Particle-based solar thermochemical and thermal energy storage

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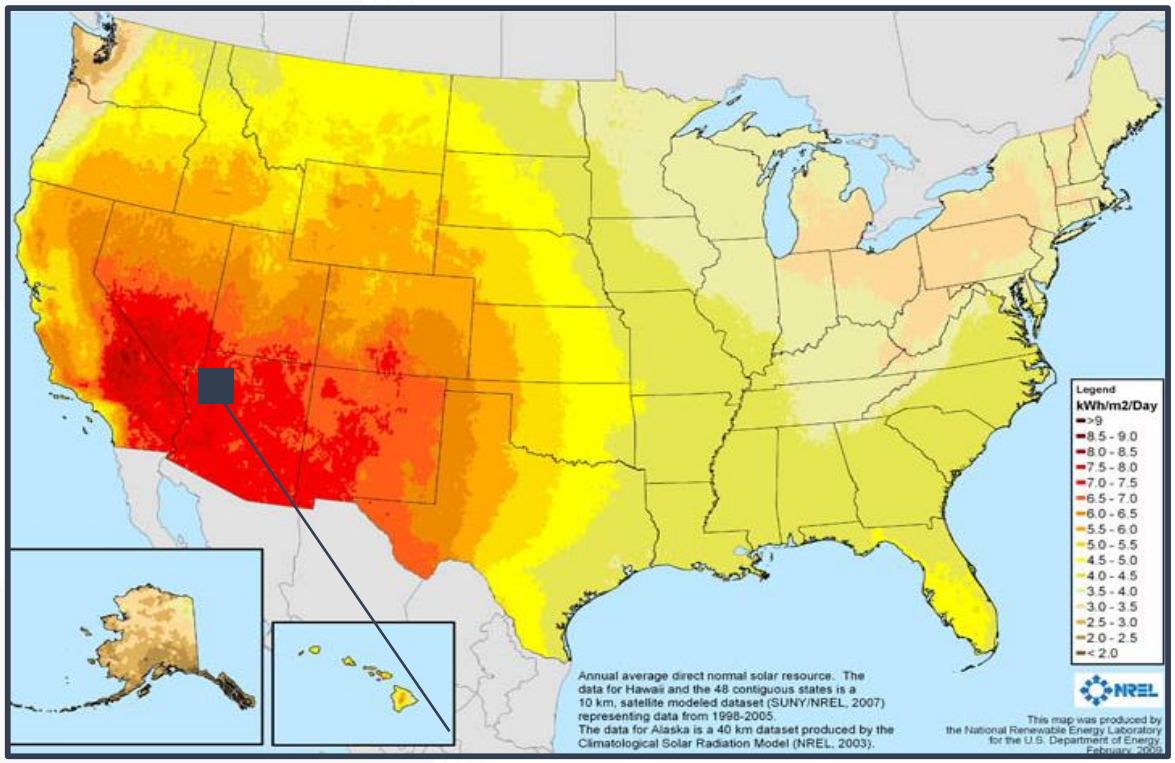
Solar potential and limitations

Annual solar irradiation in the United States

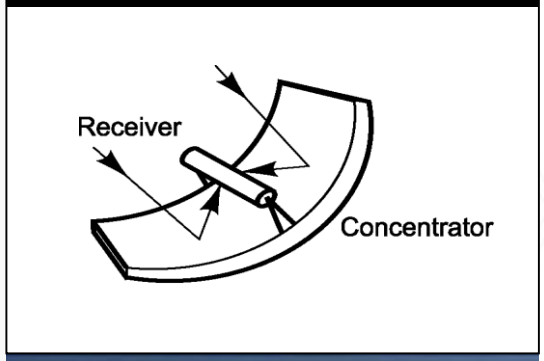
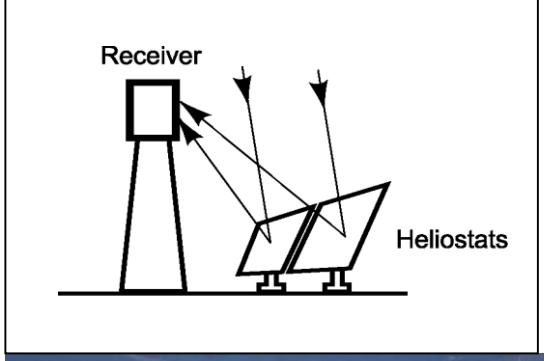
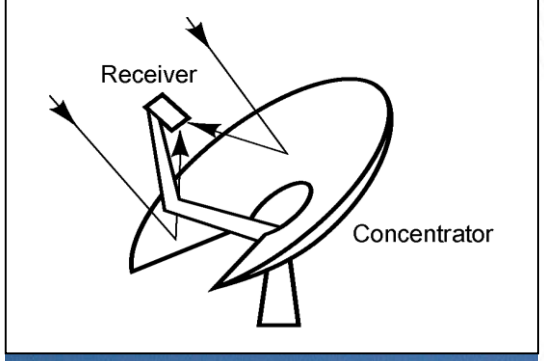


