Solarthermal Redox-based Water Splitting Cycles

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[c]Sandia National Laboratories

[d]ETH Zurich

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Project ID No. PD028

This presentation does not contain any proprietary, confidential or otherwise restricted information

Overview

Timeline

- Start: 6-1-2005
- End: 9-30-2014
- 90% completed

Budget

- Total Project Funding
  - 2005-2012: $1,427K DOE
  - $401,750 Cost Share
- Funds received in FY13
  - $250,000 (subcontract from SNL)
  - $62,500 Cost Share
- Planned FY2014 Funding
  - $200,000 (subcontract from SNL)
- Cost Share Percentage: 20%

Barriers

U. High-Temperature Thermochemical Technology

V. High-Temperature Robust Materials

W. Concentrated Solar Energy Capital Cost

X. Coupling Concentrated Solar Energy and Thermochemical cycles

Partners

National Renewable Energy Laboratory (NREL)

Sandia National Laboratories (SNL)

ETH Zurich (ETHZ)

Relevance

Overall Objective

- Develop efficient robust materials and operation methods for a two-step thermochemical redox cycle that will achieve the DOE cost targets for solar hydrogen:

($14.80/kg H_2 in 2015; $3.70/kg H_2 in 2020; ultimately $2/kg H_2)

- Develop a scalable solar-thermal reactor design that will achieve the DOE cost targets for solar hydrogen.

Objectives this period

- Develop understanding of "hercynite cycle" chemistry, multi-tube reactor performance, and Red/Ox behavior
  - Kinetics and chemistry
  - Isothermal (IT) vs pseudo-isothermal (PIT) vs. temperature swing (TS)
  - Understanding IT, PIT &. TS efficiencies
- Develop continuous particle flow reactor & materials concept with independently controllable Red/Ox conditions
  - Analyze Surround Sun design
  - Develop Particle Flow Reactor design enabling broader reactor optimization
  - H2A Analysis
  - Identify critical research challenges for future investigation

2013 Milestone – "Synthesize a cobalt ferrite/alumina "hercynite cycle" active material and demonstrate isothermal redox water-splitting in a stagnation flow reactor at a temperature of 1350°C yielding a H_2 production per gram of total mass of active material > 100 μmoles/g active material." (> 200 μmoles/g active material achieved)

Approach

Red/Ox Thermal Cycling

- Understanding the activity of Red/Ox materials and its impact on type of cycling (isothermal, pseudo-isothermal, temperature-swing) and reactor efficiency.

Materials Design and Properties

- Develop a more detailed understanding of Red/Ox materials mechanisms and, hence, methods to improve materials performance

Reactor Design

- Design a reactor which is scalable to large sizes, is comprised of suitable containment materials and is tunable for specific active materials.

- Demonstrate materials robustness, reactor operability on-sun and cost-effectiveness via H2A analysis

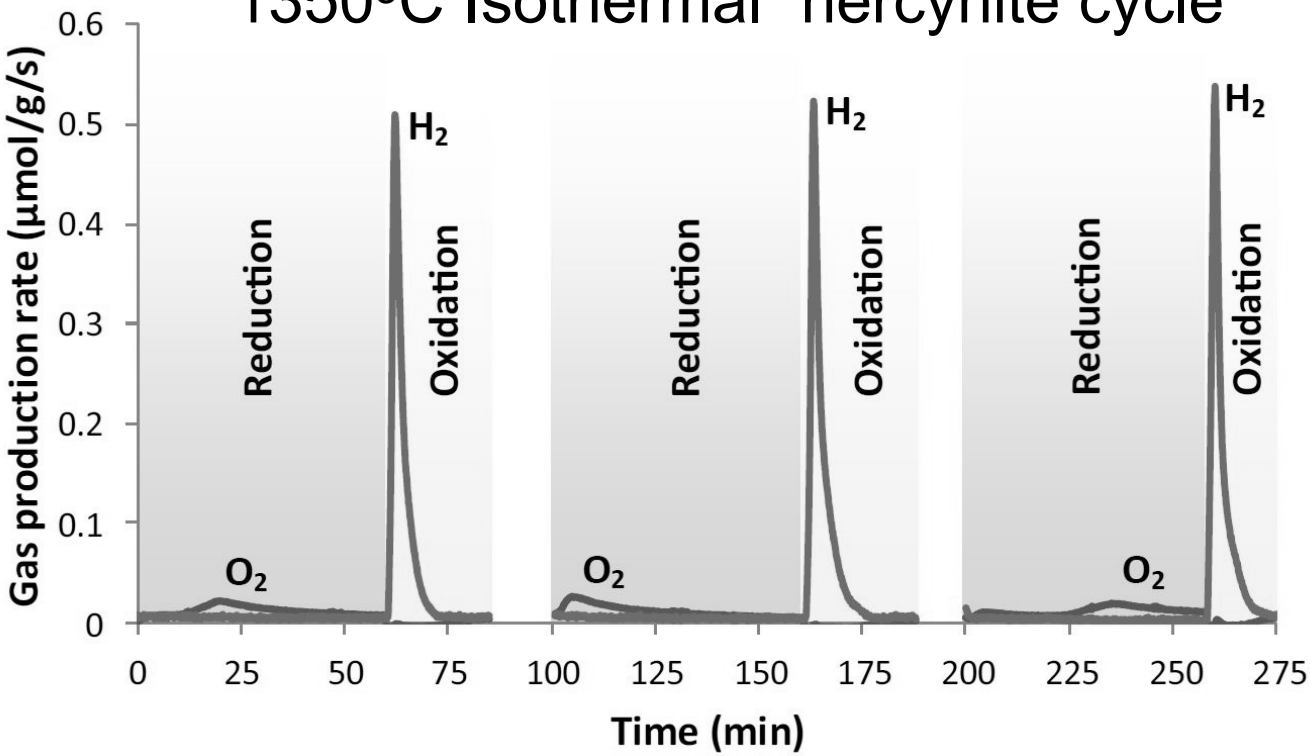
Efficient, Cost Effective H_2

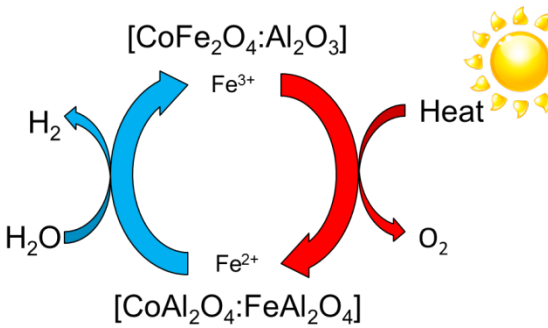
Broadening Red/Ox Design Space

Red/Ox Thermal Cycling

- Oxidation temperatures up to the reduction temperatures are possible (enables expanded design space)
- Higher oxidation temperatures reduce kinetic limitations

1350°C Isothermal "hercynite cycle"





Take-Away

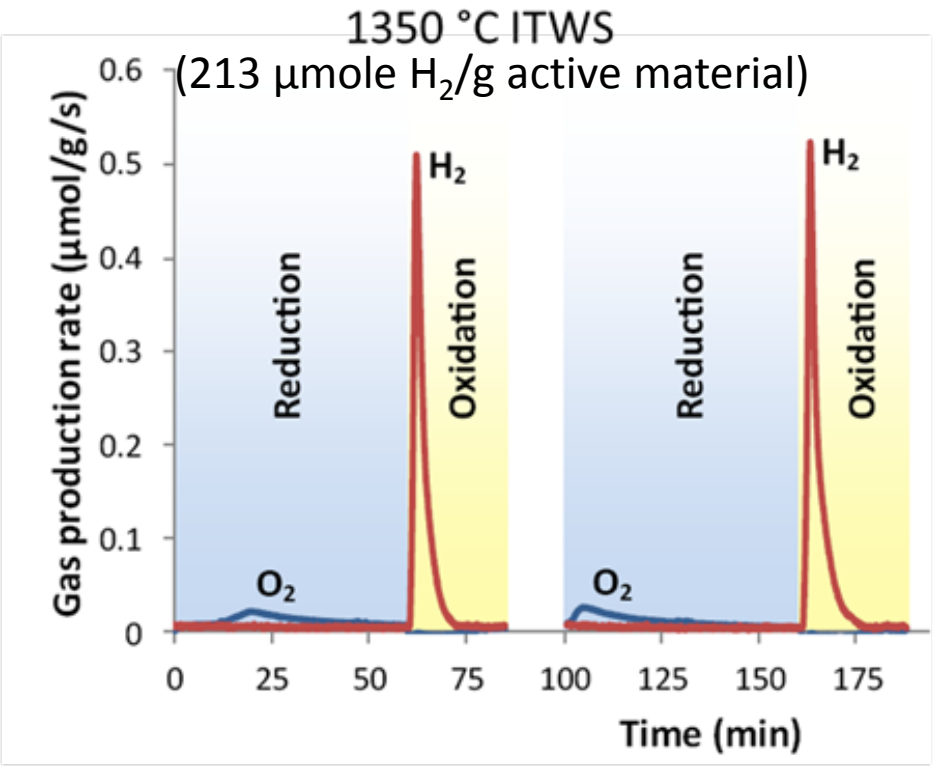
It is possible to produce substantial H_2 by operating isothermally & without simultaneous Red/Ox occurring using the "hercynite cycle"

