SAND2013-5725C

Thermochemical Cycle of a Mixed Metal Oxide for Augmentation of Thermal Energy Storage in Solid Particles

July 16, 2013

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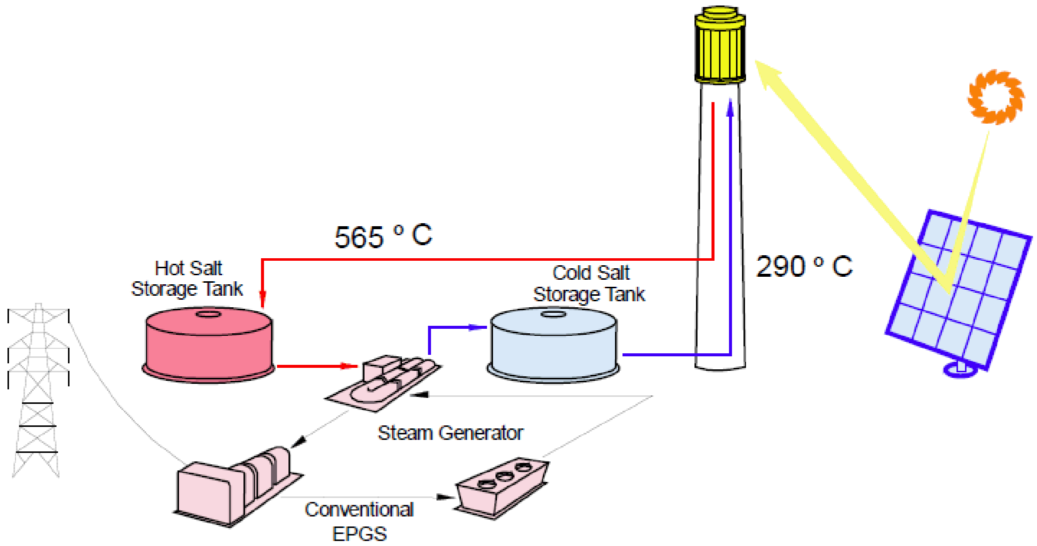
Outline

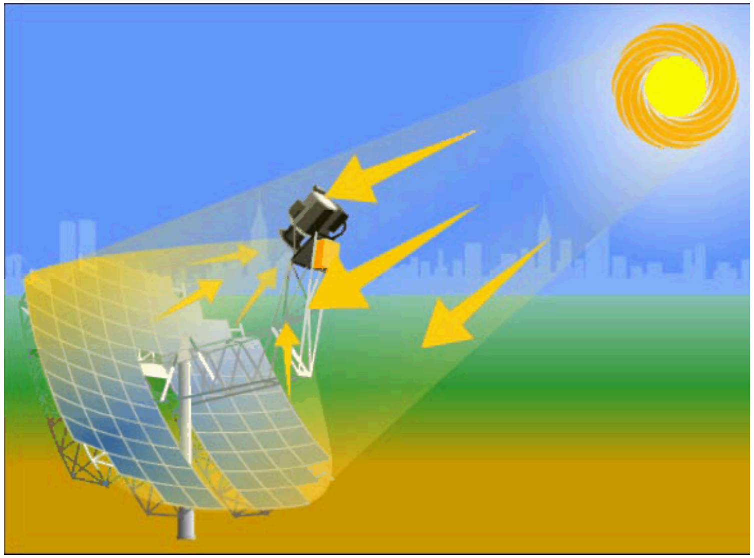
- Description of CSP/TES
  - Description of thermochemical energy storage
- Description of "Boosting"
  - Possible concepts
- Hercynite Reaction
  - Thermodynamic predictions
  - Experimental data
- Conclusion
- Suggestions for Future Work

Concentrated Solar Power

- Solar Thermal Power
- Thermal Energy Storage

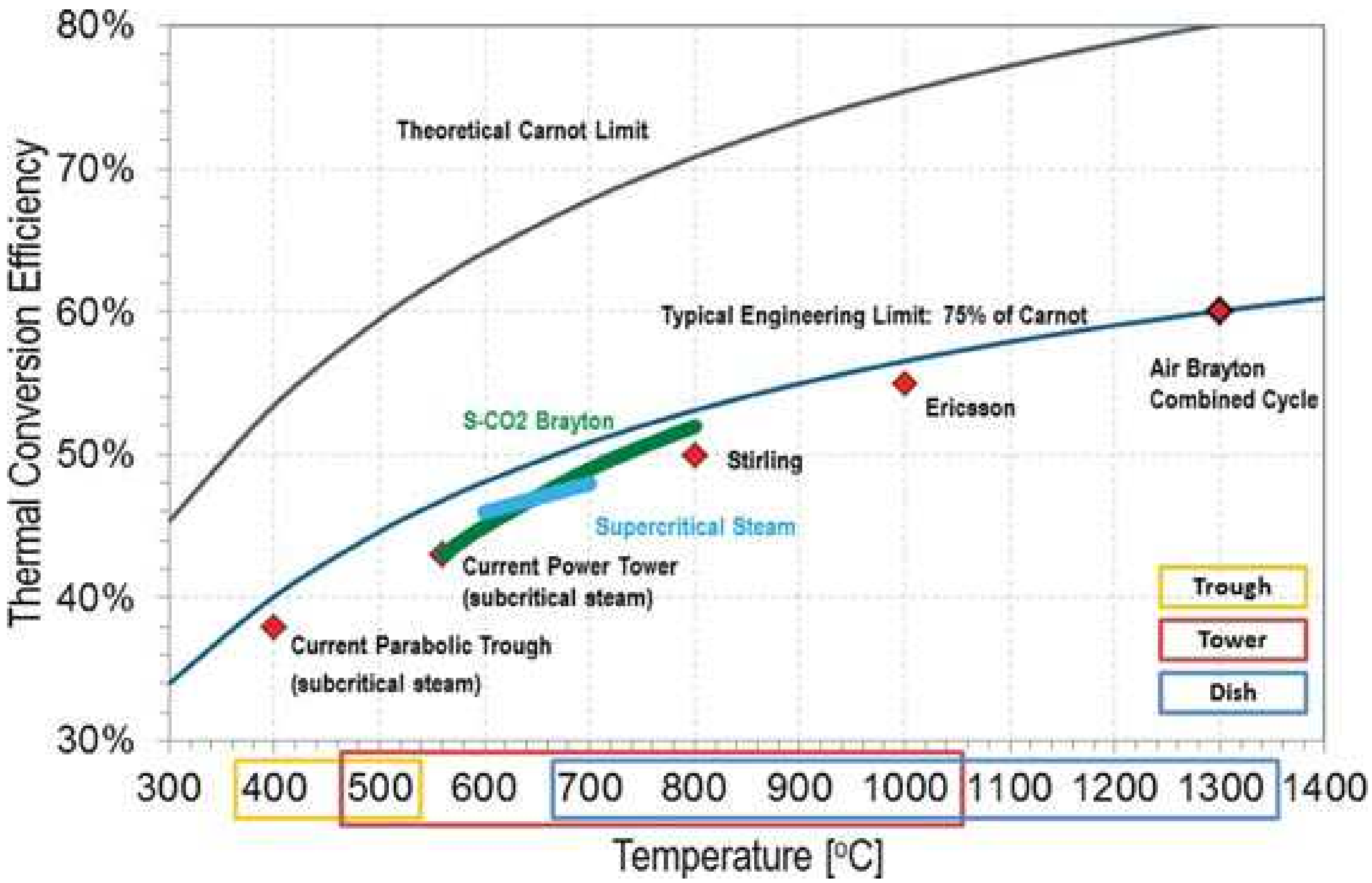


- Central Receiver
  - Heliostats ~50% of Plant Capital Costs
- Parabolic Dish
  - No Storage, Space Limitations



G. J. Kolb, *et al.*, Sandia National Laboratories SAND2007-3293, June 2007.
G. Glatzmaier, National Renewable Energy Laboratory NREL/TP-5500-52134, August 2011.

High Temperature Operation

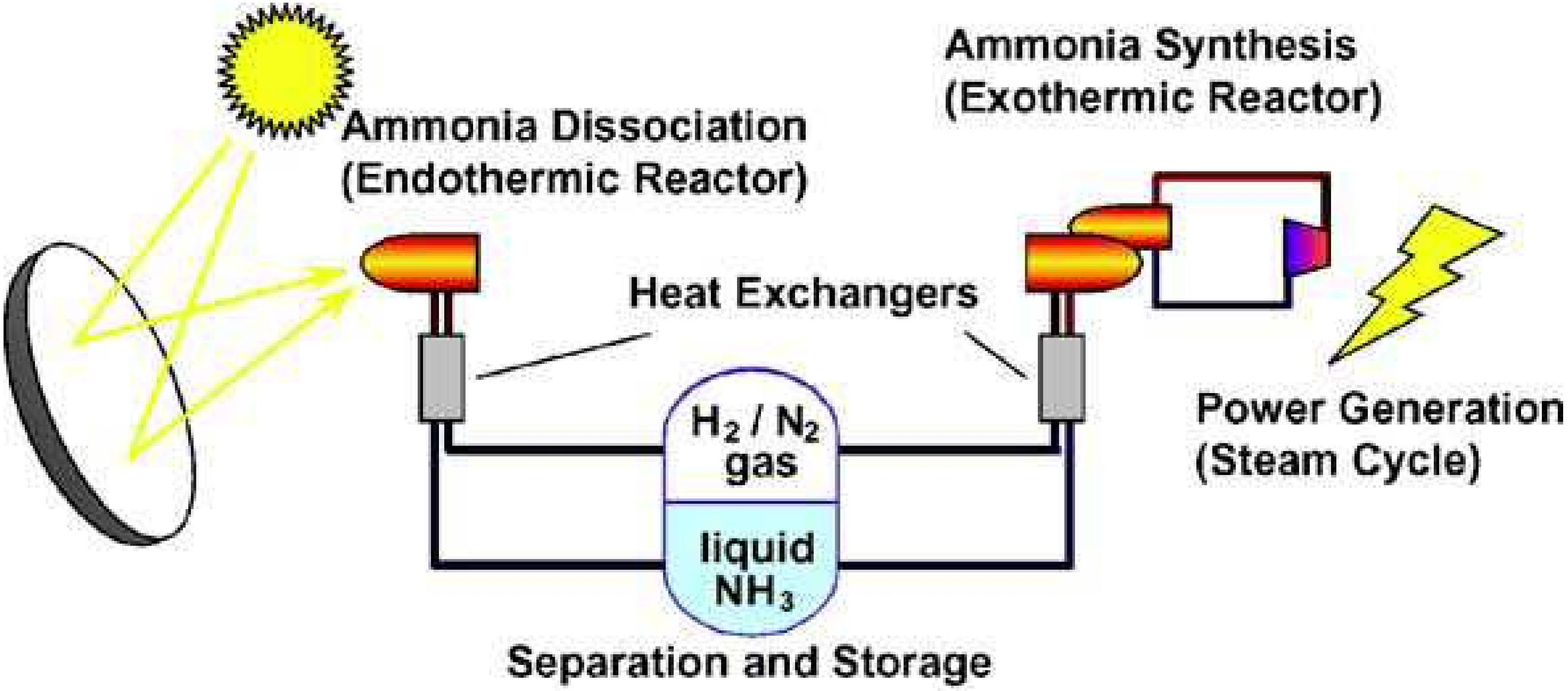


- More efficient thermal-to-electric conversion
- Higher thermal losses

N. P. Siegel, *Wiley Interdisciplinary Reviews: Energy and Environment,* vol. 1, pp. 119-131, 2012.

Thermochemical Energy Storage

- Ammonia Synthesis



$$NH_3 + DH \rightleftharpoons 1/2N_2 + 3/2H_2$$

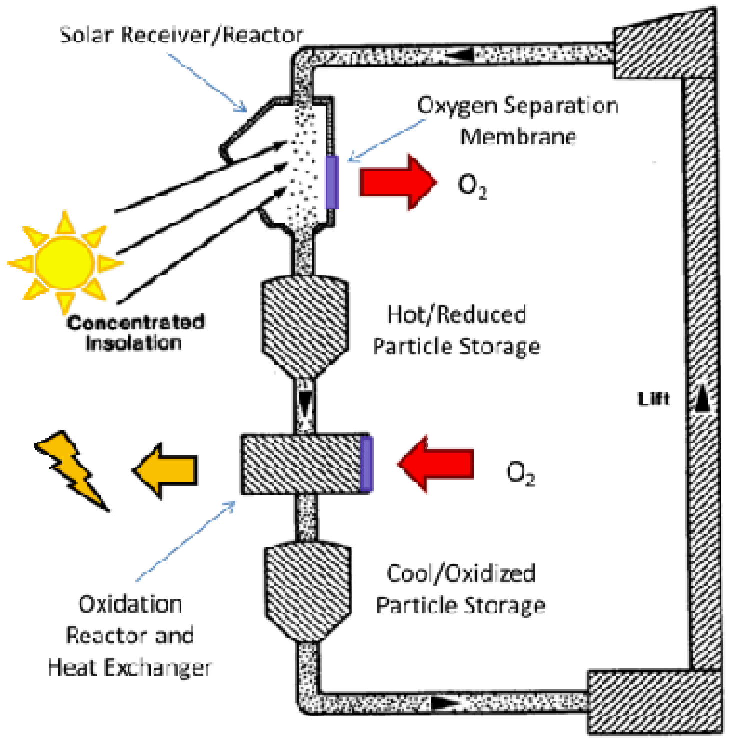
K. Lovegrove, *Solar Energy*, vol. 76, pp. 331-337, 2004.

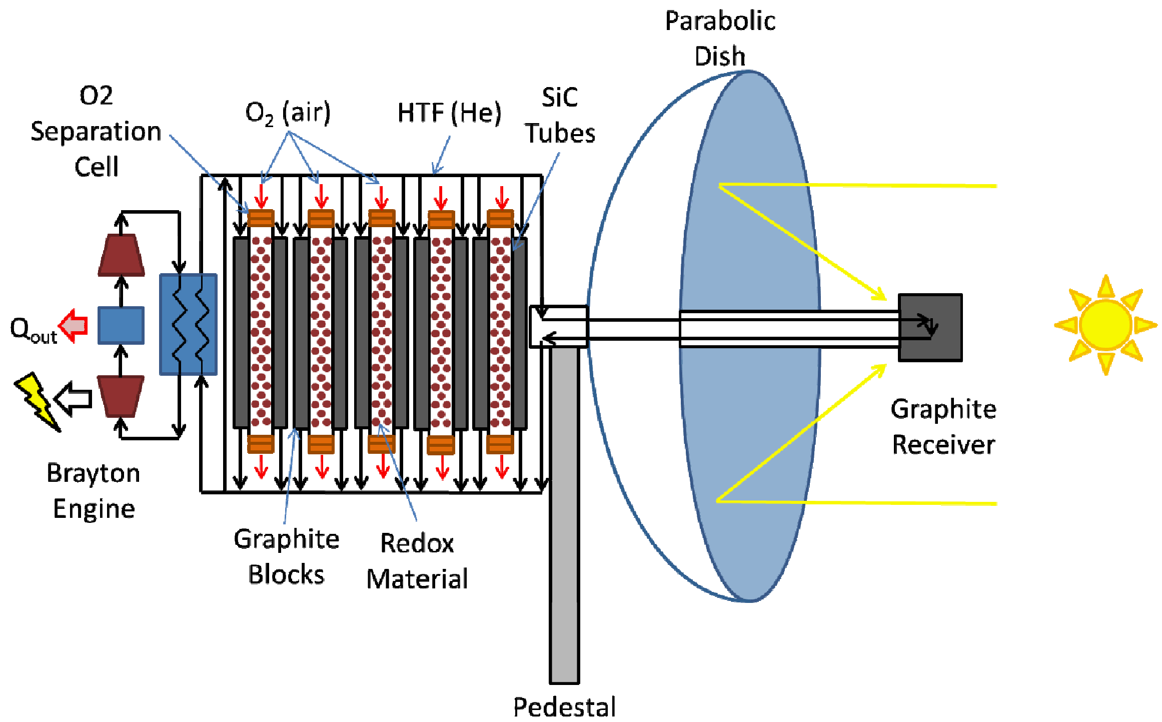
Thermochemical “Boosting”

- Sensible AND Thermochemical Energy Storage
  - $Q_{sensible}(T) = \int_{T_0}^{T} C_p(T')\, dT'$
  - $Q_{thermochem}(T, [O_2]) = \Delta H_{rxn}(T, [O_2]) \cdot x$
- Augmenting effective heat capacity
  - Increased energy storage density
- Increased exergetic efficiency ($Ex = \left(1 - \frac{T_0}{T}\right) Q$)
  - Keeping reactants at temperature
  - Higher upper limit of exergetic efficiency

	T_{high}	T_{low}	Exergy Loss
Ammonia Cycle	700°C	500°C	11.26%
“Hercynite Cycle”	**1200°C**	**1150°C**	**0.90%**

Potential Systems



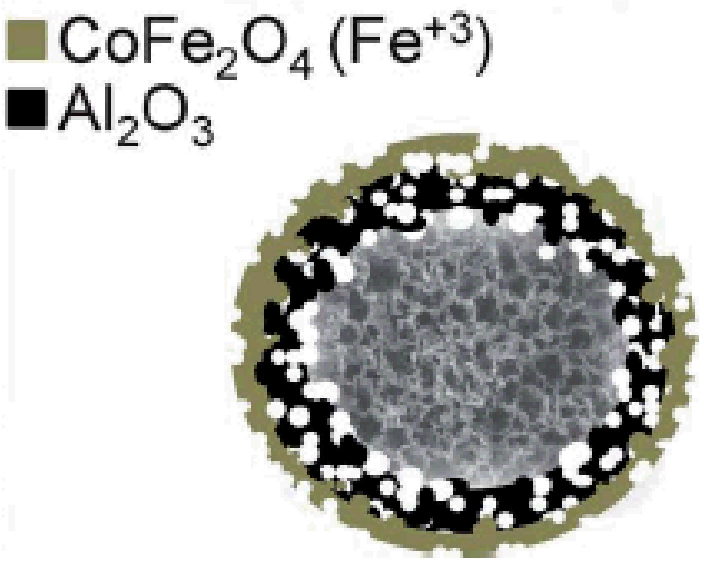


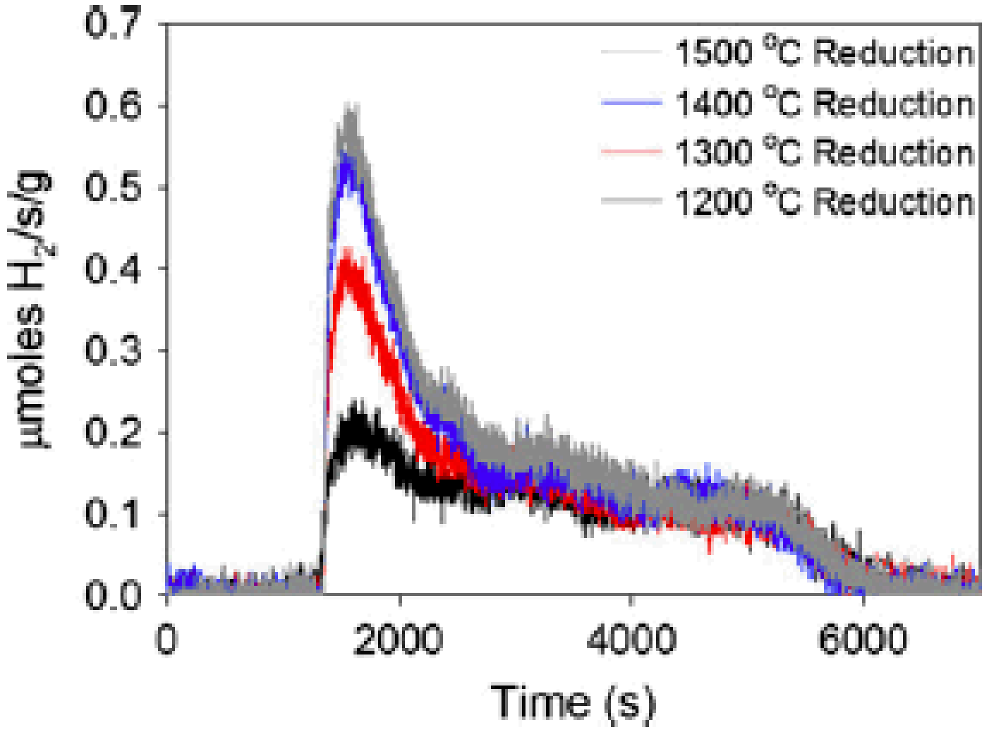
- Moving or Stationary Solid Media
- Direct vs Indirect Storage
- Pros and Cons to each

Hercynite Reaction

$$CoFe_2O_4 + 3\,Al_2O_3 \leftrightarrow CoAl_2O_4 + 2\,FeAl_2O_4 + \tfrac{1}{2}\,O_2$$

- Water/CO_2 Splitting





D. Arifin, *et al.*, *Energy & Environmental Science,* vol. 5, pp. 9438-9443, 2012.

J. R. Scheffe, *et al.*, *International Journal of Hydrogen Energy,* vol. 35, pp. 3333-3340, 2010.

Hercynite Cycle for Boosting

- Why Hercynite Cycle?

