Solar-thermal Ferrite-Based Water Splitting Cycles

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Project ID No. PD_10_Weimer

Overview

Timeline

- 6-1-2005
- 9-30-2010
- 75% completed

Budget

•Total Project Funding

$900,000 DOE

$225,000 Cost share

•Funds received in FY09

$ 0

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

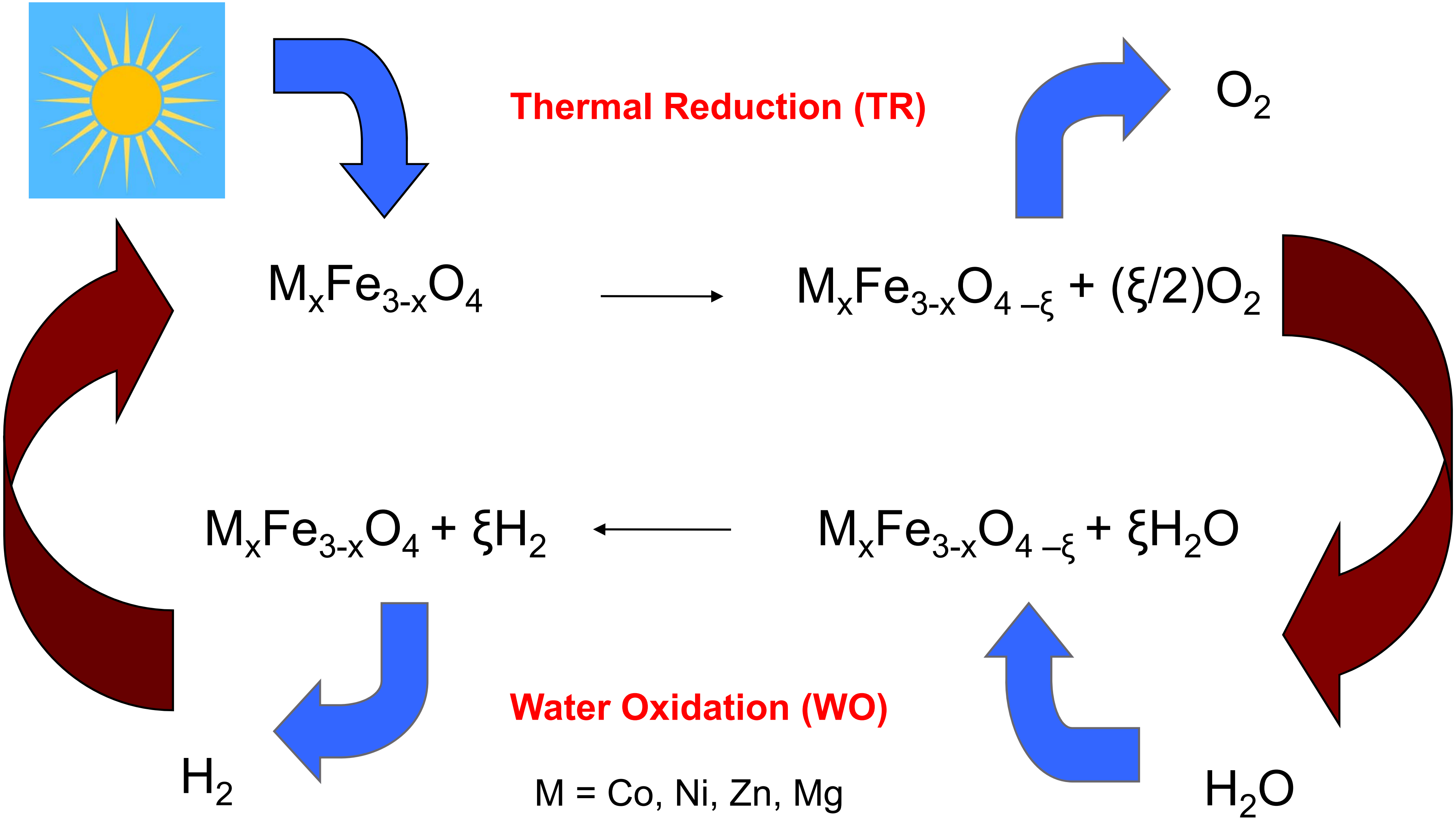
Partners

Swiss Federal Research Institute (ETH Zurich)