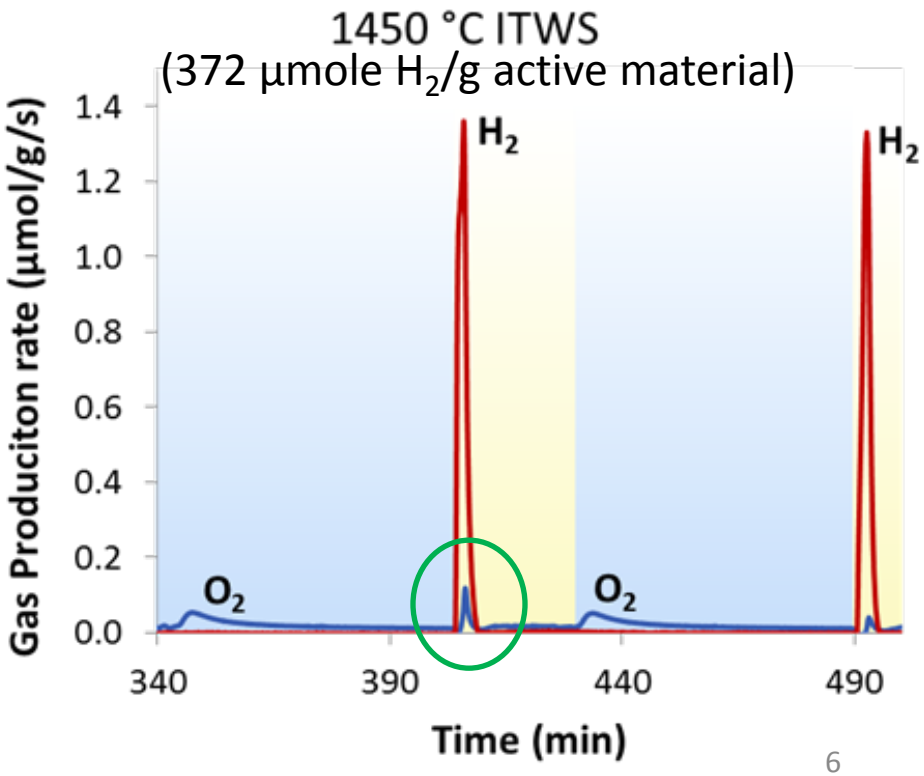
Muhich, C.L. et al., Science, 341, 540-542 (2013)

Need for "Pseudo-Isothermal" Operation

Red/Ox Thermal Cycling

- Oxidation temperatures that are too high can induce simultaneous O_2/H_2 production (below right)
- Such processes can be cycled "pseudo-isothermally" where the T_{red}-T_{oxid} is minimized (i.e. ≤ 150°C); e.g. 1500°C T_{red} / 1350°C T_{oxid}





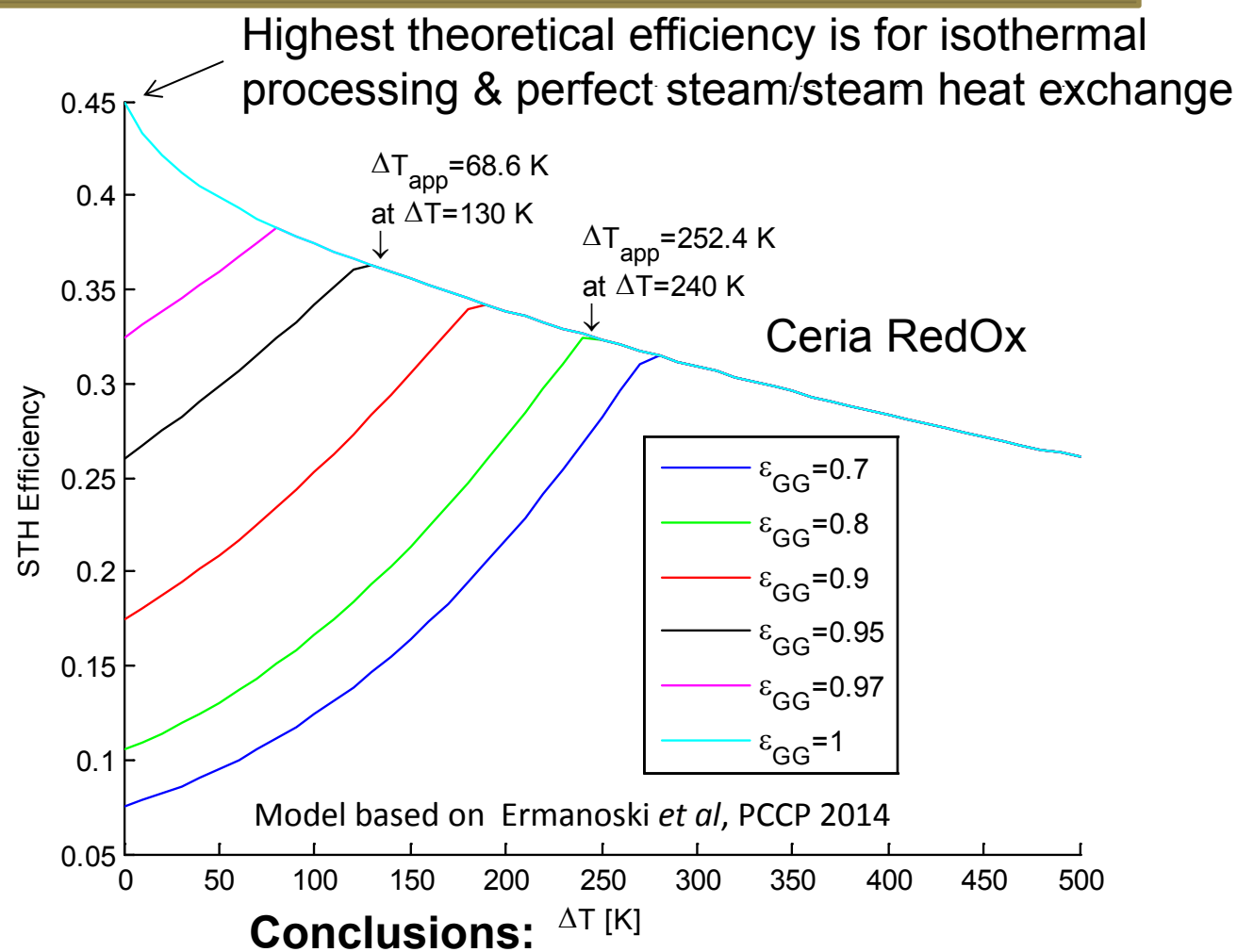
Accomplishments & Progress

Efficient Gas-Gas heat recuperation enables high efficiencies and low ΔT

Red/Ox Thermal Cycling

Parameters:

- T_{red} = 1800K
- P_{red} = 10 Pa
- Solid heat recuperation = 0.5
- ε_{GG} : gas/gas recuperation efficiency
- T_{app}: temp. difference between ox steam and inlet steam after gas/gas recuperation
- ΔT_{opt}: highest theoretical efficiency



