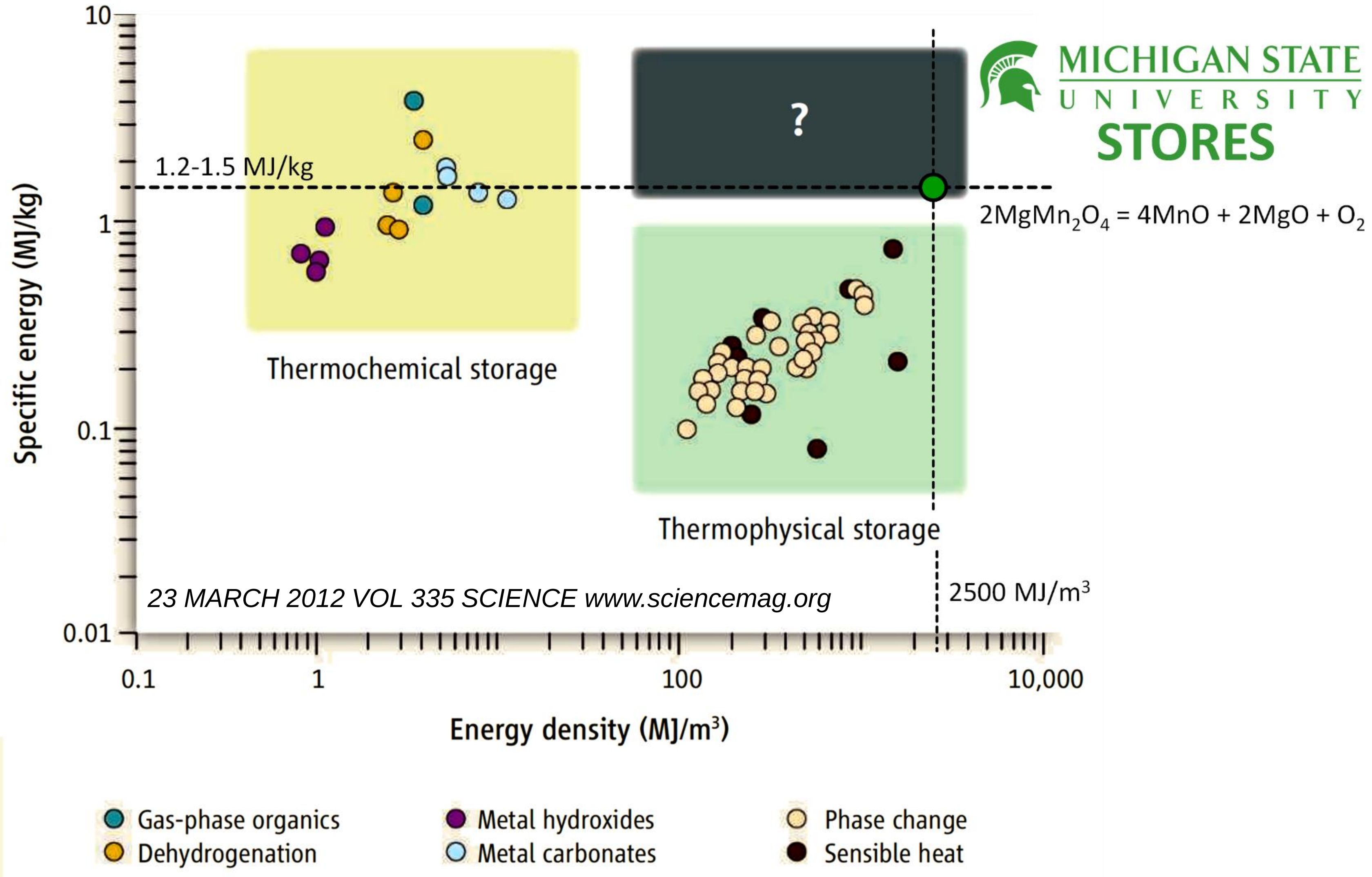
Utilization of Solid State Fuel

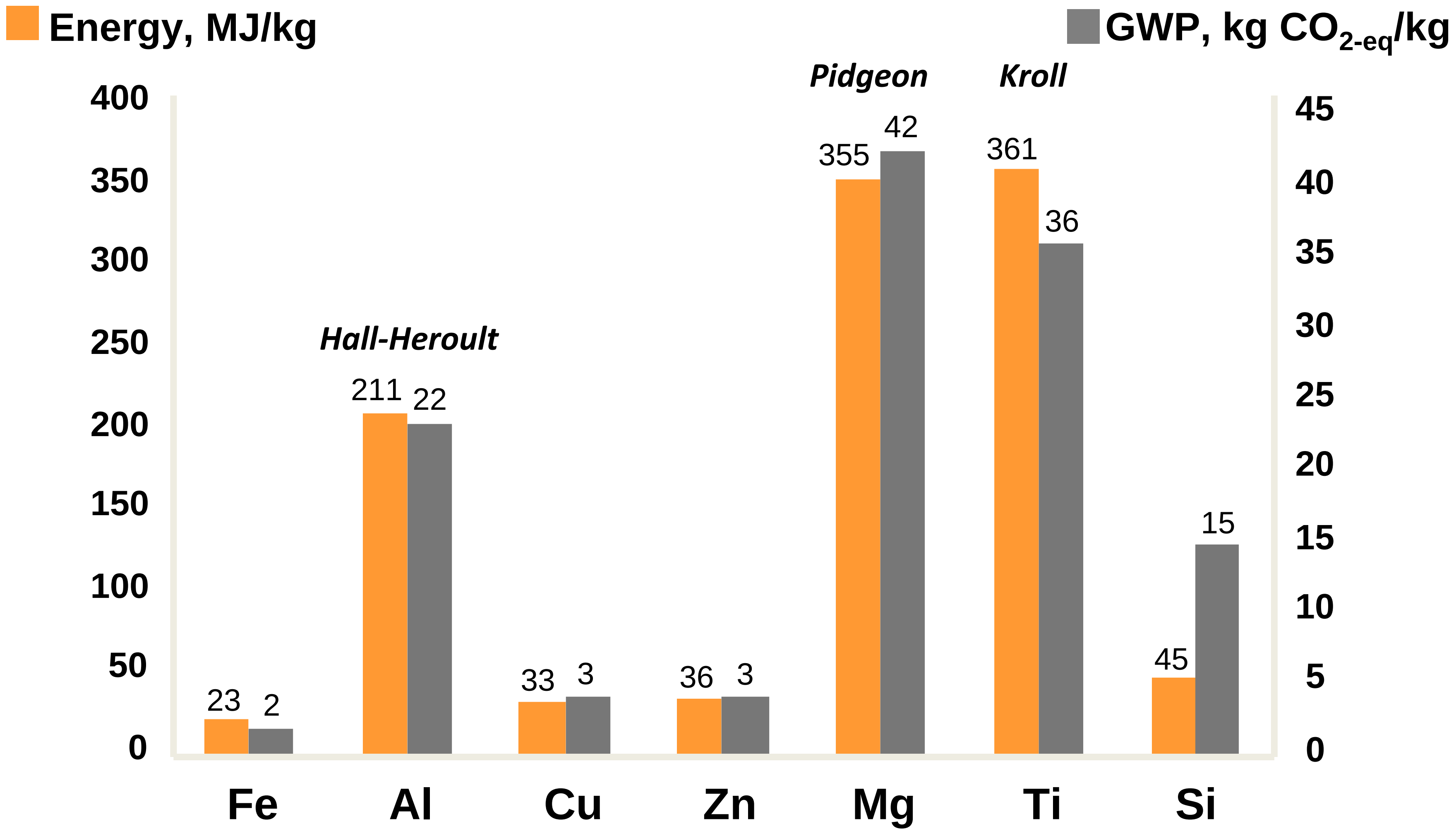


In Search of the ideal "Thermal Battery"



Low Carbon, Low Energy, and Low Cost Production of Metals

10% of global GHG emissions are a result of metal production[1]



[1]Stephen Lezak, Charles Cannon and, Thomas Koch Blank, Low-Carbon Metals for a Low-Carbon World: A New Energy Paradigm for Mines, Rocky Mountain Institute, 2019, http://www.rmi.org/url here.

