SunShot
U.S. Department of Energy

CSP Program Summit 2016

High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage (PROMOTES)

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Project Team

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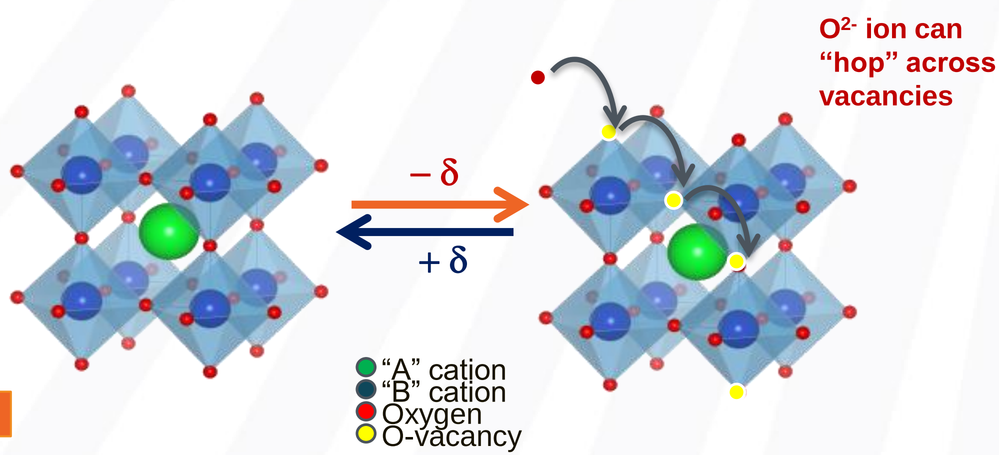
Problem Statement and Objective

Enabling technologies are needed to store and deliver thermal energy to high-temperature (> 1000 °C), high-efficiency power cycles, e.g. Air Brayton. The technology must be low cost ($\$15/kWh_{th}$), which demands high energy density solutions.

We will systematically develop, characterize, and demonstrate a robust and innovative storage cycle based on novel metal oxides with *mixed ionic-electronic conductivity* (MIEC). Thermal energy is stored as chemical plus sensible potential in these materials through a reversible reduction-reoxidation reaction. The product of the cycle will be air at T ≥ 1000 °C for integration with an air Brayton system. The tested system and validated models will indicate the ability to achieve thermal storage costs ≤$\$15/kWh_{th}$ and total available enthalpy ≥ 1500 kJ/kg.



Value Proposition

Thermochemical energy storage (TCES), wherein thermal energy is converted and stored indefinitely as chemical energy, can boost energy storage density. Redox active mixed ionic electronic conducting metal oxides (MIECs) with their elegantly simple redox chemistry, approach an ideal medium for high temperature TCES in many respects:

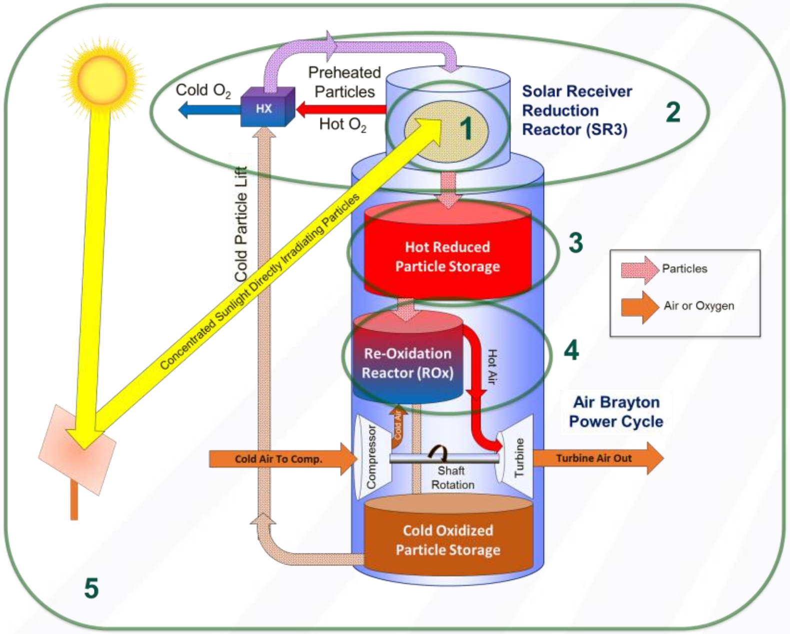
- They are robust and high temperature stable.
- The reduction/oxidation reactions are highly selective, highly reversible, and can be conducted open loop in air.
- MIEC properties enhance reaction kinetics.
- Particle approaches are complimentary to Falling Particle Receiver technology.
- Particulates can act as both a storage and heat transfer media.

We will capitalize on the unique characteristics of MIECs so that the potential of TCES may be realized.

Project Concept

1. New MIEC materials enable high temperature, high energy density storage

5. Systems and technoeconomics to predict cost and performance and to guide development efforts



2. SR3: A particle receiver tailored to metal oxide reduction reactions

3. Hot Storage Bin: High temperatures (T > 1000 °C) and an O_2-free environment

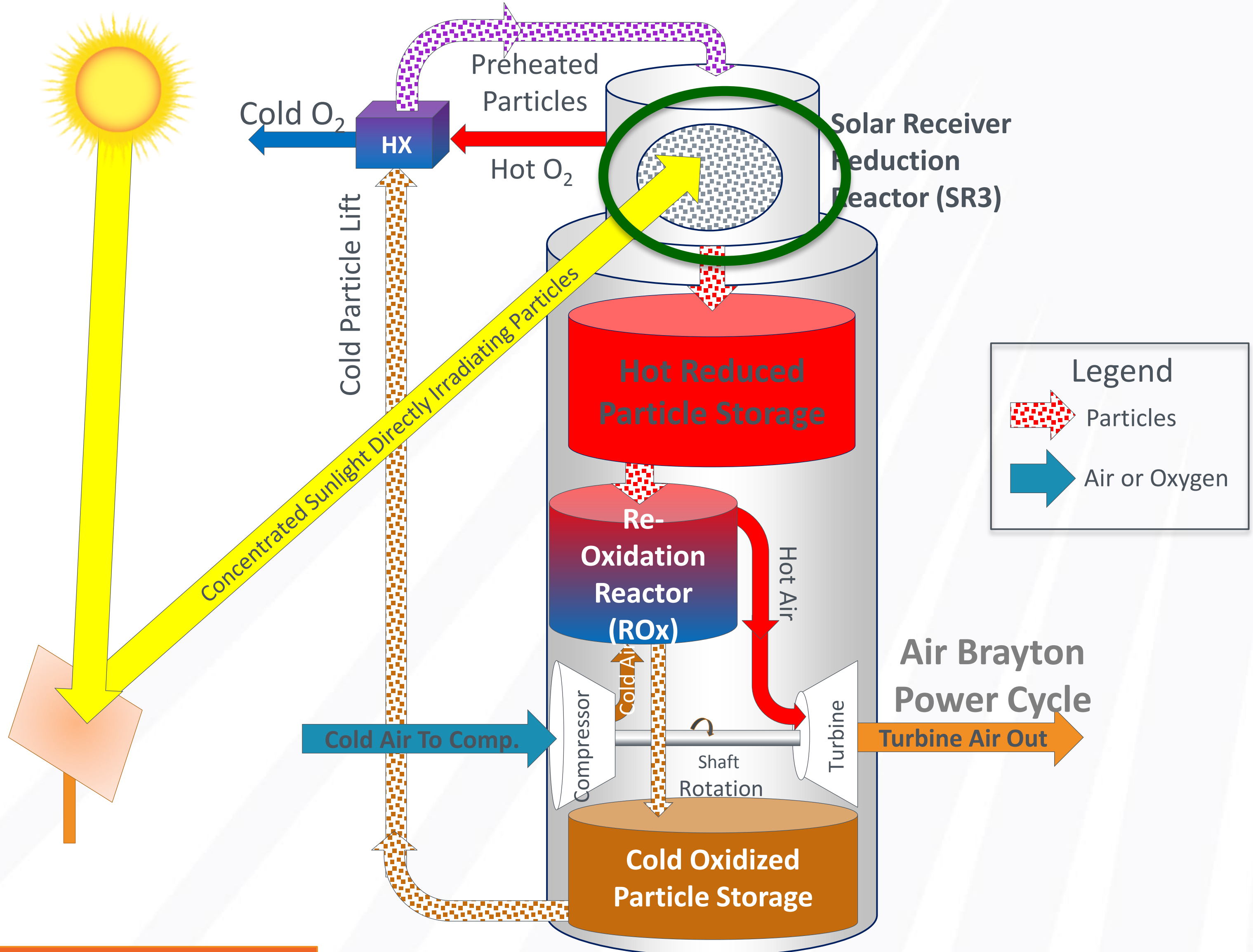
4. ROx: Reoxidation reactor --replaces the combustor in a power block. Compressed air acts as both reactant and heat transfer fluid. High pO_2 facilitates heat recovery at high temperatures. Open cycle – no gas storage.