Limitations of Solar Energy

- **Dilute:** Maximum direct-normal solar irradiance of 1 $kW \cdot m^{-2}$
- **Intermittent:** Solar energy can only be harvested when the sun is shining
- **Unequally distributed:** Optimal areas for harvesting solar energy are near the equator away from population centers

10% conversion to a usable form of energy in an area 126 ×126 km^2 could have supply all the energy needs n the United States

Concentrating solar irradiation

Trough	Tower	Dish
Solar concentrations of < 100 suns	Solar concentrations of 500 – 2500 suns with secondary	Solar concentrations of 5000 – 10,000 suns
		
		

Steinfeld and Meier,
Encyclopedia of Energy
2004, 623-637

Maximum work potential extraction

$$\eta_{overall,ideal} = \eta_{absorption}\eta_{Exergy} = \underbrace{\left(1-\frac{\sigma T^4}{I_{DN}C}\right)}_{\frac{\dot{Q}_{solar}-\dot{Q}_{re-radiation}}{Q_{solar}}} \cdot \underbrace{\left(1-\frac{T_{ambient}}{T}\right)}_{\text{theoretical work potential from heat (exergy)}}$$

$$\eta_{overall,ideal} = 0 \rightarrow T_{stagnation} = \left(\frac{I_{DN}C}{\sigma}\right)^{0.25}$$

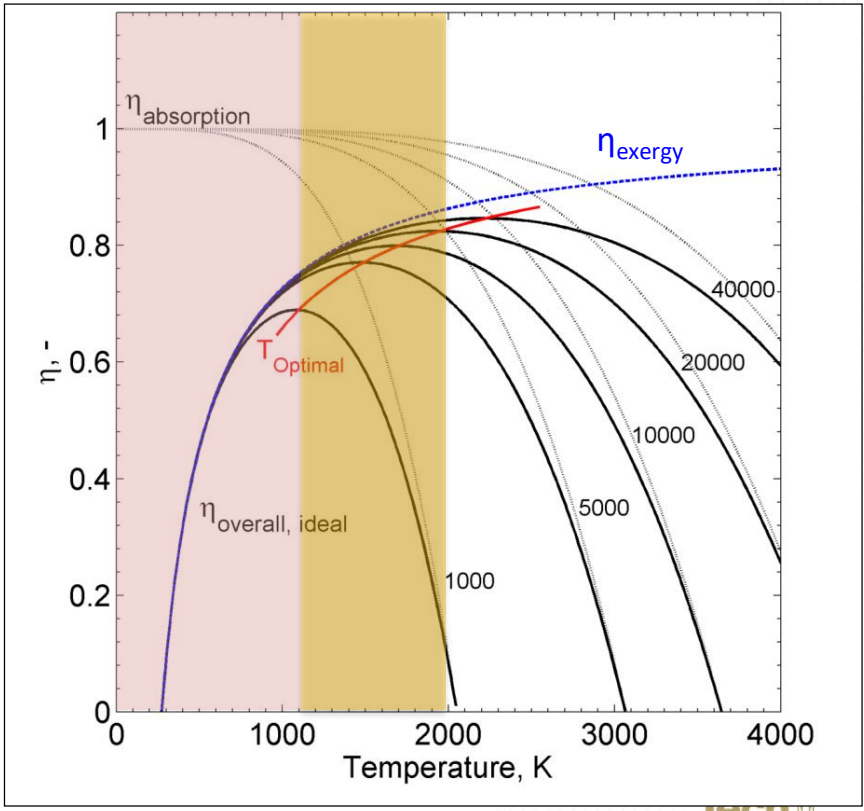
$$\frac{\partial \eta_{overall,ideal}}{\partial T_{optimal}} = 0$$

$$0 \rightarrow \left(T_{optimal}\right)^5 - 3/4\,T_{ambient}\left(T_{optimal}\right)^4 - \left(\frac{T_{ambient}I_{DN}C}{4\sigma}\right) = 0$$

C	1000 suns	5000 suns	10000 suns
$T_{stagnation}$	2049 K	3064 K	3644 K
$T_{optimum}$	1106 K	1507 K	1724 K

nuclear range

ideal thermochemical cycles



Sensible thermal energy storage media molten salts

Advantages

- Relatively inexpensive
- High energy density
- Low vapor pressures
- Discharges at constant conditions

Disadvantages

- High melting points (~200 °C Solar Salt)
- Low thermal conductivites
- Relatively low temperatures of stability (~585 °C Solar Salt)
- Relatively hard to pump and corrosive