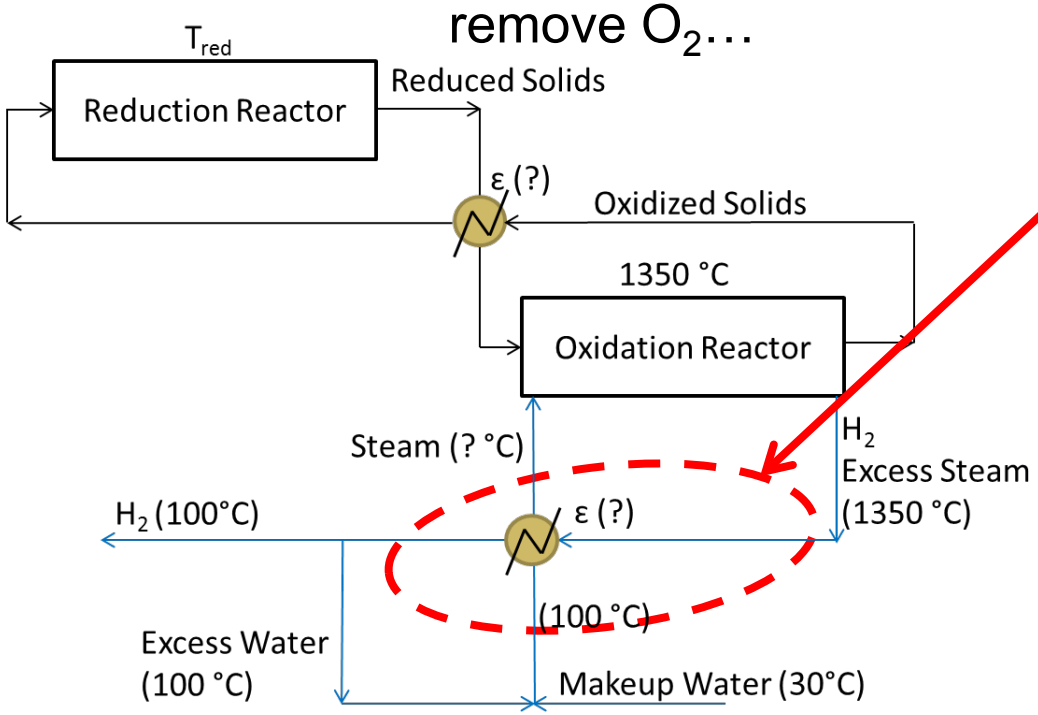
Conclusions:

- ε_{GG} has large positive impact on efficiency
- ε_{GG} is negatively correlated with ΔT_{opt}
- Kinetic effects will lower efficiency and shift ΔT_{opt} to lower values

Key Factors for Efficient Water Splitting

Red/Ox Thermal Cycling

Process efficiency is highly dependent on: (a) properties of Red/Ox materials – optimal T_{red}-T_{oxid}, kinetics, and robustness (cyclability)…; and (b) reactor design – reliability, scalability, ability to recuperate heat, ability to efficiently remove O_2…



<u>Staged steam / steam heat exchange is key</u>

Inconel: 100°C to 1000°C
Ceramic: 1000°C to >1350°C

"heating gases to 1200°C is almost guaranteed, 1300°C should work, 1500 °C could be possible, and even hotter may be possible"

Isothermal operation with perfect steam/steam heat exchange is theoretically most efficient Red/Ox

Accomplishments & Progress

<u>Active Ceramic Heat Exchanger Development</u>

Ceramatec (http://www.ceramatec.com/applications/heat-exchangers.php)
HTI (http://www.heatxfer.com/)
AGC (http://www.agcc.jp/2005/en/environment/03_04.html)

"Hercynite Cycle" Red/Ox Most Likely Reduces Through O Vacancy Formation

Materials Design and Properties

Using density functional theory (DFT), high temperature In-situ XRD, and SEM/EDS to identify "hercynite cycle" mechanism

- "Hercynite cycle" operates through an O vacancy mechanism
- Spinels enable high Fe content
- Al provides structural stability

Various reaction mechanism energies

	Displacement	Mixed Displacement	O Vacancy
Red	165 kJ/mol	150 kJ/mol	318 kJ/mol
Ox	77 kJ/mol	80 kJ/mol	-76 kJ/mol

Displacement mechanism

$CoFe_2O_4 + 3Al_2O_3 \rightarrow CoAl_2O_4 + 2FeAl_2O_4 + 1/2\ O_2$

$CoAl_2O_4 + 2FeAl_2O_4 + H_2O \rightarrow H_2 + CoFe_2O_4 + 3Al_2O_3$

Mixed displacement mechanism

$CoFe_2O_4 + 3Al_2O_3 \rightarrow Co_{0.5}Fe_{0.5}Al_2O_4 + 1/2\ O_2$

$Co_{0.5}Fe_{0.5}Al_2O_4 + H_2O \rightarrow H_2 + CoFe_2O_4 + 3Al_2O_3$

O-vacancy mechanism

$\mathbf{Co_{0.5}Fe_{0.5}Al_2O_4 \rightarrow Co_{0.5}Fe_{0.5}Al_2O_{4-\delta} + \delta/2\ O_2}$

$\mathbf{Co_{0.5}Fe_{0.5}Al_2O_{4-\delta} + \delta H_2O \rightarrow \delta H2 + Co_{0.5}Fe_{0.5}Al_2O_4}$

$\delta H_2O \rightarrow \delta H2 + \delta/2\ O_2$

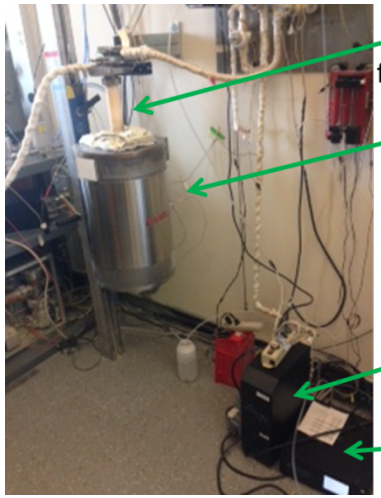
Accomplishments & Progress

Pseudo-isothermal water splitting

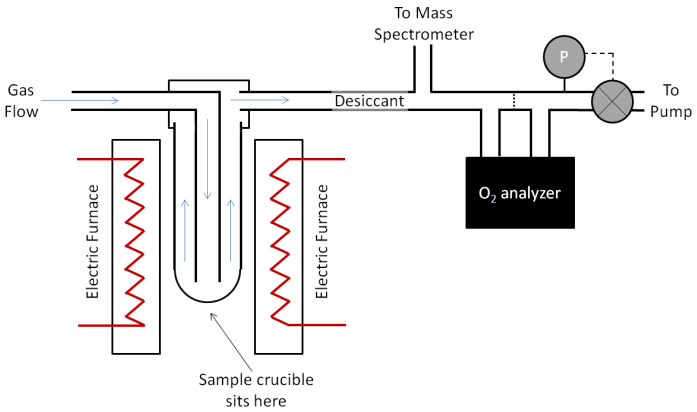
Materials Design and Properties

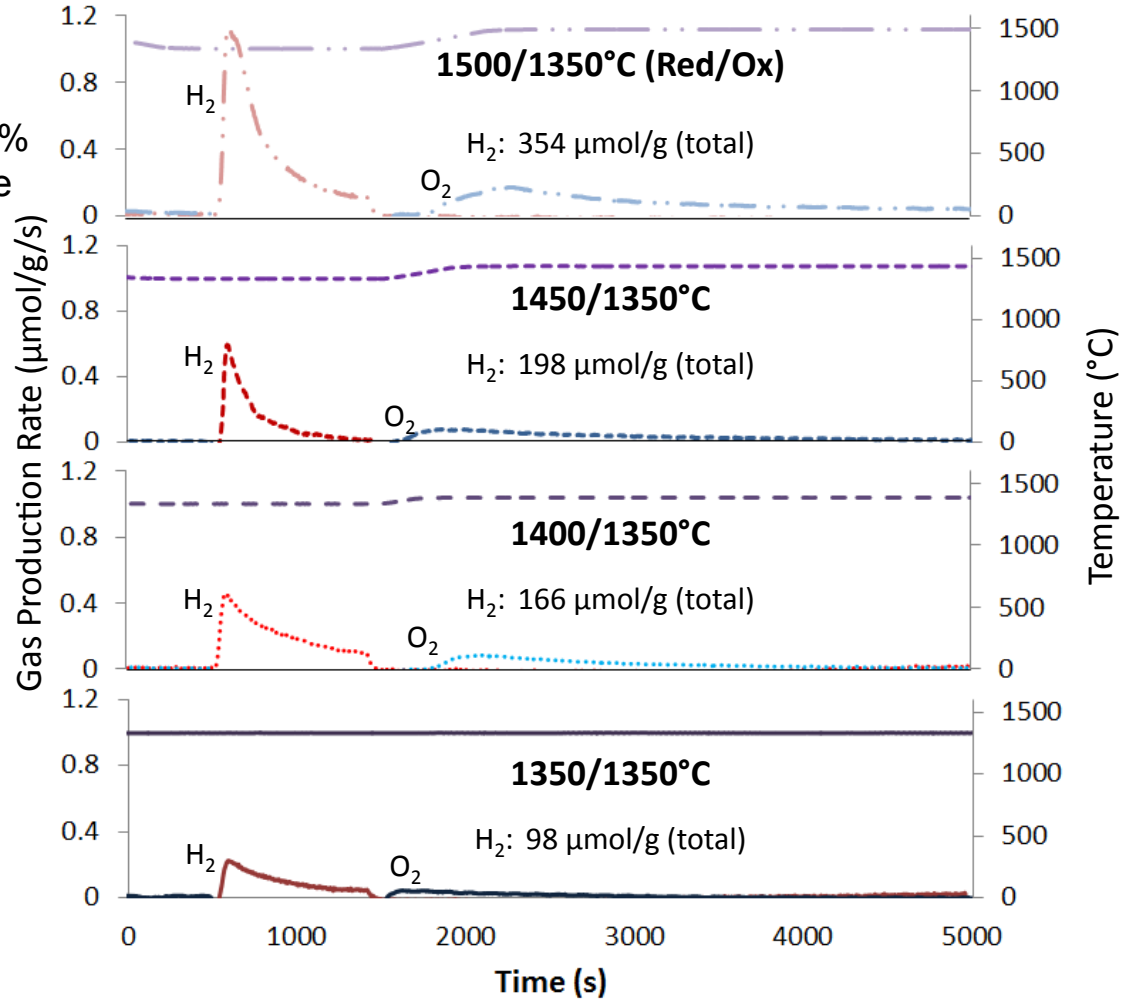
Reduction: 60 min at T_{red} in 300 sccm He