Phase 1: Develop & Characterize materials & TE models → Phase 2: Midscale Component Development and Demo → Phase 3: Develop large-scale reactor and test on-sun

Milestones

SOPO Task # M.S. #	Task Title and Milestone Description (High Level)
1.1	**Identify MIEC Material**
M1.1	*Material identified that meets project metrics*
1.2	**Design, Build and Validate Stagnation Flow Reactor**
M1.2	*Validate that SFR can achieve necessary heating rates, be used to measure reaction kinetics,and be used to evaluate stability of materials*
1.3	**Design of Storage Bins for 1000 °C, Reduced Particles**
M1.3	*Storage materials identified consistent with project metrics*
1.4	**Implement Thermodynamic and Techno-economics Models**
M1.4	*Validate that the system can achieve sufficient thermal efficiency, exergy efficiency, and cost effectiveness*
2.1	**Measure Reaction Kinetics**
M2.1	*Demonstrate accurate determination of kinetic parameters*
2.2	**Solar Receiver/Reactor/Reducer (SR3) Modeling and Design**
M2.2	*Identify design that achieves receiver outlet > 1000 °C and meets project metrics*
2.3	**Fabricate and Test Laboratory-scale SR3; Finalize Design of Demonstration-scale SR3**
M2.3	*Demonstrate particle temperature between 1000 and 1350 °C at lab scale*
2.4	**Evaluate Ability of ROx to Provide 1200°C at the Brayton State Points**
M2.4	*Reactor design completed with modelling showing the ability to achieve sufficient power to the air Brayton powerblock under defined constraints*
2.5	**Build and Test a Small Scale ROx Oxidizer Reactor**
M2.5	*Ramp to 1200 °C in less than 5 minutes*
2.6	**Balance of Plant Design**
M2.6	*Cost-effective materials and components identified*
2.7	**Benchmarked Thermodynamics System & Detailed Sub-system Models**
M2.7	*Validate that the system can achieve sufficient thermal efficiency, exergy efficiency, and cost effectiveness*
3.1	**Demonstration-Scale (≥100kWt) On-Sun System Testing**
M3.1	*Successful demonstration*

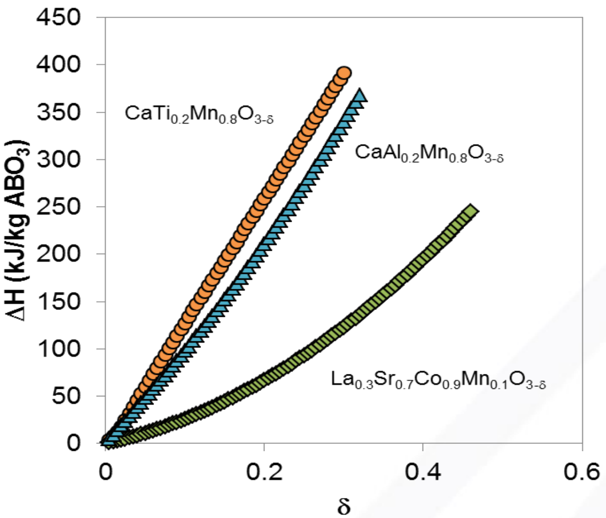
1. Materials

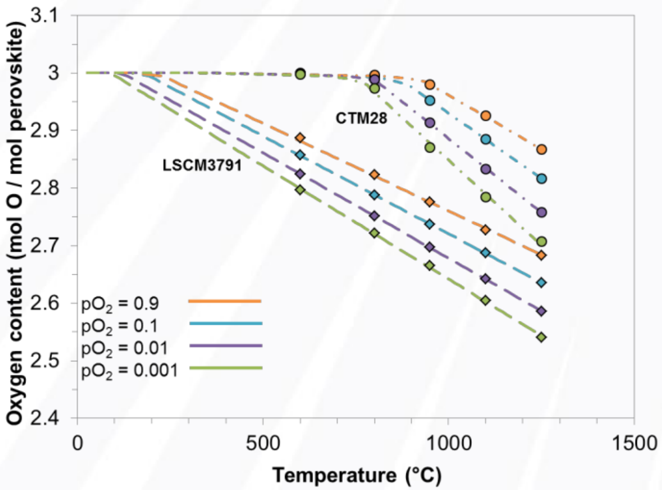


Preheated Particles
Cold O_2
HX
Hot O_2
Solar Receiver Reduction Reactor (SR3)
Cold Particle Lift
Concentrated Sunlight Directly Irradiating Particles
Hot Reduced Particle Storage
Legend
Particles
Air or Oxygen
Re-Oxidation Reactor (ROx)
Hot Air
Cold Air
Air Brayton Power Cycle
Cold Air To Comp.
Compressor
Turbine
Turbine Air Out
Shaft Rotation
Cold Oxidized Particle Storage

Materials: Reaction Enthalpy

$$ABO_3 + \Delta H_{rxn} \leftrightarrow ABO_{3-\delta} + \delta/2\ O_2(g)$$



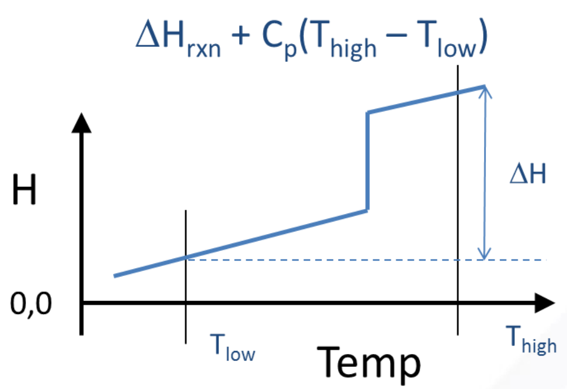


- First generation: Investigated/characterized LSCM, LSCF, and related perovskite families to identify baseline composition, LSCM3891, with high redox capacity ($\delta = 0.46$) and reasonable ΔH_{rxn} (242 kg/kJ)
- Second generation: Low-cost earth-abundant compositions CXM (X = Ti, Al)
  - Lower redox capacity compensated by higher T_{red} → Stronger M-O bonds and storage of higher-quality heat
  - Smaller molecular weight results in higher specific heat, and therefore mass-specific total enthalpy