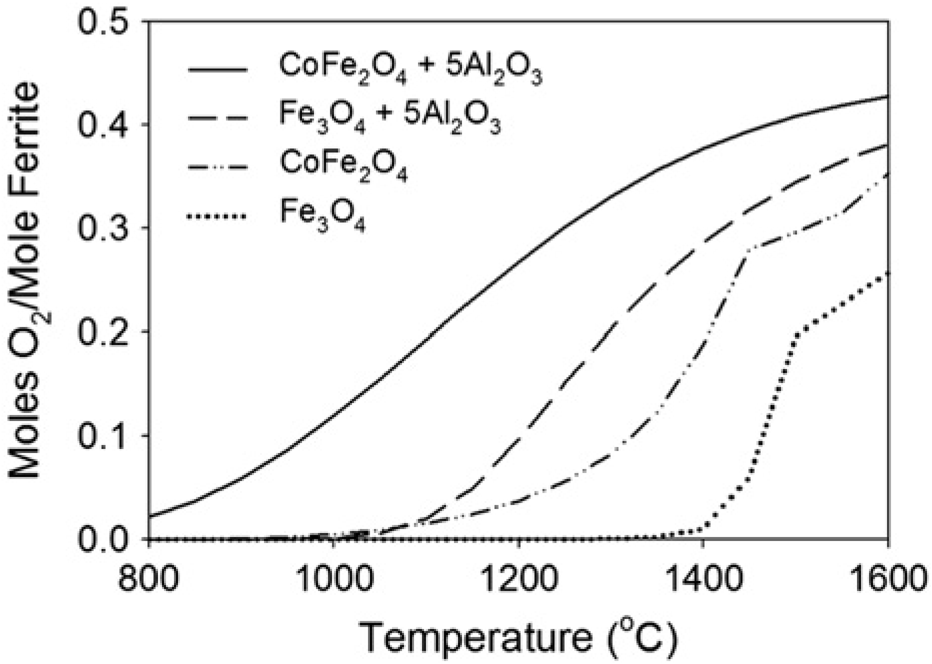
- Chemical Components

CarboHSP Composition	wt-%
Al_2O_3	83
SiO_2	5
TiO_2	3.5
Fe_2O_3	7.0
Other	1.5

http://www.carboceramics.com/CARBO-HSP/

N. P. Siegel, *et al.*, *Journal of Solar Energy Engineering,* vol. 132, p. 021008, 2010.

- Reaction Temperatures



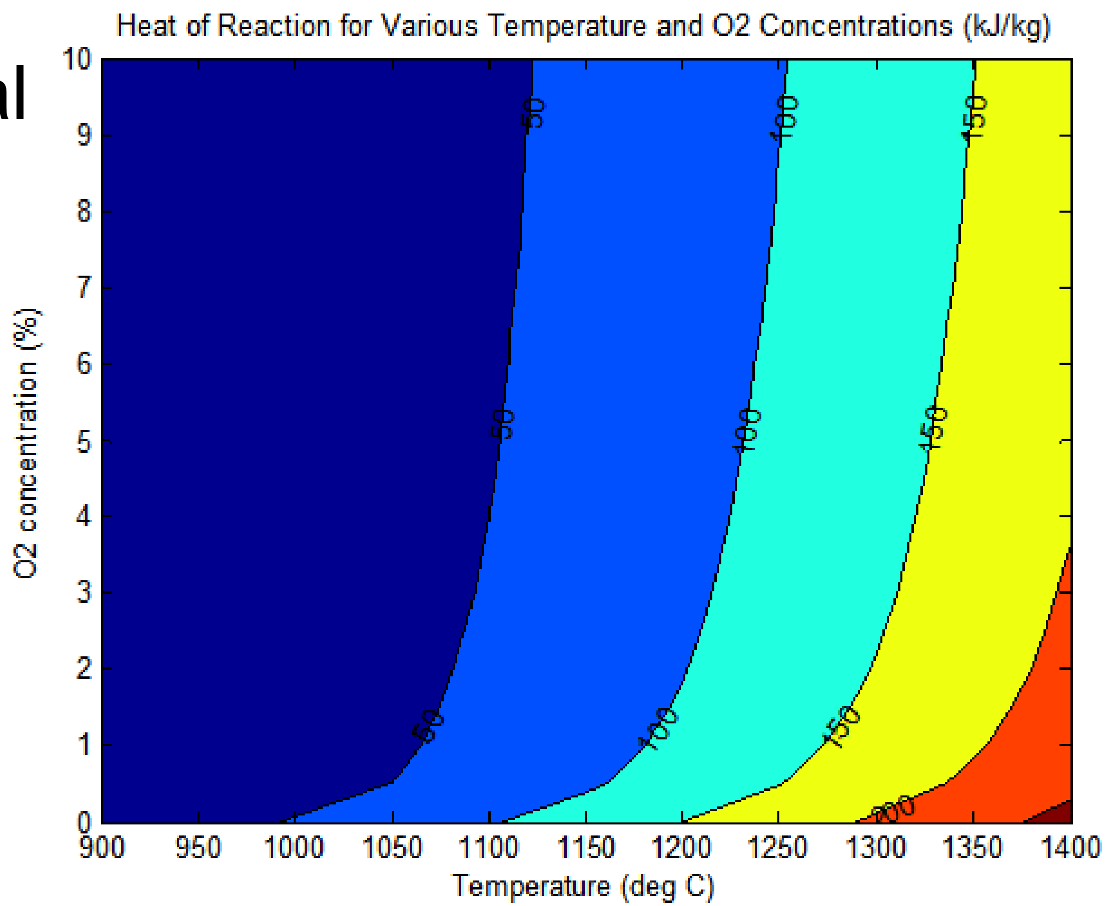
J. R. Scheffe, *et al.*, *International Journal of Hydrogen Energy,* vol. 35, pp. 3333-3340, 2010.

Thermodynamic Predictions

- FACTSage™ Proprietary Software
- Gibbs free energy minimization
- Specific initial materials and conditions
- Software calculates composition and state of material at thermodynamic equilibrium
  - Also calculates changes from initial conditions

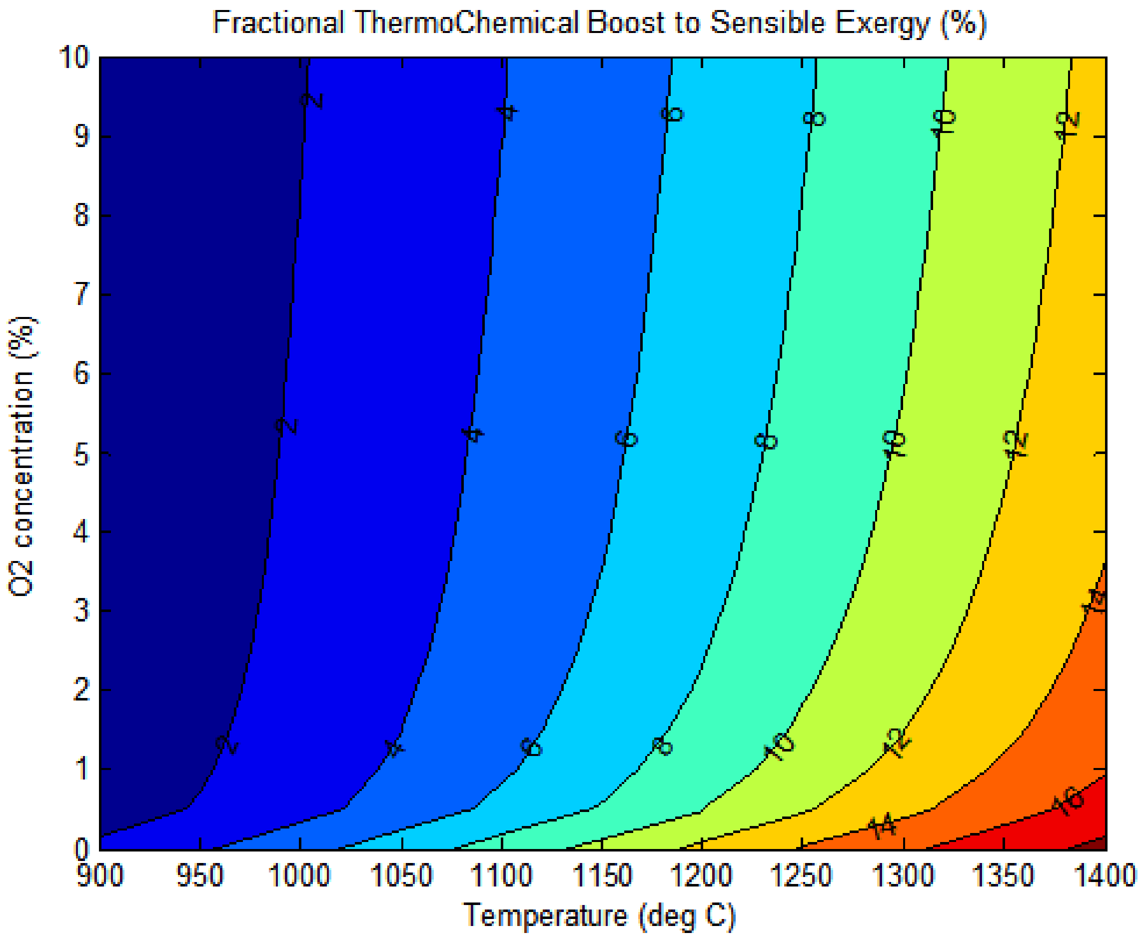
FACT – Temperature and O_2 Study

- Calculated reaction enthalpy in isothermal cycling
- Solid Material with Argon (reduction) or Oxygen (oxidation)
- Normalized per unit mass
- Corrected for any enthalpy changes in gas phase



FACT – Comparison to Exergy

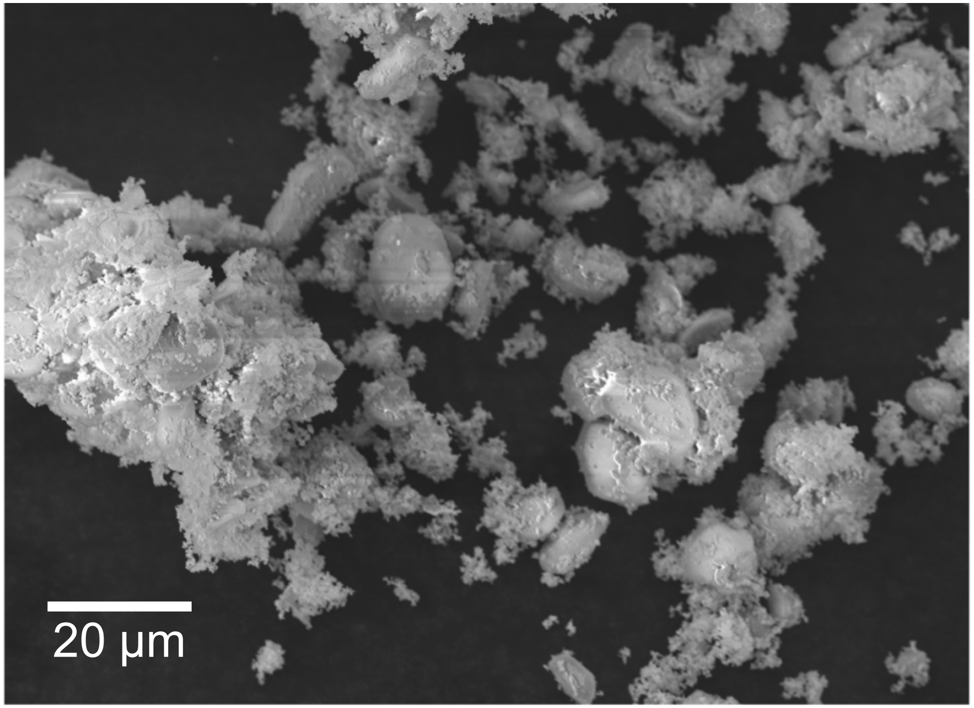
- Sensible energy calculated from ambient (23°C)
- Sensible energy calculated in Excel
- Calculated thermochemical fraction of sensible energy
- Maximum is 18.5%



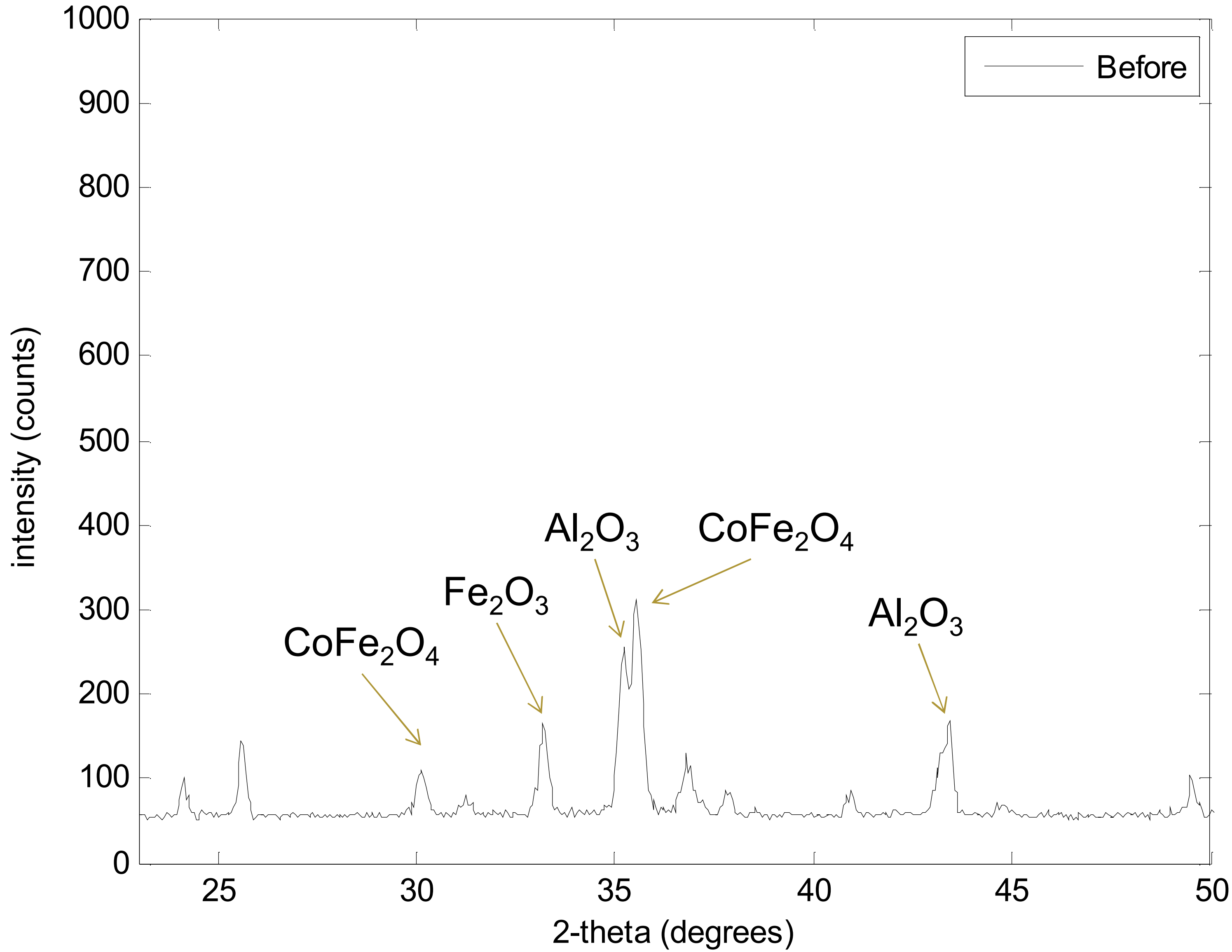
E. S. Domalski and E. D. Hearing, *NIST Chemistry WebBook, Standard Reference Database Number 69*, P. J. Linstrom and W. G. Mallard, Eds., Gaithersburg, MD: National Institute of Standards and Technology.