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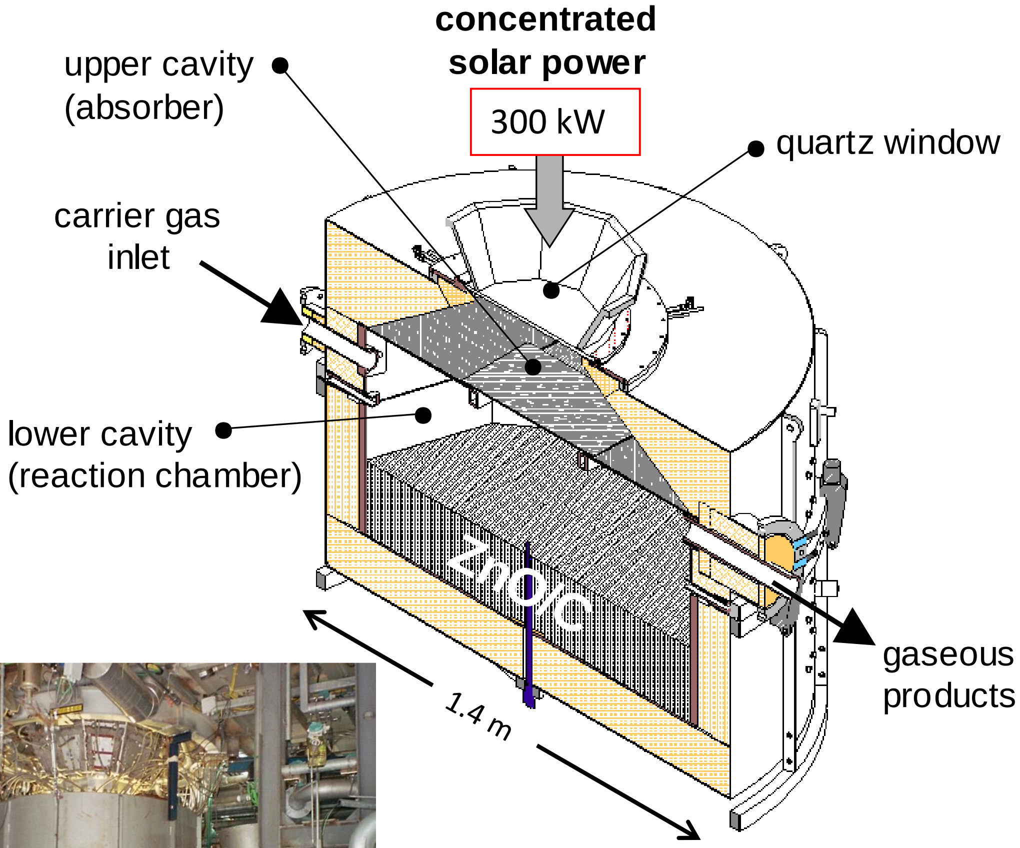
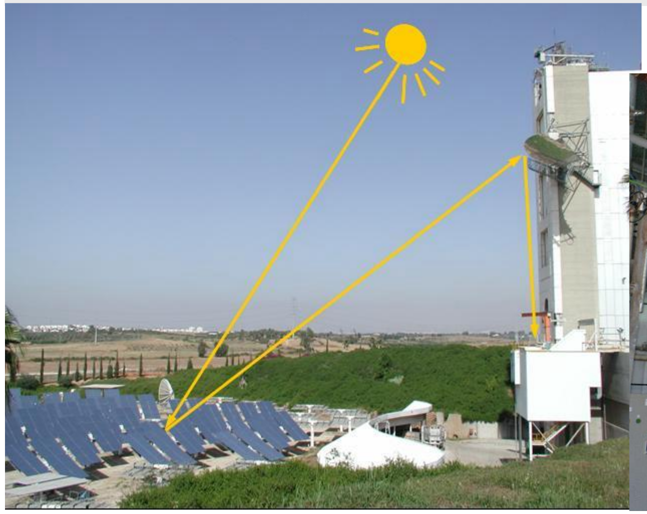
Solar Carbothermic Production of Zn Demonstration