Oxidation: 15 min 50% $[H_2O]$ in 200 sccm He



85% active "hercynite cycle" material



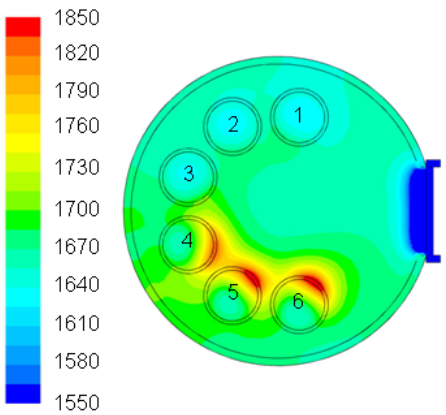


Higher reduction temperatures coupled with ΔT prevent simultaneous Red/Ox, enable high H_2 generation and capacity

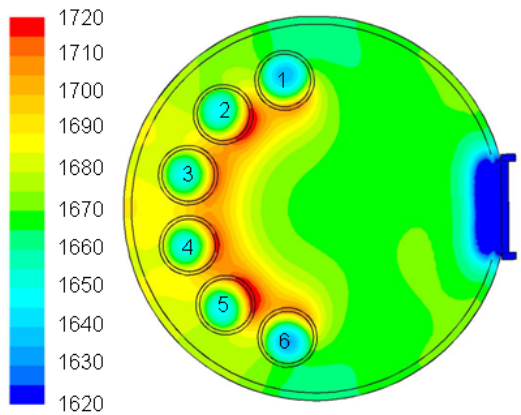
Accomplishments & Progress

Multi-tube Reactor Design Limitations

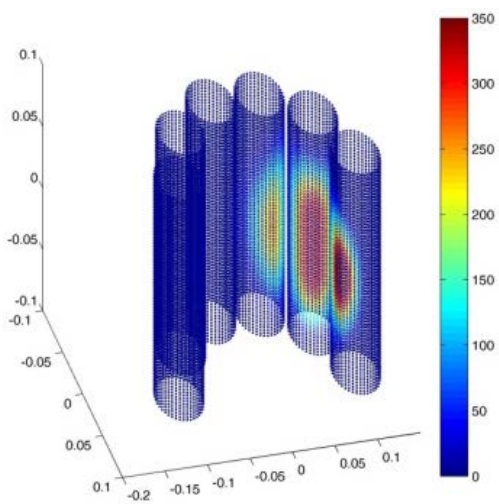
Reactor Design



Temperature Swing



Isothermal



Results for Multi-tube reactor design:

- Limited ΔT achievable in the tube based design due to radiation between tubes.
- Large ΔT within the tubes limits use of materials packed into reactor.

Need new reactor design

Principles for particle flow reactor:

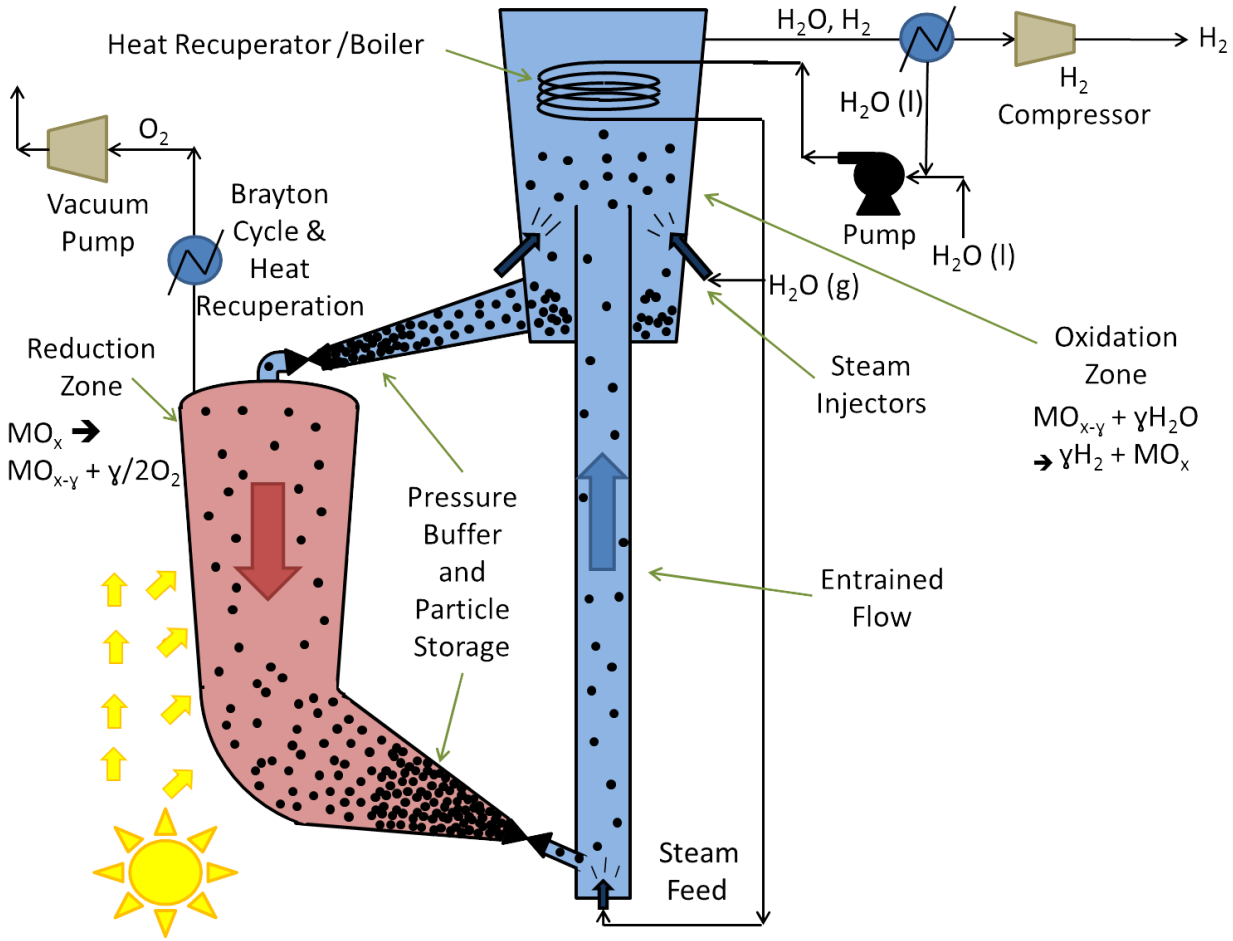
- Separate containment for Red/Ox
- Use flowing particles to enable even heating
- Decouple Red/Ox times

Solar Thermal Particle Flow Reactor

Reactor Design

Key Design Points

- Controllable ΔT; reaction decoupling
- Efficient/Scalable beam-up receiver
- Flowing "engineered" active particulate materials
- Transport limitations mitigated
- Heat recuperation
- Vacuum pumping O_2 removal

