# Flowing Particle Bed Solarthermal Redox Process to Split Water

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University of Colorado at Boulder

6/11/2015

Project ID: PD114

# Overview:
# Year 1 of 3-Year Project

## Timeline

Project Start Date: 9/1/2014

Project End Date: 8/31/2017

% Complete: 15%

## Budget

Total project funding: $2,000,000

Sub-contract to NREL: $450,000

Total recipient cost share: $6,250

Total DOE funds spent*: $109,203

*as of 3/31/2015

**TRL 2 → TRL 3**

## Technical Barriers Addressed

S. High-temperature robust materials

W. Materials and catalysts development

X. Chemical reactor development and capital costs

## Partners/Collaborators

National Renewable Energy Laboratory (NREL), Golden, CO

- Solar testing facility and capabilities

Musgrave Group*, CU Boulder

- Active materials discovery and DFT modeling (*NSF/DOE Funding – joint FOA)

Alan Lewandowski, Consultant

- Solar field design

# Relevance:
# Renewable Efficient Hydrogen Generation

***Project Objective:* Design and test individual components of a novel flowing particle solarthermal water splitting system capable of producing 50,000 kg $H_2$/day at a cost < \$2/kg $H_2$**

- Identify and develop high-performance active material formulations
- Synthesize flowable, attrition-resistant, long-use spherical particles from low-cost precursors
- Demonstrate high-temperature tolerant, refractory, non-reactive containment materials
- Construct flowing particle redox test system and test components of system
- Monitor progress toward cost target by incorporating experimental results into frequently updated detailed process model and H2A
- On-sun production for a full solar day
- Move from TRL 2 to TRL 3

***This Reporting Period:***

✓ Demonstrated production of spherical spray dried active materials (**Barrier W**)
✓ Started construction of flowing particle redox test system (**Barrier X**)
✓ Developed model to understand process efficiency and sensitivity of parameters
✓ Developed improved understanding of hercynite cycle chemistry (**Barrier W**)

# Approach:
# Iterative Materials and Reactor Development

## Reactive Particles

Produce and characterize reactive materials and engineered particles

- M1.5: SFR will be upgraded with improved mass spec and steam feeding systems. FY15Q3 (75% done)
- GNG1: Spray dried particles that produce ≥150 µmol H2/g. FY15Q4 (50% done)
- GNG2: Spray dried particles that produce ≥150 µmol H2/g and lose ≤10% reactivity between 100th and 200th cycle. FY16Q4 (10% done)

## Reactor Design

Construct lab particle flow reactor system to test the individual sections of the reactor design.

- M3.1: Particle flow Redox test system constructed and operated at up to 1500°C. FY15Q4 (50% done)
- GNG4:Demonstrate operation of particle flow redox test system by reducing/oxidizing >1g of active material. FY15Q4 (25% done)

## Efficient, Cost Effective $H_2$

Ongoing updates to the process model and H2A to reflect current and future reactive materials properties

## Containment Materials

Develop thermal shock resistant containment materials that are compatible with steam and redox materials.

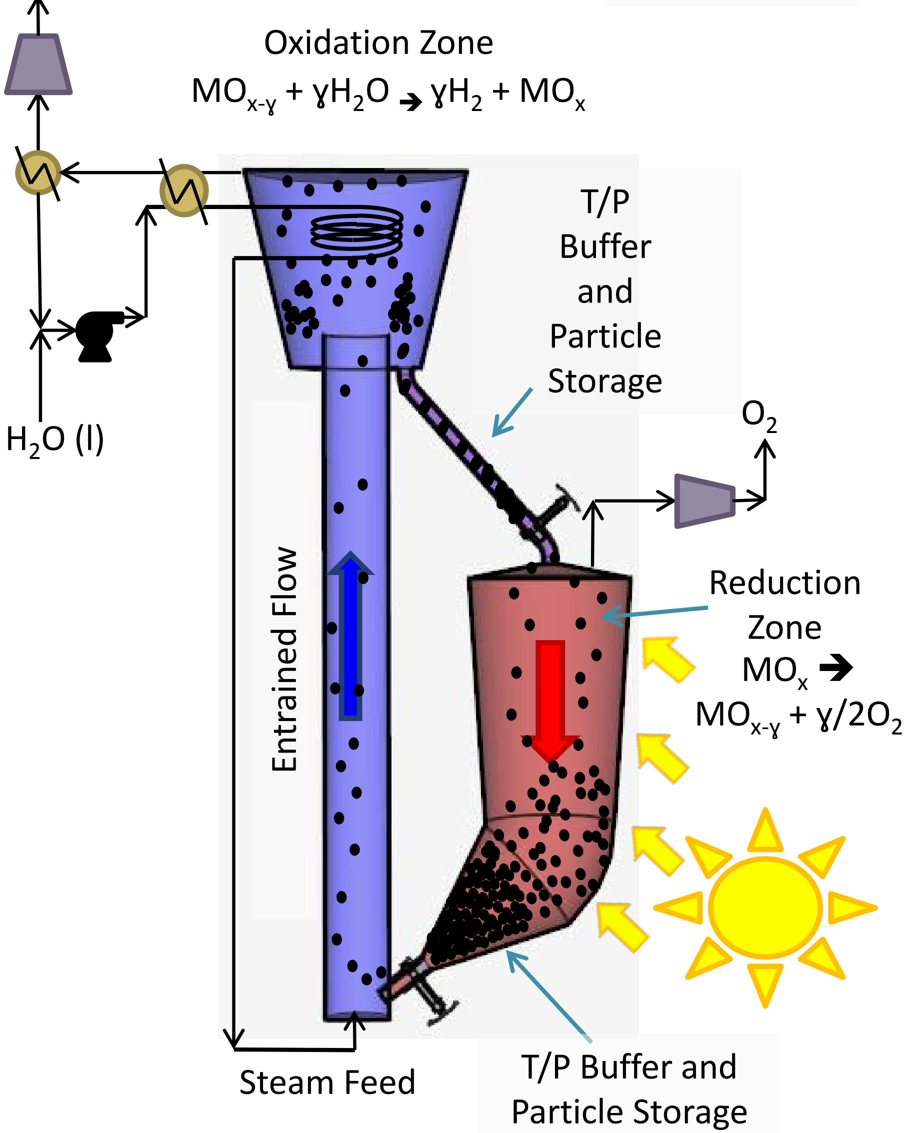
- M2.1: Synthesis and characterization of coated SiC powders. FY16Q4 (10% done)
- M2.2: Selection of preferred coating material based on TGA runs. FY16Q4 (0% done)
- M2.4: Coated containment tube system constructed. FY16Q1 (5% done)
- GNG4: Coated SiC with ≥25% reduction in steam reactivity. FY16Q4 (0% done)

## On-Sun Production

Future production of $H_2$ with reactive engineered particles (FY17)

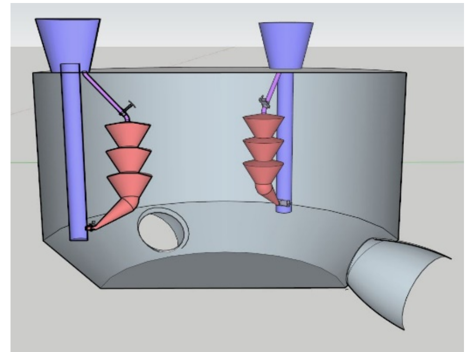
# Accomplishments and Progress: Updated Reactor Design

## Reactor Unit Concept (not to scale)

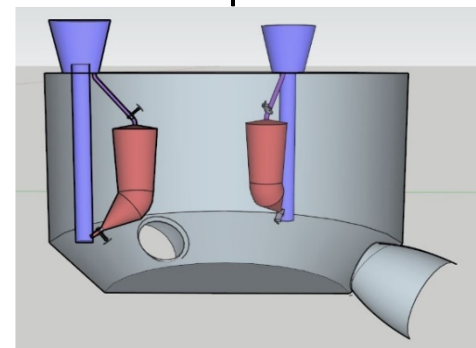



## Updated Receiver Design

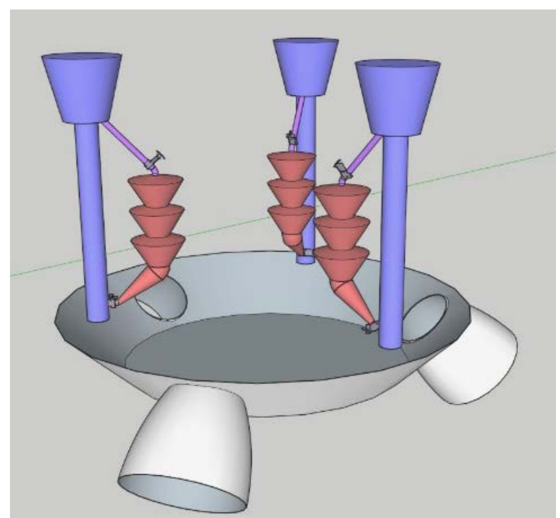
Vacuum:

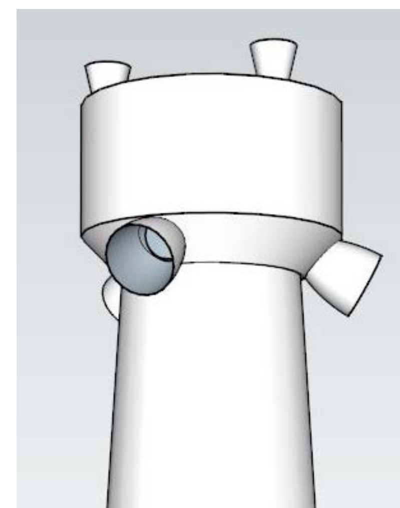


Inert Sweep:



Multiple reactor units on top of central receiver

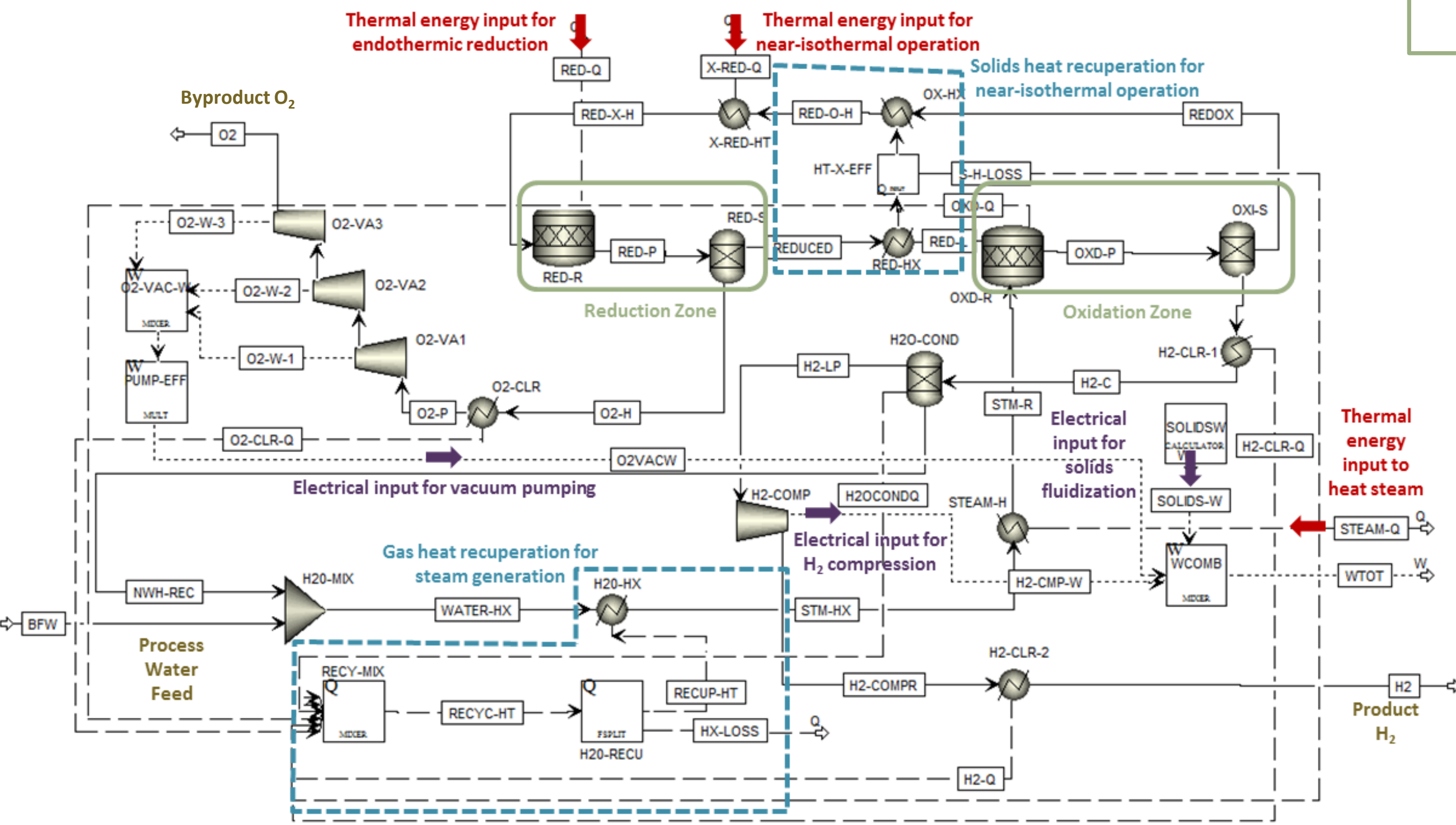




# Accomplishments and Progress: H2A AspenPlus® Process Model

***AspenPlus process model updated to incorporate experimental results***

- Updated reaction enthalpies from DFT calculations
- Updated temperature-dependent material activities from SFR experimental results




*AspenPlus Process Flow Diagram*

***Model expanded to incorporate more operation conditions***

- Added excess steam flow to facilitate thermodynamically favorable oxidation conditions
- Added capacity to operate at near-isothermal conditions (with solids heat exchange)
- Added staged vacuum
- Added work for solids fluidization
- Added blocks for simple sensitivity analysis of heat exchanger effectiveness

# Accomplishments and Progress: H2A Techno-Economic Analysis

Updated H2A with new solar field model

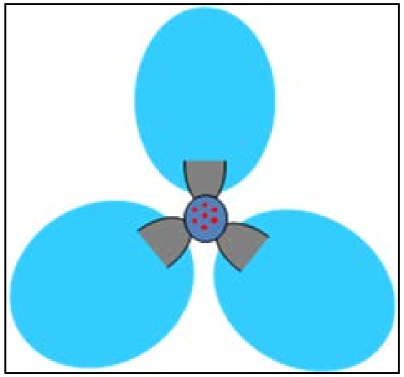
- Three solar fields direct to one central tower with three secondary concentrators
- Ideal setup for 160 MW plant is 4000x concentration with one 249 m central tower

More detailed capital costs of high temperature reactor components

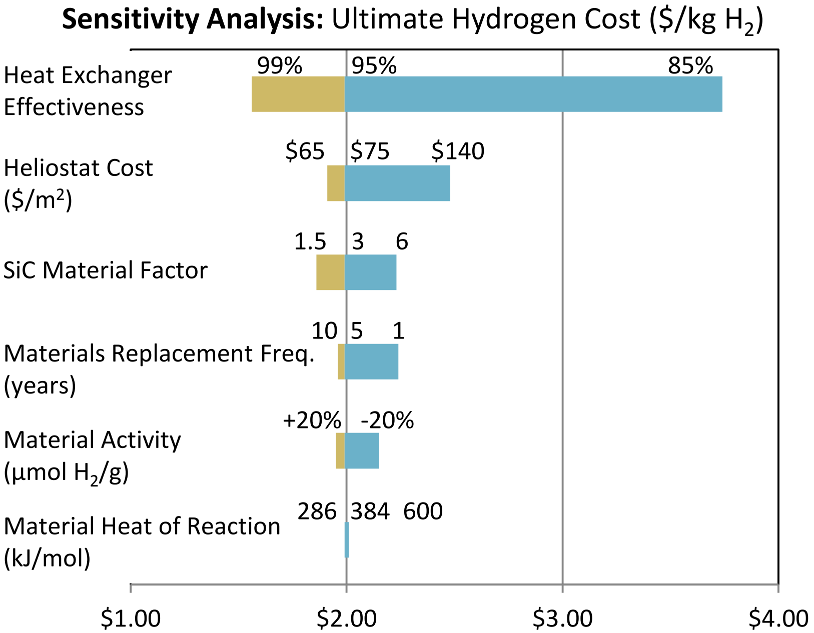
- Used updated system design and CapCost software to estimate unit cost of SiC reactors

***Updated H2A predicts system will achieve \$2/kg $H_2$ ultimate cost goal***

| Cost Drivers | 2015 | 2020 | Ultimate |
|---|---|---|---|
| Heat exchanger effectiveness | 85% | 90% | 95% |
| SiC material factor (x higher than carbon steel) | 6 | 5 | 3 |
| Replacement frequency (years) | 2 | 5 | 5 |
| Material activity (µmol $H_2$/g) | 354 (current material measured value) | 389 (10% greater than current material) | 425 (20% greater than current material) |
| Enthalpy of reaction (kJ/mol) | 384 (current result of DFT model for hercynite) | 346 (10% lower than current result) | 307 (20% lower than current result) |
| Cycle time (min) | 20 | 9 | 5 |
| Heliostat cost (\$/m²) | \$140 | \$75 | \$75 |
| **Cost $H_2$ (\$/kg)** | **\$14.67** | **\$3.64** | **\$1.99** |