- Solar power input, Q_{solar} = 300 kW
- Solar concentration, C = 1500 suns
- Reactor temperature, $T_{reactor}$ = 1500 K
- Zn production rate = 45 kg/h
- Zn purity = 95%
- Thermal efficiency:

$$\eta_{thermal} = \frac{\Delta H}{Q_{solar}} = 30\%$$

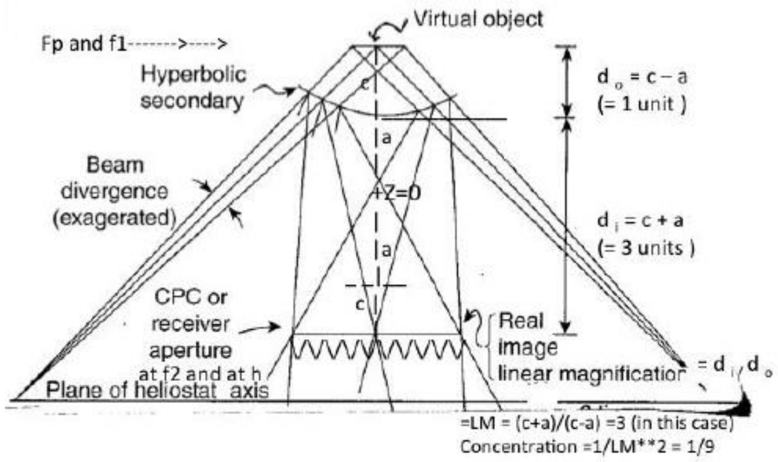


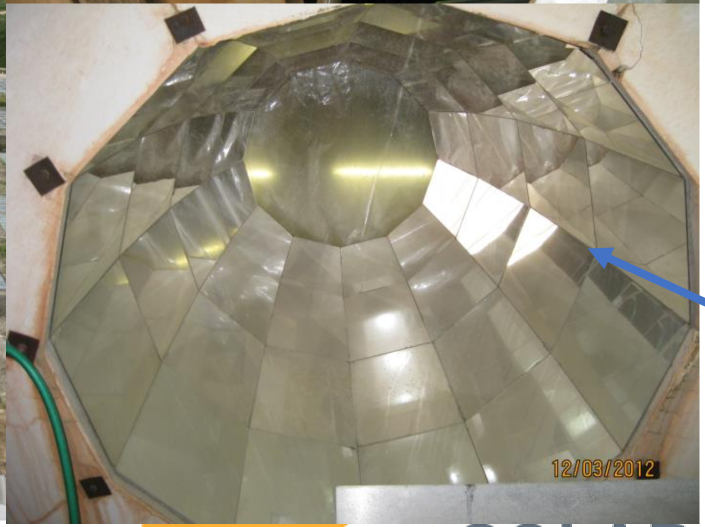


Weizmann Institute, Rehovot, Israel

- ASME J. Solar Energy Eng. 129, 190-196, 2007.

Weizmann Institute—Demonstration of Solar Thermochemical Processing Industrial Scale-up