Objectives

- Research and develop a cost effective (\$4/kg H_2 at plant gate) ferrite-based solar-thermal thermochemical water – splitting cycle through theoretical and experimental investigation
- Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option

Relevance – Simple 2-Step Thermochemical H_2O Splitting Cycle



Thermal Reduction (TR)

O_2

$$M_xFe_{3-x}O_4 \longrightarrow M_xFe_{3-x}O_{4-\xi} + (\xi/2)O_2$$

$$M_xFe_{3-x}O_4 + \xi H_2 \longleftarrow M_xFe_{3-x}O_{4-\xi} + \xi H_2O$$

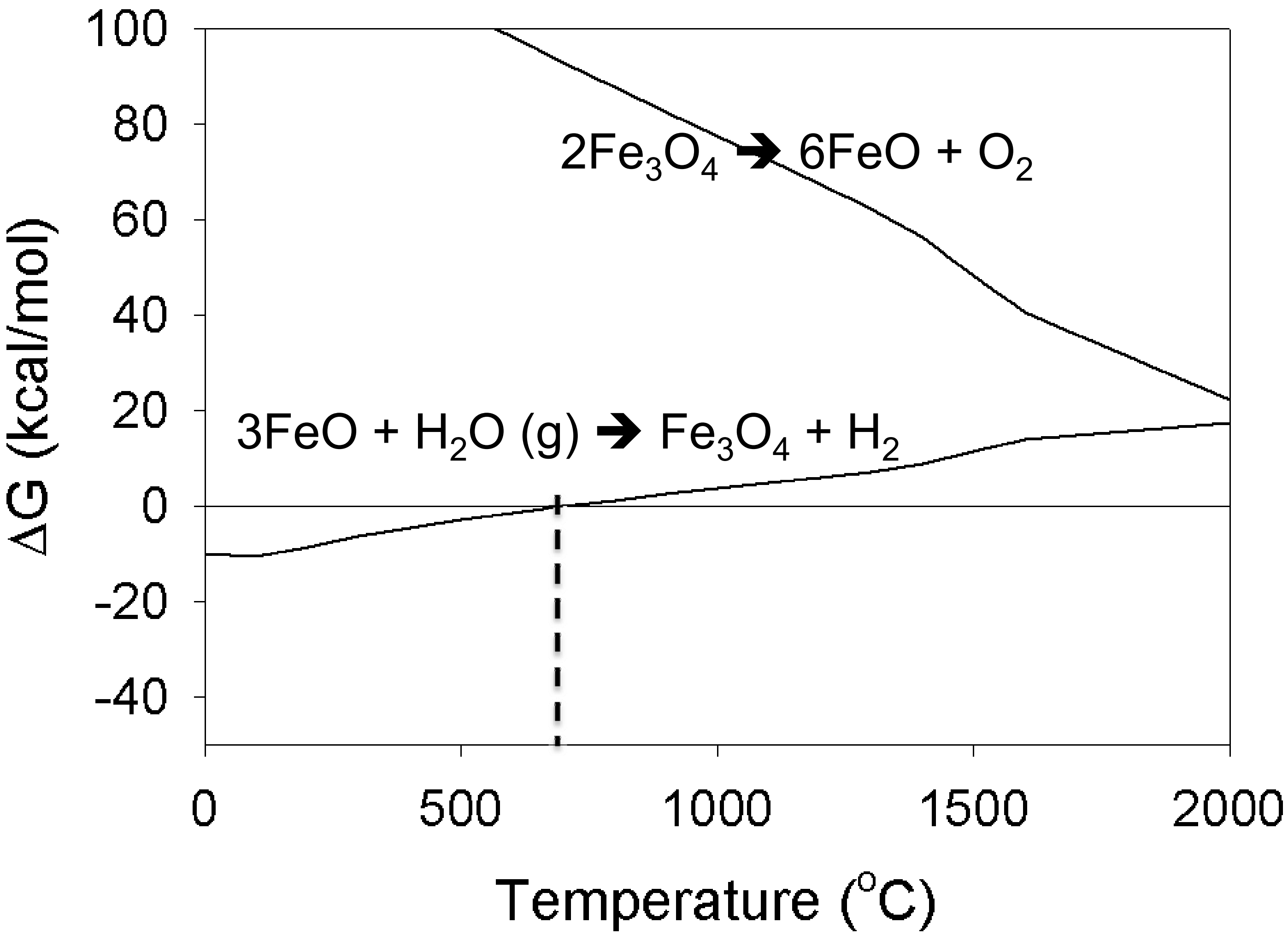
Water Oxidation (WO)