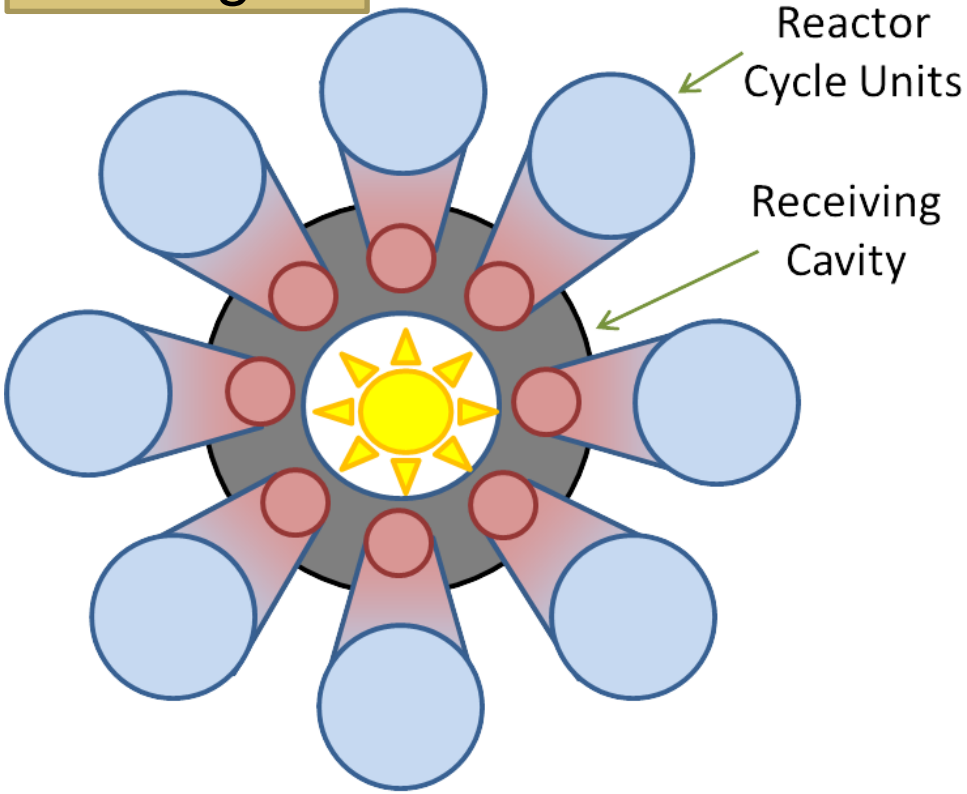


Robust Particle Flow is Critical

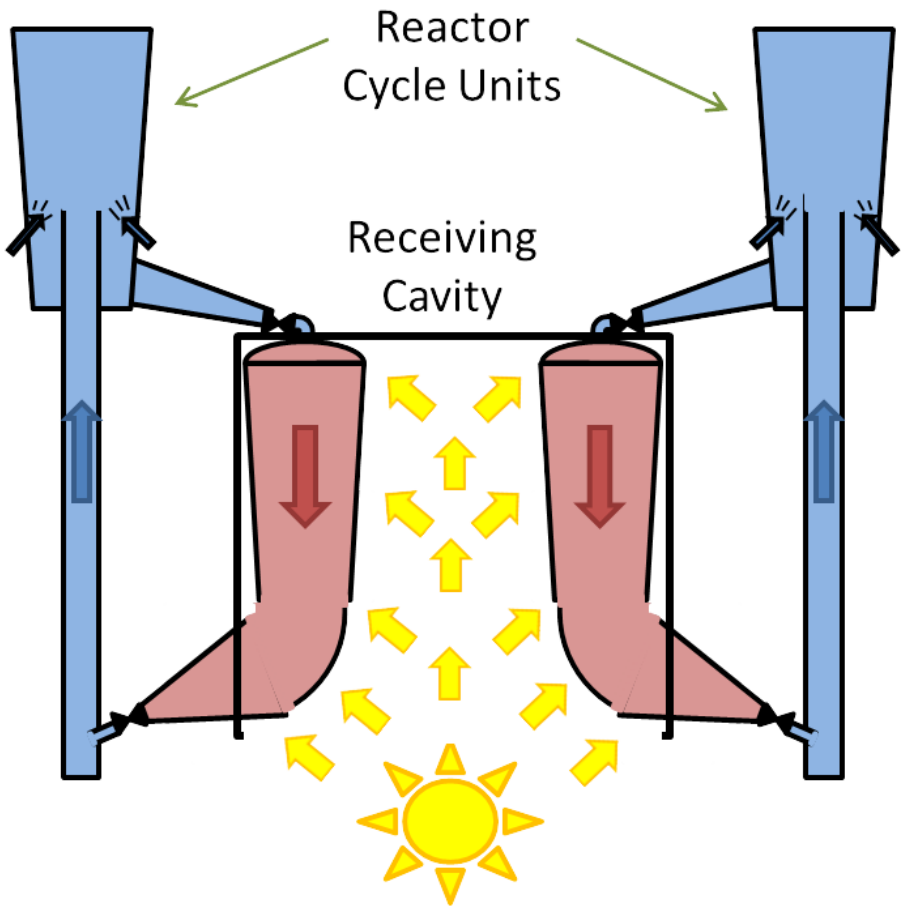
Accomplishments & Progress

Solar Thermal Particle Flow Reactor

Reactor Design



Top View



Side View

Accomplishments & Progress

Annual Particle Replacement Costs

Materials Design and Properties

Spherical particles minimize attrition & material deposition on colder surfaces by thermophoresis which are essential for long term, safe operation: **fabricate spray died particles**

"Engineering design" of Red/Ox particles to minimize replacement cost, C, is critical

Spray dried particles can operate up to a calculated lifetime of 396,000 cycles based on 1000 °C; 1000 hr runs for chemical looping combustion[1] (> 11 yr lifetime)

[1]C. Linderholm, *et al.*, *Fuel,* vol. 88, pp. 2083-2096, 2009.

- High reactivity/fast kinetics decreases flow rate for particles between reduction and oxidation reactors
- Durable particles increase number of cycles

Particle Robustness

$$C = \frac{8sryf}{n}$$

f	$2.00/kg H_2	
	Cycles	Years
0.1	10,561	0.30
0.3	31,683	0.90
0.5	52,805	1.51
0.7	73,926	2.11
1.0	105,609	3.01

C: replacement cost

s: materials cost

r: flow rate

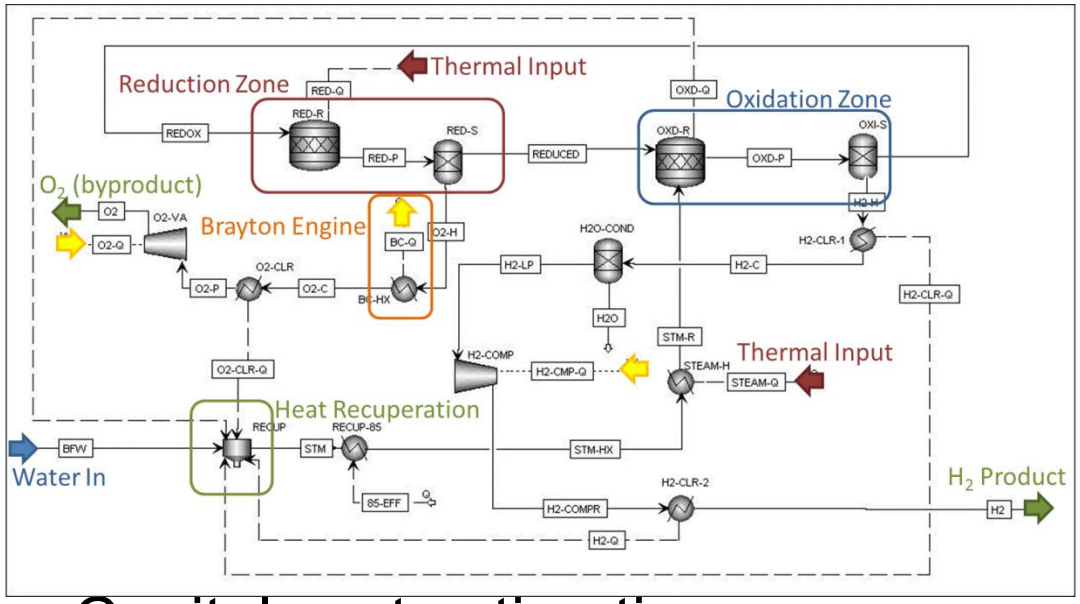
y: cycle days/year

f: fraction of replacement cost from reprocessing of material

n: cycles before replacement

- L.-S. Fan, *Chemical Looping systems for Fossil Energy Conversions*. American Institute of Chemical Engineers (AIChE) and John Wiley & Sons, Inc., 2010.