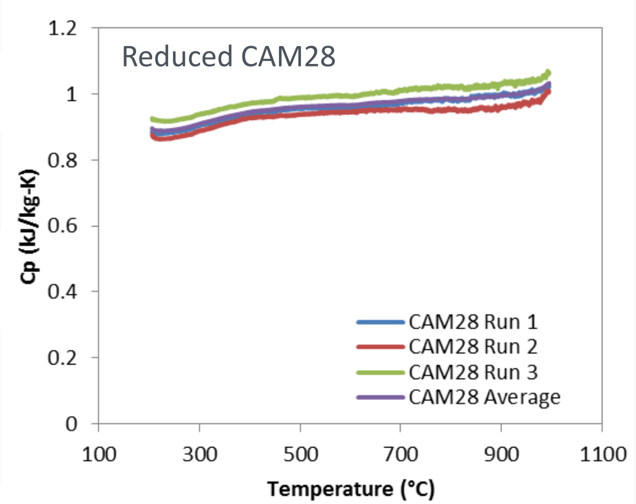
Materials: Total Storage Capacity

$$\Delta H_{tot} = \Delta H_{rxn} + C_p\Delta T$$

Chemical + Sensible Energy Storage



Measured heat capacity as a function of temperature

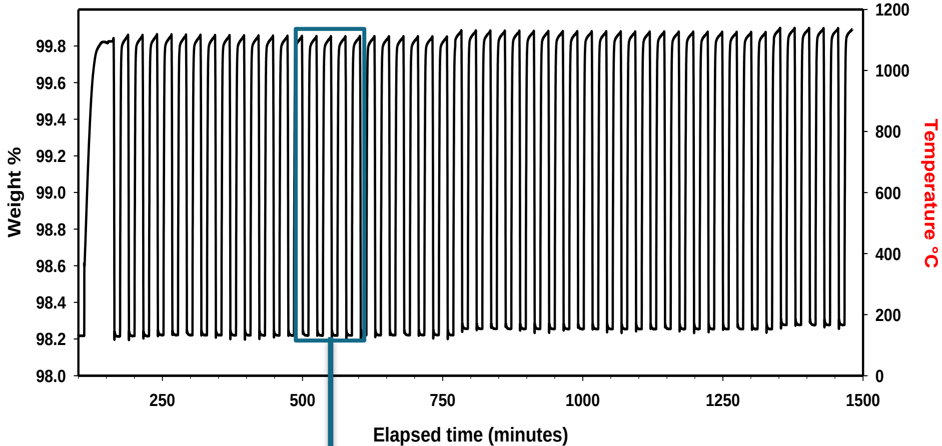


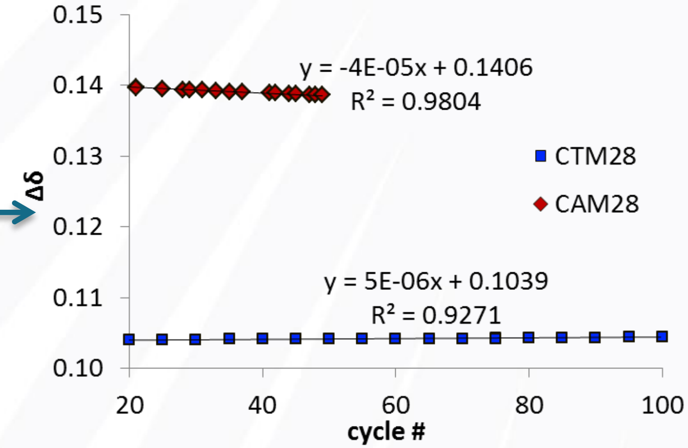
Candidate material	Mol weight (g/mol)	T_{red} Onset (°C)	Max δ	ΔH_{rxn} (kJ/kg) (at δ_{max})	C_p (kJ/kg-K)	ΔH_{tot} (kJ/kg)
LSCM3791	209.5	343	0.461	242	*0.595	837
CTM28	141.6	901	0.293	393	*0.881	1274
CAM28	135.8	759	0.322	371	*0.910	1281

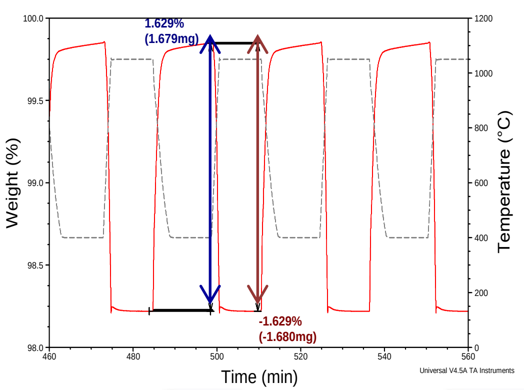
*Estimated Values: C_p = 3R·N (J/mol-K) = 15R, T_{high} = 1200 °C, T_{low} = 200 °C