H_2

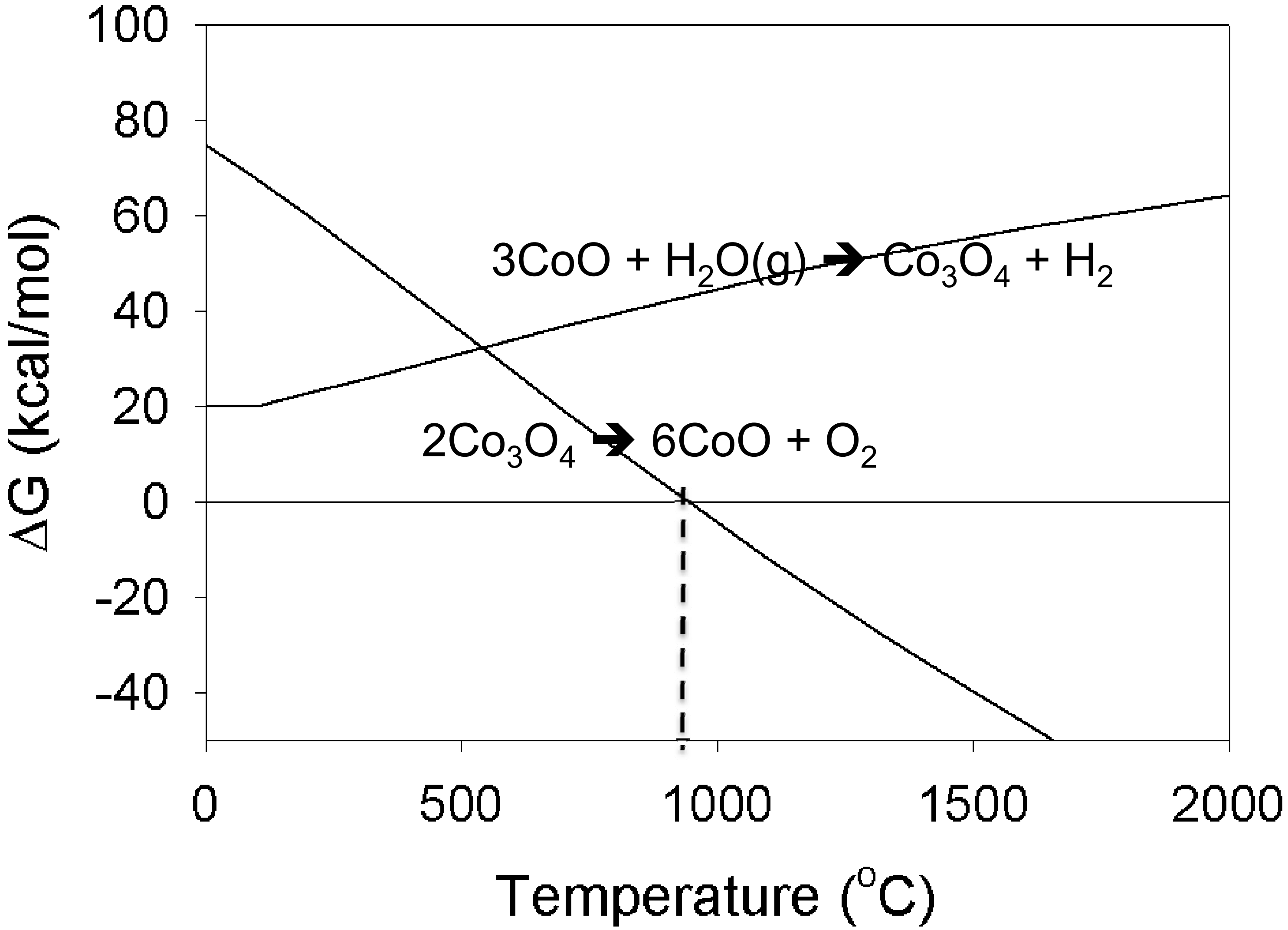
M = Co, Ni, Zn, Mg

H_2O

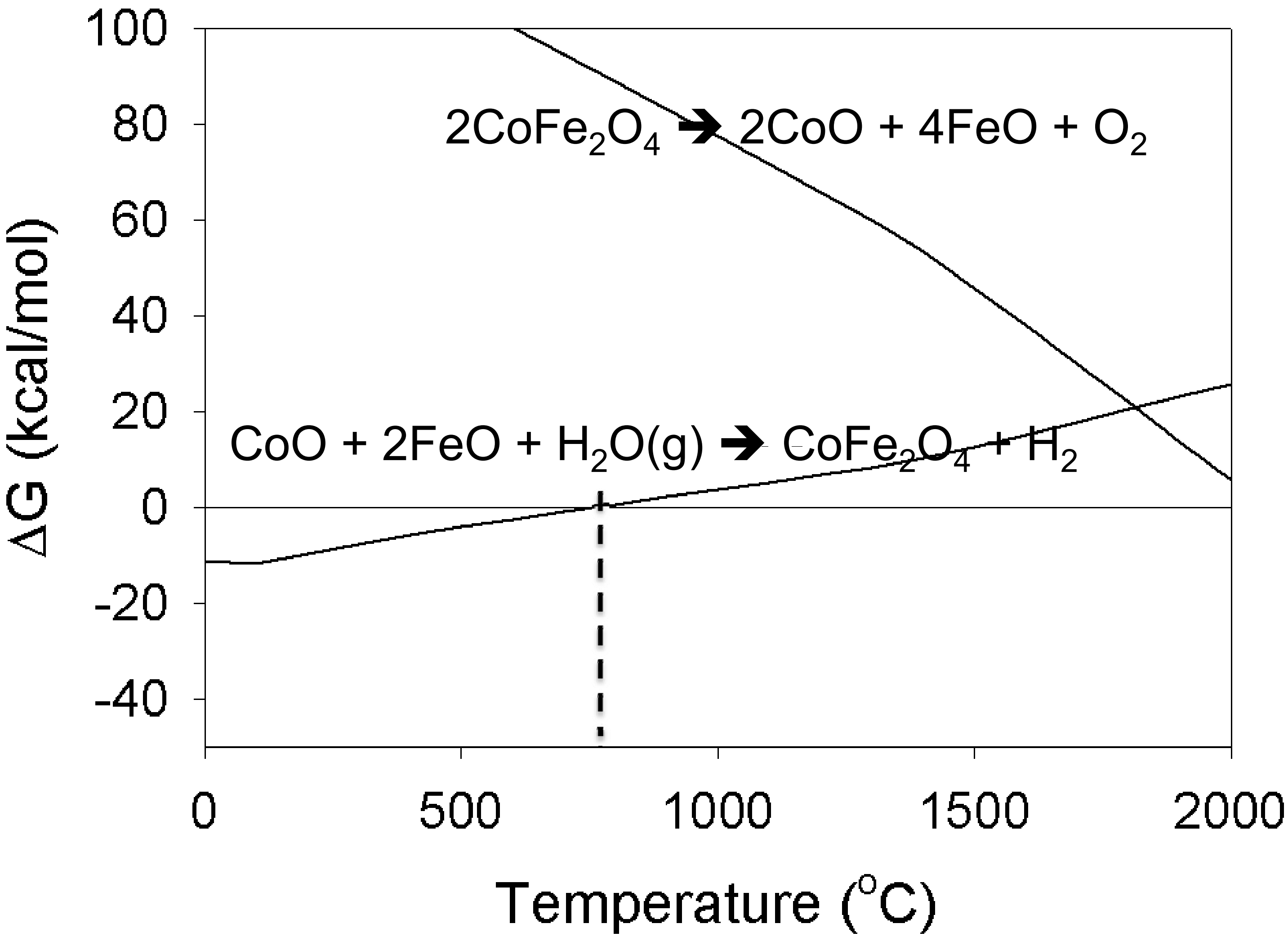