Experimental Set Up

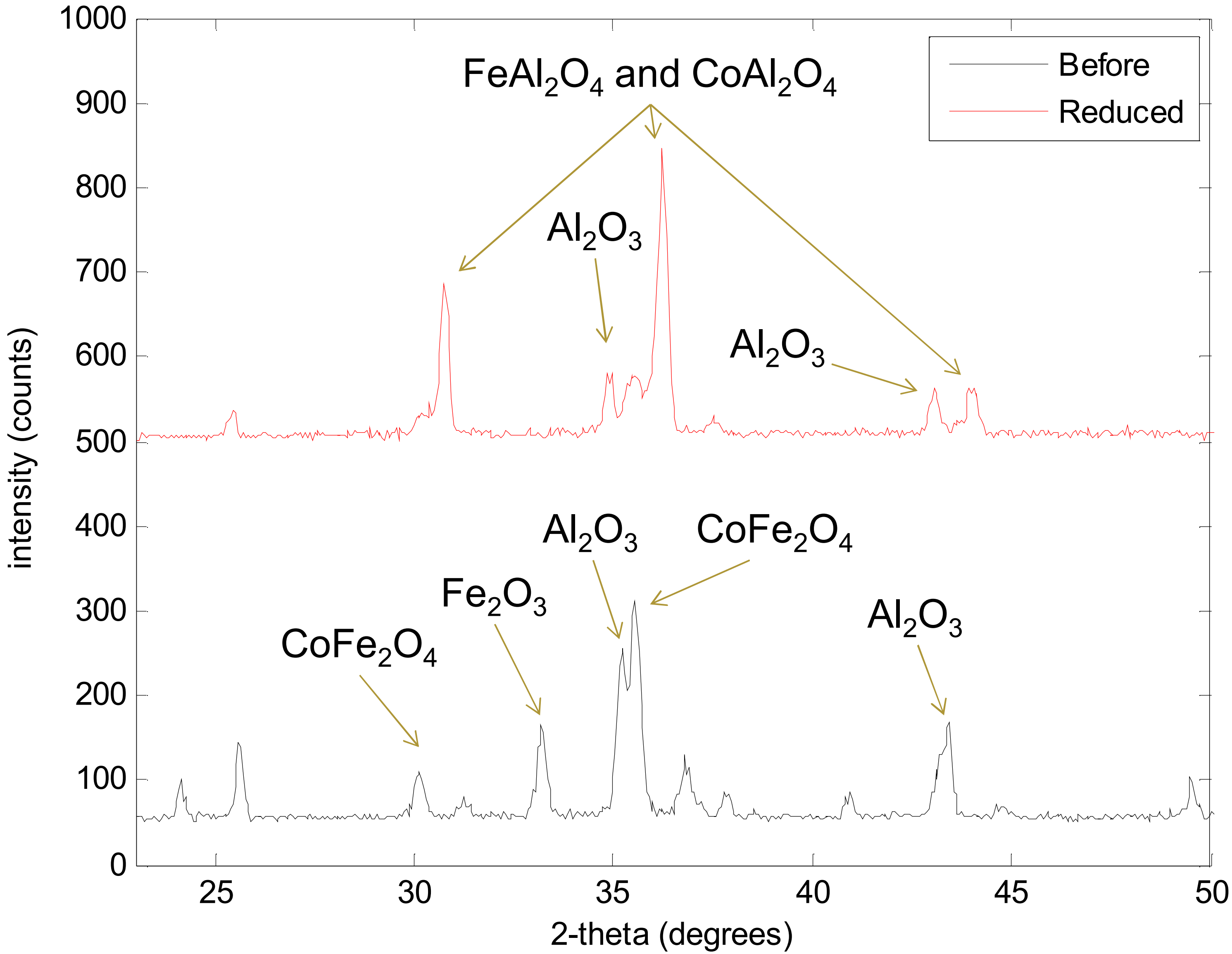
- Physically Mixed Powders
  - "Base Powder"
    - 1:1:3 Molar Ratio $CoO:Fe_3O_4:Al_2O_3$
  - "Alumina-6 and -9"
    - 1:1:6 and 1:1:9 Molar Ratio $CoO:Fe_2O_3:Al_2O_3$
  - Calcined at 850°C
- HT-XRD in-situ
- NETZSCH STA 409 CD TGA/DSC



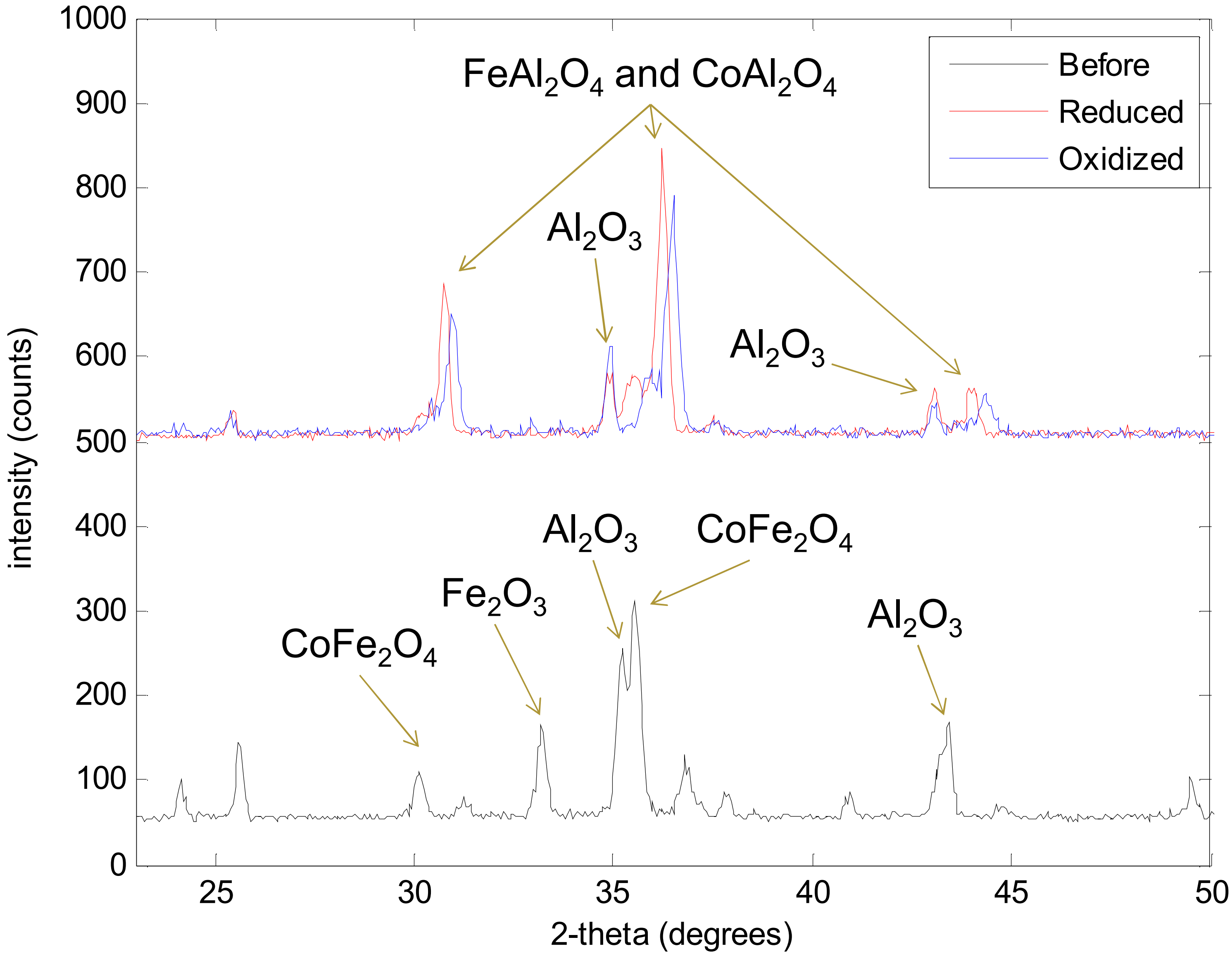
Selected Peaks - HT-XRD *in-situ*



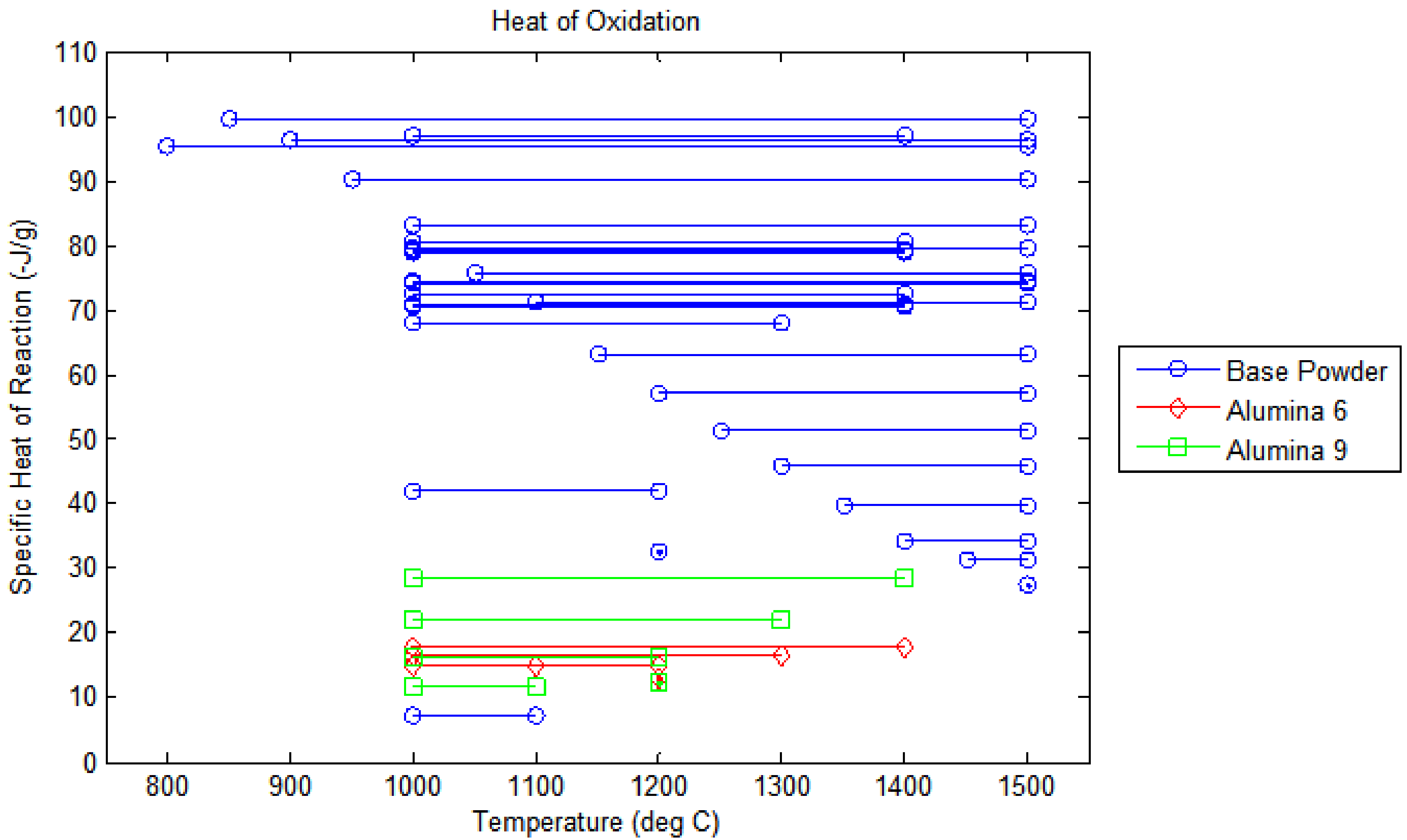
Selected Peaks - HT-XRD *in-situ*



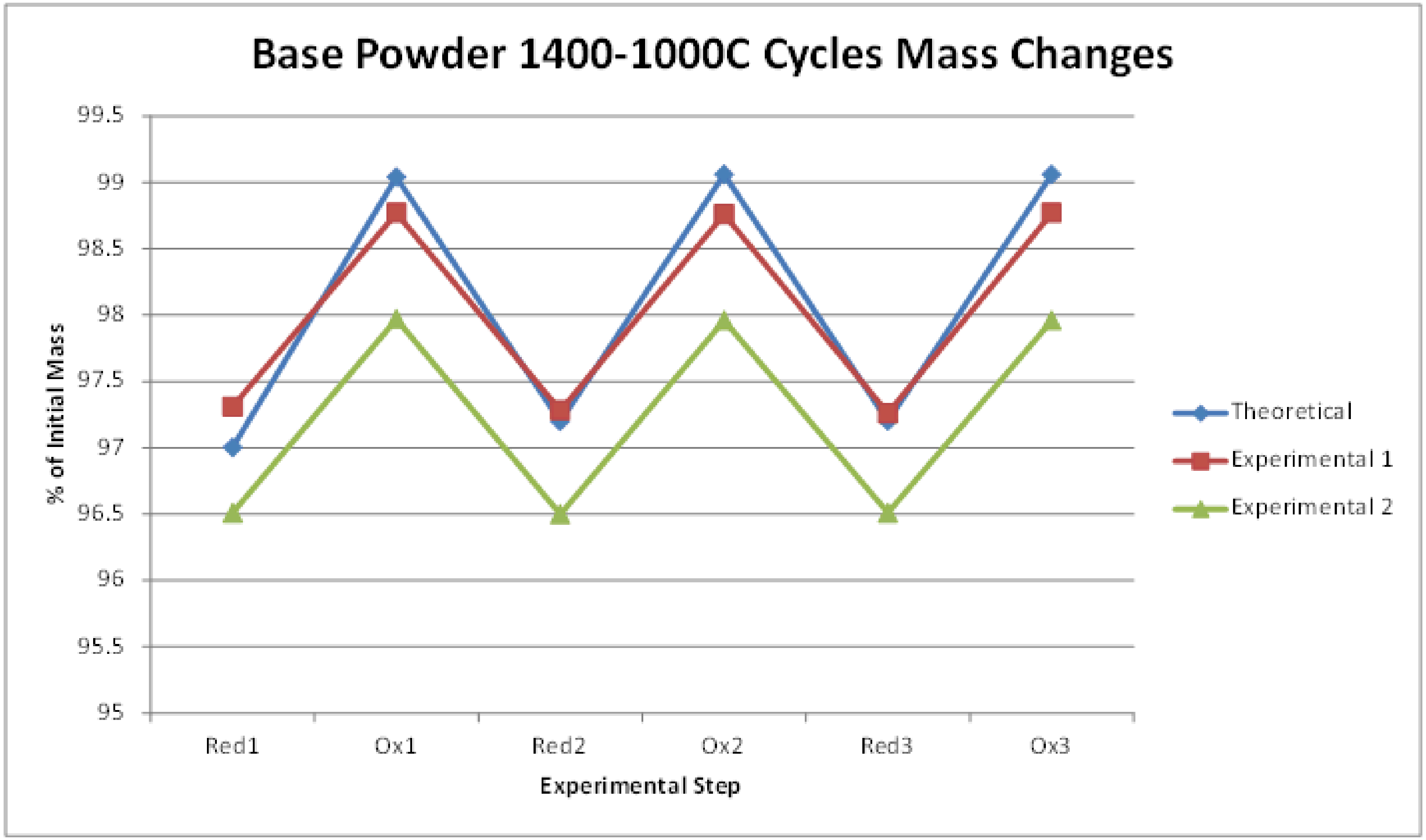
Selected Peaks - HT-XRD *in-situ*



DSC Data Summary

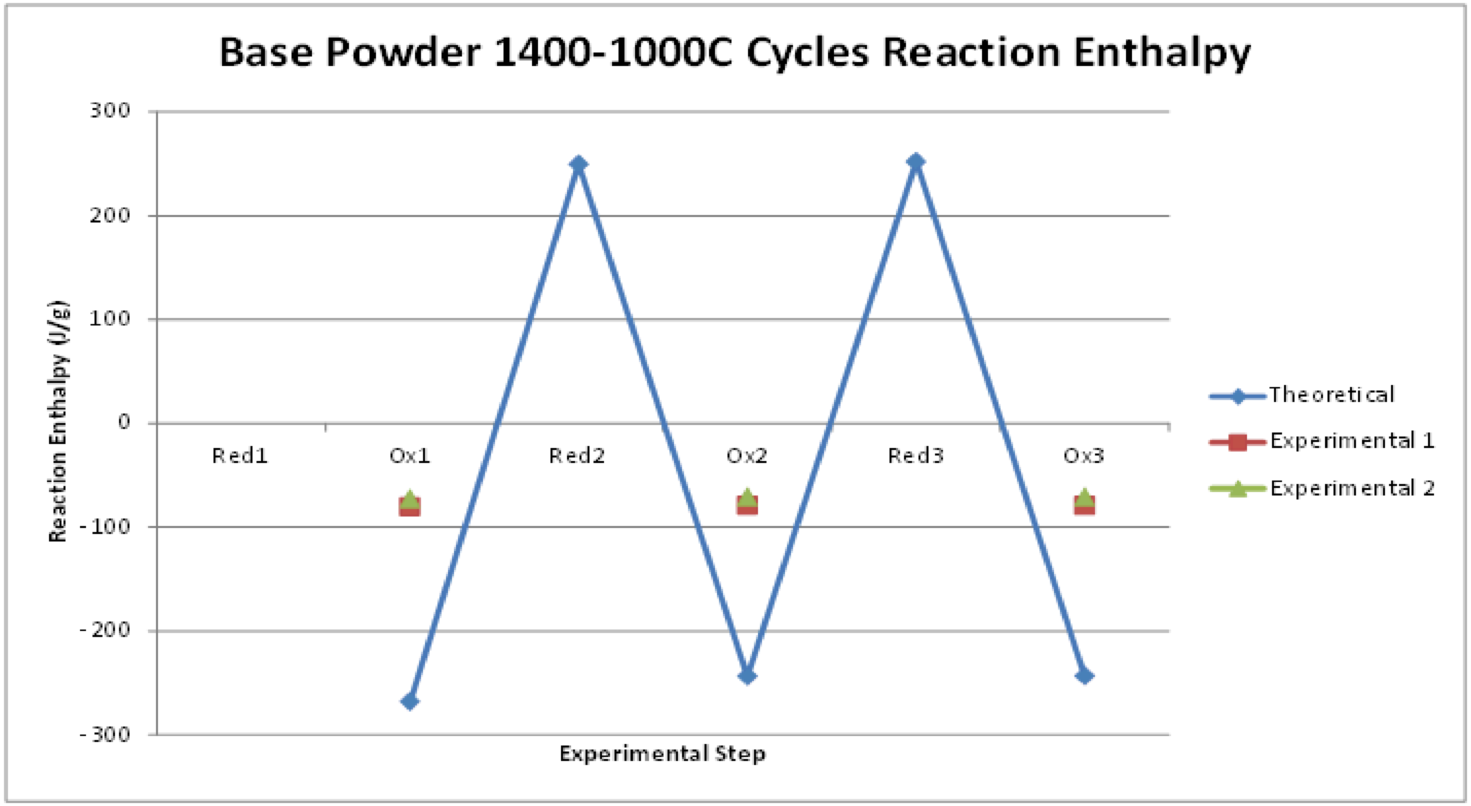


Theoretical-Experimental Comparisons



- Theoretical calculations done with FACTSage™
- "Base Powder" Material Formulation