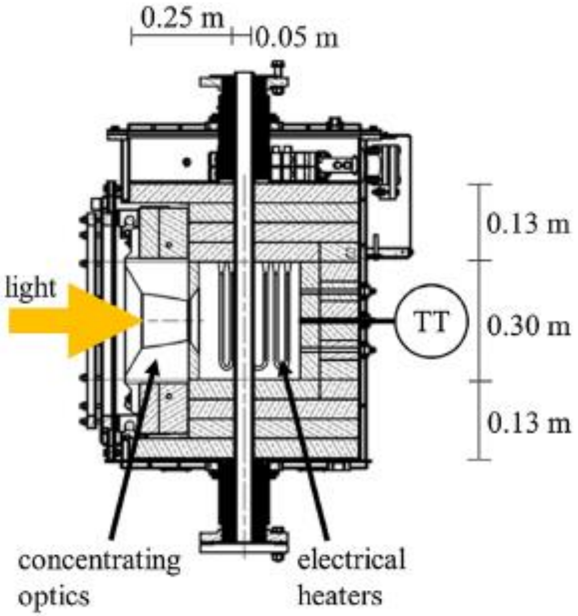


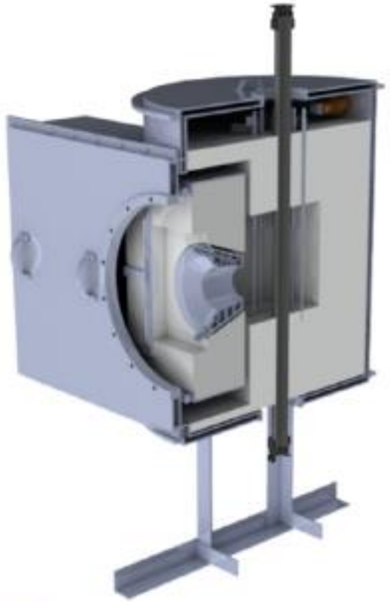


Hyperbolic Beam Down

Secondary Concentrator

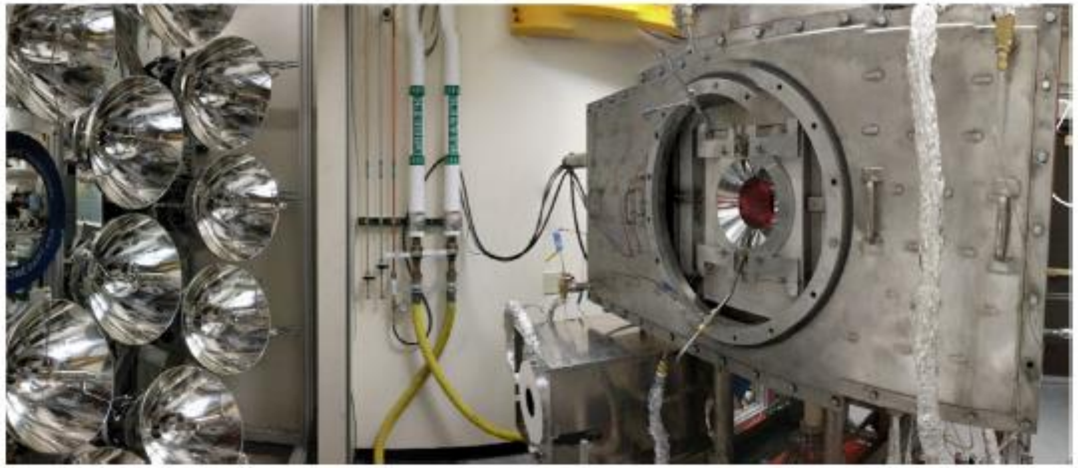
Solar Magnesium Production –Falling Particle Reactor