Fe_3O_4 Redox Thermodynamics



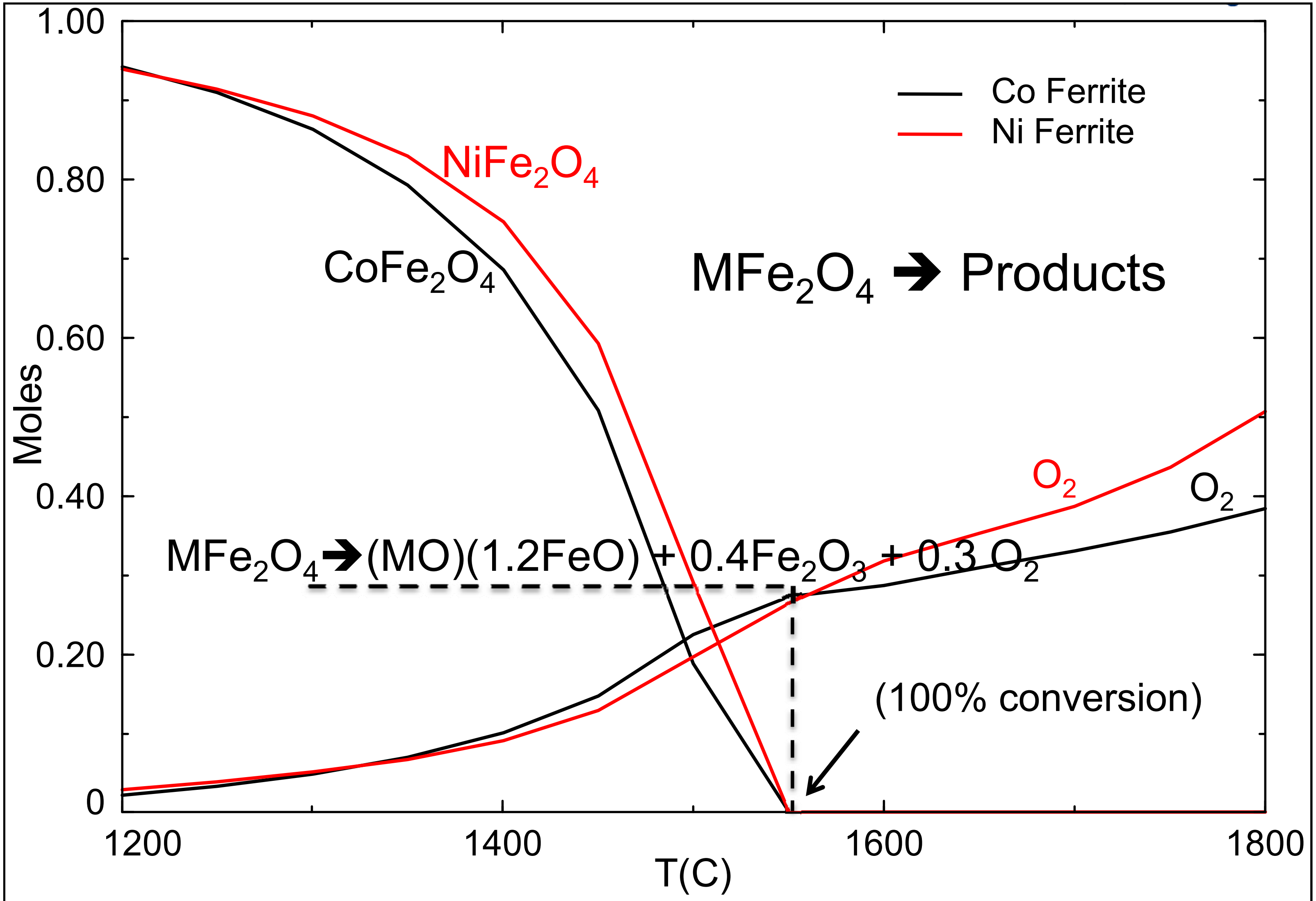
Co_3O_4 Redox Thermodynamics



$CoFe_2O_4$ Redox Thermodynamics