Predictions for Reaction Enthalpy



- Not necessarily due to material formulation
- Probably not kinetic limitations
- Difference most likely due to:
  - Experimental error
  - Reactant contact

Conclusions

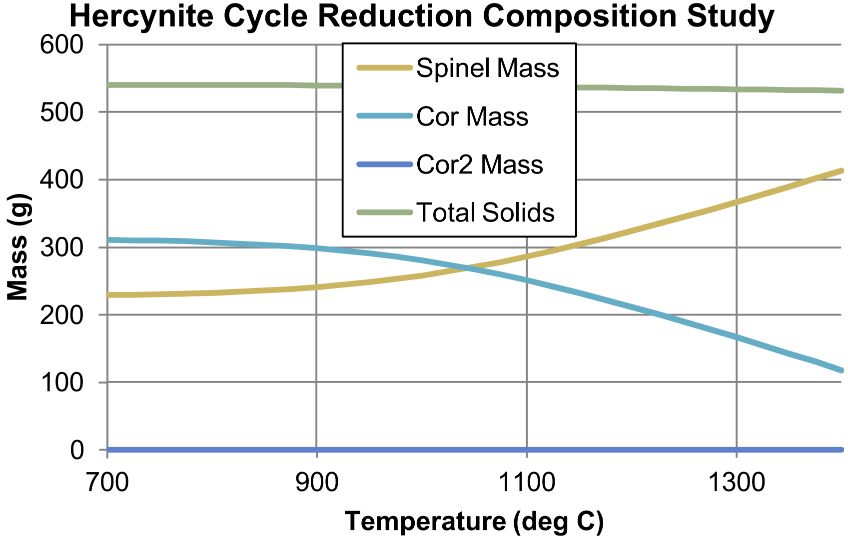
- Thermochemical energy storage “boost” from Hercynite cycle can be up to ~19% of sensible
  - Will be lower due to kinetic/reactivity limitations and parasitic loads
  - This is probably not enough to be useful
- Preliminary results are informative
  - Matching cycle to sensible energy ranges
  - High specific reaction enthalpy is critical
  - Demonstration of isothermal energy storage
  - Additional experimental verification needed

Suggestions for Future Work

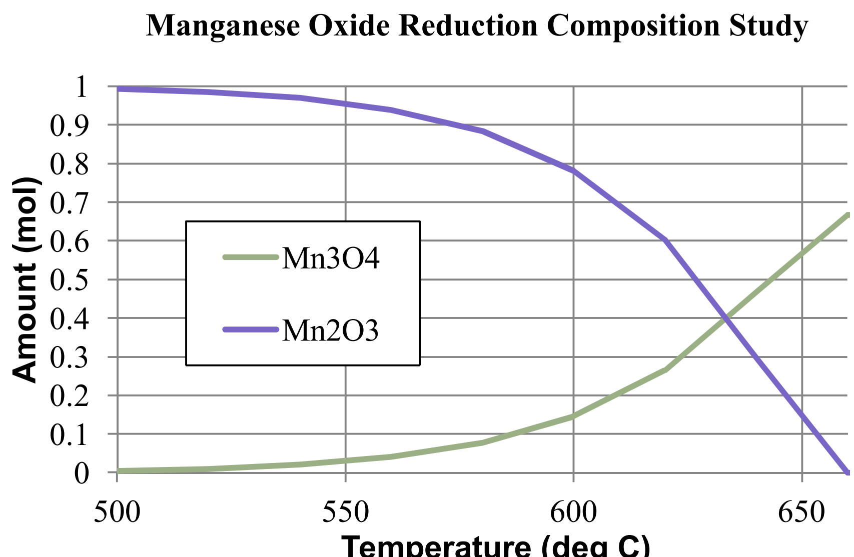
- Better exploration of “design space” for thermochemical boost
  - Thermodynamic and experimental
  - Other materials are promising
- Mass and Energy system model for more in-depth energy and exergy analysis
  - Explore potential improvements to cycle process and chemistry
  - Evaluate thermochemical benefit vs parasitic losses

New Materials

Reaction	ΔH_{red}
$Fe_2O_3 \leftrightarrow 2/3\ Fe_3O_4 + 1/6\ O_2$	471 kJ/kg
$Co_3O_4 \leftrightarrow 3\ CoO + 1/2\ O_2$	901 kJ/kg
$Mn_2O_3 \leftrightarrow 2/3\ Mn_3O_4 + 1/6\ O_2$	205 kJ/kg
$Mn_3O_4 \leftrightarrow 3\ MnO + 1/2\ O_2$	853 kJ/kg
$CoFe_2O_4 + 3\ Al_2O_3 \leftrightarrow CoAl_2O_4 + 2\ FeAl_2O_4 + 1/2\ O_2$	131 kJ/kg



- Cobalt and manganese oxide look promising
  - High energy density
- Manganese oxide lower cost



Acknowledgements

- Sandia National Laboratories · U.S. Department of Energy · NNSA National Nuclear Security Administration
  - Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
  - CSMP
  - Kristin Meyer
  - Mark Rodriguez
  - Kalvis Terauds

- Team Weimer

Works Cited

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- E. S. Domalski and E. D. Hearing, "Condensed Phase Heat Capacity Data," in *NIST Chemistry WebBook, Standard Reference Database Number 69*, P. J. Linstrom and W. G. Mallard, Eds., ed. Gaithersburg, MD: National Institute of Standards and Technology.
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- N. P. Siegel, "Thermal energy storage for solar power production," *Wiley Interdisciplinary Reviews: Energy and Environment,* vol. 1, pp. 119-131, 2012.

Questions?

Additional Slides

High Temperature Operation

- Improvement of Power Cycle Efficiency
  - Carnot Efficiency $\eta = 1 - \frac{T_{cool}}{T_{hot}}$
- Current materials do not operate at these temperatures

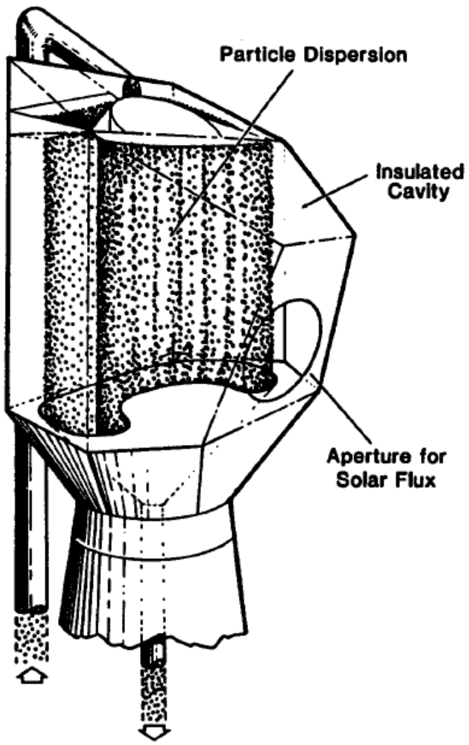
Alloy	Max. Operating Temp.
Inconel 625	982°C
Stainless 347	899°C

- Containment materials would need to be rated (or insulated) for higher temperatures
  - $$$

Hercynite Cycle for Boosting

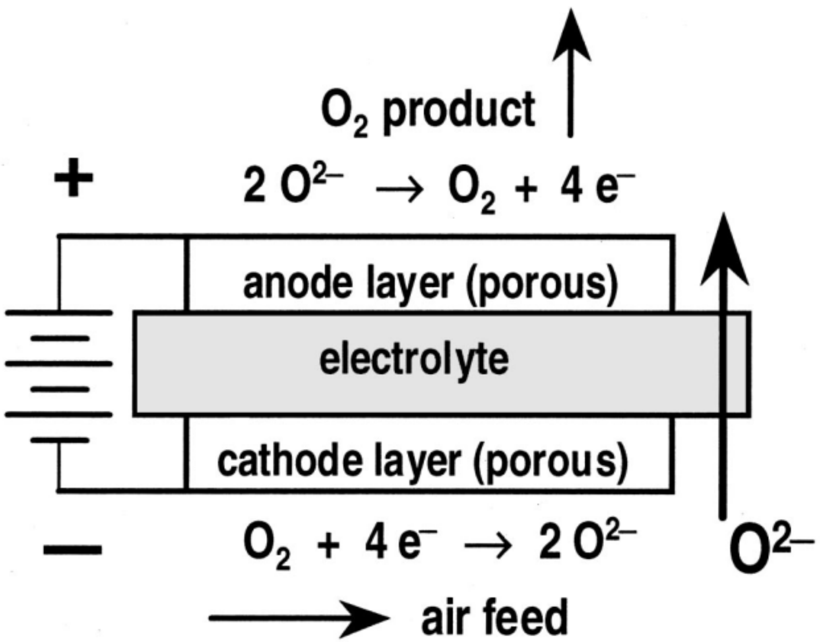
- Why Hercynite Cycle?

- Direct Heating



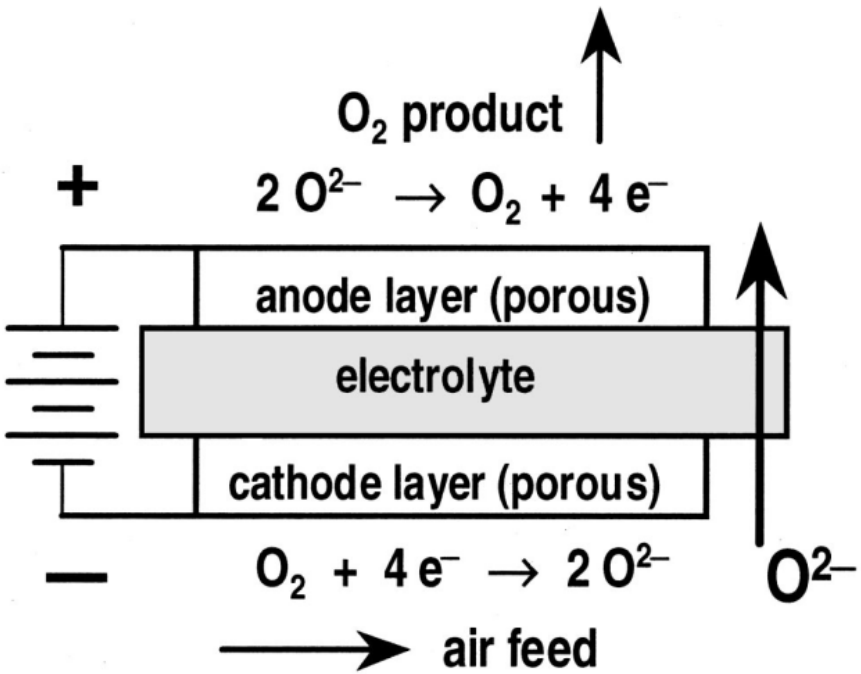
J. M. Hruby, Sandia National Laboratories SAND86-8211, 1986.

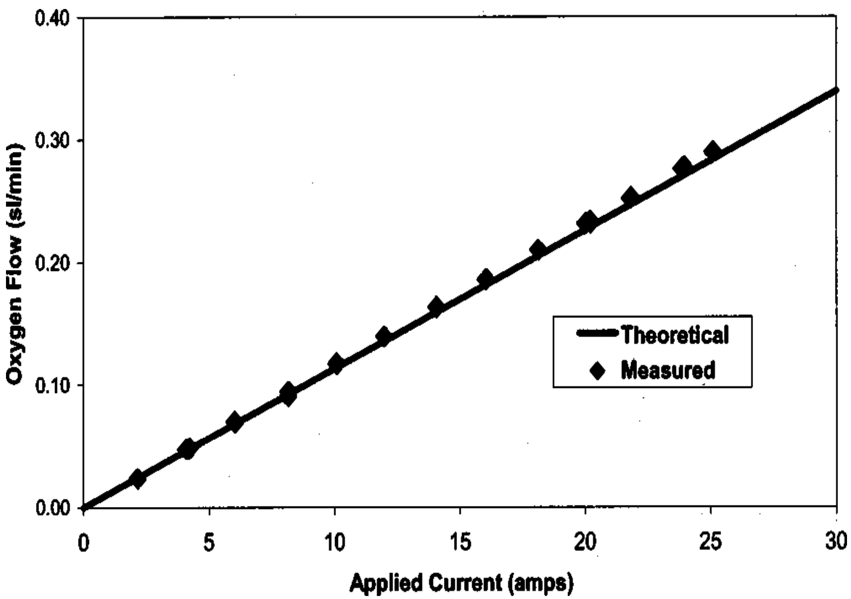
- Oxygen Control



D. L. Meixner, *et al.*, *Journal of the Electrochemical Society,* vol. 149, pp. D132-D132, 2002.

Oxygen Control

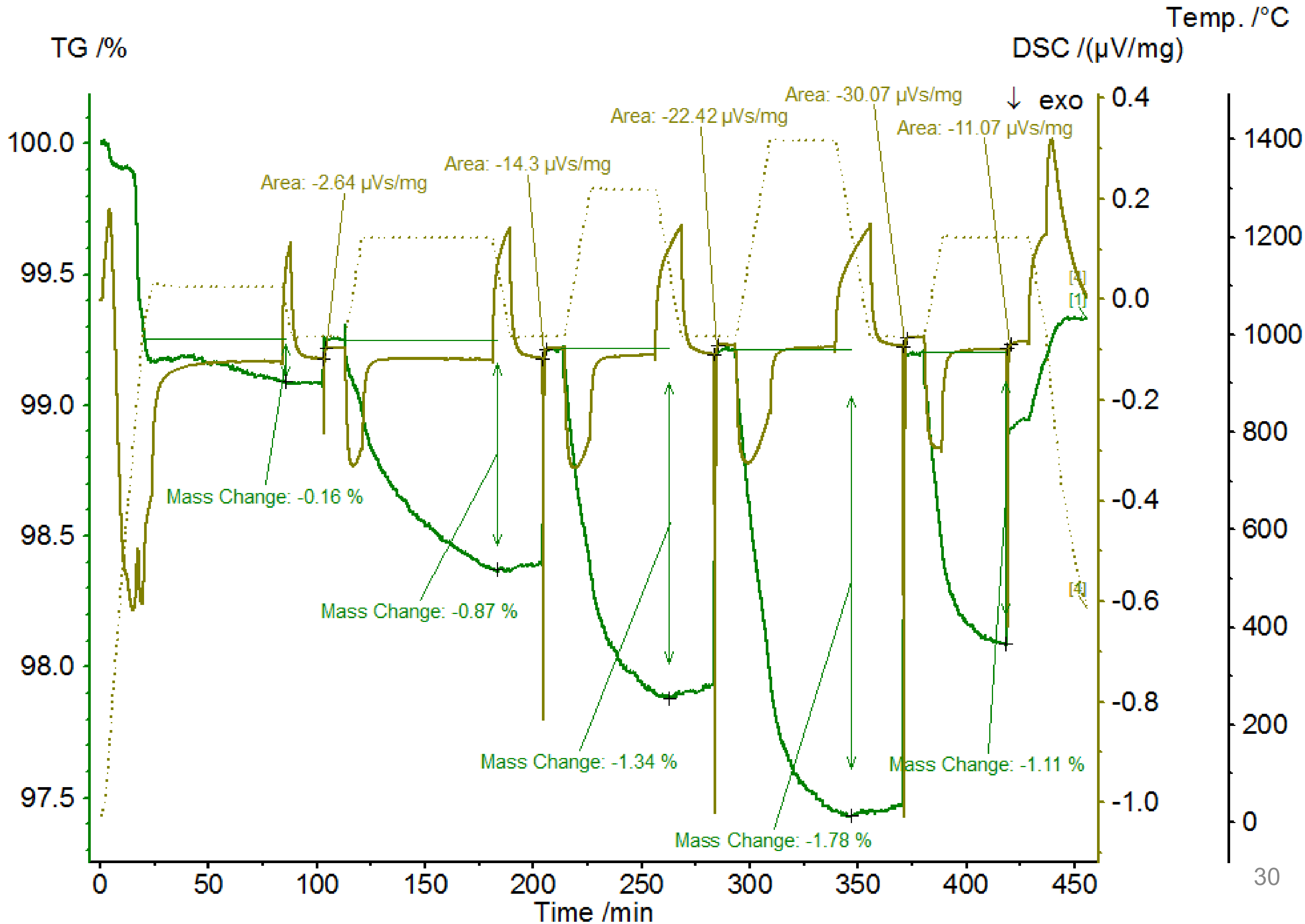




$$Q_{O_2} = \frac{I}{4F} N_{cells}$$

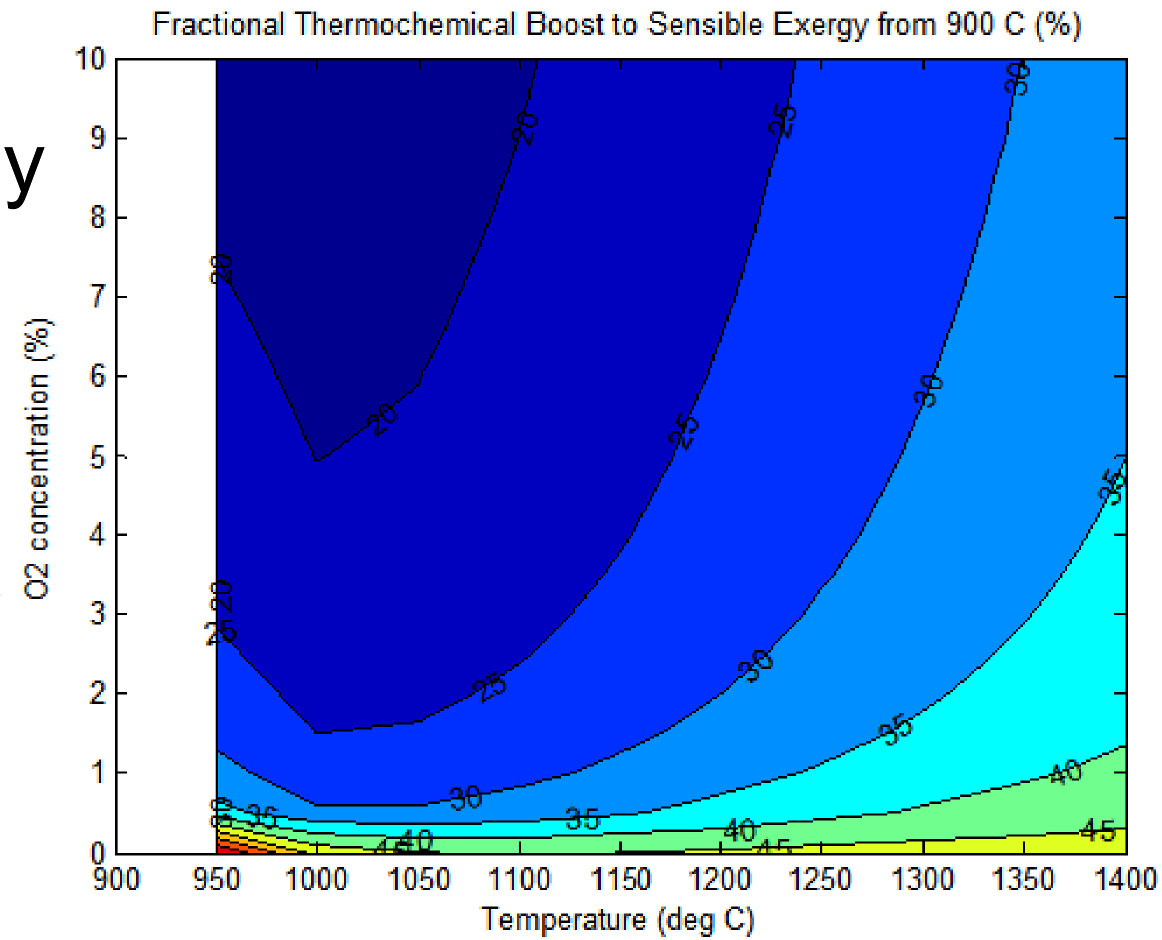
D. L. Meixner, *et al.*, *Journal of the Electrochemical Society,* vol. 149, pp. D132-D132, 2002.