Materials: Cycle-to-Cycle Stability

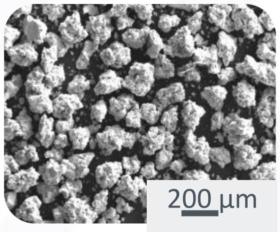
Extended thermal redox cycling in TGA



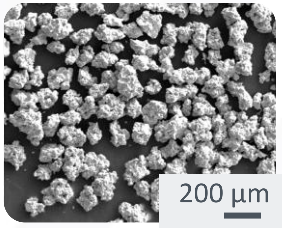




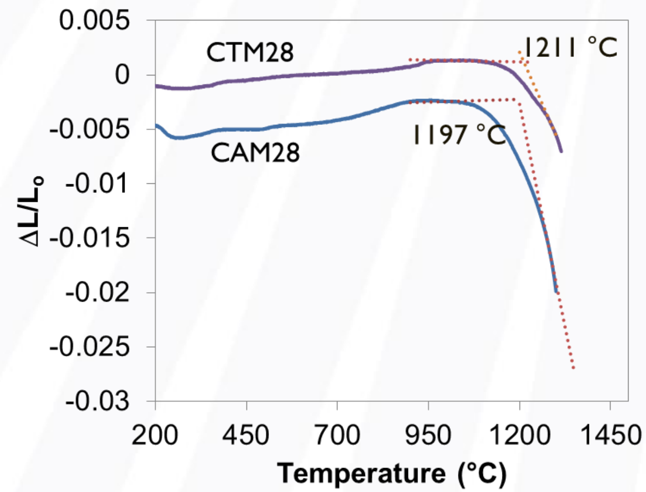
Before



After



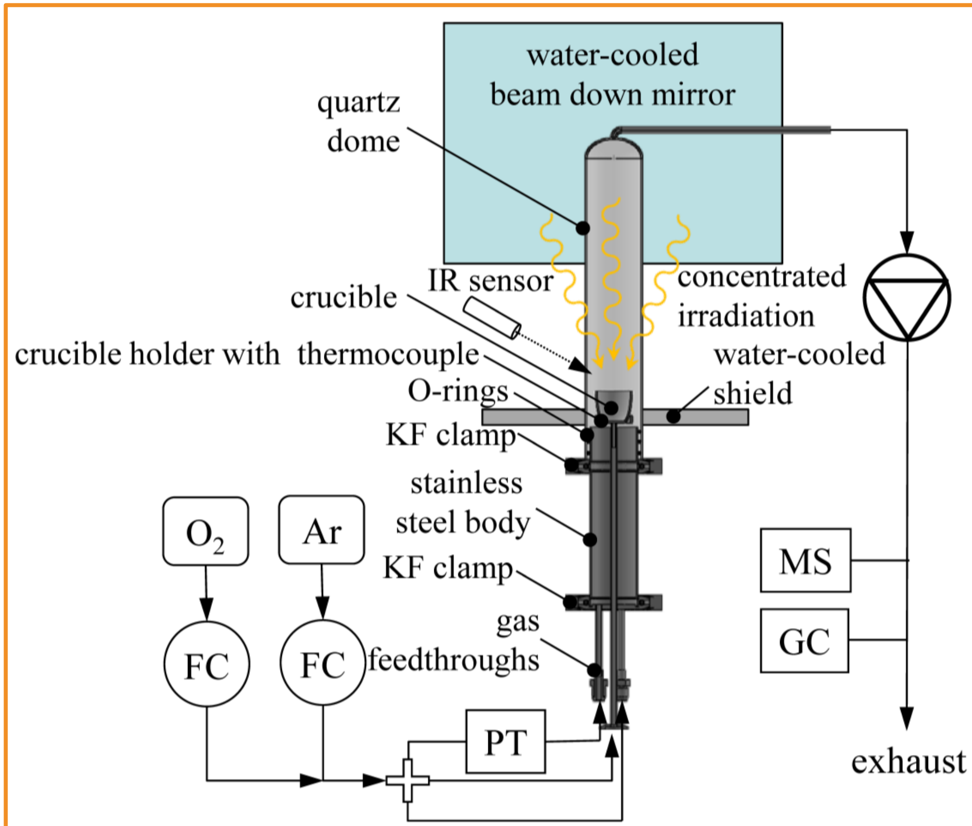
SEM of cycled particles



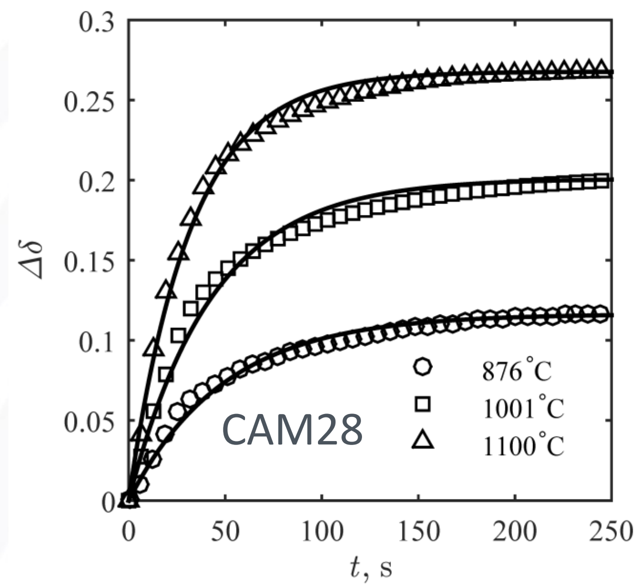
Sintering (dilatometry) of compressed pellets (worst case)

Materials: Reaction Kinetics

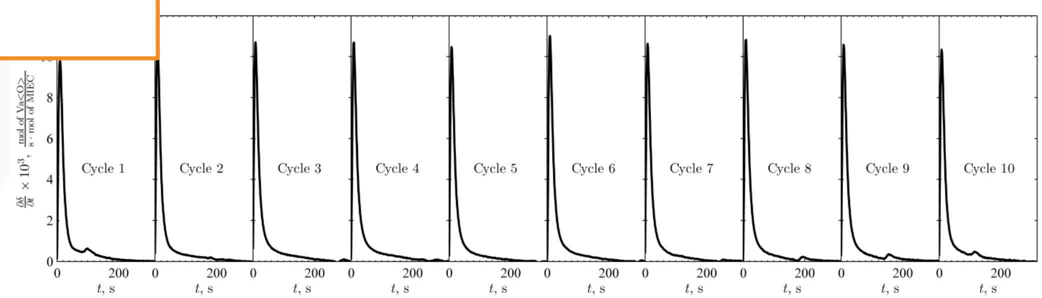
“Upflow reactor” coupled to high flux solar simulator measures oxidation kinetics



Upward Flow Reactor (UFR) employs ultrafast heating rates > 50 K/s enabling measurement of MIEC kinetics.

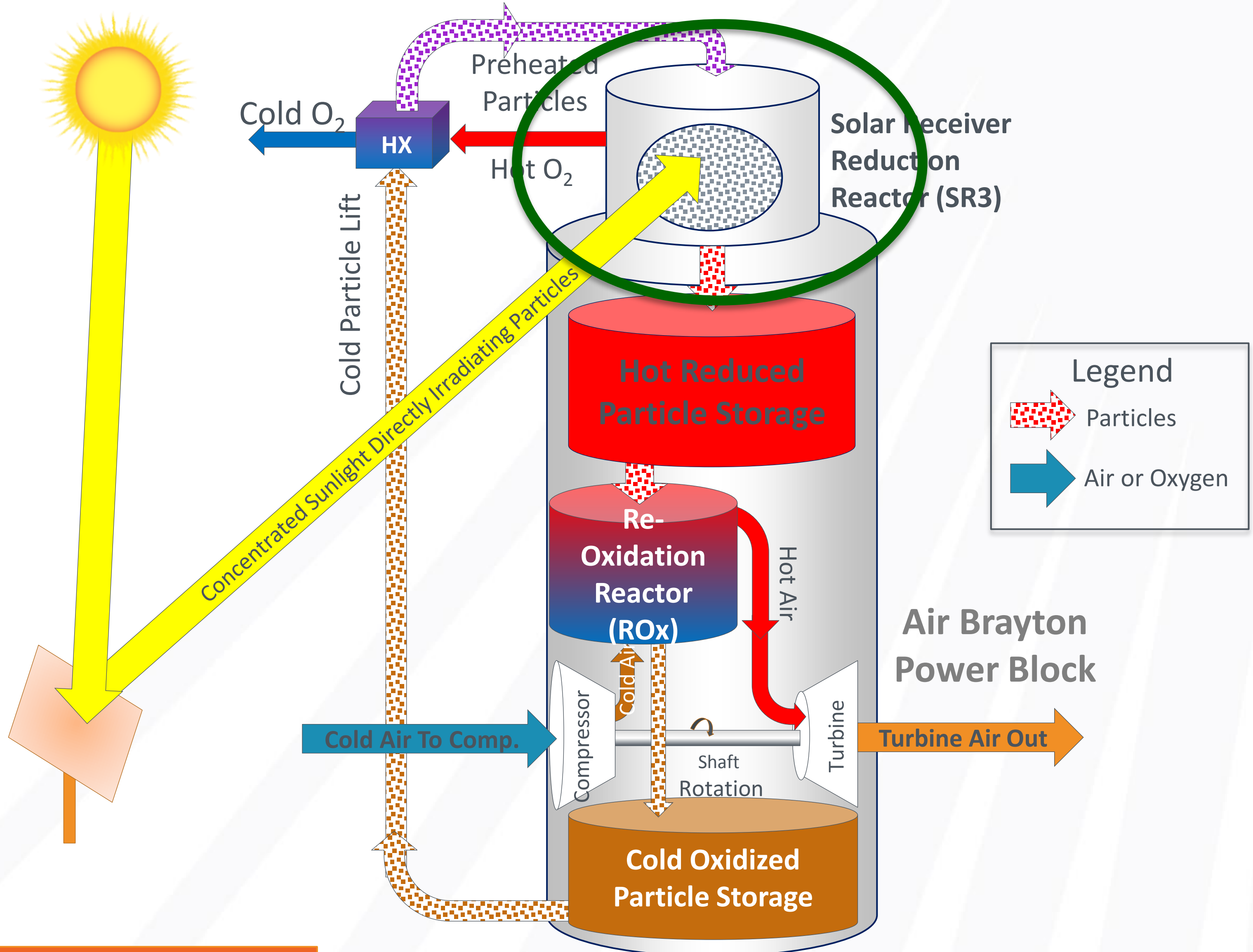


Experimental data for CAM28 reduction (mass spectrometry, validated with GC) vs. models (lines)