*Concept cartoon of new three-lobed solar field design*




***Heat exchanger effectiveness, high-temperature SiC reactor materials costs, and active material replacement frequency and activity are major cost drivers that this project seeks to impact***

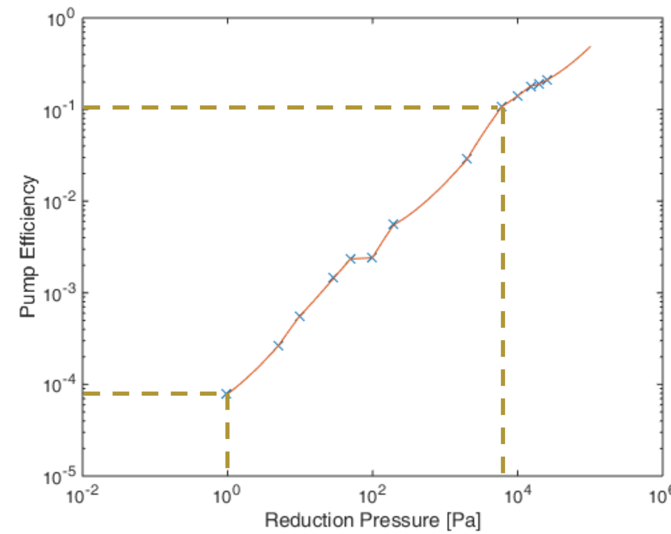
# Accomplishments and Progress: Low Vacuum Pump Efficiency

**Simple vacuum reduction leads to low efficiency**

- Vacuum pumps are inherently less efficient than atmospheric or positive-pressure pumps
- Low pressure useful for chemical thermodynamics, but leads to low efficiency