TGA/DSC Data - Energy Flows

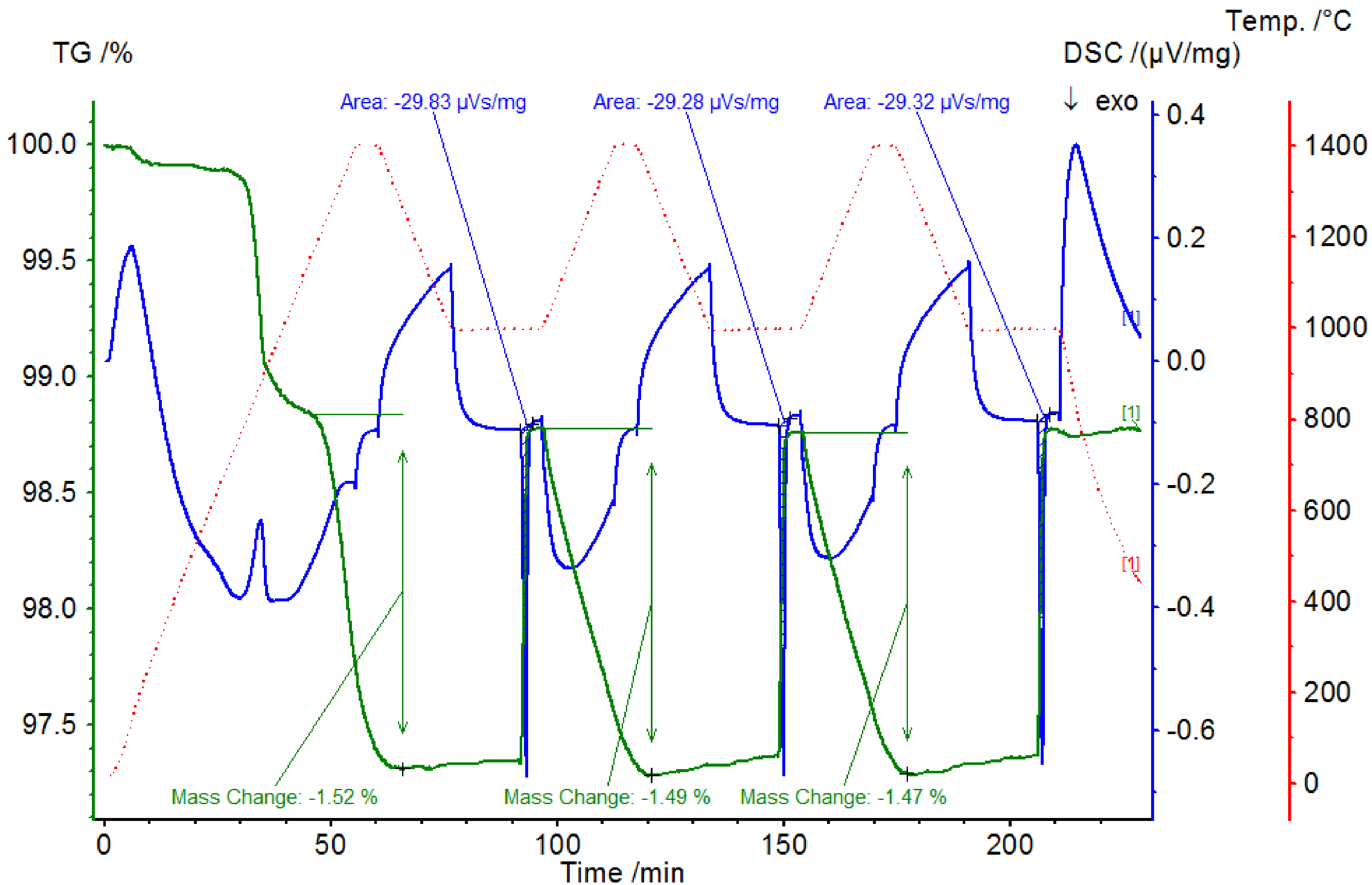


FACT – Comparison to Limited Exergy

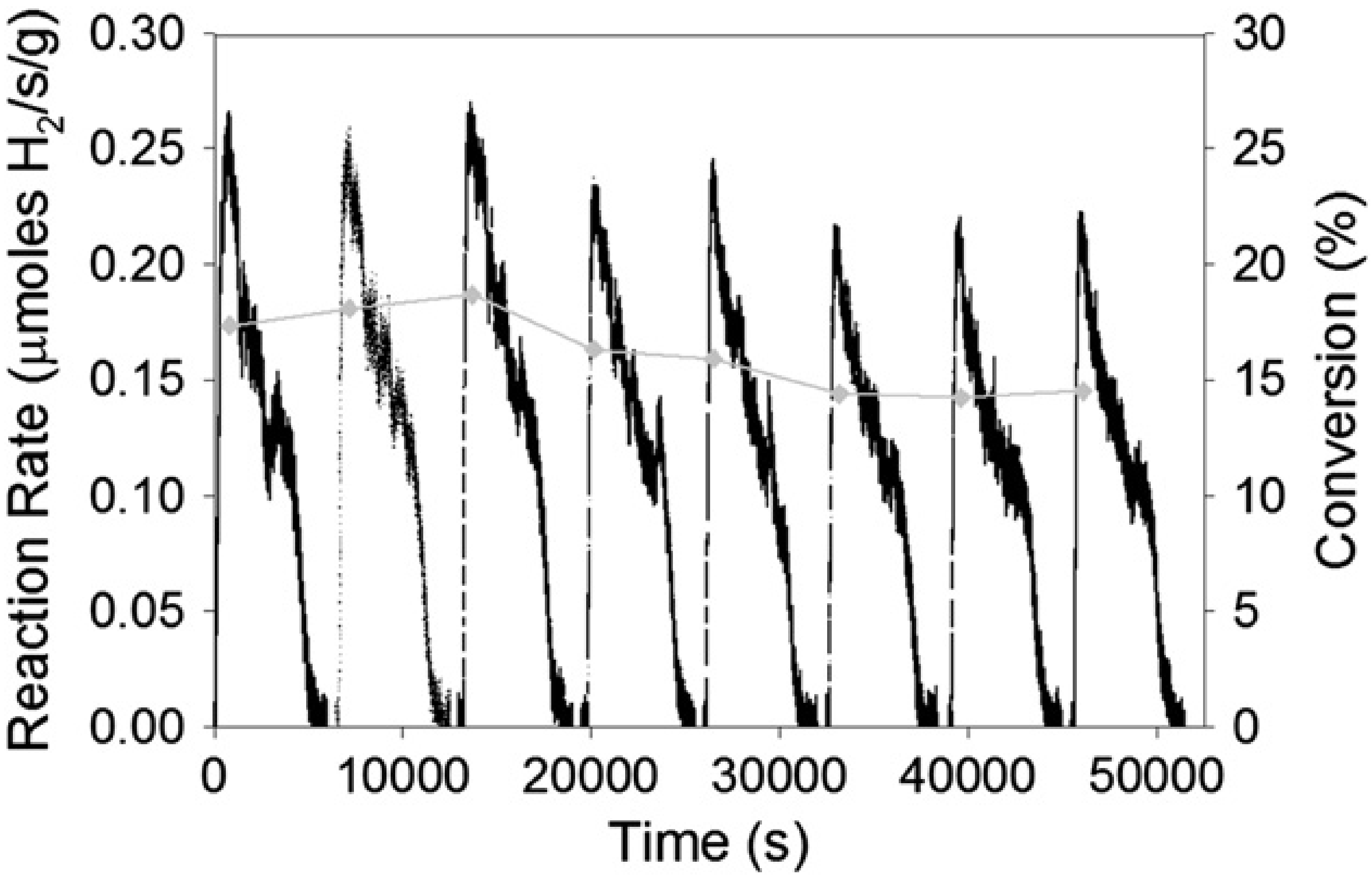
- Reaction enthalpy compared to exergy from 900°C
  - Not very realistic
- Maximum is 66.1%



Repeatable Cycles



Repeatable Cycles



J. R. Scheffe, *et al.*, *International Journal of Hydrogen Energy,* vol. 35, pp. 3333-3340, 2010.

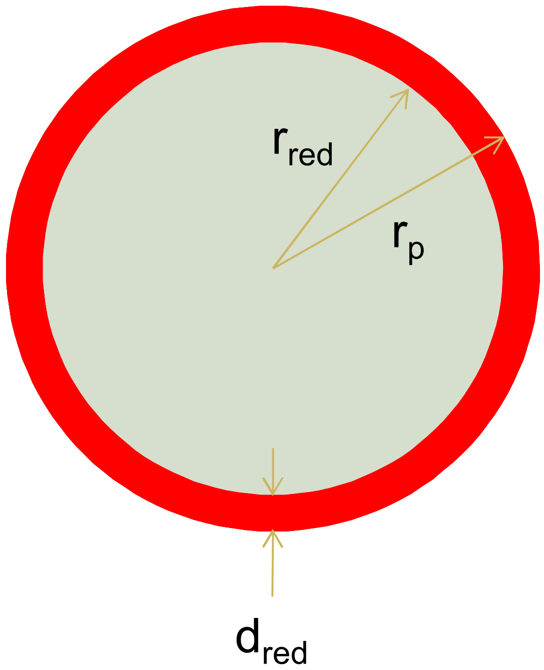
Reaction Extent

- Volume Reduced:

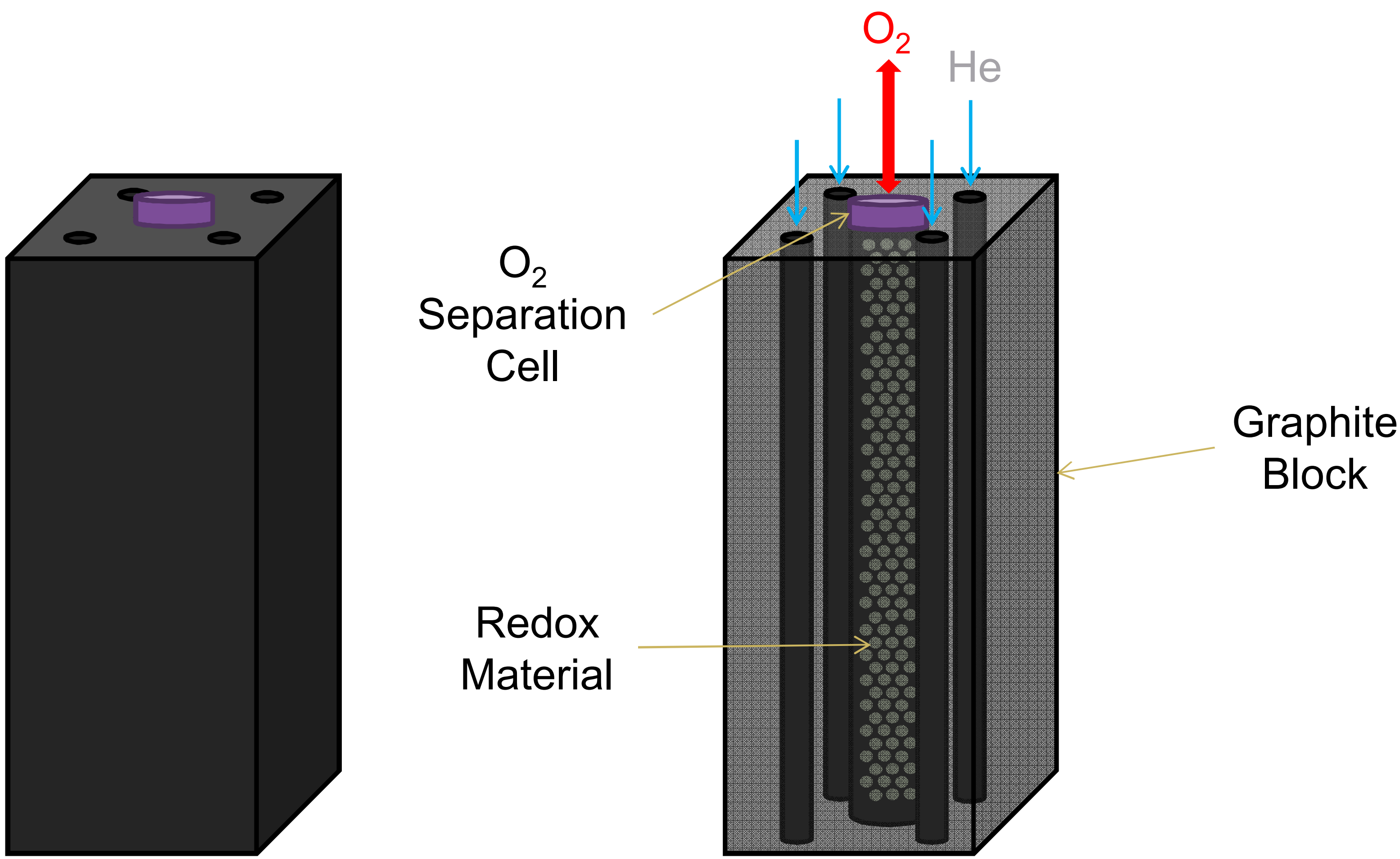
$$V_{red} = \frac{4}{3}\pi({r_p}^2 - {r_{red}}^2)$$

- Particle diameter = 100 µm
- Reduction Depth = 6.69 µm
- Volume fraction reduced:

35%



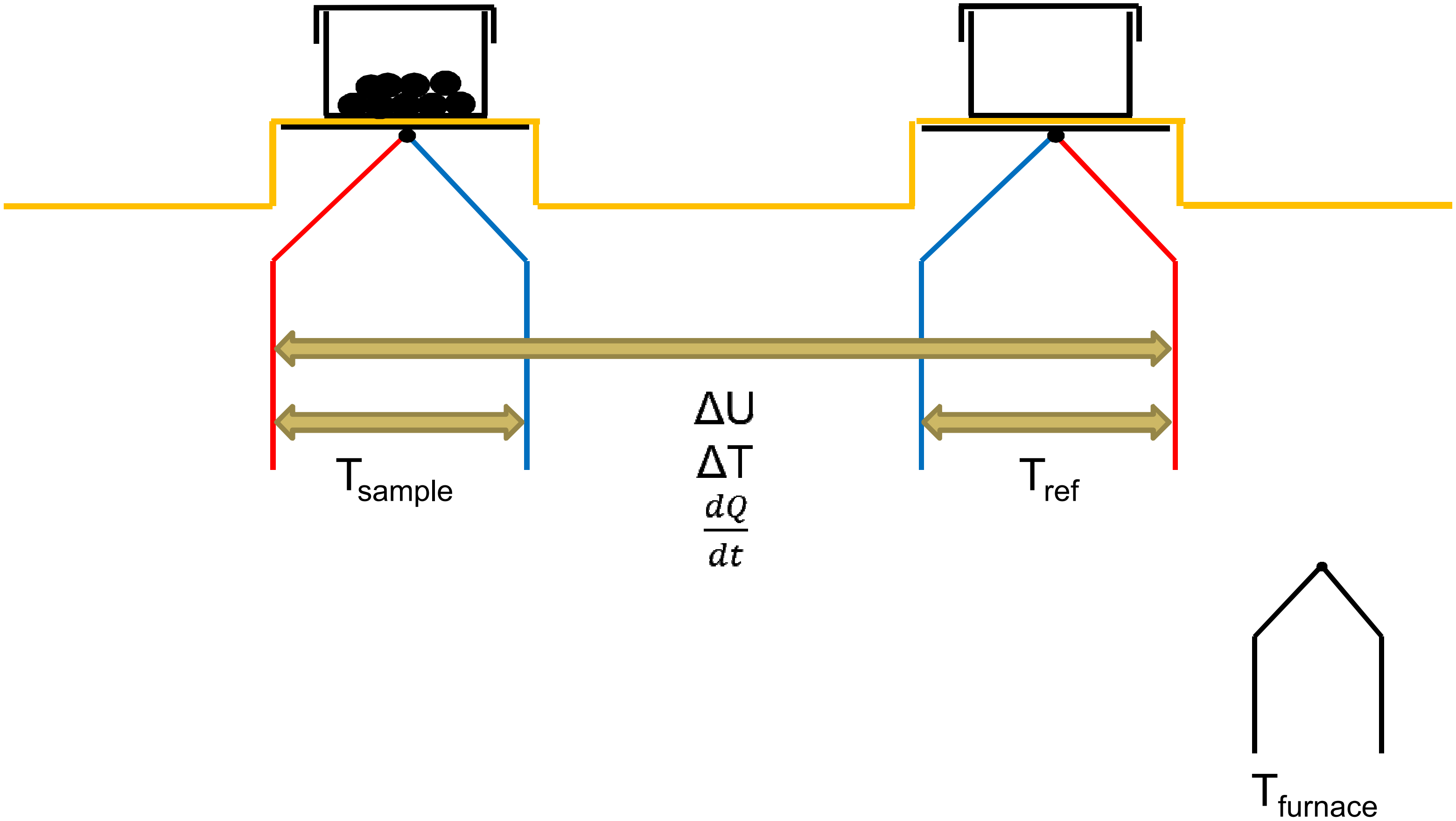
Thermochemical/Thermal Storage Unit (SUN-TSU)