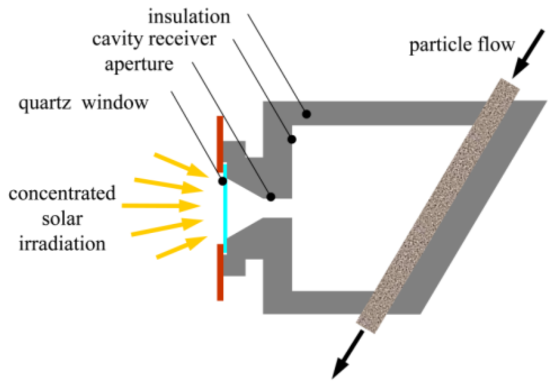
UFR results quantify/verify stability of reaction kinetics with cycling

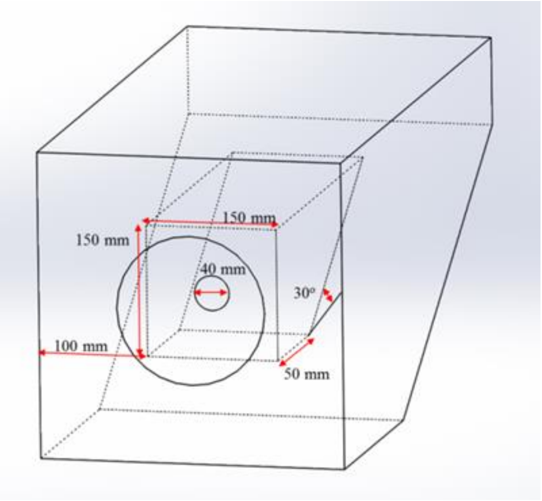
2. Solar Receiver Reduction Reactor (SR3)



SR3: Inclined plane particle flow reactor modeling

Directly-irradiated inclined plane solar thermochemical reactor concept

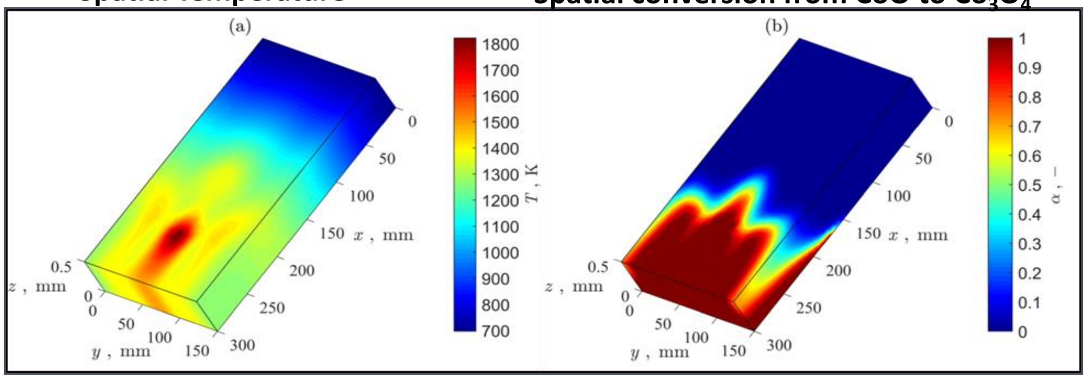




Material properties for simplified mass and heat transfer model	
M-35 buster type alumina	k = 0.27 W/m·K ε = 0.5 for 0 <λ < 4 μm ε = 0.95 for 4 <λ < 12 μm ε = 0.8 for λ > 12 μm
Quartz Window	ε = 0.9 for 0 <λ < 0.1 μm ε = 0.01 for 0.1 <λ < 5 μm ε = 0.9 fr λ > 5 μm
Co_3O_4 / CoO particles	k =7.5 - 10 W/m·K ε_{eff} = 0.85

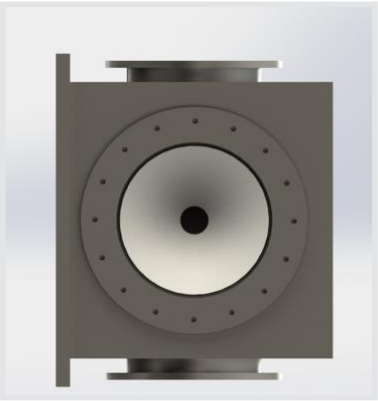
- Model couples heat and mass transfer (including particle flow) with chemical kinetics, reactor optics, and material limitations.
- Co_3O_4 used as stand-in for CAM28 pending further data collection/refinement

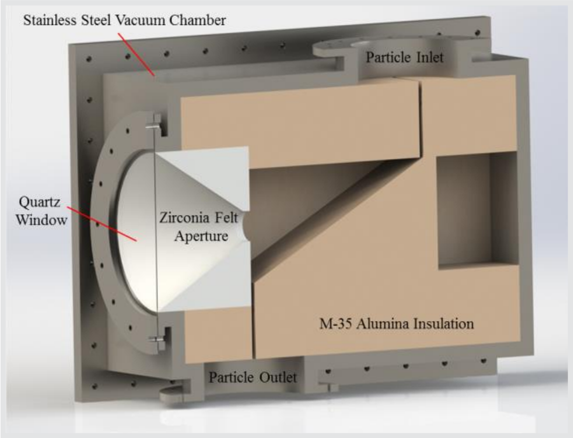
Spatial Temperature **Spatial conversion from CoO to Co_3O_4**