H2A Economics are Promising



Plant Capacity	50k kg H_2/day
Total Capital Investment	$70M
Tower Height	134 m
Number of Heliostats	4940
H2A H_2 Price	$1.97 / kg H_2

- Capital cost estimations
  - Scaled from previous analyses or estimated cost of material
  - Solar field/tower calculated from DELSOL3
- Operating cost estimations
  - Incorporated input streams, utilities, byproducts
  - Replacing all active material every 3 years
- *"Living" H2A for "hercynite" cycle 1st pass complete*

Accomplishments & Progress

Collaborations

- High-flux Solar Furnace On-sun Operations at NREL
- Laser-assisted Stagnation Flow Reactor Operations at Sandia – Livermore (one Ph.D. student in-place at all times; two students in summer, 2013)
- Long term materials testing – ETH Zurich
- Future Reactor system modeling - ANU

Weaknesses Addressed

- Weakness – Not enough time was spent on reactor design and scale-up
- Addressed – A major effort was made in modeling the multi-tube reactor configuration – a paper has recently been accepted for publication in Solar Energy.

- Weakness – Active materials with Red/Ox reaction back and forth may offer integrity challenges that will only be apparent after repeated cycling
- Addressed – A current task is to operate for at least 100 cycles using the Gold IR furnace at partner ETH Zurich; further, we propose making "engineered particles" that are flowable and attrition resistant; we recognize the value of understanding C=8sry/n $/yr

- Weakness – there are more advanced reactor concepts under development that might be suitable to achieve an additional raise in the efficiency of the process
- Addressed – We are proposing a particle flow reactor with a flexible ΔT and ΔP, and efficient "beam-up" design to minimize convection and multiple solar reflection losses, high-temperature mechanical parts prone to break, and scale-up limitations as well as thermophoretic deposition challenges on quartz windows; we are focused on flowable/attrition resistant active "engineered particles" and proper containment materials.

Future Work

- Red/Ox cycling
  - Incorporate Red/Ox extents from “hercynite cycle” and new materials into model to determine “optimal” ΔT
- Materials Design and Properties
  - Increase range of “hercynite cycle” pseudo-isothermal data
  - Assess long term materials stability in a gold IR furnace at ETH-Zurich over > 200 cycles
  - Determine long term stability of spray dried particles
  - Develop improved “hercynite cycle” and perovskite materials for STWS using high through-put screening methods
  - Investigate improved materials extent of reduction for various P_{O2} and P_{H2O}
- Reactor Design
  - Develop CFD model for new particle flow reactor design
  - Investigate ALD coatings on SiC to develop suitable containment materials
- Efficient H_2 production
  - Improve H2A analysis by including additional kinetics/thermodynamic data
  - Interface with heat exchanger producers to develop high T systems

Summary

- Red/Ox cycling
  - Obtained Rasirc Rainmaker© steam generator
  - ΔT down to 0 (isothermal Red/Ox) is possible, enabling large design space for optimization
  - Optimal ΔT is dependent on active materials, gas/gas heat transfer efficiency and temperature of H_2/H_2O separation
- Materials Design and Properties
  - "Hercynite cycle" appears to operate through O vacancy mechanism (preliminary)
  - Developed oxidation kinetics for high temperature CO_2 splitting
  - "Pseudo-isothermal" processing enables high reduction extent and rapid oxidation kinetics without simultaneous reduction/oxidation occurring
  - Obtained Büchi Lab bench spray drier
- Reactor Design
  - Surround sun reactor doesn't enable large ΔT, and temperature is not easily controllable
  - Developed particle flow reactor concept to avoid this problem
- Efficient H_2 production
  - Carried out H2A analysis on the new reactor concept and found we can meet the price and efficiency targets but not the tower or materials cost targets

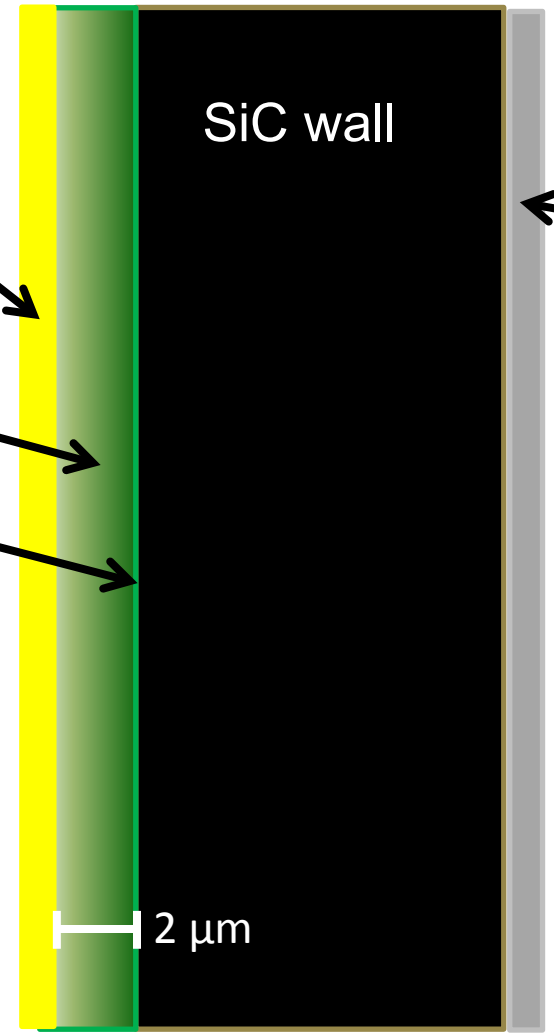
Acknowledgements:

- 27 Peer-reviewed scientific papers published since 2012;
- 5 U.S. Patents issued since 2012;
- Four students won 1st Place Poster Competition and two took 2nd Place in the past three Annual AIChE Meetings in Minneapolis (2011), Pittsburgh (2012) and San Francisco (2013)

Technical Backup Slides

Overcoming Reactor Materials Challenges

T = 1350°C, released O_2
(reduction reactor step)
or
T = 1350°C, flowing $H_2O(v)$
(oxidation reactor step)



<u>Overall Al_2O_3 ALD</u>

$Al_2(CH_3)_6$ (TMA) + $3H_2O$ ➔ Al_2O_3 + $6CH_4$
T = 175°C

<u>Overall SiO_2 ALD</u>

$SiCl_4$+ $2H_2O$ ➔ SiO_2 + 4HCl
T = 327°C or
TMA + tris(tert-pentoxy)silanol (TPS) ➔
T = 175°C

Future Work

[1]J. I. Federer, *et al.*, Oak Ridge National Laboratory Report No. ORNL/TM-11828, 1991.
[2]R. Krishnamurthy, *et al.*, *J. Am. Ceram Soc,* vol. 88, pp. 1099-1107, 2005.
[3]M. L. Auger, *et al.*, *J. Am. Ceram Soc,* vol. 83, pp. 2429-2435, 2000.
[4]S. M. Zemskova, *et al.*, *Journal De Physique Iv,* vol. 11, pp. 861-867, Aug 2001.

STH Efficiency Calculation Efficiency

- Adapted from Ermanoski *et al. (PCCP, 2014)*
- $\eta_R = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_A}$
  - $\dot{n}_{H_2} = \frac{\dot{Q}_{TH}}{Q_{mol}}$, $\dot{Q}_{TH} = A \times \dot{Q}_A - P_{rad}$, $\dot{Q}_A = \frac{\dot{n}_{H_2} Q_{mol}}{A - \frac{\epsilon \sigma T_{wall}^4}{\zeta_{1sun} \eta_{optic} C}}$, $P_{rad} = \epsilon \sigma \frac{\dot{Q}_A}{\zeta_{1sun} \eta_{optic} C} T_{wall}^4$
  - $Q_{mol} = Q_{TR} + Q_{SH} + Q_{AUX}$
    - $Q_{TR} = \Delta H_r$ and $Q_{SH} = \frac{C_P}{\Delta \delta} \Delta T (1 - \varepsilon_R)$
    - $Q_{AUX} = \left(Q_{H_2O} + Q_{pump} + Q_{mech} + Q_{sep}\right) - \left(Q_{MOX} + Q_{SH,L} + Q_{O_2}\right)$
      - $Q_{H_2O} = \left(C_P^{H_2O} MW_{H_2O} (n_{wh} + 1)(T_{OX} - T_{amb}) + \Delta H_{vap}^{H_2O} MW_{H_2O}\right)$
        $-\varepsilon_{GG}\left(C_P^{H_2O} MW_{H_2O} n_{wh} (T_{OX} - T_{amb}) + C_P^{H_2} MW_{H_2} (T_{OX} - T_{amb}) + \Delta H_{vap}^{H_2O} MW_{H_2O}\right)$
      - $Q_{pump} = \frac{(P_{amb} - P_{TR})\left(\frac{n_{O_2} RT^\circ}{P^\circ}\right)}{\eta_{pump}}$
      - $Q_{sep} = \frac{T_{OX}}{\eta_{sep}} \left(\Delta S_{\text{mix}}^{H2} + \Delta S_{\text{mix}}^{H2O} - \Delta S_{\text{mix}}^{initial}\right)$
      - $Q_{MOX} = \Delta H_r - \Delta H_{cH_2}^\circ$
      - $Q_{SH} = \frac{C_P}{\Delta \delta} \Delta T \varepsilon_R$
      - $Q_{O_2} = C_P^{O_2} MW_{O_2} n_{O_2} (T_{red} - T_{amb})$