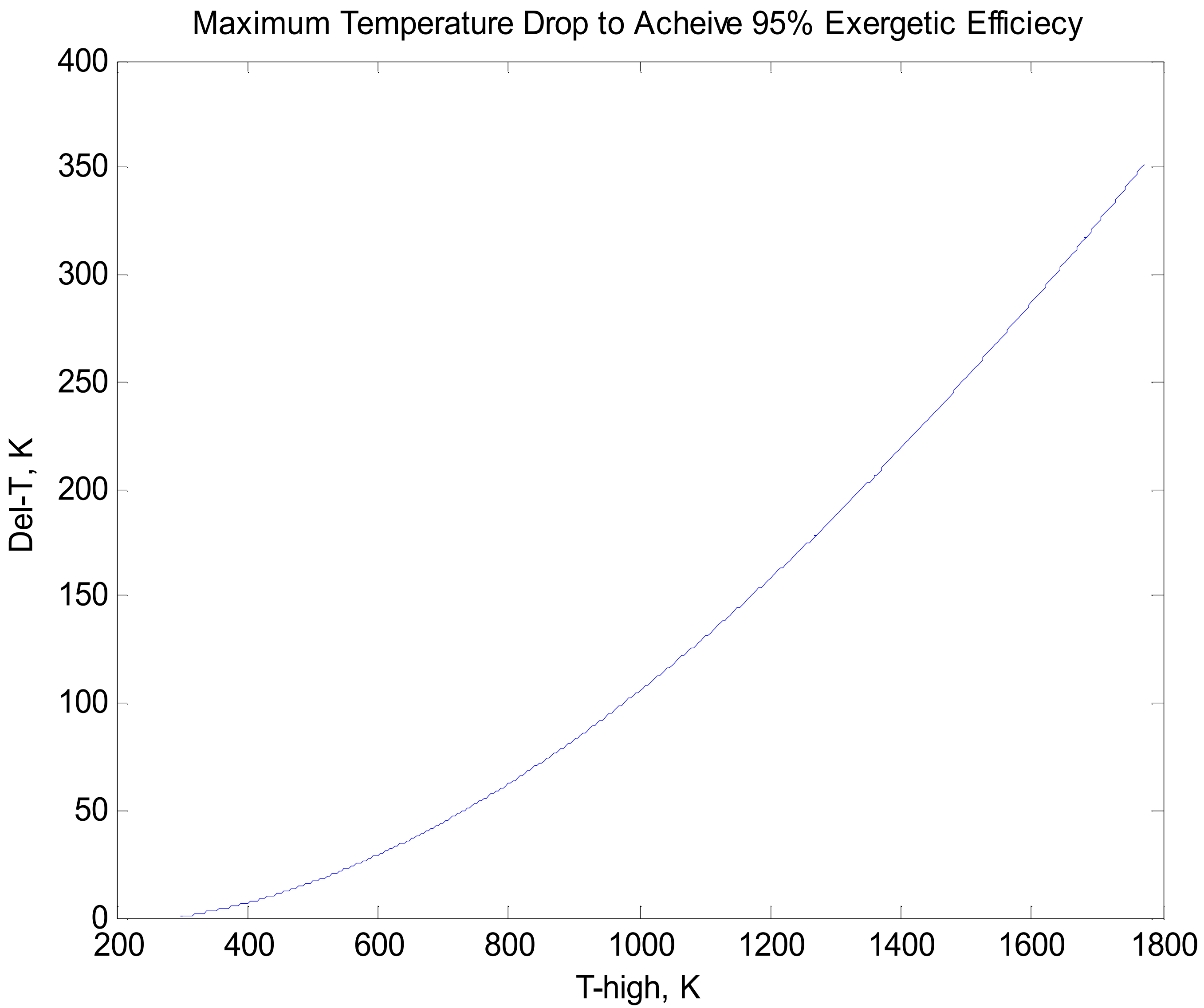
Issues with TGA-DSC Data

- Al_2O_3 crucible used for previous runs
- Al_2O_3 becomes "heat transparent" at high temperatures
  - Al_2O_3 is transparent in far-infrared and part of the mid-infrared spectrum
  - Radiative heat travels through crucible to sample
  - Gives false exotherms and/or exothermic shift
- Very little (any?) information available in the literature