Solar Salt – 60% $NaNO_3$/40% KNO_3

Thermal and thermochemical energy storage with particles

Advantages

- Directly irradiated
- Low-cost, abundant media (*e.g.* sand, casting media)
- Higher operating temperatures/ efficiency
- Existing bulk transport, storage technologies
- Various receiver configurations available

Sensible thermal energy storage media

- High thermal capacitance
- High solar absorptance
- Enhanced heat transfer due to small particles

Thermochemical storage media

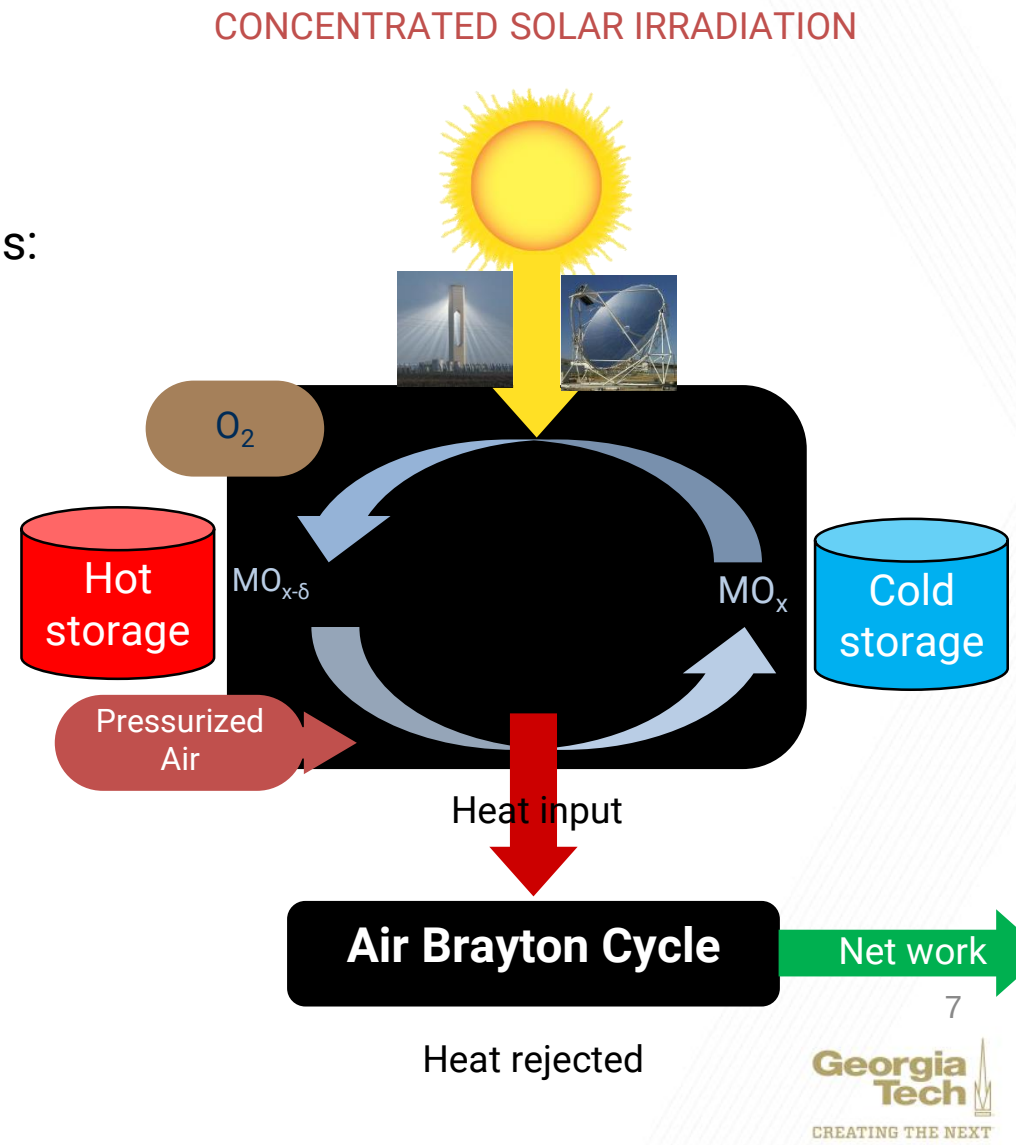
- Increased energy power densities
- Maintains higher temperatures during the exothermal release of heat

Solar thermochemical heat storage concept for integration into an Air Brayton cycle

- Solar thermochemical energy storage via a two-step solar thermochemical cycle for integration in an Air Brayton cycle based off of redox-active materials:

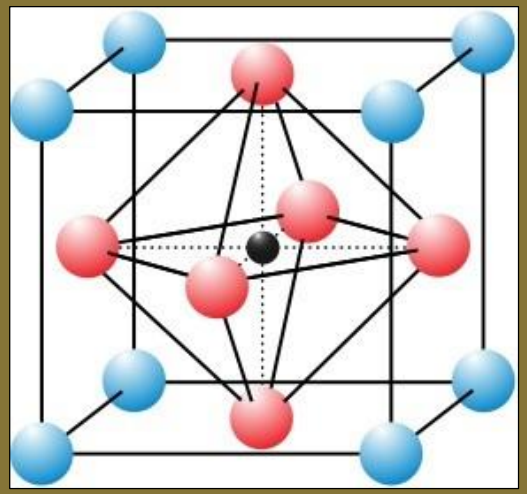
$$MO_{x-\delta} + \frac{\delta}{2} O_2 \rightleftharpoons MO_x + \Delta h$$

- Enables heat storage in both a chemical and sensible form
- The added chemical storage increases the energy densities of the material to better account for intermittency of sunlight



Design constraints for solar receiver

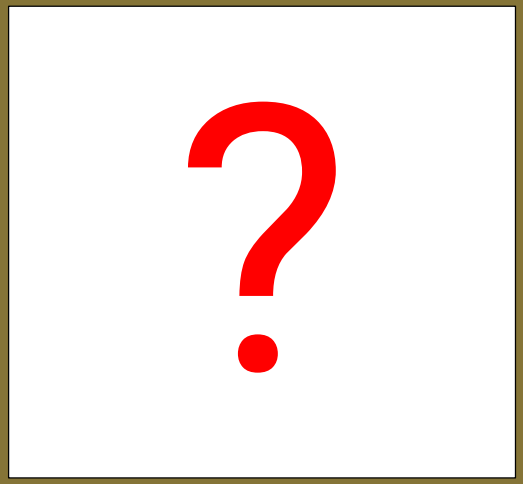
Redox-active materials development



Cation substitution to “tune” MIEC materials for

- Increased redox capacitance and reaction enthalpy
- Faster kinetics from increased oxygen mobility
- Optimized thermodynamics
- CAM28 particles

Thermochemical reactor development



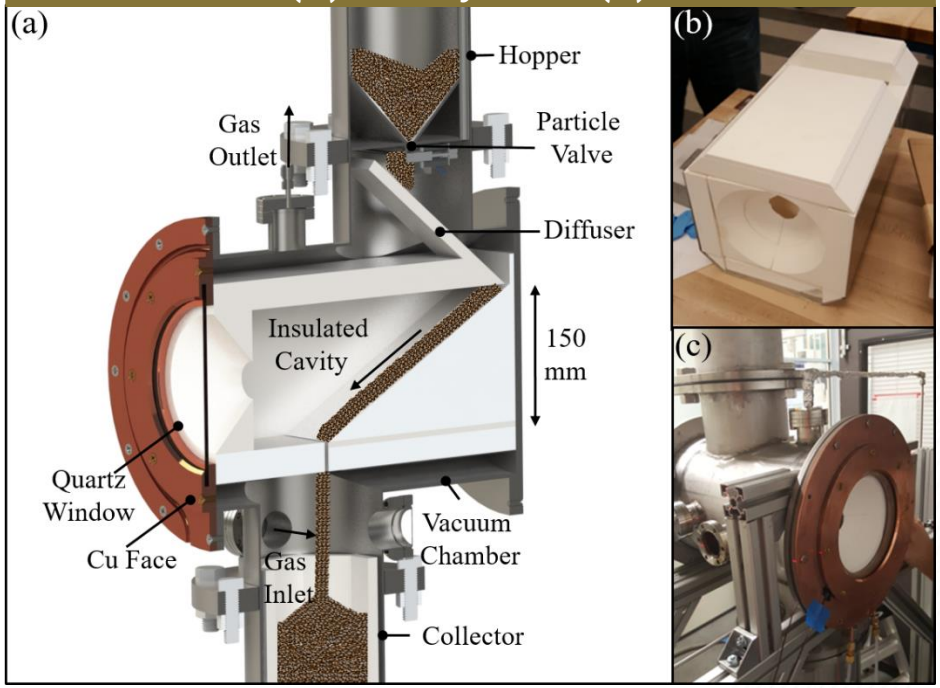
Thermochemical reactors must also be designed for

- Optimal absorption of concentrated solar irradiation
- Specific solar concentrating facilities
- Redox-active materials and residence times

5 kW_{th} Solar Thermochemical Inclined Granular-Flow Reactor (STInGR)