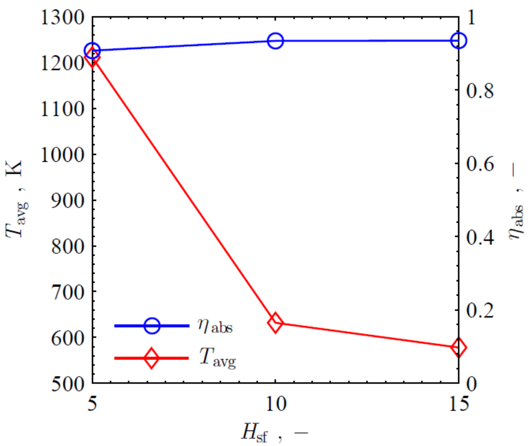


SR3: Inclined plane particle flow reactor demonstration

Design and construction of lab-scale SR3 underway

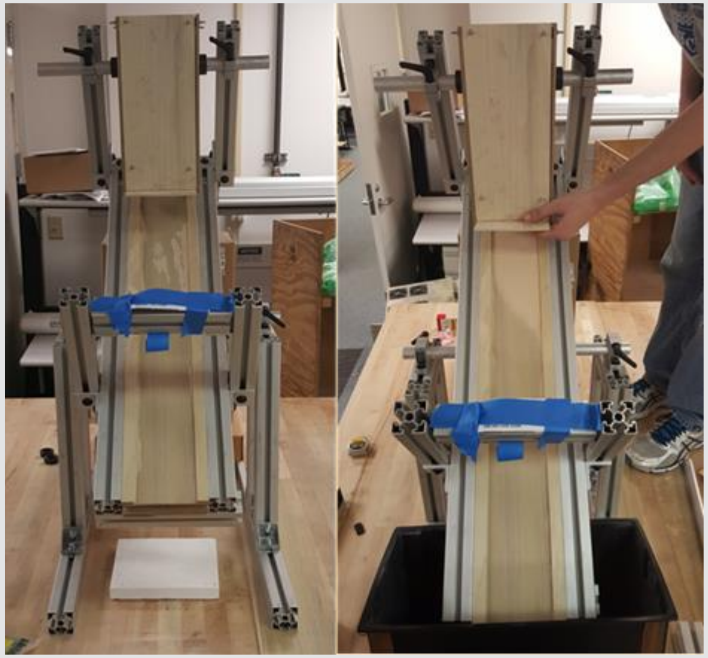




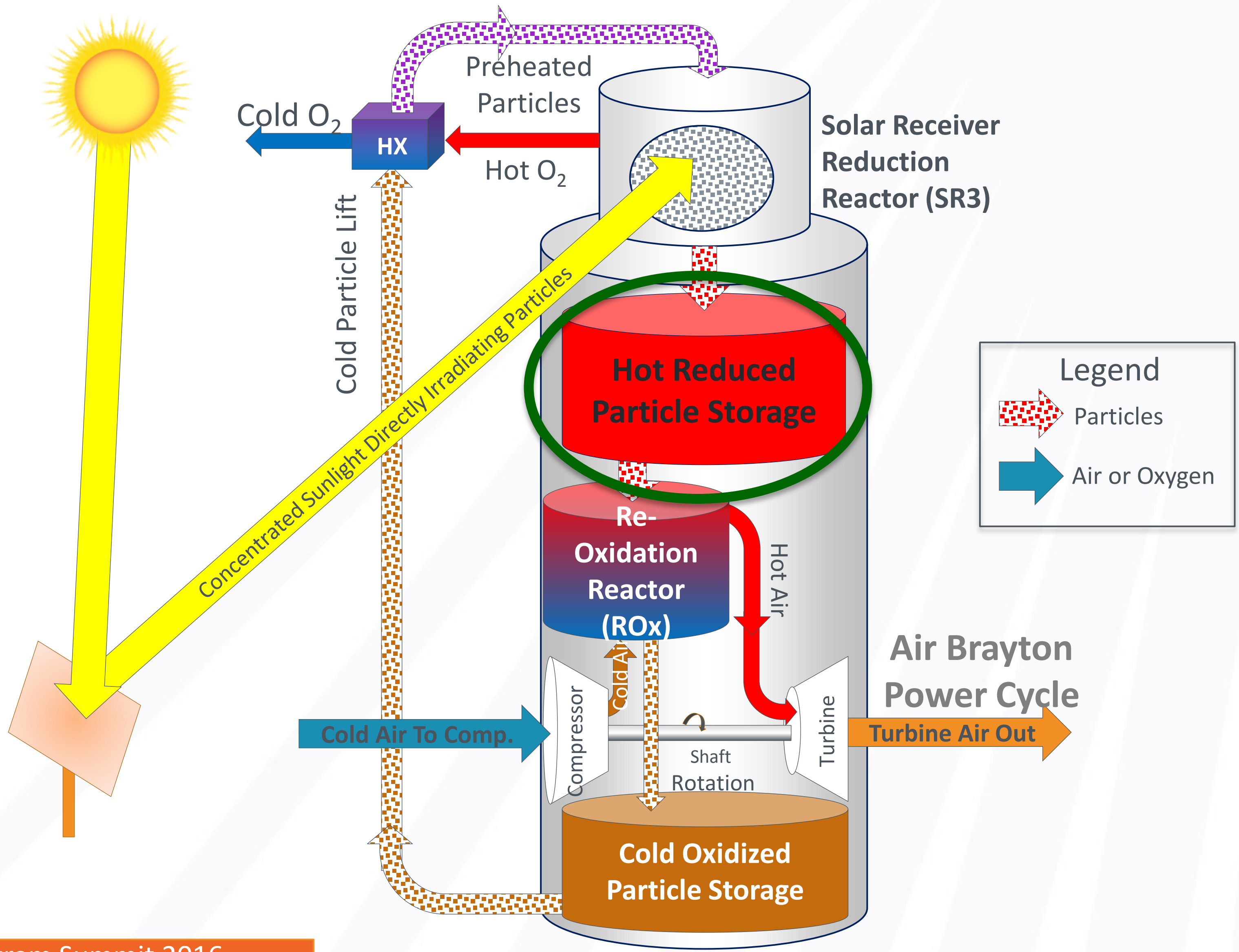


(Left) Parametric study illustrating variation in average particle temperature and energy absorption efficiency as a function of particle bed thickness

Tilt rig constructed to characterize particulate flow down inclined planes and validate models in support of SR3 design and modeling



3. Hot Particle Storage

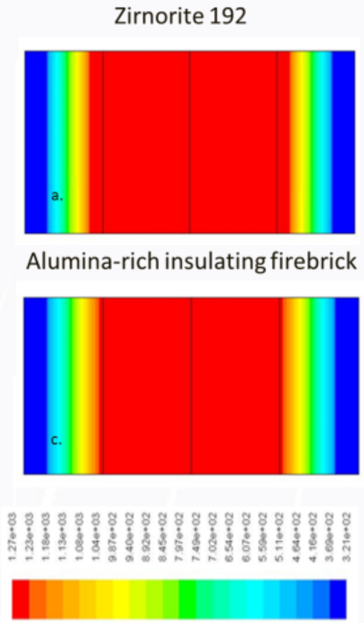


Hot Particle Storage

Design, cost, & thermal analysis of inert atmosphere hot particle storage bin

	Internal bin temperature	
	1000°C	1350°C
Temperature range in IFB (°C)	817-1000	1100-1350
Temperature range in PC (°C)	162-817	209-1100
Temperature range in EB (°C)	63-162	74-209
Temperature range in RC (°C)	45-63	51-74
Rate of heat loss (kW)	111	152
Heat loss to nitrogen (GJ)	2.0	2.7
Total energy loss over storage period (GJ)	5.2	4.4
Percentage loss of energy content	0.12%	0.18%