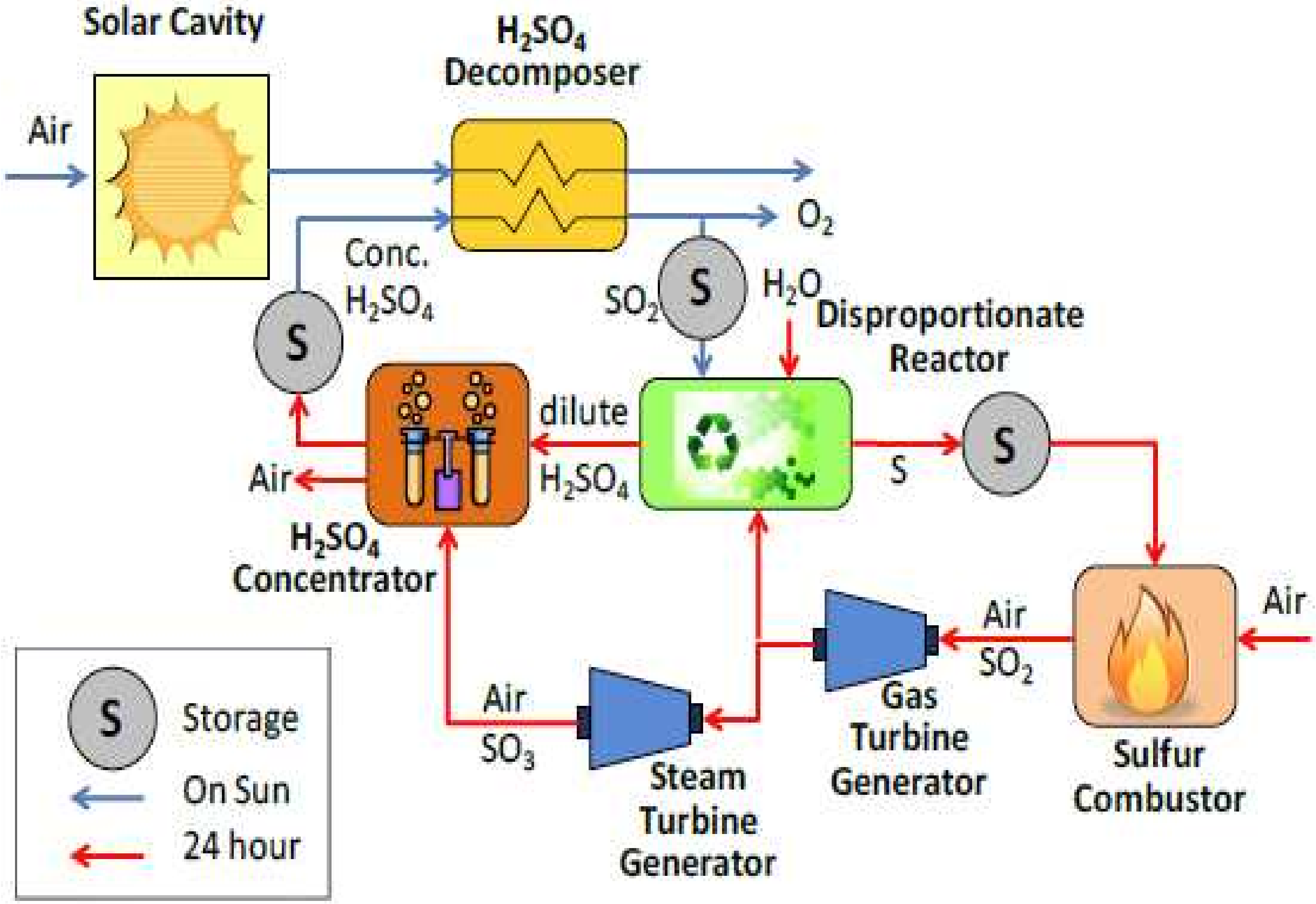
TGA-DSC Setup



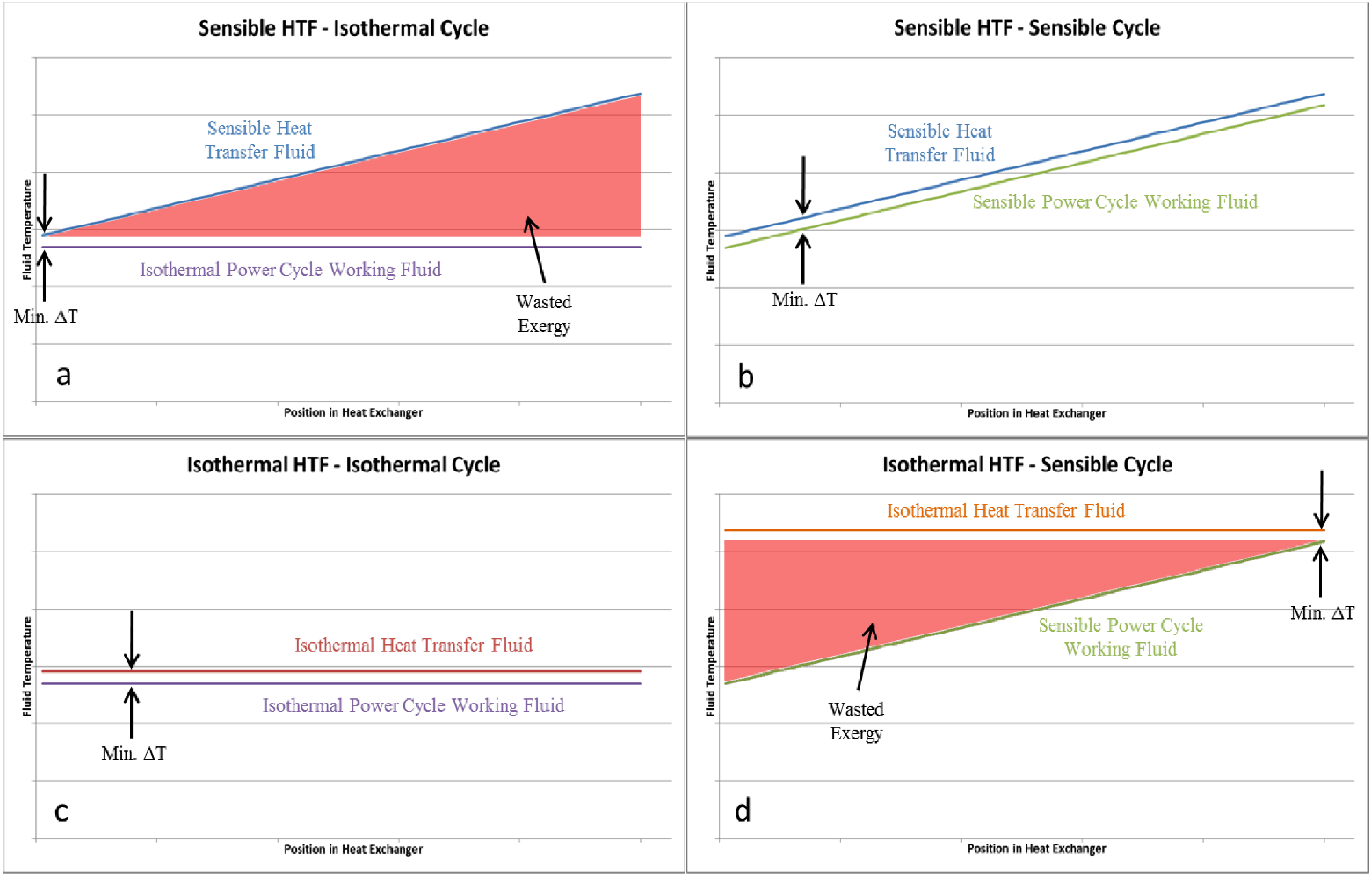
95% Exergetic Efficiency



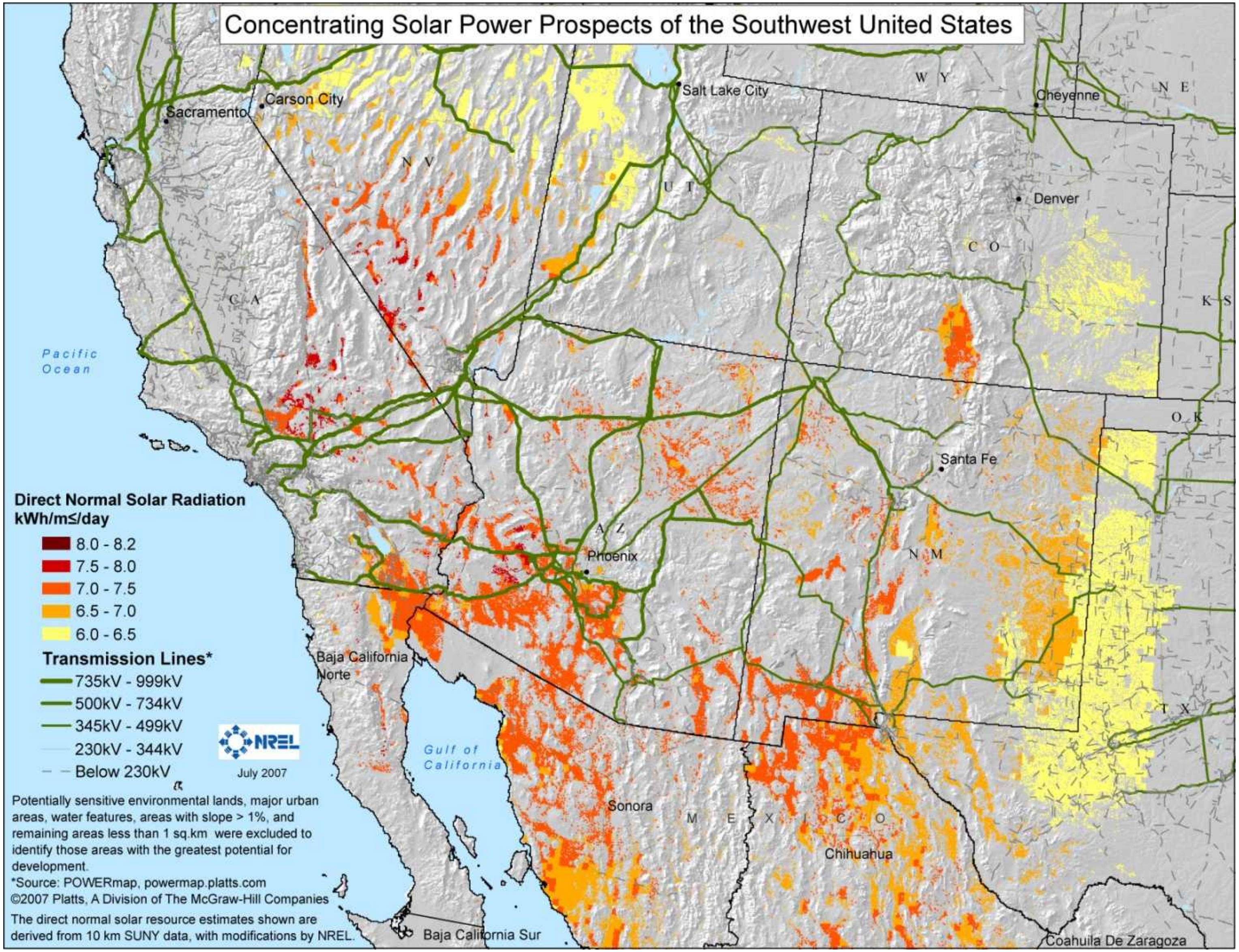
Sulfur Process



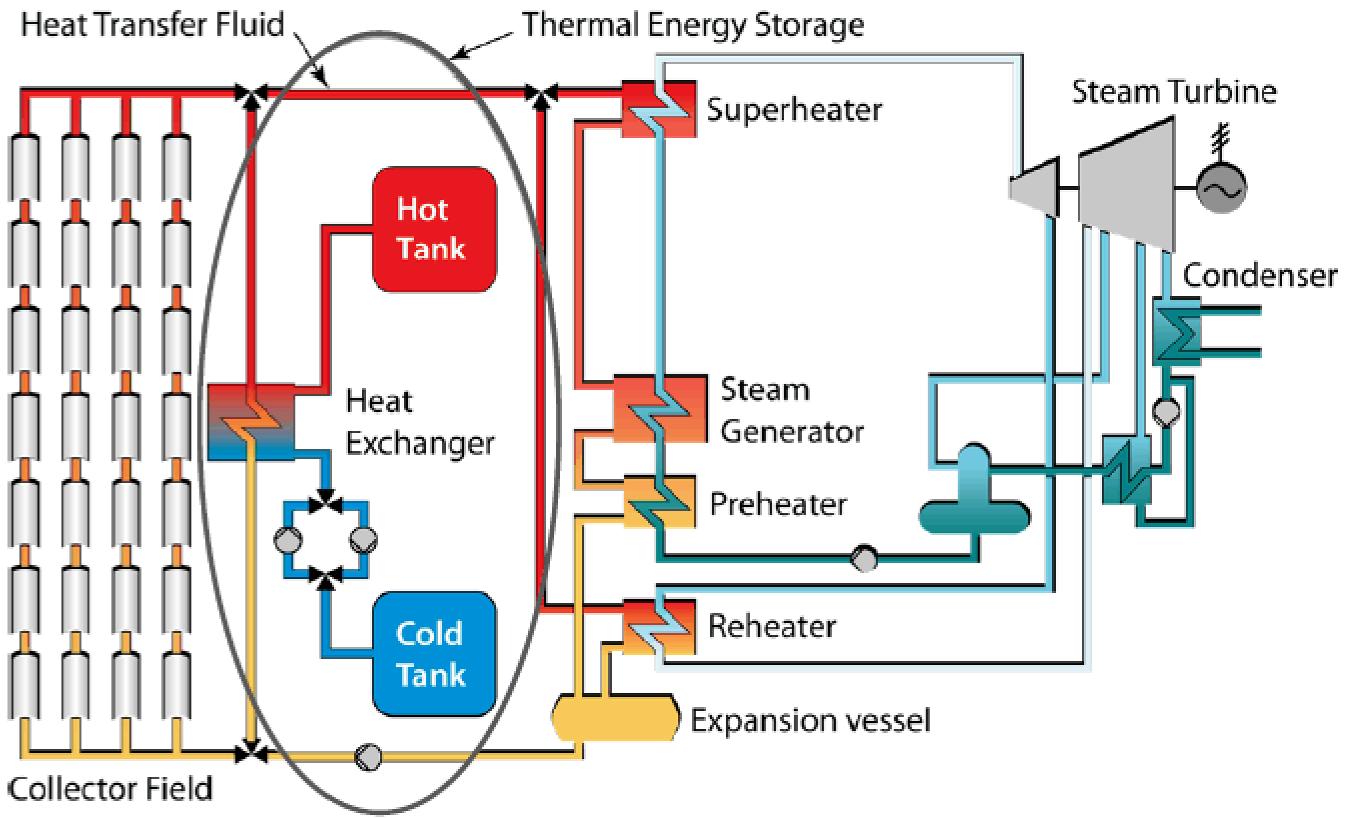
Power Cycle Matching



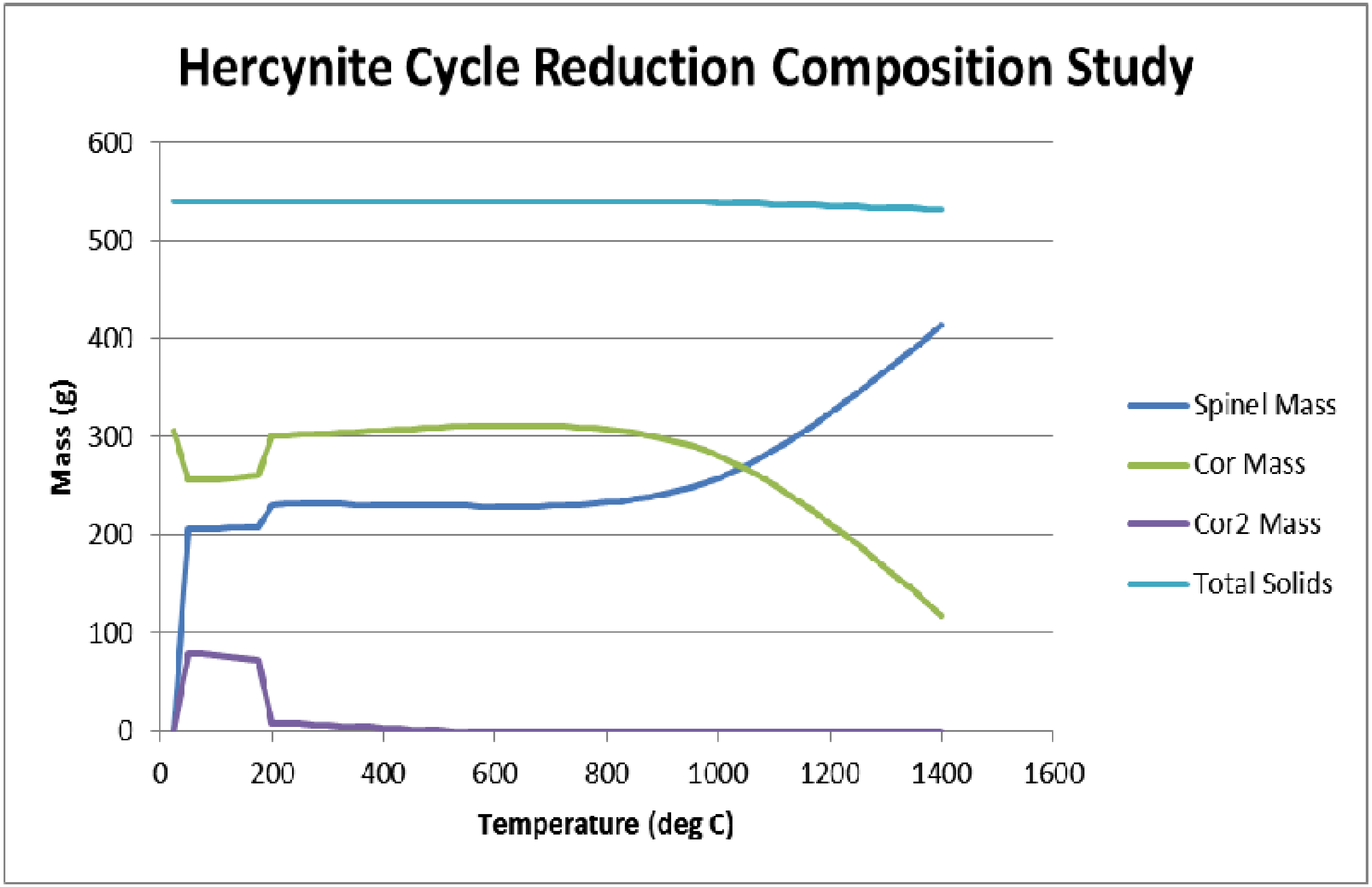
Desirable Solar Resource



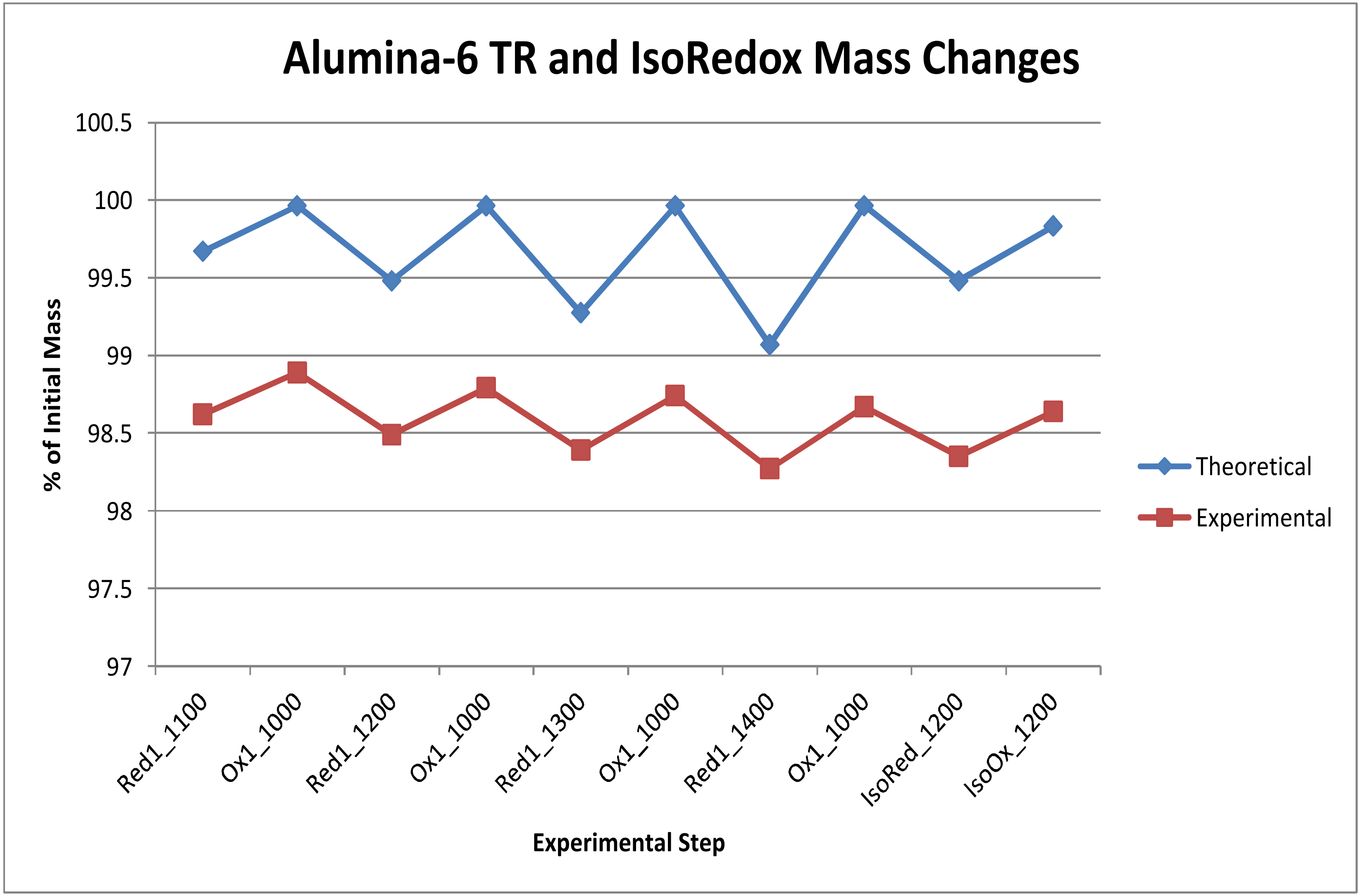
Parabolic Trough



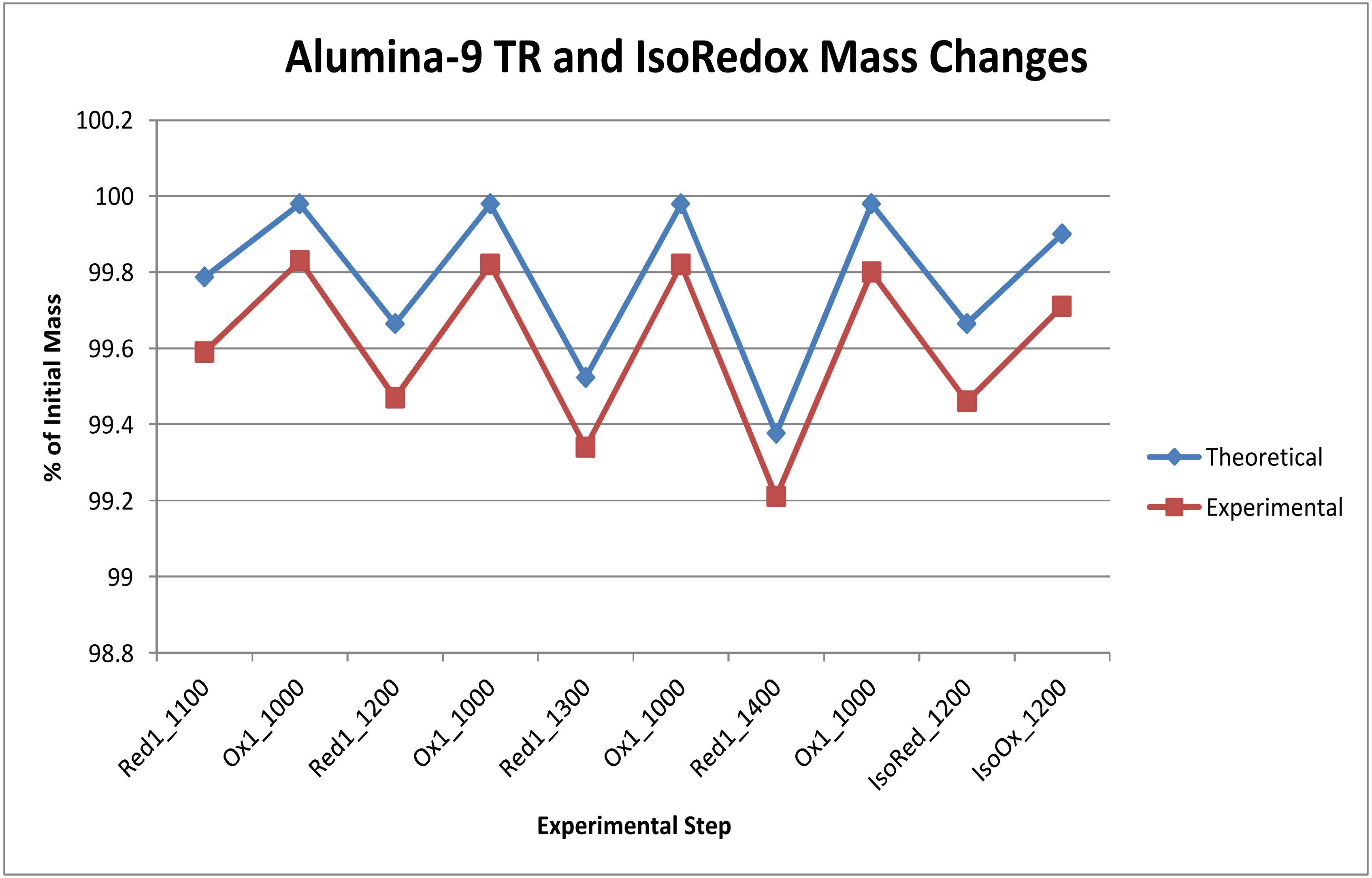
Hercynite Cycle Composition



Alumina-6 Experimental Comparisons

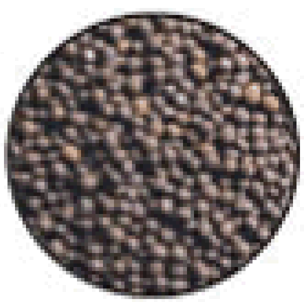


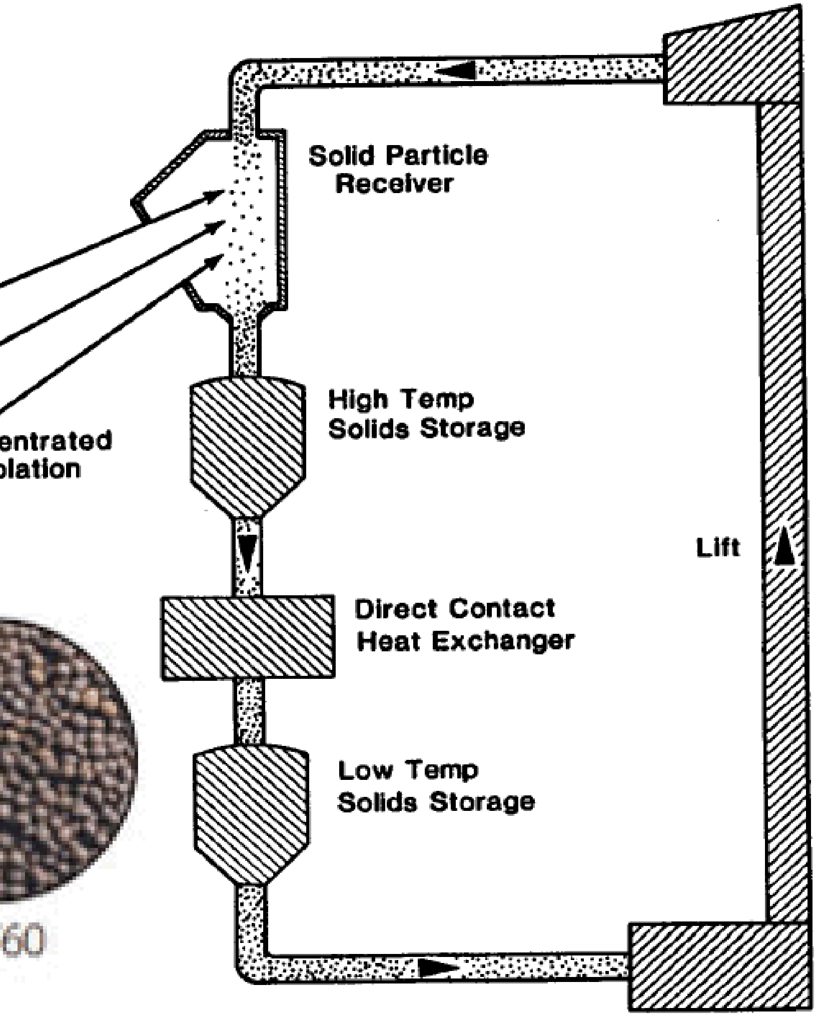
Alumina-9 Experimental Comparisons



Solid Particle Receivers

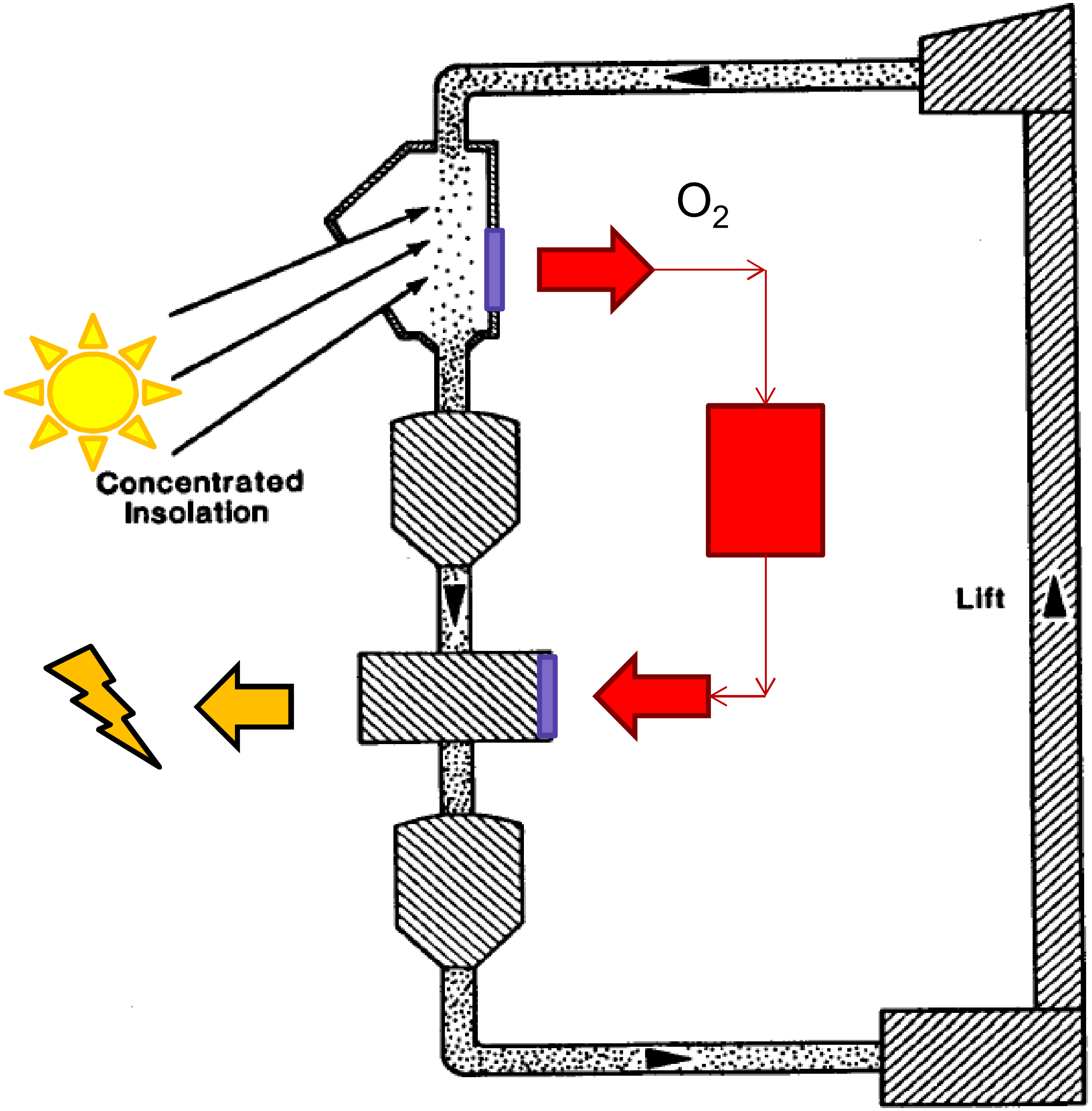
- Solid Particle "Heat Transfer Fluid"
- Operation at much higher temperatures
- Moving particles is a challenge
- Initially studied in late 1970's to mid-1980's
  - Currently being studied again