- Thermochemical energy storage of solar energy within a dense, granular flow of reactive particles
- Aluminosilicate insulated cavity inserted within steel, cylindrical vacuum chamber
- Reactor sealed using steel flanges, hopper / collector cylindrical assemblies, quartz window
- Incident irradiation introduced through quartz window using HFSS, concentrated on 40 mm diameter aperture
- Residence time controlled by variable inclination angle, mass flow rate, slope roughness
- Reactor capable of receiving various granular media, specifically tuned for $CaAl_{0.2}Mn_{0.8}O_{3-\delta}$

Solar thermochemical reactor (a) schematic, (b) cavity, and (c) assembled



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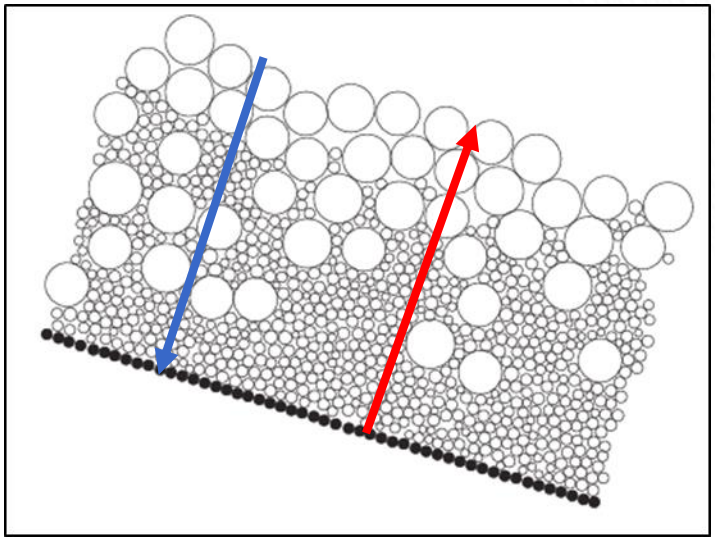
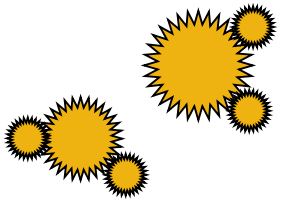
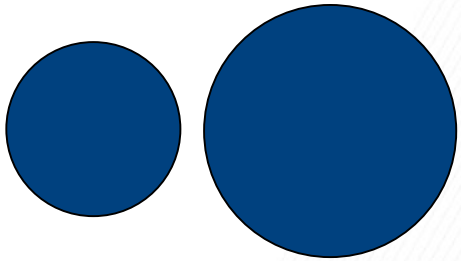
Granular flow theory

- Bulk transport influenced by competing time scales
  - Inter-particle contact time versus $\left(\frac{\partial u}{\partial z}\right)^{-1}$
- Bulk transport sensitive to development of small population of long-lived contacts
  - Electrostatic forces
  - Cohesion
  - Particle shape, size interactions
  - Soft particles
  - Temperature effects (*e.g.*, particle softening, agglomeration, thermophoresis)