Bin wall construction



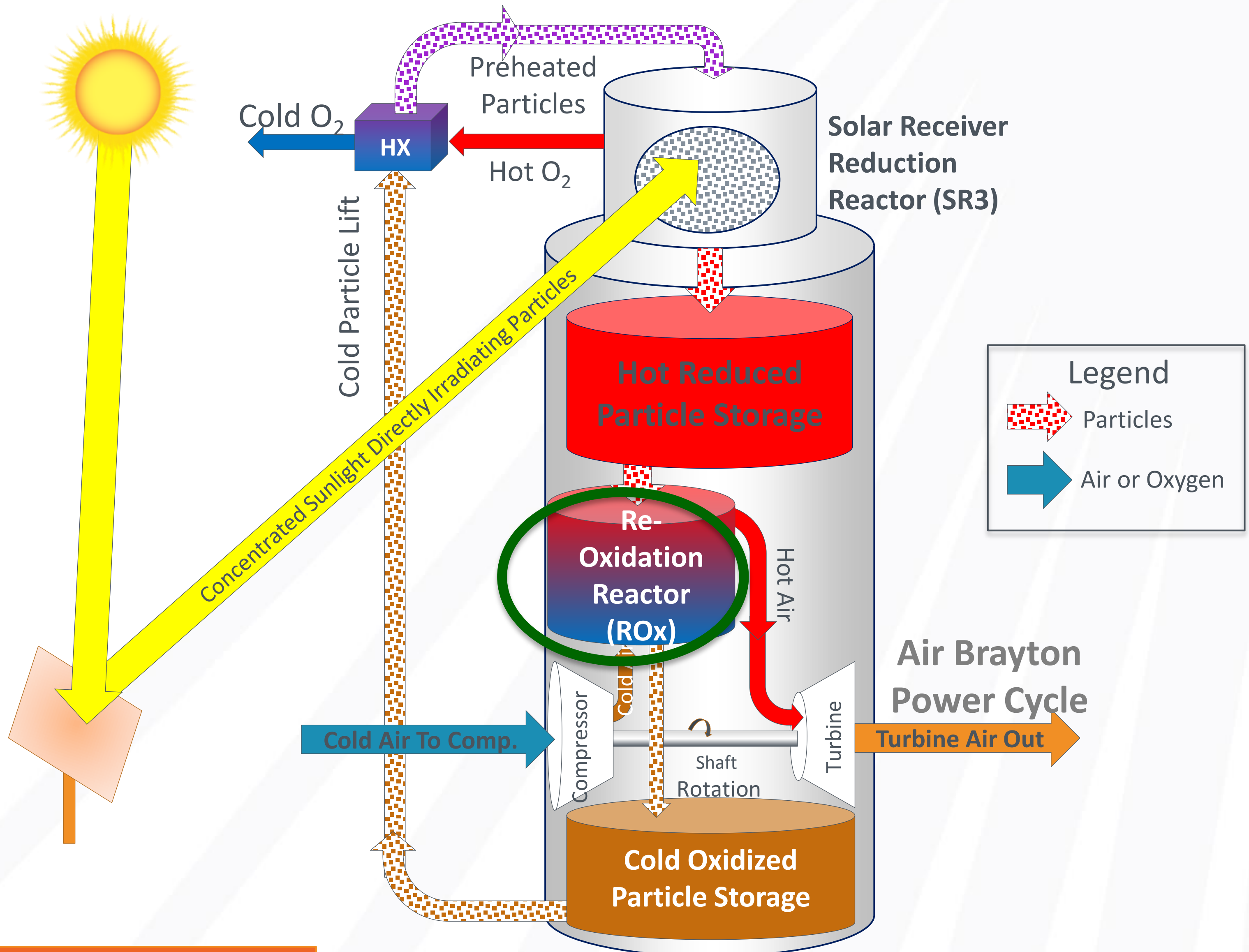
Chemical compatibility of insulating materials with MIECs: Zr-rich liners offer improved chemical resistance with thermal performance similar to conventional alumina firebrick.

	SRI HF-IB 1260	ZIRMUL	Zirnorite 699	Zirnorite 192	Silicon Carbide
Fe_2O_3	R	R	NR	NR	NR
$La_{0.8}Sr_{0.2}CoO_3$	R	R	NR	NR	NR
$SrFe_{0.5}Co_{0.5}O_x$	R	R	I	I	I
CaO	R	-	-	NR	NR
MgO	R	-	-	NR	I
$CaAl_{0.2}Mn_{0.8}O_3$	R	-	-	NR	NR
$CaTi_{0.2}Mn_{0.8}O_3$	R	-	-	NR	NR

R = Reactive; NR = Non-reactive;
I = Inconclusive; - = Not tested

Characterizing oxidation resistance of duct materials

4. ReOxidation Reactor (ROx)



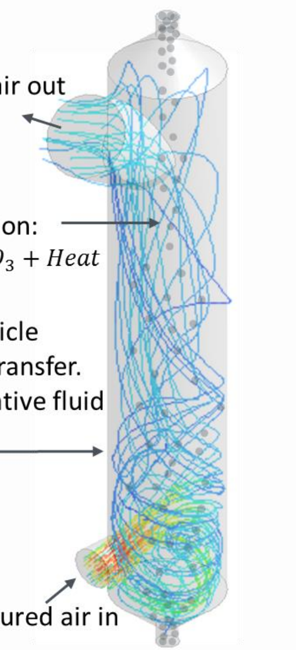
4. ROx: Design, Modeling, Demonstration

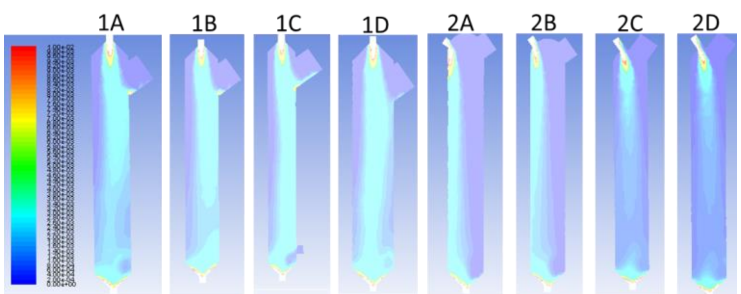
Counter-flow falling-particle design

- Flow pattern optimizes heat transfer and reaction kinetics
- Low pressure drop due to dispersed particles

Multi-phase, thermo-fluid modeling accomplished in ANSYS Fluent (right).

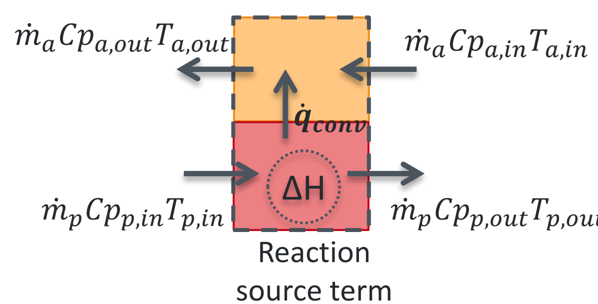
- Eulerian-Eulerian approach simulates particles as equivalent “fluid”
- Granular theory used for particle motion to capture particle-particle collisions
- Custom user-defined code to implement reactions