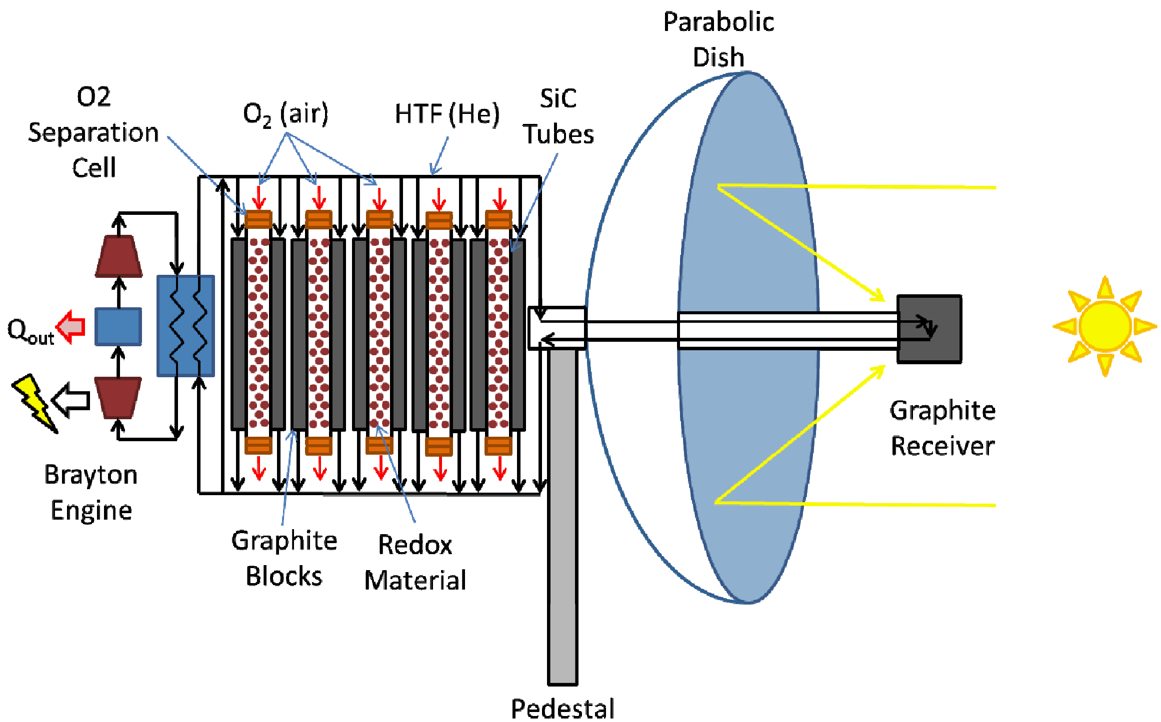
-J. M. Hruby, Sandia National Laboratories SAND86-8211, 1986.
-N. P. Siegel, *et al.*, *Journal of Solar Energy Engineering,* vol. 132, p. 021008, 2010.
-http://www.carboceramics.com/CARBO-HSP/

Potential Systems - CASPR



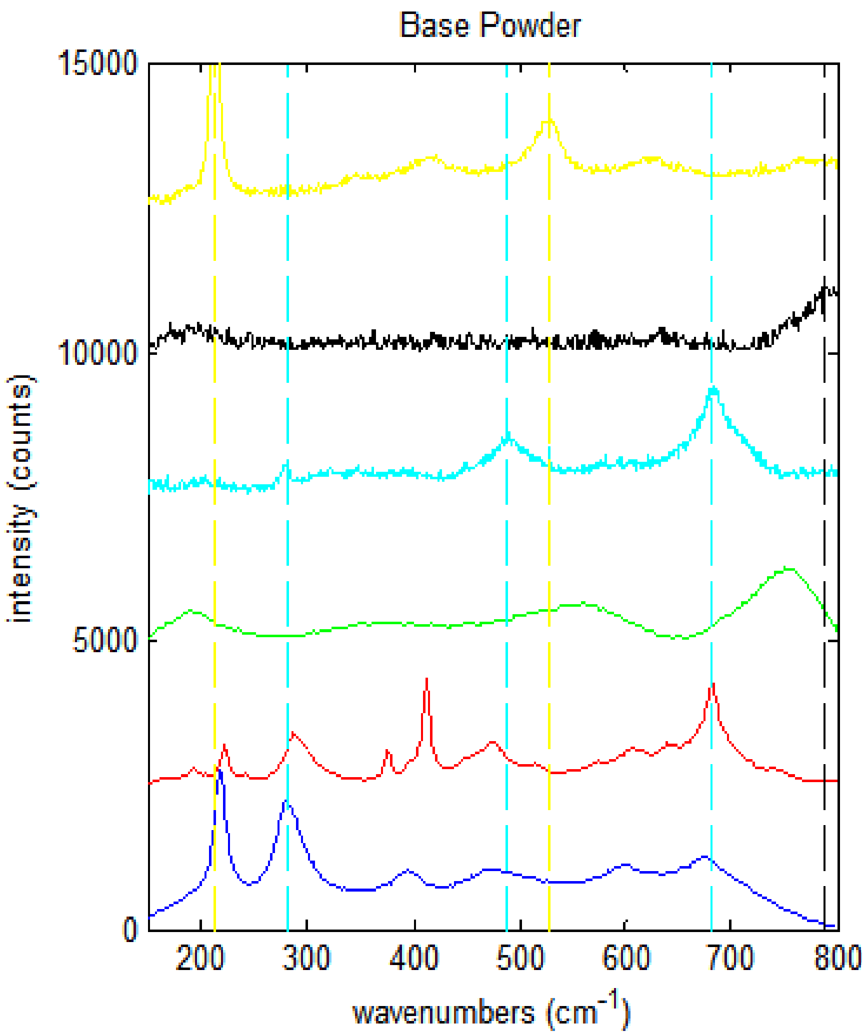
- Chemically augmented solid particle receiver
- Benefits
  - Direct utilization of heat in particles
- Issues
  - Moving particles can be difficult at high temperatures
  - Controlling atmosphere can be difficult at large scale

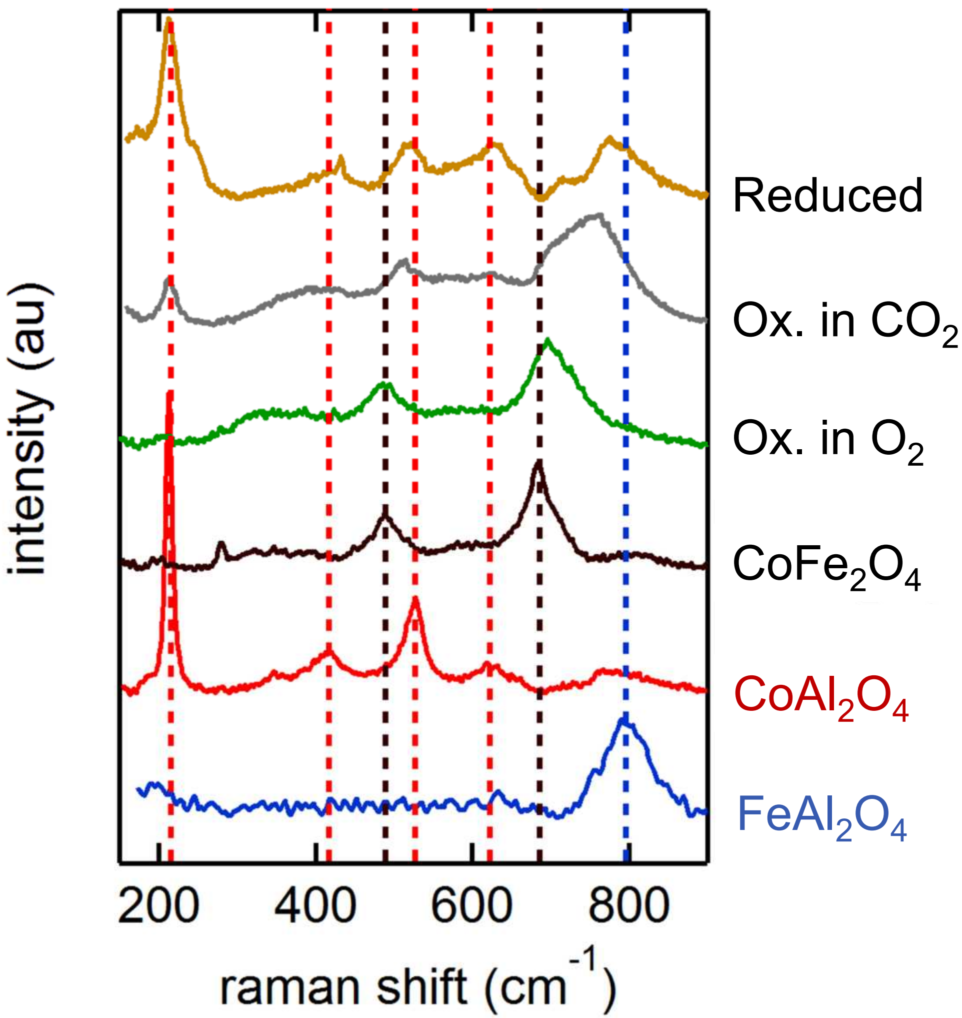
Potential Systems - CASES



- Chemically Augmented Stationary-solid Energy Storage
- Benefits
  - No moving particles
  - Could help put useful storage on dishes
- Issues
  - Indirect storage can have efficiency losses

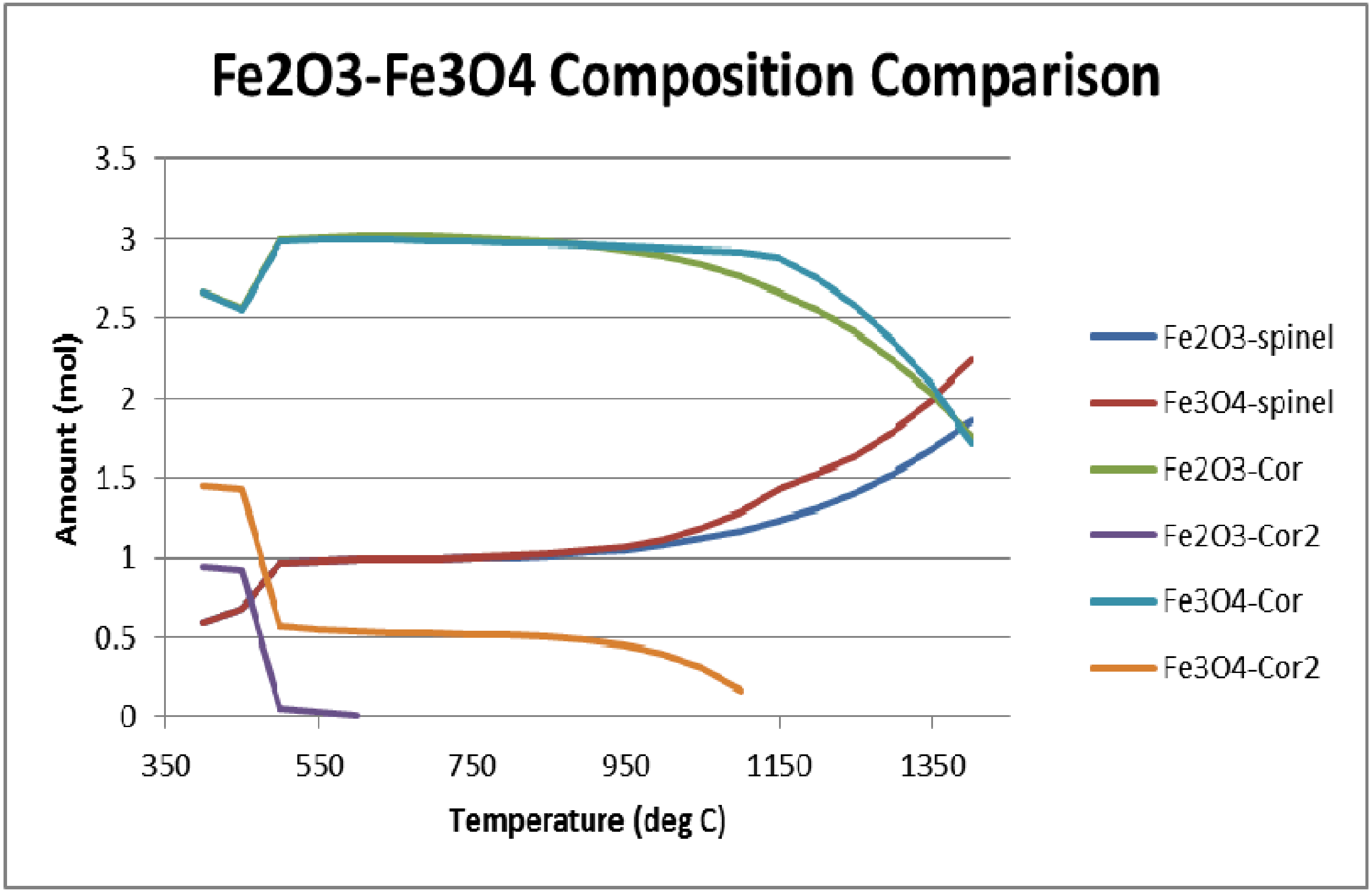
Raman - ALD Samples





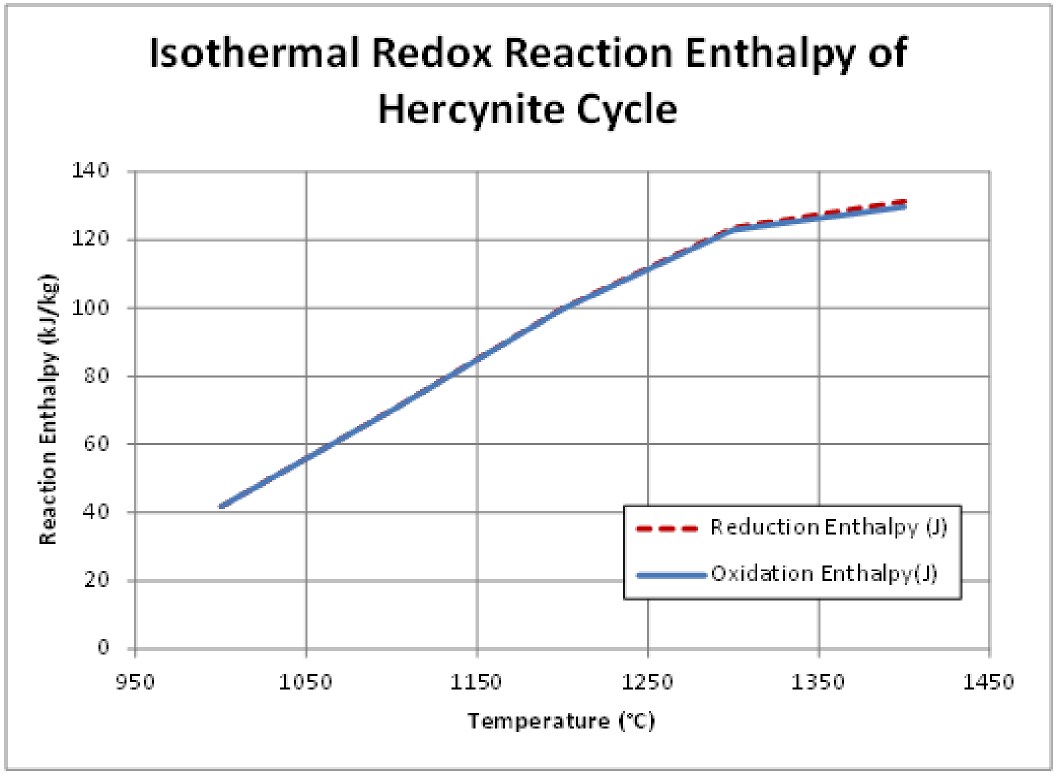
D. Arifin, *et al.*, *Energy & Environmental Science,* vol. 5, pp. 9438-9443, 2012.

Fe_2O_3-Fe_3O_4 Synthesis Comparison



FACT – Isothermal Cycling

- Calculated reaction enthalpy in isothermal cycling
- Solid Material with Argon (reduction) or Oxygen (oxidation)
- Normalized per unit mass
- Corrected for any enthalpy changes in gas phase



Considerations for Other Materials

- Cobalt Oxide of interest
- Desirable Traits
  - High specific reaction enthalpy
    - 901 kJ/kg @ 800°C
    - 265 kJ/kg for hercynite
  - Small ΔT for full reaction
- Potential Issues
  - Sintering
  - Toxicity