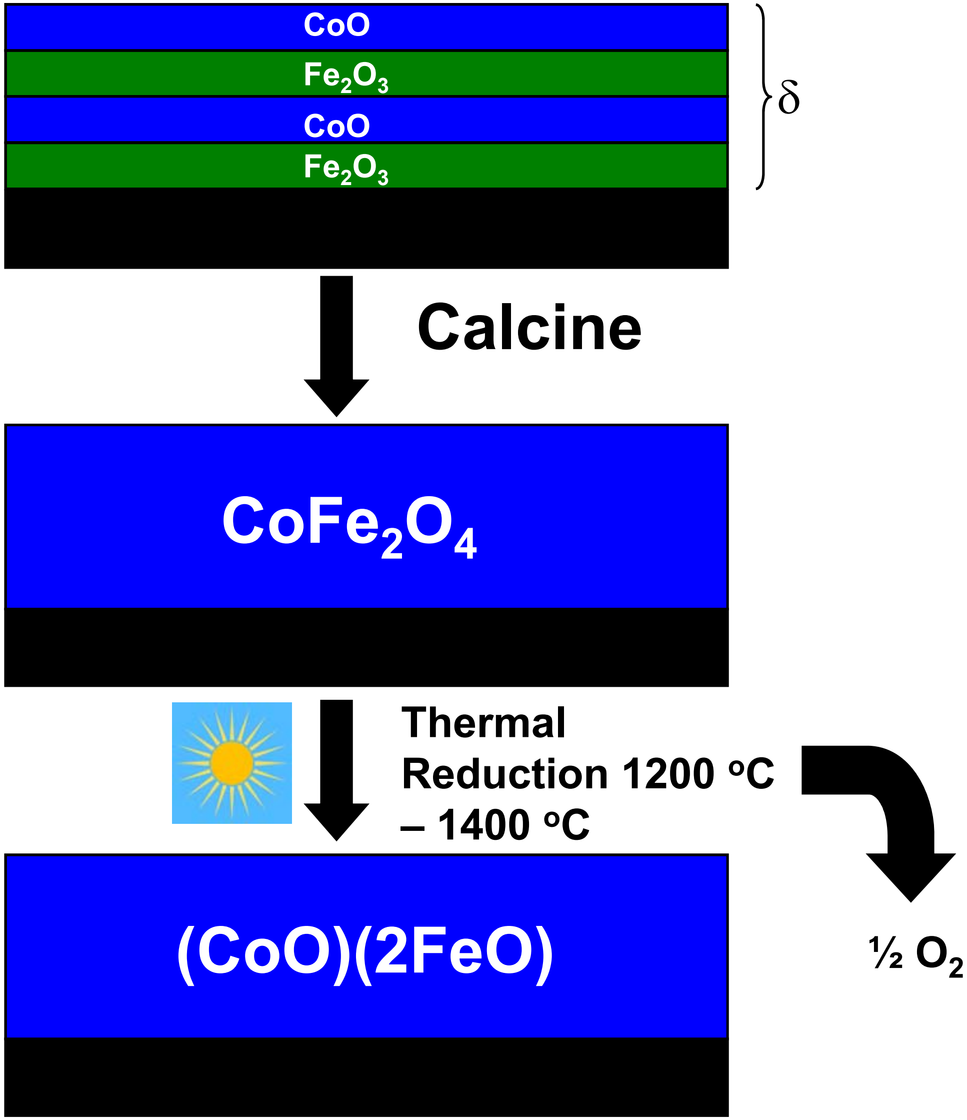
Approach - Free Energy Minimization Theoretical Limit (P = 0.001 Mpa)



Approach - Scientific Hypothesis

- Particle ALD will provide for ultra-high surface area ferrite materials having enhanced reaction rates