Jagged shapes susceptible to long-lived contacts

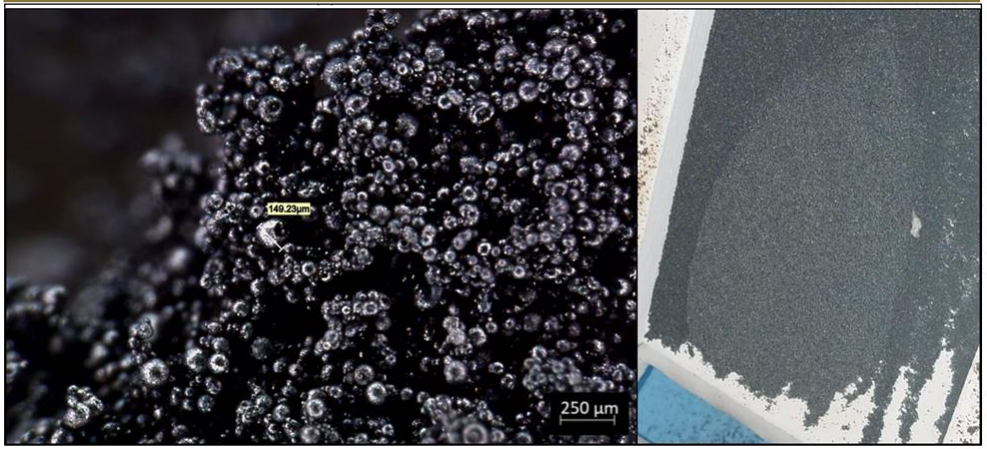


Spherical shapes susceptible to binary particle interactions

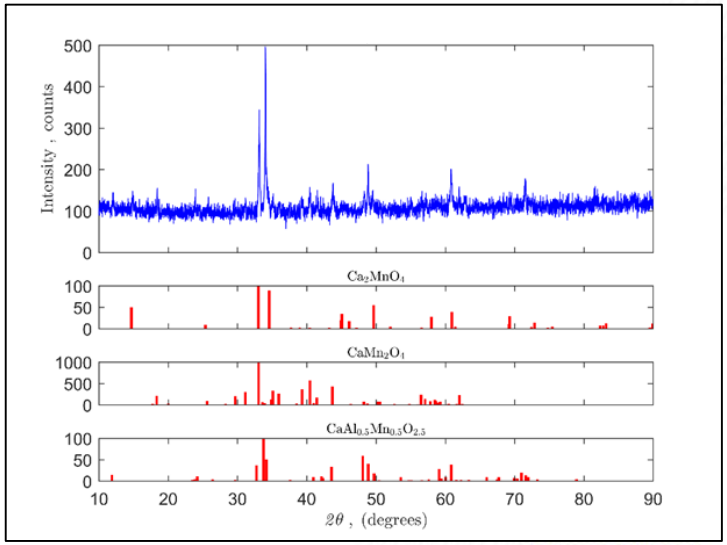
Experimental results from solar reactor

- Severe agglomeration of CAM28 powders observed to occur at T > 900 °C.
- Agglomeration observed at similar temperatures for high-density spray-dried calcium manganites with common impurities used in chemical looping combustion.
- Common impurities of spray-dried calcium manganites observed in XRD analysis of materials.

Agglomerates from as viewed by optical microscopy (left) and along the slope (right)



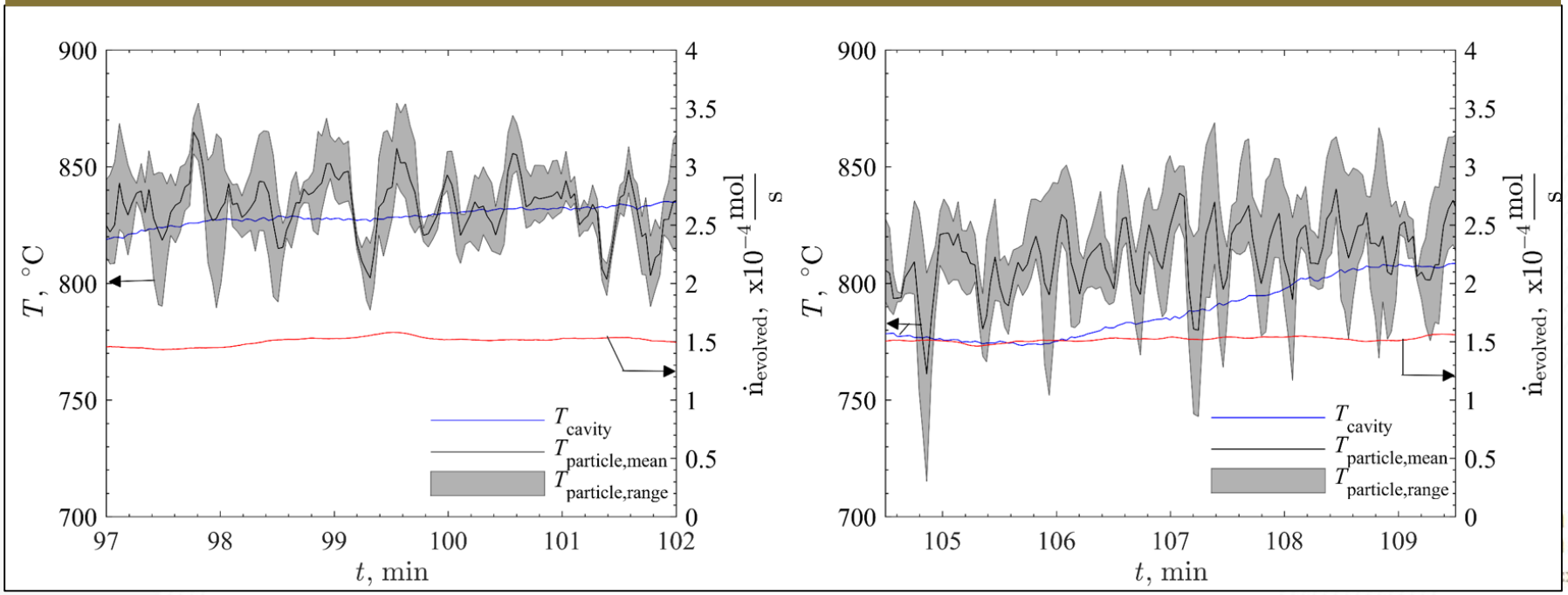
Peak intensities from X-ray diffraction for (top) Coorstek particles cycled repeatedly through the 5 kWth reactor during high flux solar simulator experimentation and (bottom) for potential phase impurities Ca_2MnO_4, $CaMn_2O_4$, and $CaAl_{0.2}Mn_{0.8}O_{2.5}$ samples