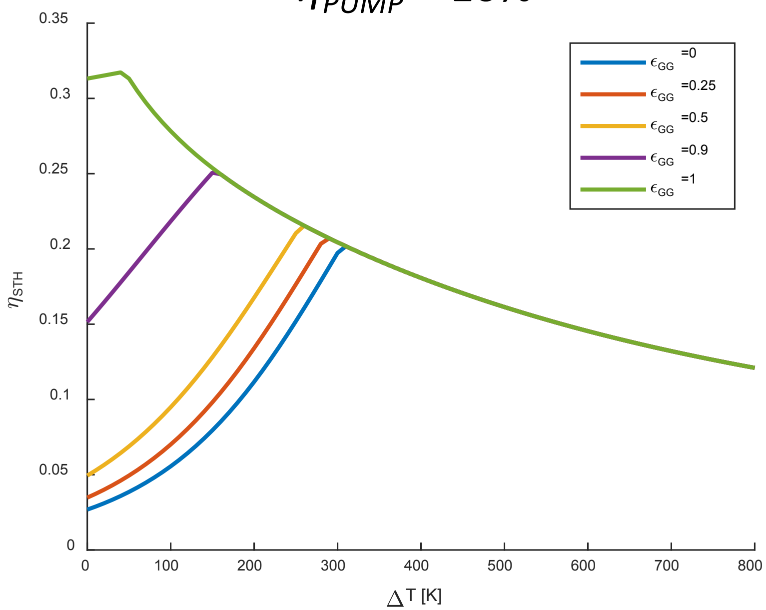
*$T_{RED}$ = 1800 K*
*$p_{RED}$ = 1 Pa*

*Calculations based on ceria active material*

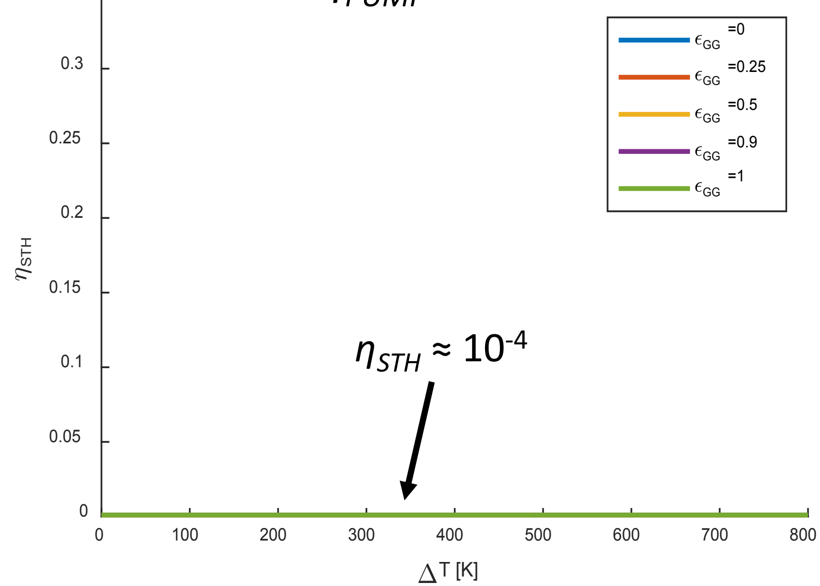



B. Bulfin, *et al.*, *Energy & Fuels*, 29, pp.1001-1009, 2015

$\eta_{PUMP}$ = 10%



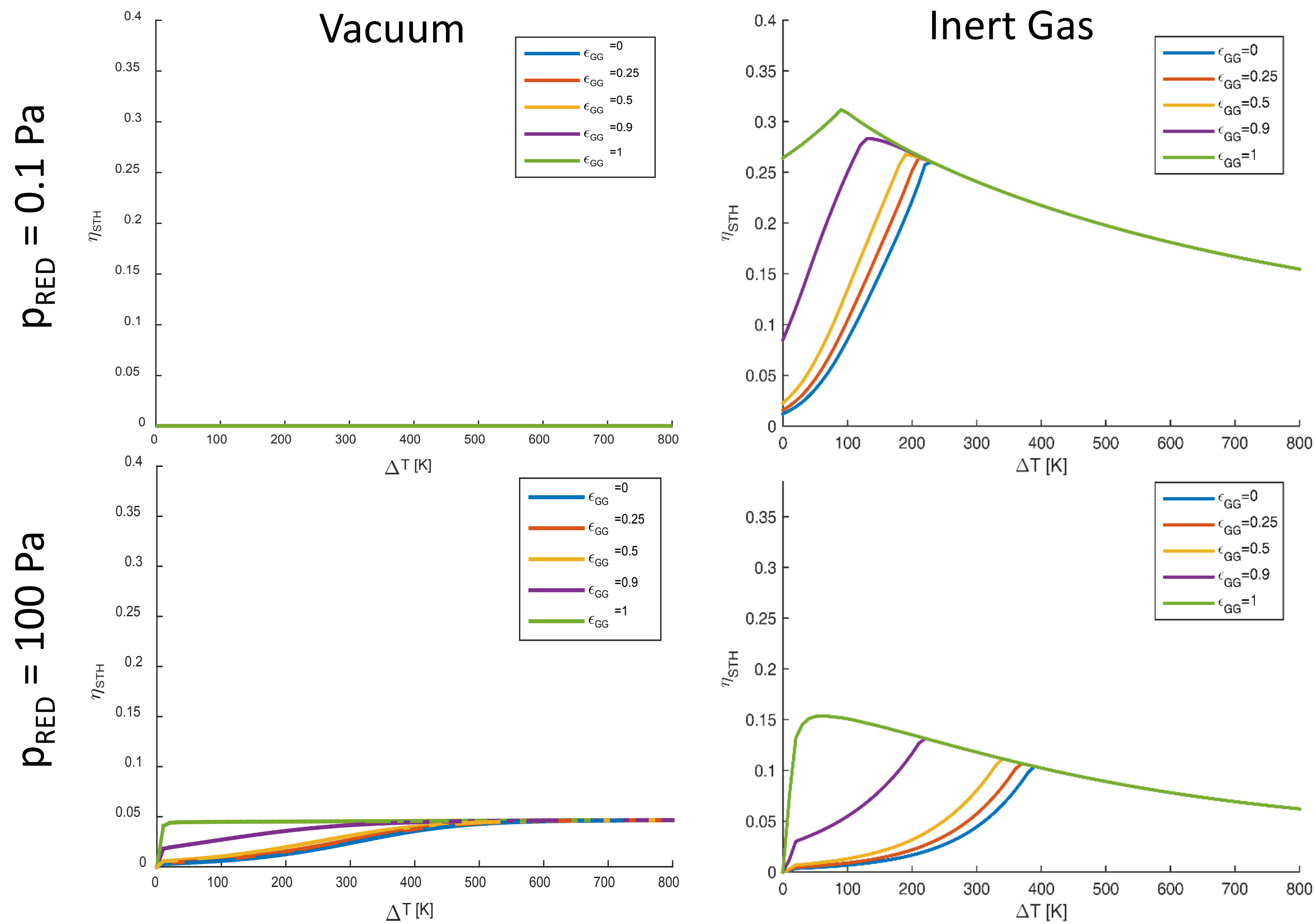

$\eta_{PUMP}$ = 0.08%



# Accomplishments and Progress: Inert Gas Reduction Shows Promise

**Inert sweep gas enables higher efficiency**

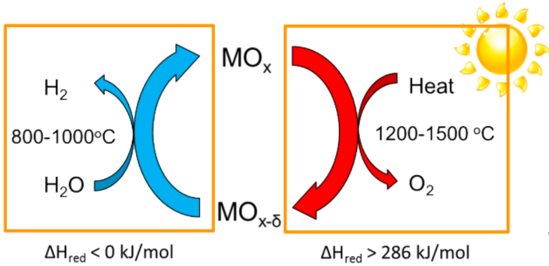
- Estimating energy required to separate $O_2$/inert
- Increased extent of reduction reduces steam required for oxidation
- Can also increase reduction reaction rate (not considered here)




*Calculations based on ceria active material*
*$T_{RED}$ = 1800 K*

# Accomplishments and Progress: Understanding materials and predicting properties

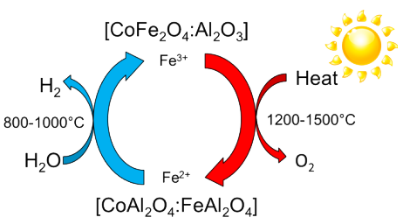
## Computational materials analysis




Use the reduction enthalpies to predict STWS abilities

Overall:
$H_2O \rightarrow H_2 + 1/2\ O_2$ ($\Delta H_{ws}$ = 286 kJ/mol)

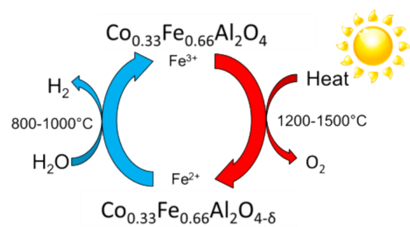
**Displacement mechanism**




$\Delta H_{red}$ = 150 kJ/mol

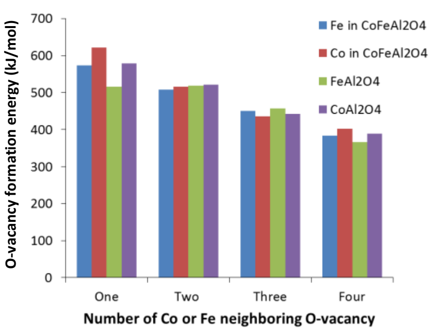
Not thermodynamically viable

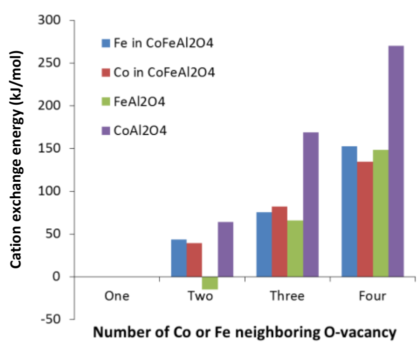
**O-vacancy formation mechanism**




$\Delta H_{red}$ = 384 to 621 kJ/mol

Thermodynamically viable



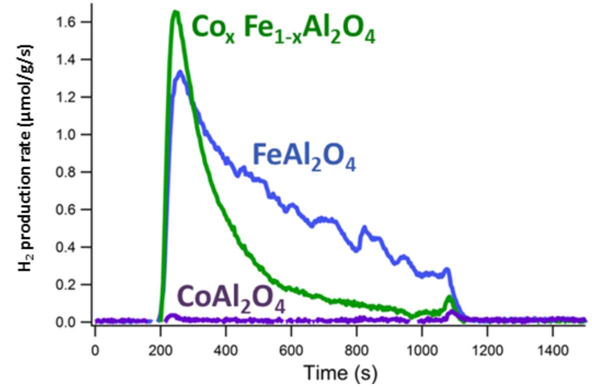



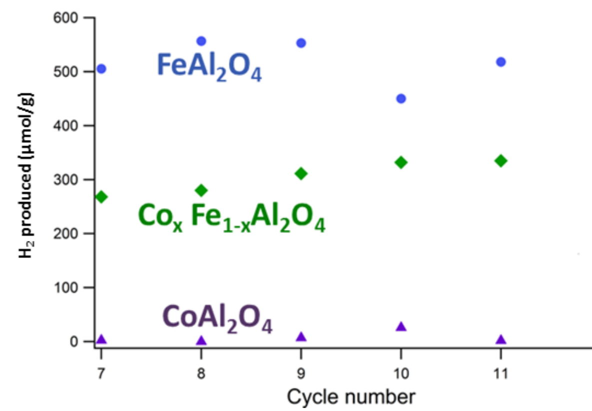

**Predicted relative $H_2$ production capacity:**

$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$

1: 0.7 : 2X10$^{-4}$

## 1500/1350 near-isothermal water splitting




**Measured relative $H_2$ production capacity:**

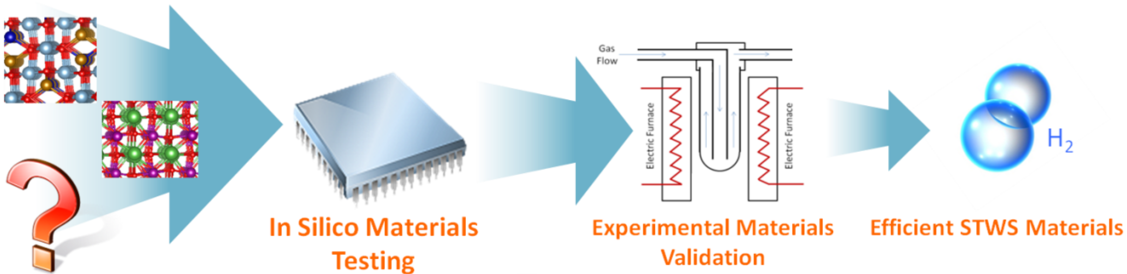
$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$

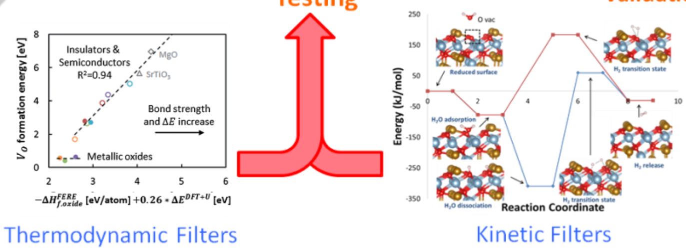
1: 0.6 : 0

- ✓ **Predicted STWS capability and mechanism of different materials**
- ✓ **Computational predictions were validated experimentally**
- ✓ **Co-doping induces a production/kinetics tradeoff**

# NSF "Sister" Project
# Materials Genome Initiative based STWS Materials Development

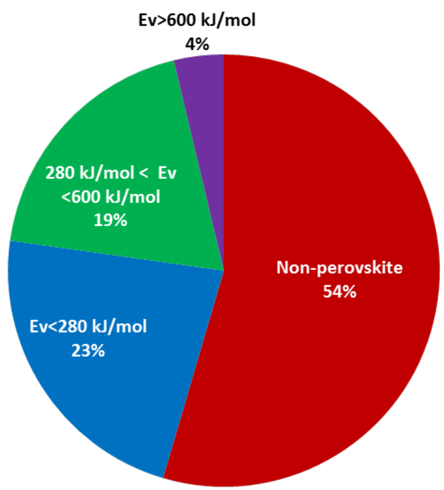
## Project Technical Approach




We apply fundamental materials science, chemistry and physics to discover promising materials using an **integrated computational, theory and experimental approach**. Computation will using state-of-the-art electronic structure theory, which will allow us to develop design rules for new materials and develop **digital data base** for material screening. **Integration with experiments** and **cross team work with the DOE project and SABIC** will then validate and help refine materials assessment metrics. This enables computational prototyping of materials integrating theory and experimentation using both thermodynamic and kinetic filters.