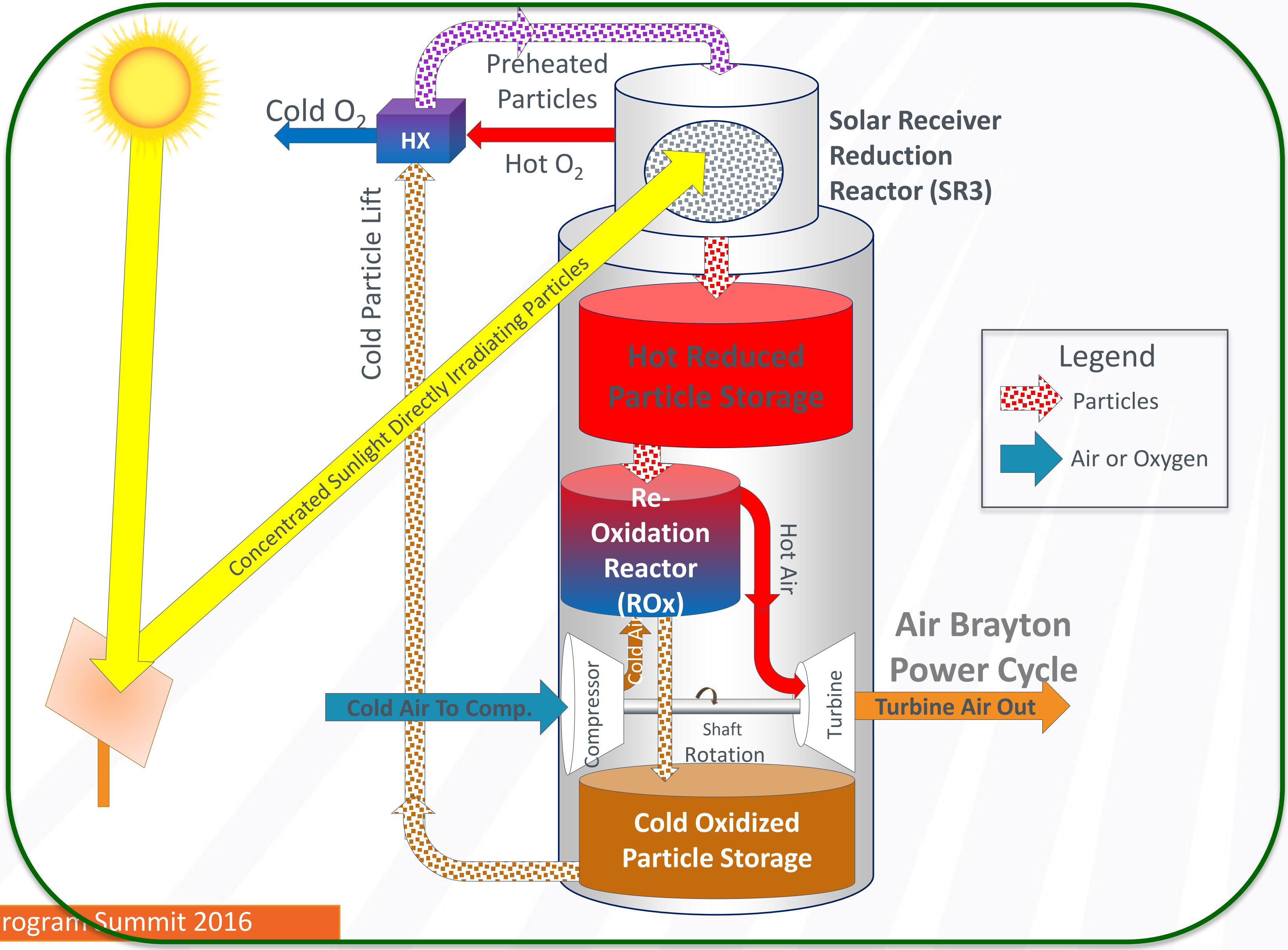
Fabricating a lab-scale (~2.5 kW) ROx demonstration unit – geometry optimized via Fluent modeling.

1-D model to bound parameter space, define inputs to 3D models



Functions of T: ρ_a, v_a, μ_a, Cp_a, Cp_p, Re/Nu/Pr, h, δ_{equil}

5. Technoeconomics and Systems

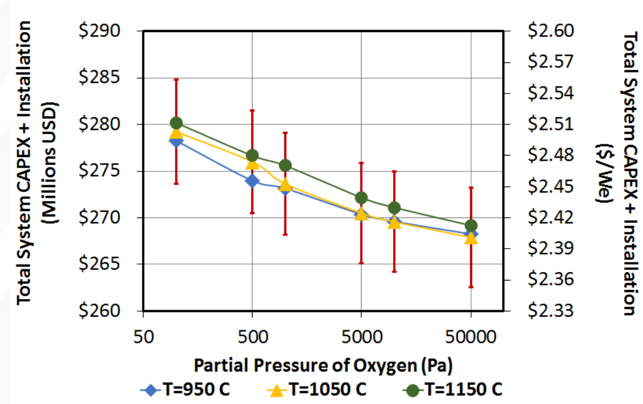


5. Technoeconomic modeling

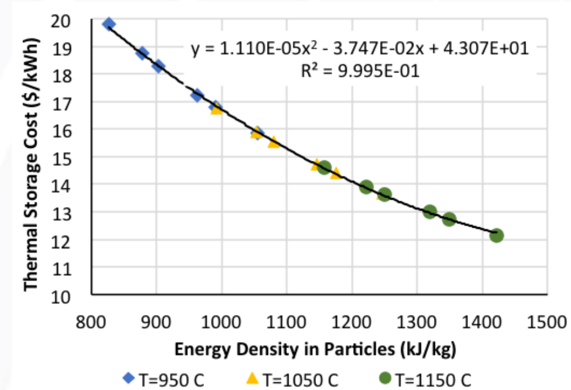
TE and performance models at various scales are continually updated and refined as new data is available. Information shown incorporates data for CAM28 and assumes a scale of 111.7 MWe.

Component List	Cost	% of Total
SR3	$ 31,990,464	8.3%
Vacuum Pump	$ 26,597,883	6.9%
Particles	$ 11,123,973	2.9%
Tower	$ 10,967,142	2.8%
Elevator	$ 1,129,862	0.3%
Heat Exchange	$ 1,865,733	0.5%
Storage Hot	$ 3,593,935	0.9%
Storage Lower Hopper	$ 2,355,678	0.6%
Storage Upper Hopper	$ 1,247,124	0.3%
ROx Reactor	$ 1,696,460	0.4%
Controls	$ 3,523,857	0.9%
Solar Field	$ 68,403,311	17.7%
Power Block	$ 93,583,548	24.3%
Balance of Plant	$ 16,276,905	4.2%
Contingency & Indirect	$ 64,519,742	16.7%
Owner's Cost	$ 46,640,498	12.1%
Multiple Components/Total	$ 385,516,114	

- Particle inventory sensitive to temperature of the incoming air, SR3 operation, and the fabrication factor
  - Particle cost estimated at $8.50/kWh$_{th}$ based on CAM28 reduced at 1050 °C and 200 Pa pO_2 (δ=0.203), residual particle heat = 388 °C after ROx
- Storage volume scales with amount of particles, cost scales more slowly
  - Estimated at $4.60/kW$_{th}$



Total system costs as a function of pO_2 and T assuming 2500 suns (2.5 MW/m^2) at the aperture.



Storage cost as a function of energy density. Data points assume CAM 28 with the energy density varying as a function of the SR3 temperature and pO_2.

Summary

- We have discovered and characterized a family of redox active MIEC oxides , CXM, which exhibit total enthalpies > 1200 kJ/kg
  - Stable at high temperatures
  - Reproducibly cycled with little loss in performance
  - Comprised of earth abundant elements
  - *To our knowledge, these materials outperform any reported oxide TCES material operating above 1000 °C*
- An inclined plane particle flow reactor was modeled and designed
  - A lab scale test rig was built to validate models
  - Construction of test reactor is underway.
- Designed storage bins and identified MIEC compatible liner materials
- A counter-flow falling-particle Re-oxidation (ROx) reactor was designed and will be constructed at lab scale
  - Multi-phase, thermo-fluid modeling accomplished in ANSYS Fluent
- Techno-economic modeling is underway, with constant refinement as new data is obtained
  - Current results show that the storage cost goal of $\$15/kWh_{th}$ is achievable

Path to Market

The path to market strategy builds on previous experience and is composed of three elements:

1. Follow a system-level design strategy that leverages existing technology whenever possible
2. Provide a robust and scalable TCES solution
3. Partner with key players from the global CSP community to maximize deployment opportunity

Protecting the financial investments of potential commercial partners is considered critical, hence IP protection through the patent process is a priority. Filings to date include:

- US Application SD12749.1/S132468: Redox-active Oxide Materials for Thermal Energy Storage. (Ambrosini, Miller, Gill)
- Provisional patent application (62169109: Redox-active Oxide Materials for Thermal Energy Storage. (Babiniec, Coker, Miller, Ambrosini)
- Provisional patent application (62130847): An Air Brayton Cycle Integrated with Solar Thermochemical Storage. (Loutzenhiser, Jeter)

Thank You