Experimental performance

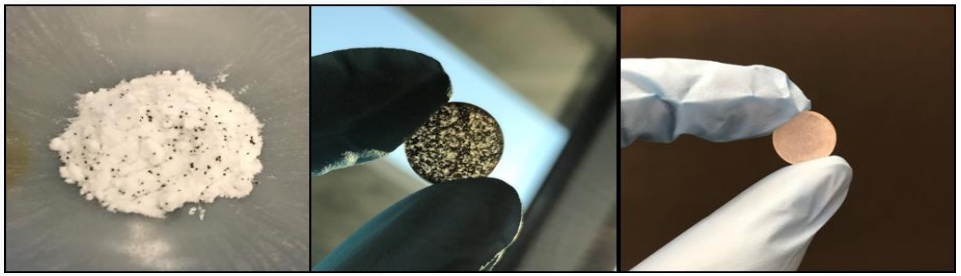
- Severe agglomeration avoided if $\bar{T}$< 875 °C.
- Replicated steady state experiments performed with $\dot{Q}_{\mathrm{HFSS}}$= 2.7 $\mathrm{kW_{th}}$ with HFSS lamps 2-6.
- $\bar{T}_{\mathrm{outlet}}$= 830 – 850 °C, $\overline{\Delta\delta_{\mathrm{outlet}}}$ = 0.012, η_{th} = 0.785
- η_{th} greater than anticipated due to lower *T* and higher $\dot{m}_{\mathrm{CAM28}}$

Temporal temperature (cavity and particulate) and O_2 measurements



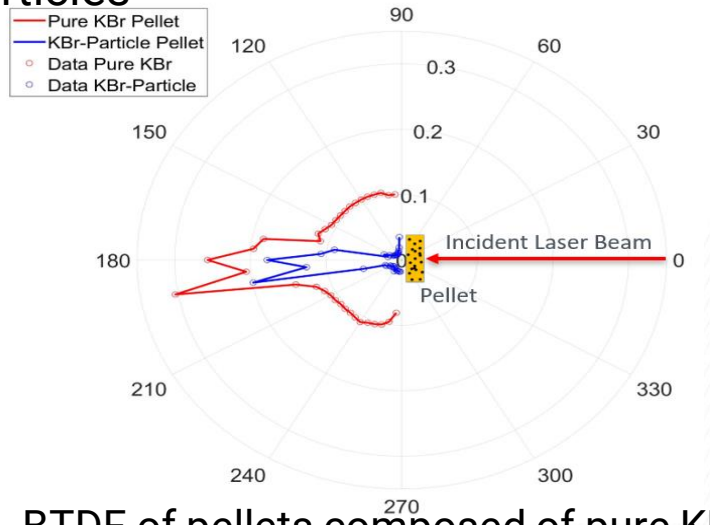
Characterization of scattering phase function setup/measurements

- Three Axis Automated Scatterometer (TAAS)
- Requires particle-KBr pellet
- Laser wavelength: 635 nm
- Pellet fabrication parameters
- 13 mm diameter, ~ 7 ton load compaction, no vacuum, powder pulverized



Fabrication of the KBr pellet with particles: (left) a mixture of KBr powder and ID50 particles; (middle) the 1% by weight KBr-particle pellet after compression; (right) a pure KBr pellet for reference

- Bi-directional Transmittance Distribution Function (BTDF)
- Preliminary results indicate strong forward scattering normal to pellet
- Similar pattern observed for both pellets, uniform decrease due to particles



BTDF of pellets composed of pure KBr powder (red) and KBr-particle mixtures of 1 wt% particles (blue)

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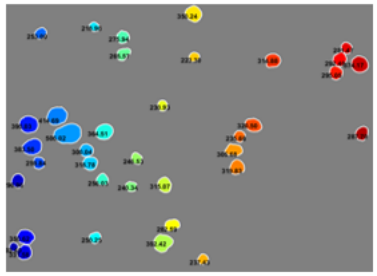
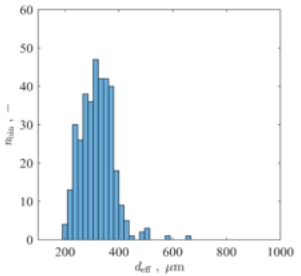
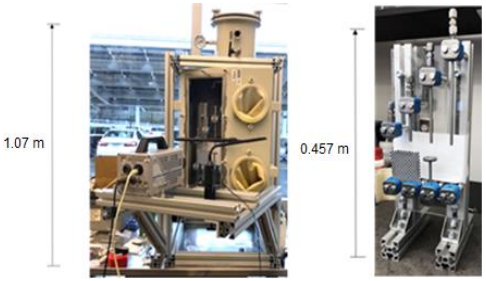
Characterization of mechanical properties up to 800 °C