## Preliminary Perovskite Results



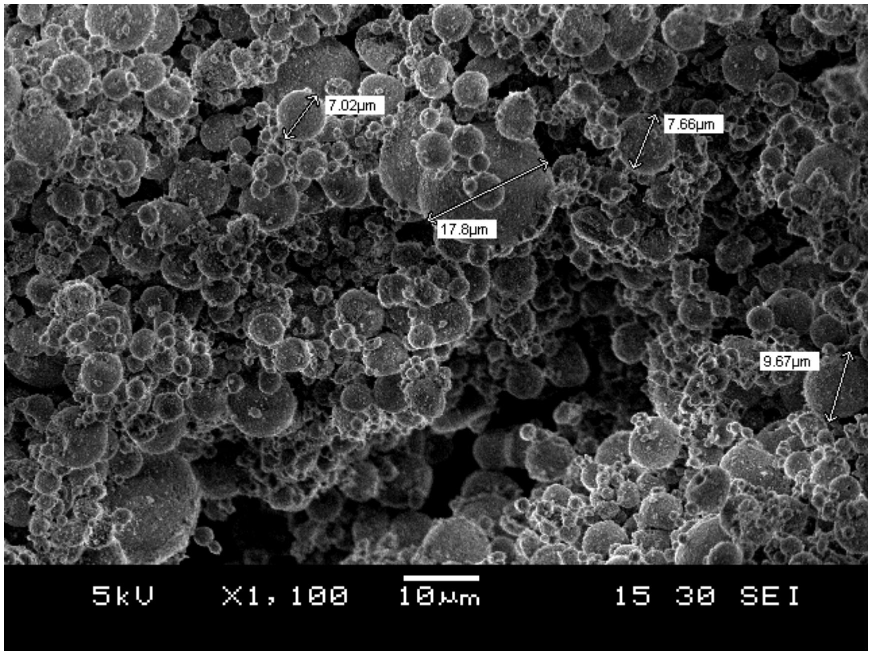

1045 materials screened
As of 4/10/2015

- Calculated predicted $E_{O\text{-}vac}$ for 1045 possible binary perovskites using method developed in our group by Deml *et al.*
- 570 materials spontaneously phase transitioned out of the perovskite structure
- 237 materials have reduction enthalpies too low to drive STWS ($E_{O\text{-}vac} < 280$ kJ/mol)
- 199 materials are potentially capable of driving STWS* ( 280 kJ/mol $< E_{O\text{-}vac} <$ 600 kJ/mol)
- 39 materials have reduction enthalpies too high for practical use as STWS materials ( $E_{O\text{-}vac} >$ 600 kJ/mol)

* *Materials were not analyzed for thermal stability or fabrication practicality*

# Accomplishments and Progress: Engineered Particles – Preliminary Characterization

***>2g Hercynite active material synthesized by spray drying and characterized for composition, particle size, and surface area***




*Spray dried hercynite spherical particles after calcining at 850°C for 8 hours*

XRD analysis after calcining shows **hercynite** and iron oxide (hematite) peaks, and ICP results show **elemental content in agreement with intended stoichiometric ratios**

Chemical composition from ICP: $Co_{0.4}Fe_{0.66}Al_{2.1}$

Spray drying can produce engineering particles that are active, robust, flow-able, and cost effective

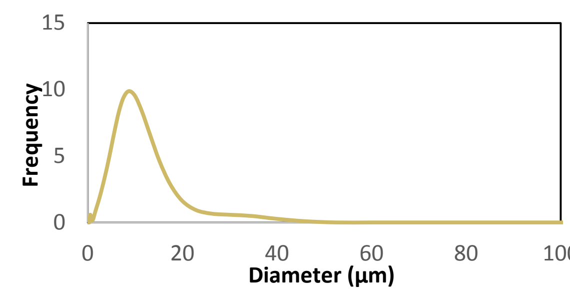
$$C = \frac{8sryf}{n}$$

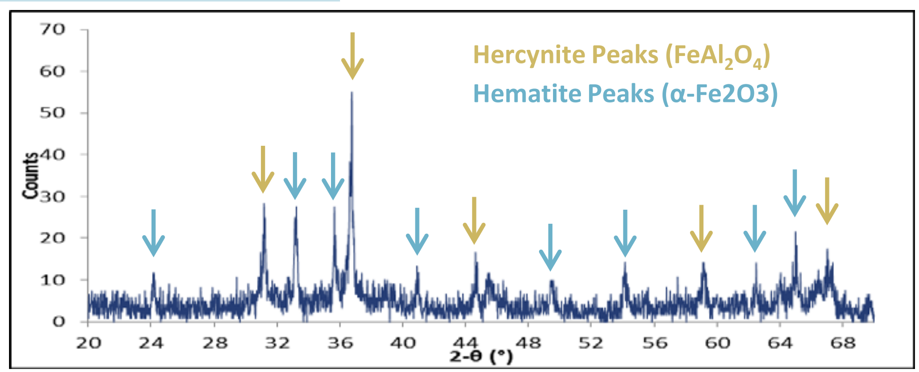
C: annual replacement costs
s: flow rate
r: cost per particle
y: operational days per year
f: fraction of original cost
n: number of cycles before replacement

L.-S. Fan, *Chemical Looping systems for Fossil Energy Conversions*. AIChE and John Wiley & Sons, Inc., 2010.

*Preliminary spray drying has produced particles with a narrow size distribution*

Initial spray dried particles are **spherical** and have a mean particle size of **7μm** and a surface area of **23 m²/g**

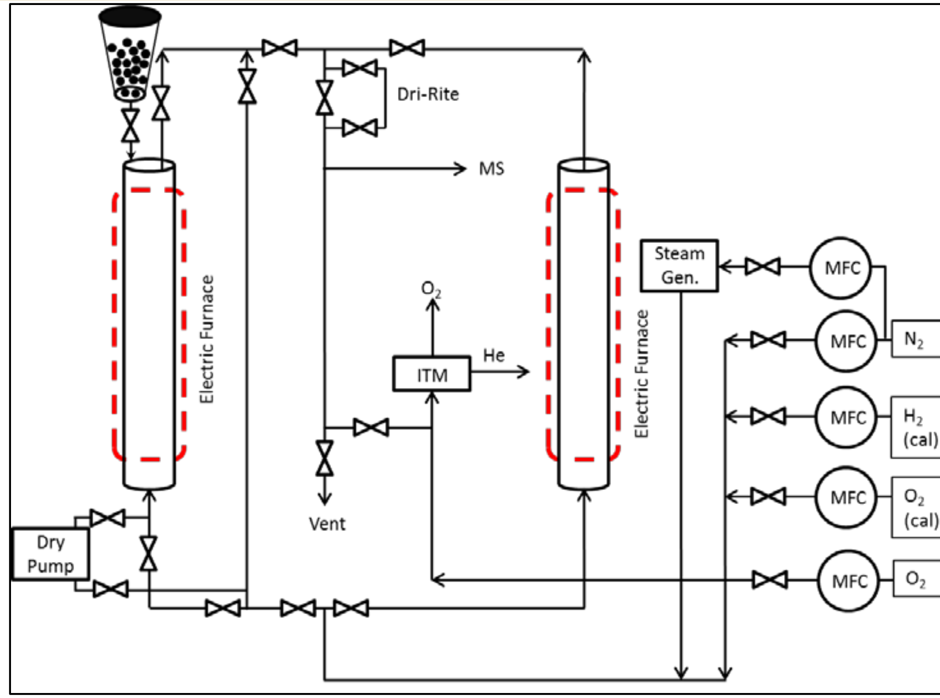


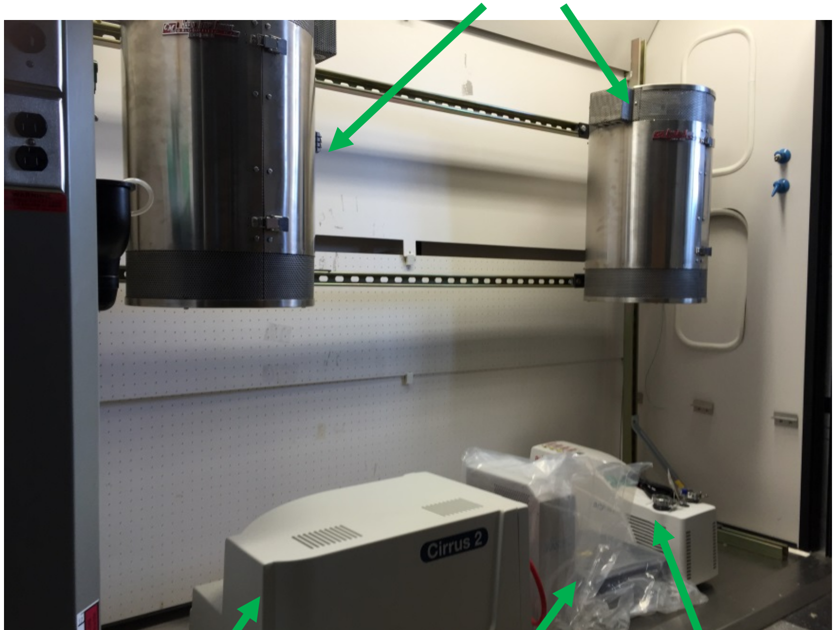



# Accomplishments and Progress: Progress of Particle Flow Reactor System

## Particle Flow Reactor Lab System

- Test reduction and oxidation zones with spray dried particles
- Reduce particles as they are flowing down an alumina tube under vacuum
- Oxidize particles in a fluidized bed with steam
- Perform comparison studies of inert gas sweeping versus vacuum pumping.