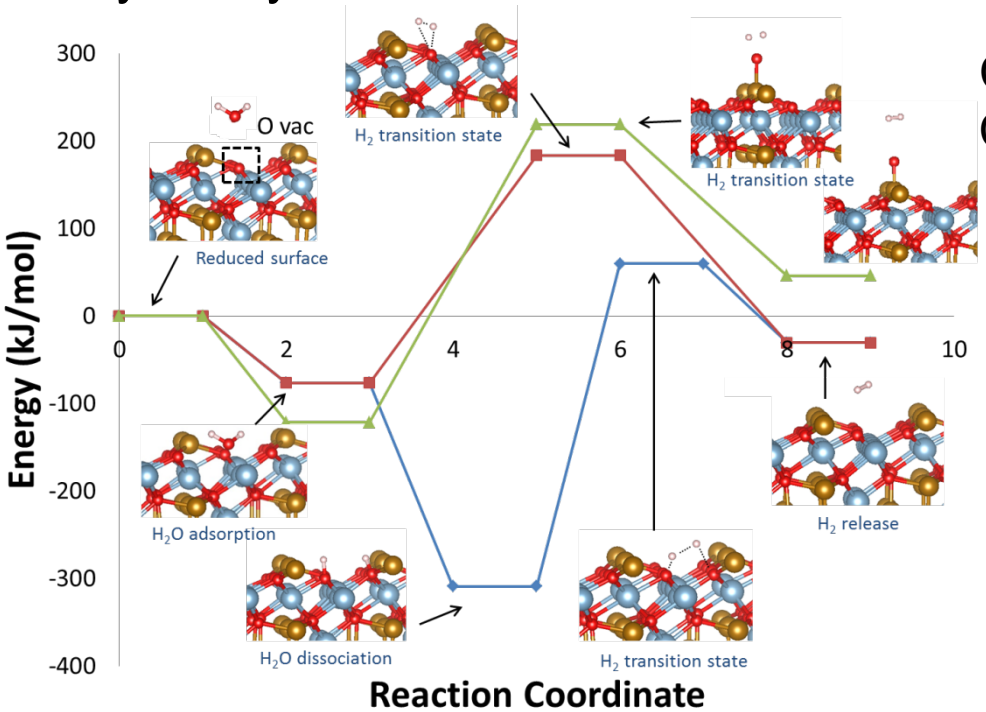
"Hercynite Cycle" Red/Ox Most Likely Reduces Through O Vacancy Formation

Materials Design and Properties

Using density functional theory (DFT), high temperature In-situ XRD, and SEM/EDS to identify "hercynite cycle" mechanism

Various reaction mechanism energies

	Displacement	Mixed Displacement	O Vacancy
Red	165 kJ/mol	150 kJ/mol	318 kJ/mol
Ox	77 kJ/mol	80 kJ/mol	-76 kJ/mol



$$CoFeAl_2O_4 \rightarrow CoFeAl_2O_{4-\delta} + \delta/2\ O_2$$
$$CoFeAl_2O_{4-\delta} + \delta H_2O \rightarrow \delta H2 + CoFeAl_2O_4$$
$$\delta H_2O \rightarrow \delta H2 + \delta/2\ O_2$$

- "Hercynite cycle" operates through an O vacancy mechanism
- Spinels enable high Fe content
- Al provides structural stability

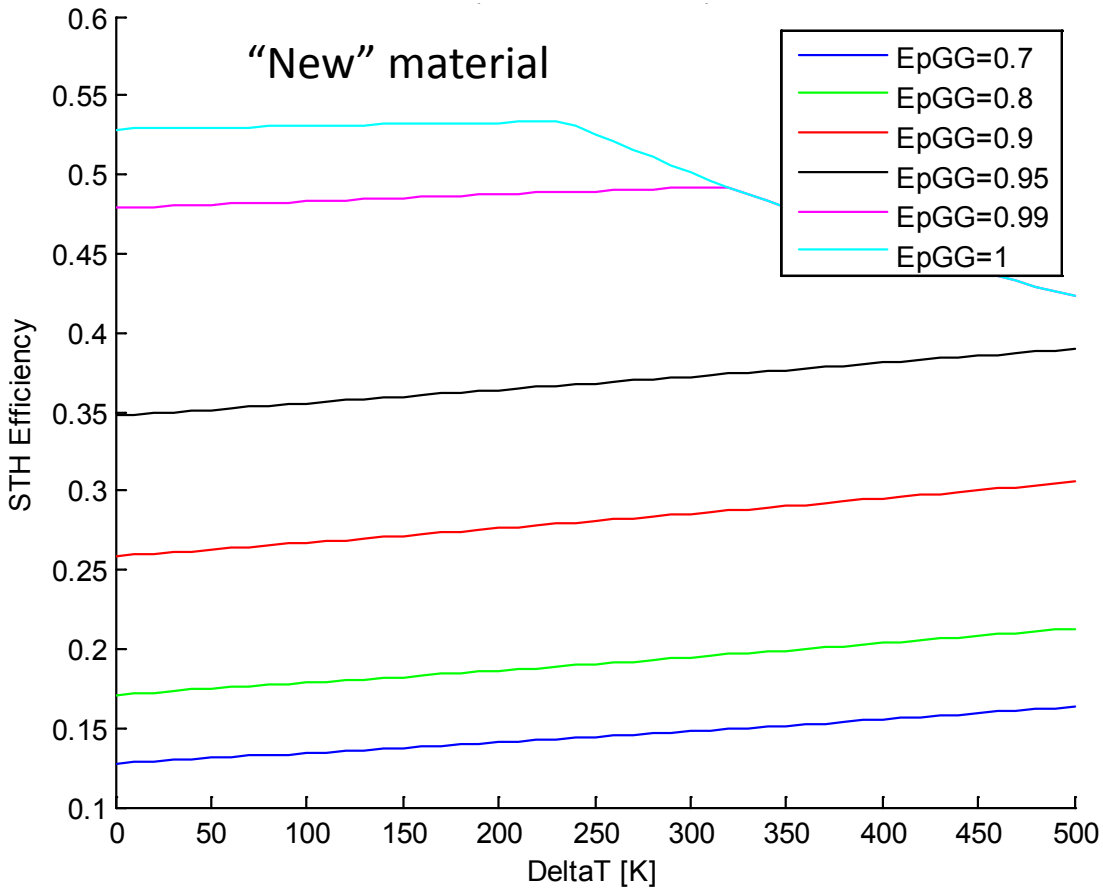
Accomplishments & Progress

Materials Dependent Properties

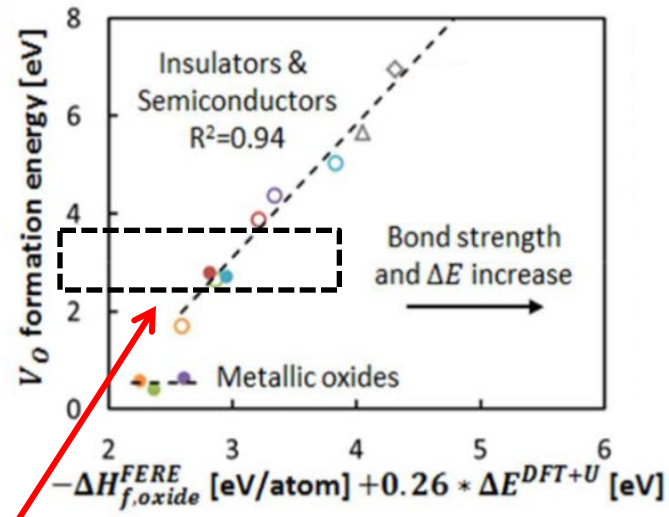
Red/Ox Thermal Cycling

Parameters:

- Degree of reduction = 0.1
- ΔH_{red} = 310 kJ/mol



New materials design:



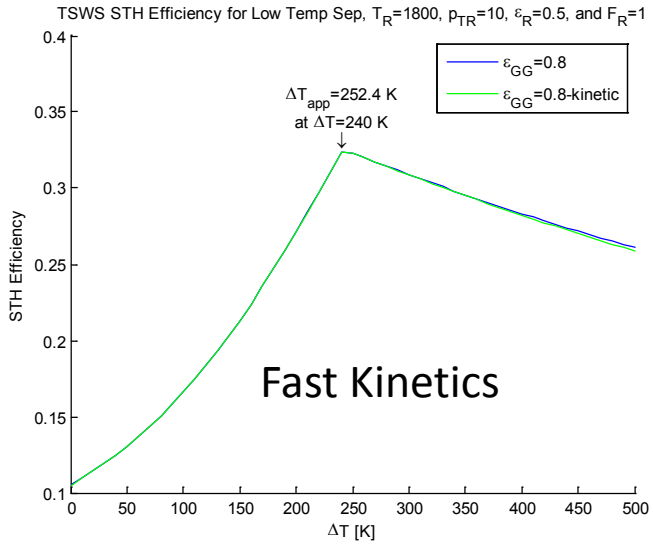
Materials properties are key in achieving high efficiencies:

- Need low ΔH_{red} (high enough for reaction)
- Large extent of Red/Ox possible

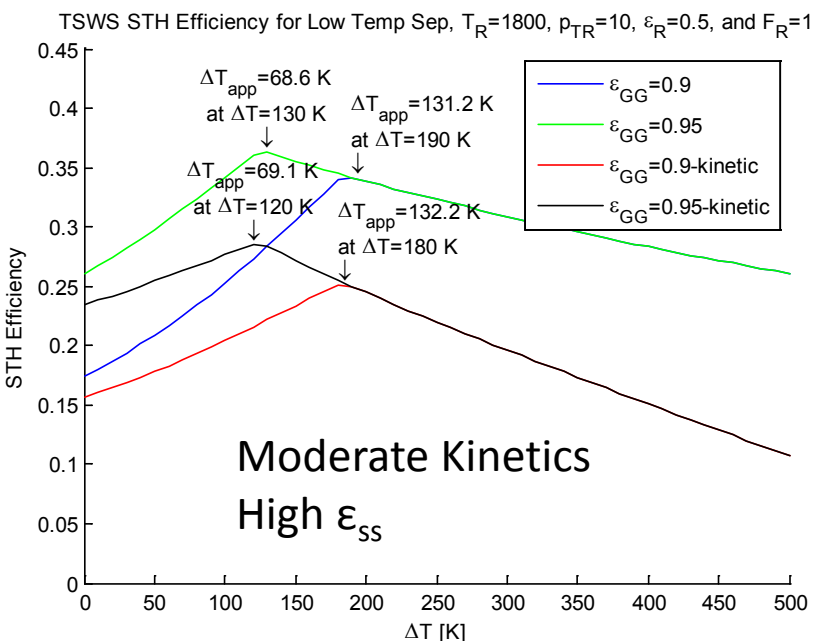
Deml, A. *et al. In press* *Energy and Environ. Sci.*

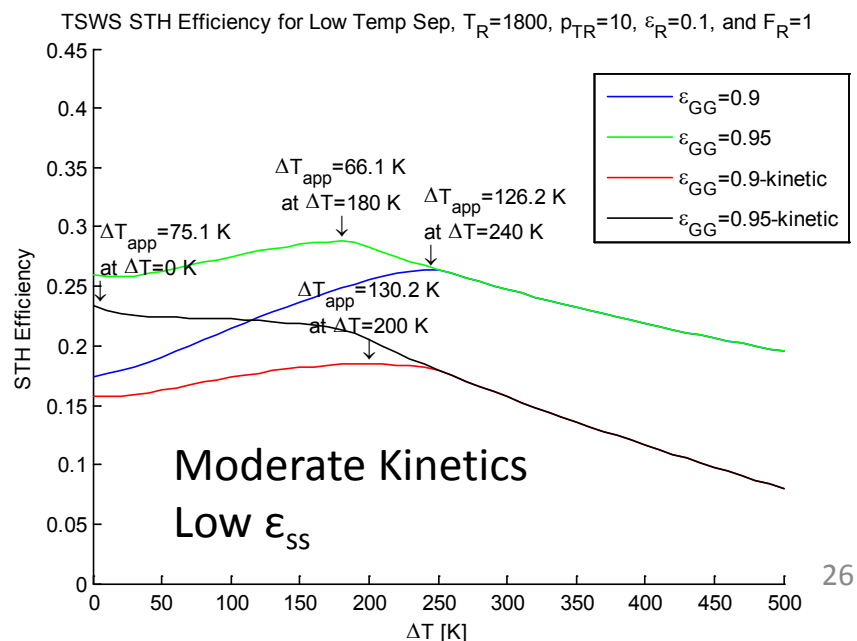
Accomplishments & Progress

Kinetic Effects on PITWS Efficiency



- Fast kinetics and high ε_{ss} approach thermo efficiency limit
- Moderate kinetics lowers overall efficiency slightly
- Low ε_{ss} shifts ΔT_{opt} to lower values





Annual Particle Replacement Costs

Materials Design and Properties

Particle Robustness

$$C = \frac{8sry}{n}$$

C: replacement cost

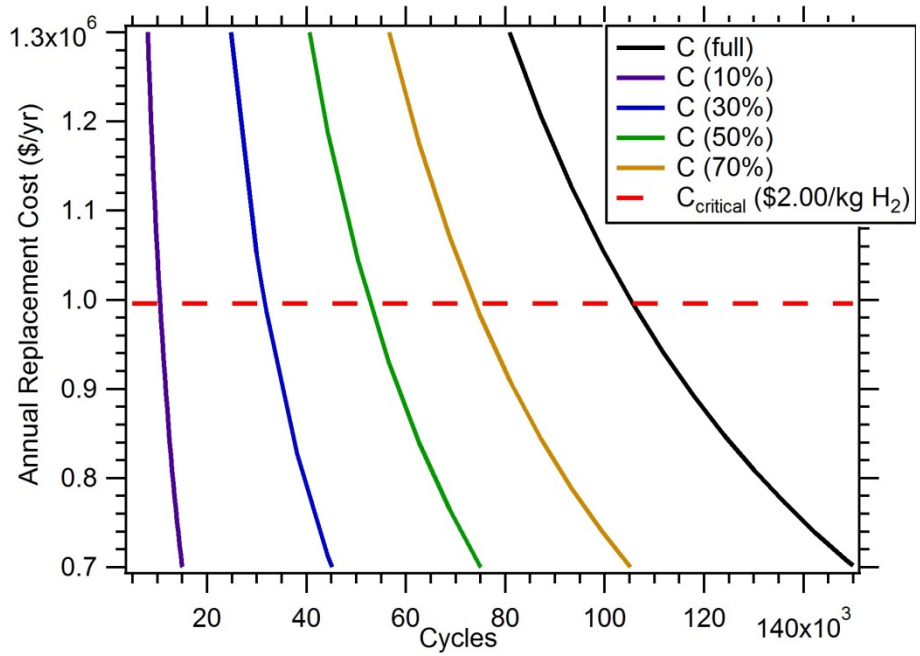
s: materials cost

r: flow rate

y: cycle days/year

n: number of cycles before replacement

Replacement Cost Fraction	$2.00/kg H_2	
	Cycles	Years
0.1	10,561	0.30
0.3	31,683	0.90
0.5	52,805	1.51
0.7	73,926	2.11
1.0	105,609	3.01



- Spray drying active materials eliminates sharp edges which tend to attrite & deposit on colder surfaces by thermophoresis
- High reactivity/fast kinetics decreases flow rate for particles between reduction and oxidation reactors
- Durable particles increase number of cycles

"Engineering design" of Red/Ox particles to minimize replacement cost, C, is critical

Spray dried particles can operate up to a calculated lifetime of 396,000 cycles based on 1000 °C; 1000 hr runs for chemical looping combustion: (= 3.75 yr lifetime for $2/kg H_2 target)

C. Linderholm, *et al.*, *Fuel*, vol. 88, pp. 2083-2096, 2009.

- L.-S. Fan, *Chemical Looping systems for Fossil Energy Conversions*. American Institute of Chemical Engineers (AIChE) and John Wiley & Sons, Inc., 2010.