MgO + C → **Mg** + CO

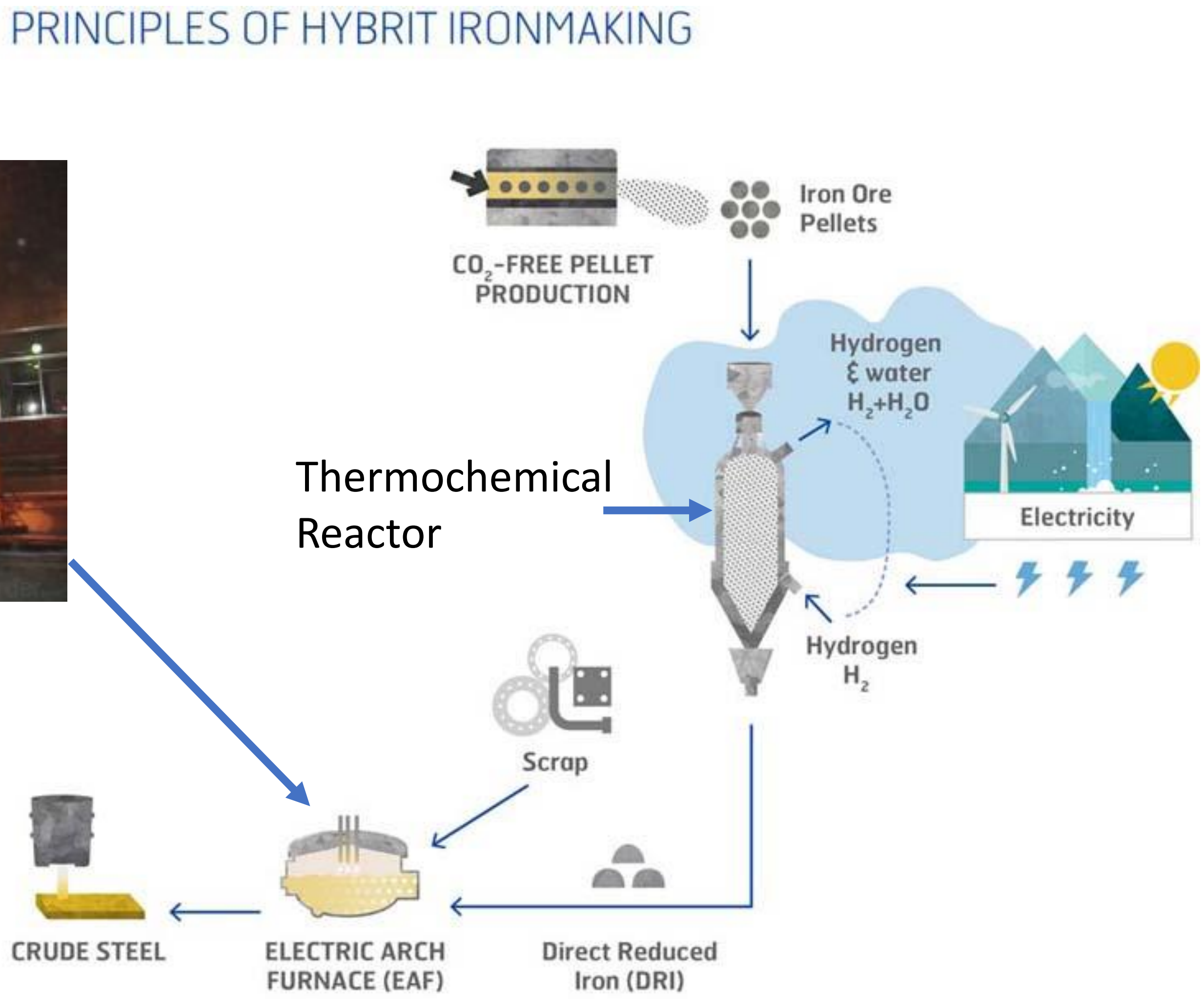
Big Blue Technologies Mg Ingot



Nowcasting, predictive control, and feedback control for temperature regulation in a novel hybrid solar-electric reactor for continuous solarthermal chemical processing

Scott C. Rowe[a,⁎], Illias Hischier[b], Aaron W. Palumbo[c], Boris A. Chubukov[c], Mark A. Wallace[d], Rachel Viger[d], Allan Lewandowski[e], David E. Clough[d], Alan W. Weimer[f,⁎]

Clean Steel Production Using Renewable Hydrogen



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Concluding Thoughts

- Solar fuel synthesis and metal extraction are feasible using high temperature redox reactions

- Robust, efficient, and cost competitive reactor technology is an enabler

- High temperature thermochemistry science and technology remains in its infancy

- Research opportunities lie in materials development; radiation, thermal, and chemical transport; chemical kinetics; reactor design; process control

- Cost competitive technology for scalable solar processing technologies is viable

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