## Current Status

- ✓ Furnaces, vacuum pump delivered and being installed
- ✓ Mass flow controllers, valves ordered
- ✓ Data acquisition and control system in progress

**System to test reduction and oxidation on track to meet Go/No-Go decision at end of Budget Period 1**

# Progress and Accomplishments: SiC Coating and SFR Upgrades

## SiC Coating

Synthesis :

- Determine the ALD deposition rate of alumina and silica
- Coat mullite ($3Al_2O_3$ $2SiO_2$) using the determined deposition rates to ensure that correct ratio is deposited
- Analyze with XRD

Analysis of coating efficacy:

- TGA will be used to expose ALD-coated SiC particles to flowing steam
- Can determine if the SiC is degrading and by what rate

Current Status

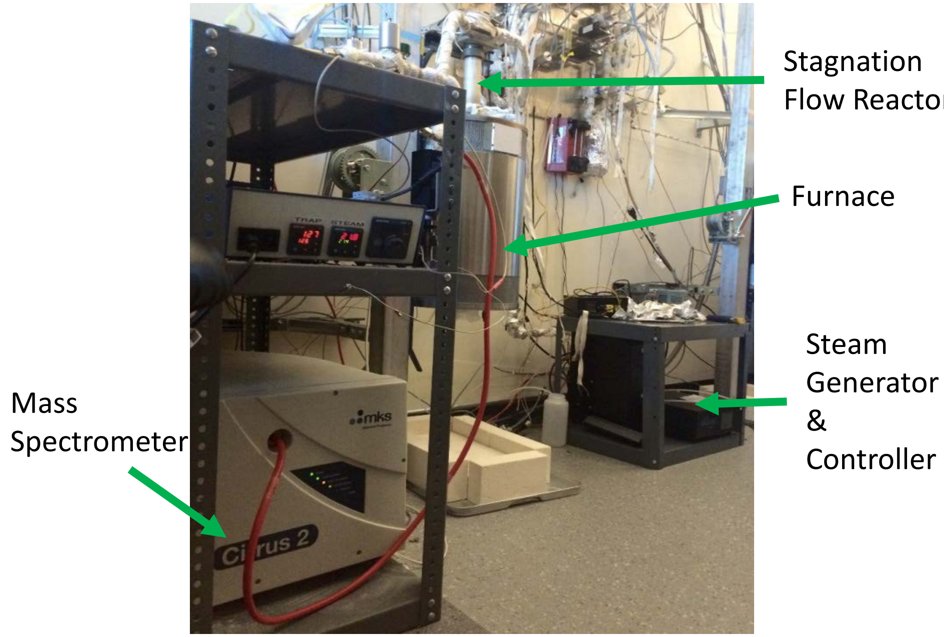
- Material-specific components of ALD reactor have been ordered
- Precursors are ready for testing

**Coating of SiC particles ready to begin**

## SFR Improvements for Long-Term Testing

- New steam generation system ordered and delivered
- Preliminary system design for long-term redox cycling has been completed
- Valves and other components have been ordered

**New MKS Cirrus™ 2 mass spectrometers installed on SFR systems for improved data quality**




Key Features of New Mass Spec

- Wide dynamic range with rapid screening speeds (up to 250 pts/s)
- Improved detection limits for gases of interest (<100ppb)
- Heated capillary inlet for more rapid signal response
- Direct Ethernet interface with software for fully automated operation and calibration

✓ ***System upgrades will allow for in-house long term materials testing***

✓ ***Upgrades are on-track to meet milestones in FY16***

# Collaborations

| Fund-Receiving Collaborator | | Project Roles |
|---|---|---|
| | National Renewable Energy Laboratory (NREL) (sub) | High Flux Solar Furnace (HFSF) user facility for process demonstration |
| | Musgrave Group, CU Boulder | Active materials discovery and DFT modeling through "sister" NSF project* |

* Funds from Joint DOE/NSF FOA

| Leveraged Collaborators (no funds received from DOE) | | Project Roles |
|---|---|---|
| | Australian National University (ANU) | Reactor models and receiver testing at solar simulator facility |
| | Saudi Basic Industries Corporation (SABIC) | Materials characterization support; supplying equipment |

# Accomplishments and Progress: Responses to Previous Year Reviewer' Comments

This project was not reviewed last year

# Remaining Challenges and Barriers: Active and Containment Materials

- Reactive Materials
  - Higher productivity needed for higher efficiency and lower cost
  - Particles must be able to flow and be entrained by steam
  - Long particle lifetimes difficult, especially at high temperature
- Reactor Design
  - Reduction may need longer residence time
  - Heat recuperation within reactor is useful but difficult
- Containment Materials Development
  - Reactor containment materials needed for high temperature reactions
  - Steam-steam heat recuperation materials needed for high temperatures
- Efficient $H_2$ production
  - More realistic costs difficult to predict for future case
  - More specific system heat integration may mean that some heat is discarded

***Project Objective:* Design and test individual components of a novel flowing particle solarthermal water splitting system capable of producing 50,000 kg $H_2$/day at a cost < $2/kg $H_2$***

# Proposed Future Work

- Reactive Materials
  - Perform detailed thermodynamic and kinetic studies of active materials (M1.3 & M1.6)
  - Validate computation work of sister NSF project (M1.1 & M1.2)
  - Demonstrate at least 150 µmol/g of spray dried active materials (GNG1)
  - Determine long term stability of spray dried particles (M1.7)
- Reactor Design
  - Construct electrically heated particle flow redox test system (M3.1)
  - Demonstrate redox cycle of at least 1 gram of spray dried active materials (GNG4)
  - Develop a solar heliostat field model to provide a flux profile over the internal surfaces of the receiver-reactor (M3.5)
- Containment Materials Development
  - Perform mullite/alumina/… ALD coatings on SiC particles (M2.1)
  - Perform TGA reactivity studies on uncoated and coated SiC particles with steam (M2.2)
- Efficient $H_2$ production
  - Update AspenPlus model and H2A with experimental thermodynamic and kinetic results and optimal operating conditions (M5.1 & M5.2)

# Technology Transfer Activities

- Methods and Apparatus for Gas Phase Reduction/Oxidation Processes; 13/857,951; being prosecuted
- Technology licensing opportunities pursued

# Summary

- Approach
  - Synergistic approach to active material, reactor design, and containment material efforts
- Reactive Materials
  - Computations results can predict $H_2$ production capacity
  - Experimental validation of computational results
  - Preliminary spray dried particles are spherical and form material composition of interest
  - Reactor test systems upgrades will improve data collection and enable long-term testing
- Reactor Design
  - Reactor concept updated with more realistic receiver concept
  - Flowing particle test system being built, on-track for Milestone completion
- Containment Materials Development
  - Preliminary deposition has begun
  - Preliminary system design complete
- Efficient $H_2$ production
  - Efficiency calculations suggest inert gas sweep reduction can be useful
  - AspenPlus simulation updated with more detailed operations and realistic assumptions
  - H2A capital costs improved, sensitivity studies underway

# Acknowledgements

# Technical Backup Slides

# Summary of Solar Plant Design Characteristics and Assumptions

| Parameter | 2015 | 2020 | Ultimate |
|---|---|---|---|
| Heliostat area ($m^2$) | 2,242,760 | 806,980 | 430,840 |
| Secondary Concentrator area ($m^2$) | 120 | 120 | 120 |
| Number of towers | 6 | 2 | 1 |
| Tower height (m) | 231 | 240 | 248 |
| Secondary concentration | 4000x | 4000x | 4000x |
| Max temperature (°C) | 1500 | 1500 | 1500 |
| Annual net thermal energy required (GWhr) | 2427 | 873 | 467 |

<u>Capital Cost Assumptions:</u>

Heliostat costs: $75/m$^2$ for cases 2020 and later, $140/m$^2$ in 2015.