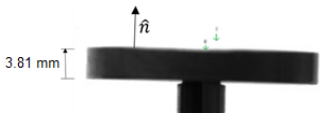
Developed a program to determine particle size distributions and roundness



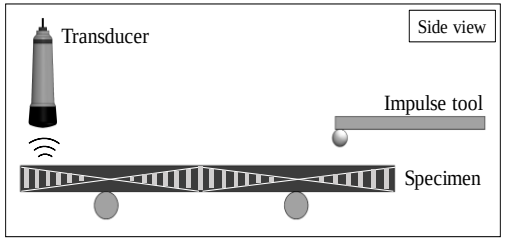


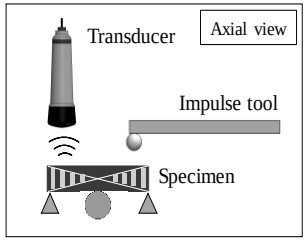
Modified a vacuum chamber coupled to a high-speed camera to measure coefficient of restitution





Developing protocols with impulse Excitation tests to determine modulus of elasticity and Poisson's ratio





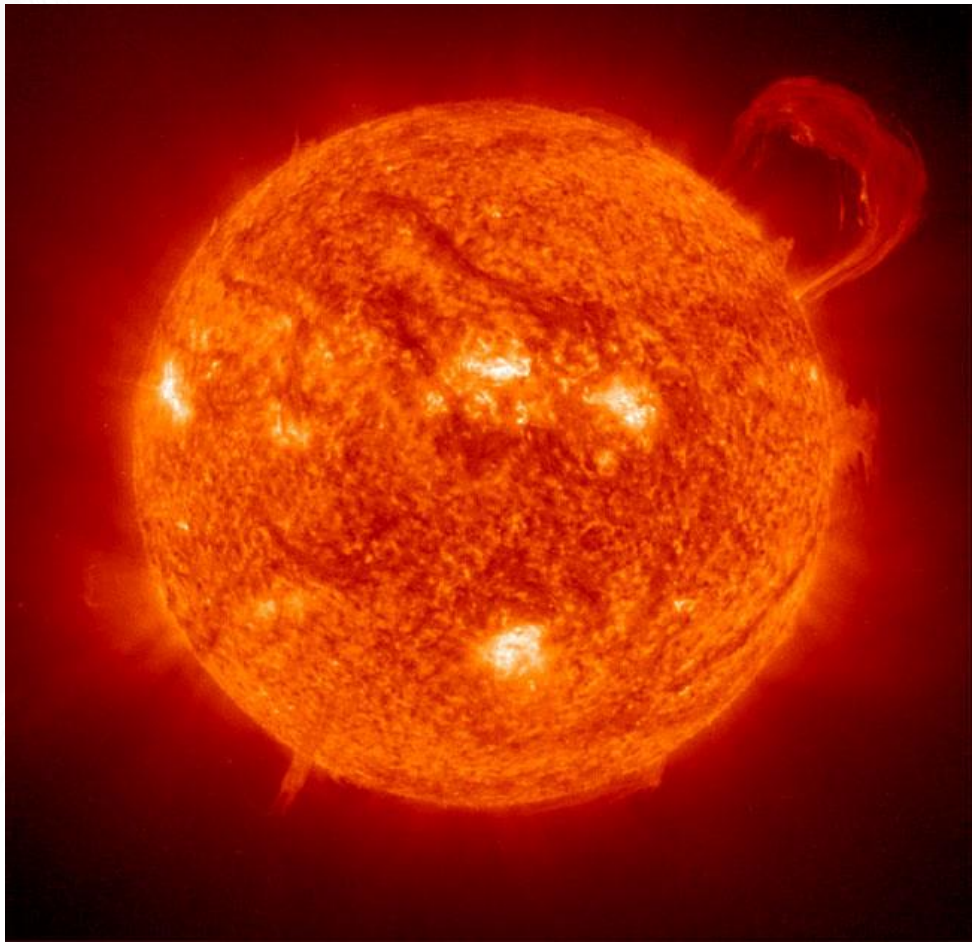
Developing a slip-stick apparatus to measure static and dynamic coefficients of friction

Conclusions and summary

- Particulate (granular) flows are excellent solar thermal energy storage media for reaching elevated temperatures and higher solar-to-electric efficiencies
- Redox-active particles for thermochemical energy storage media increase the overall power densities of the materials and allow for long-term storage
- Material properties need to be accurately characterized to design the next generation of particle heating receivers/reactors

Outlook

How does the future look?



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