Secondary concentrator costs: $1500/m$^2$

Tower cost: $\$1.5 * [600{,}000 + 17.72 * Tower\ height\ (m)^{2.392}]$

# Summary of Chemical Plant Design Characteristics and Assumptions

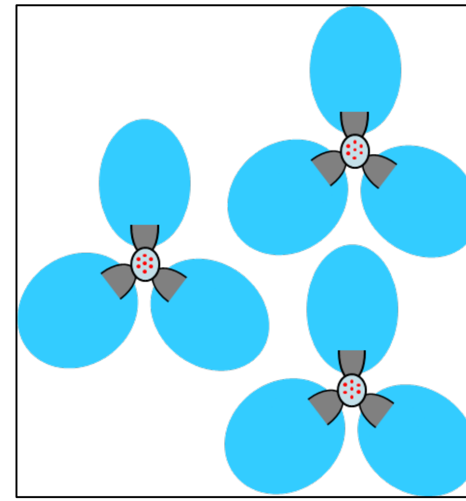
| Parameter | 2015 | 2020 | Ultimate |
|---|---|---|---|
| Gas-steam heat exchanger effectiveness | 85% | 90% | 95% |
| Solid-solid heat exchanger effectiveness | 85% | 85% | 85% |
| Reduction temperature (°C) | 1500 | 1500 | 1500 |
| Oxidation temperature (°C) | 1000 | 1250 | 1350 |
| Number of reactor units | 18 | 6 | 3 |
| Material factor for SiC | 6 | 5 | 3 |
| Cycle time (min) | 20 | 9 | 5 |
| Material activity (µmol $H_2$/g) | 354 (current material measured value) | 389 (10% greater than current material) | 425 (20% greater than current material) |
| Material heat of reaction (kJ/mol) | 384 (current result of DFT model for hercynite) | 346 (10% lower than current result) | 307 (20% lower than current result) |
| Amount of reactive material cycled (kg) | 2,900,000 | 1,200,000 | 610,000 |
| Materials replacement frequency (years) | 2 | 5 | 5 |
| Process water usage (gallons/kg $H_2$) | 2.4 | 2.4 | 2.4 |
| Byproduct O2 produced (kg/ kg H2) | 7.9 | 7.9 | 7.9 |
| Industrial electricity usage (kWh/kg $H_2$) | 9.1 | 4.9 | 3.9 |
| Annual net thermal energy required (GWhr) | 2427 | 873 | 467 |

# Solar Field Sizing Model

***Adopted new solar field sizing program developed by CPC consultant Alan Lewandowski***

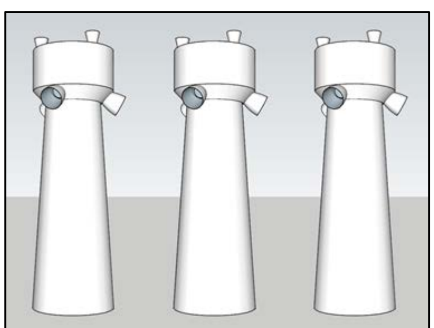
Modeling Assumptions:

- Three solar fields direct to one central tower with three secondary concentrators
  - CPC sized for ~95% intercept at design point
  - Day 82, hour 10, Latitude 30°N
- Tower height/heliostat dimension = 20
  - Sufficiently small heliostat to have no additional impact on optical performance at high incident angles
- Annual performance determined by daily modeling on single day per month for each of 12 months
- Current setup for 160 MW plant is 4000x concentration with one 248 m central tower



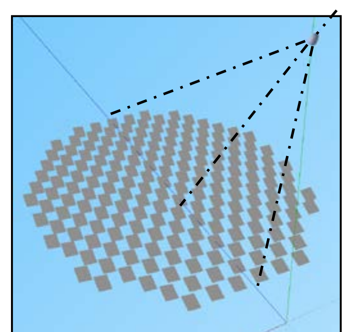
*Concept cartoon of new three-lobed solar field design with three central towers*

**Solar field sizing model outputs:**



Tower height

Number of towers



Heliostat area
Solar field area

# Capital Cost Estimates

**Chemical Plant Capital Costs**

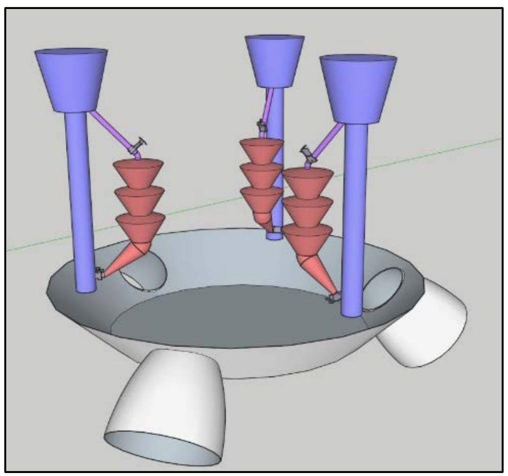
*Determined primarily by:*

- Number of towers
- Amount of active material
- Price of SiC reactors

**Solar Plant Capital Costs**

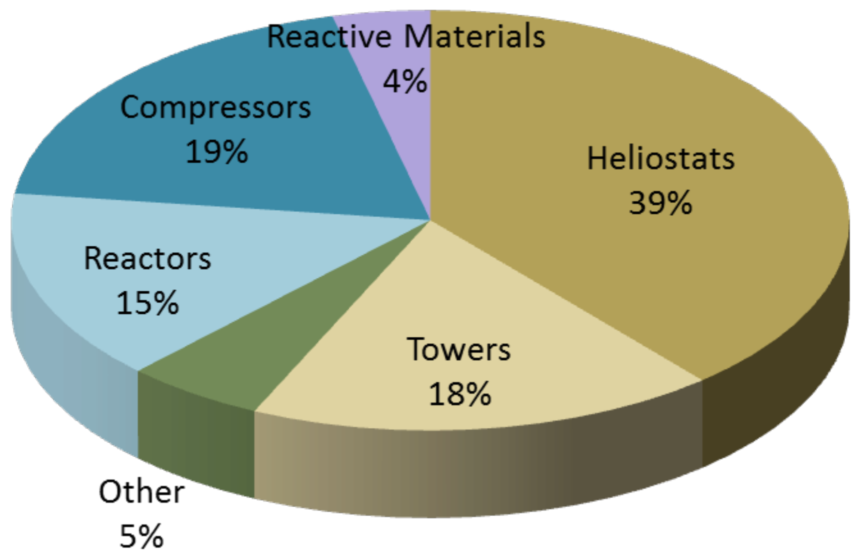
*Determined primarily by:*

- Heliostat area
- Price of heliostats
- Number of towers



- CapCost Software used to estimate bare module cost of reactors made from carbon steel, reactors adjusted with material factor for SiC
- Other chemical plant equipment estimated from costs of other projects and scaled for 50,000 kg/day plant

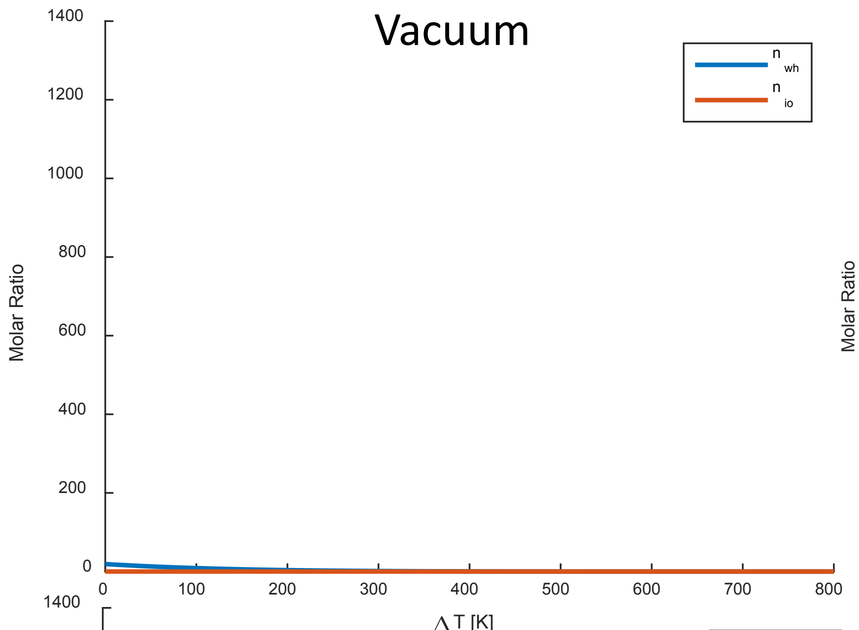
**Direct Capital Cost Breakdown for $2/kg price point**

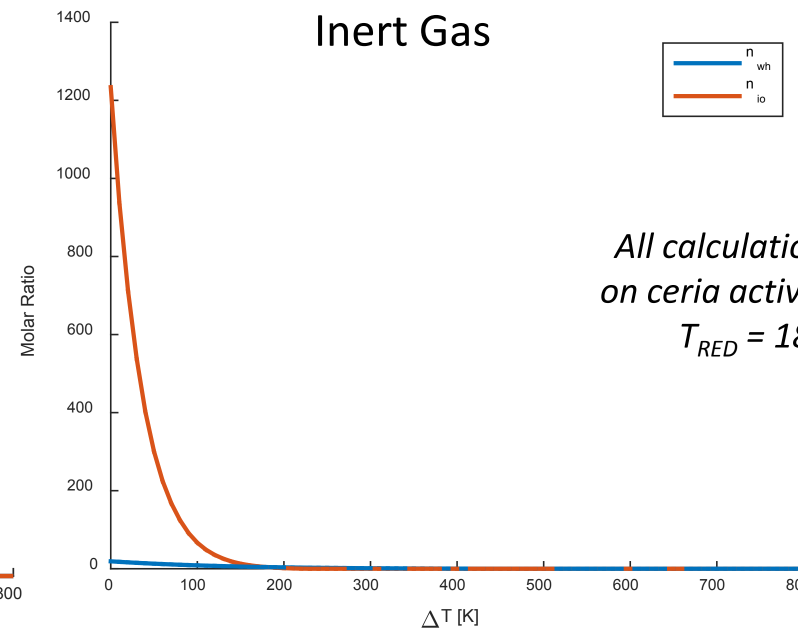



***Solar plant makes up 60% of direct capital cost***

# Inert Gas Sweep Flow Requirements

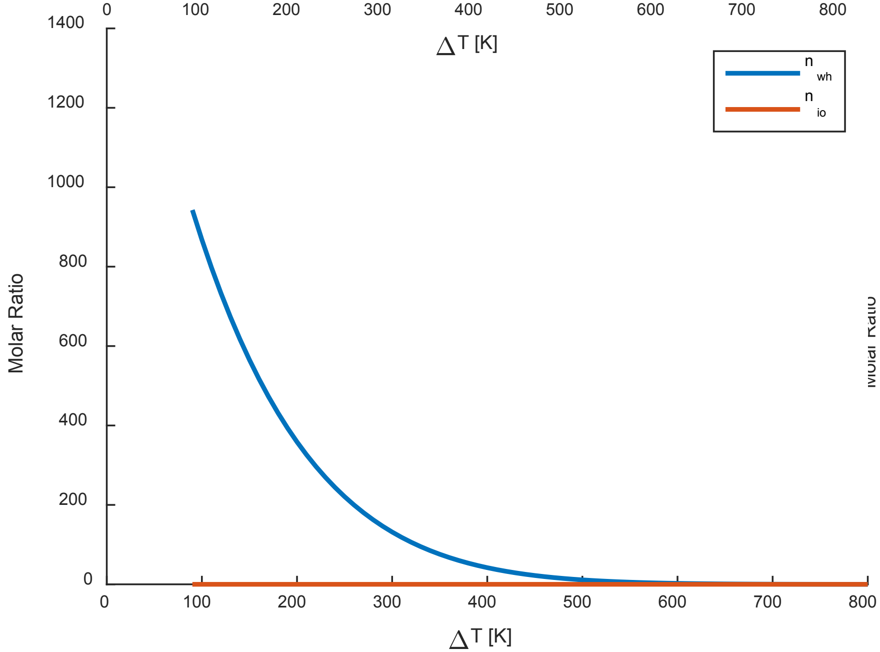
$p_{RED} = 0.1$ Pa

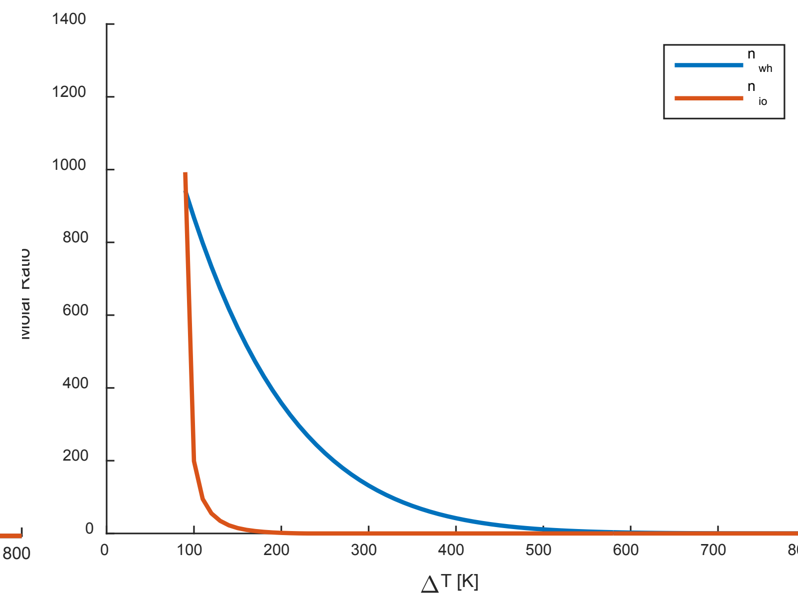



*All calculations based on ceria active material*
*$T_{RED}$ = 1800 K*

$p_{RED} = 1000$ Pa

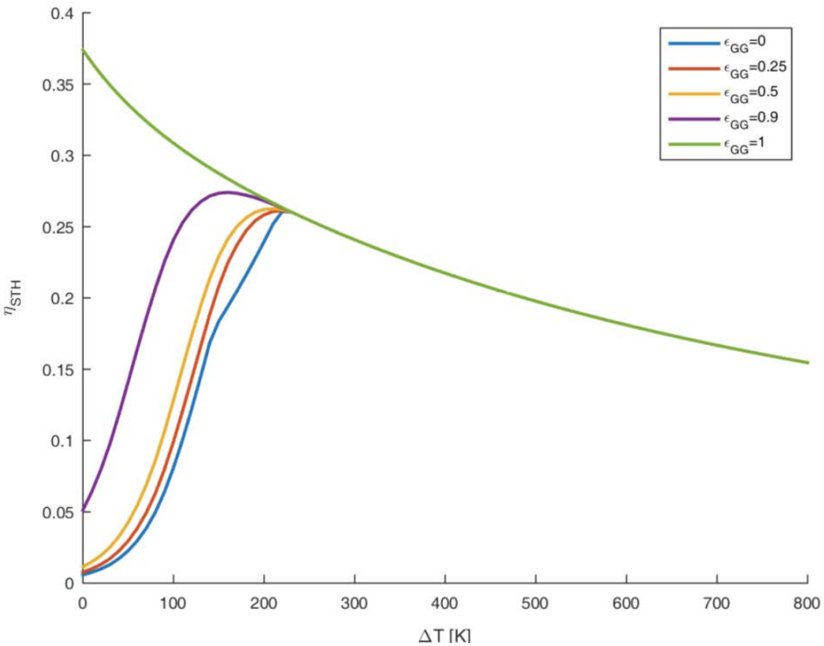


# Impact of Inert Gas Flow Above Minimum

**Base Case**

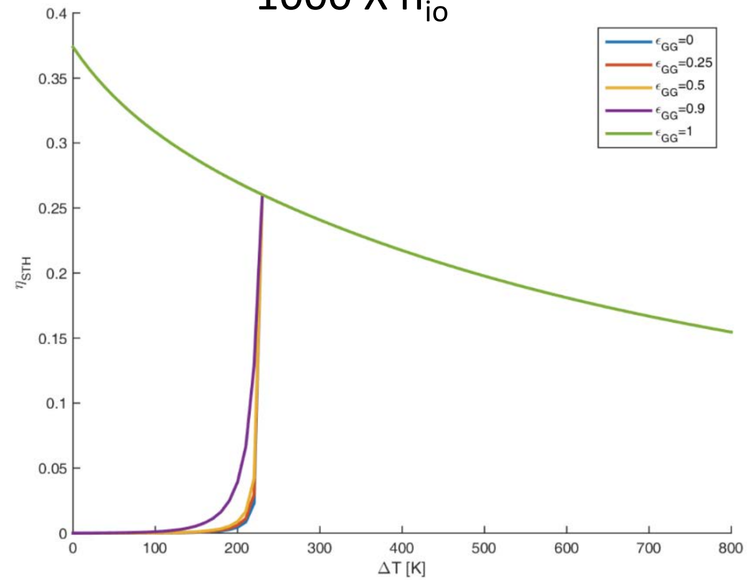
Minimum $n_{io}$




*Calculations based on ceria active material*
*$T_{RED}$ = 1800 K*

$$n_{io} = \frac{n_{N_2}}{n_{O_2}}$$

1000 X $n_{io}^{min}$




$n_{io}$ Does Not Go Below 100