Approach - ALD of $Co_xFe_{3-x}O_4$



CoO

Fe_2O_3

CoO

Fe_2O_3

δ

Calcine

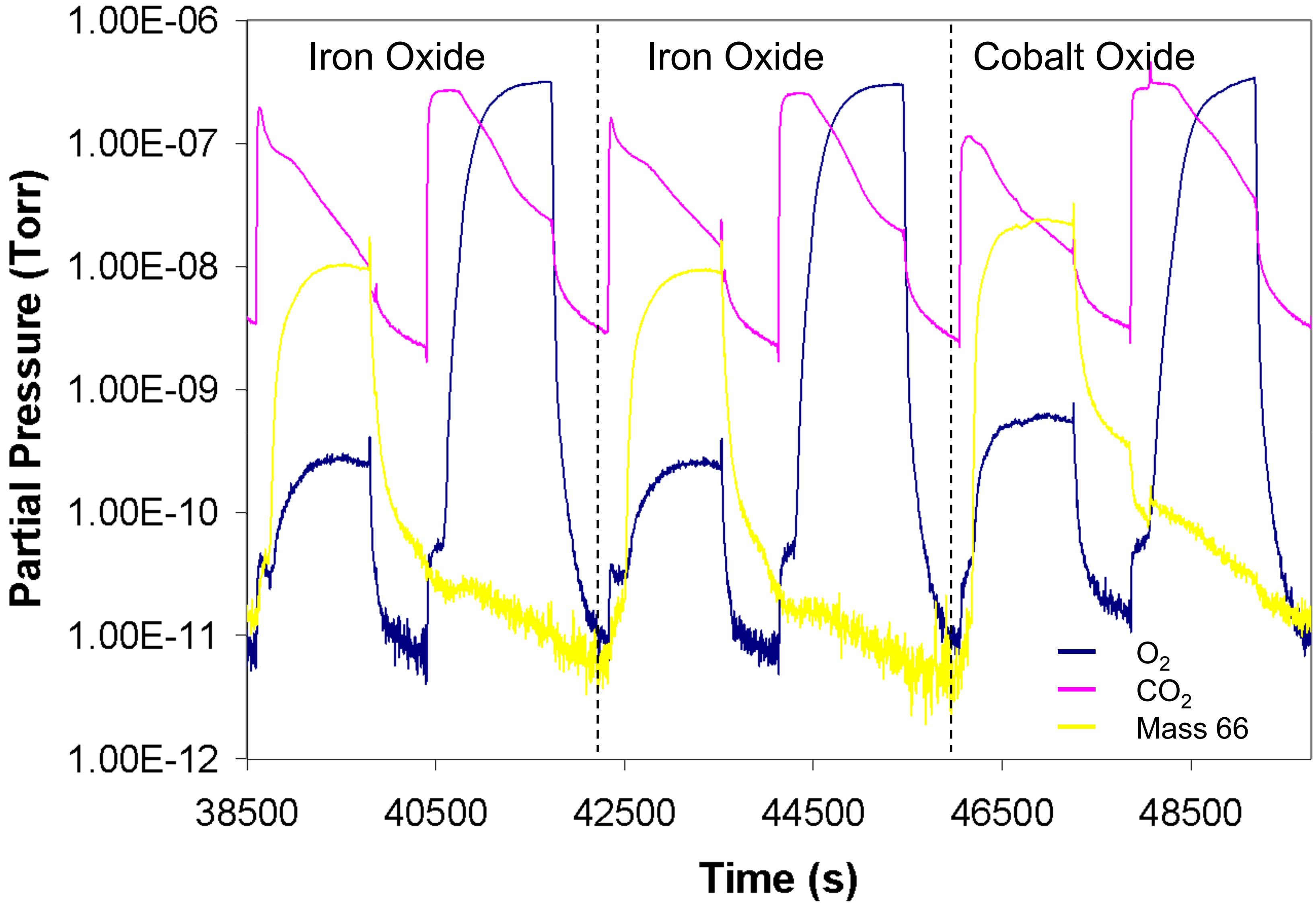
$CoFe_2O_4$

Thermal Reduction 1200 °C – 1400 °C

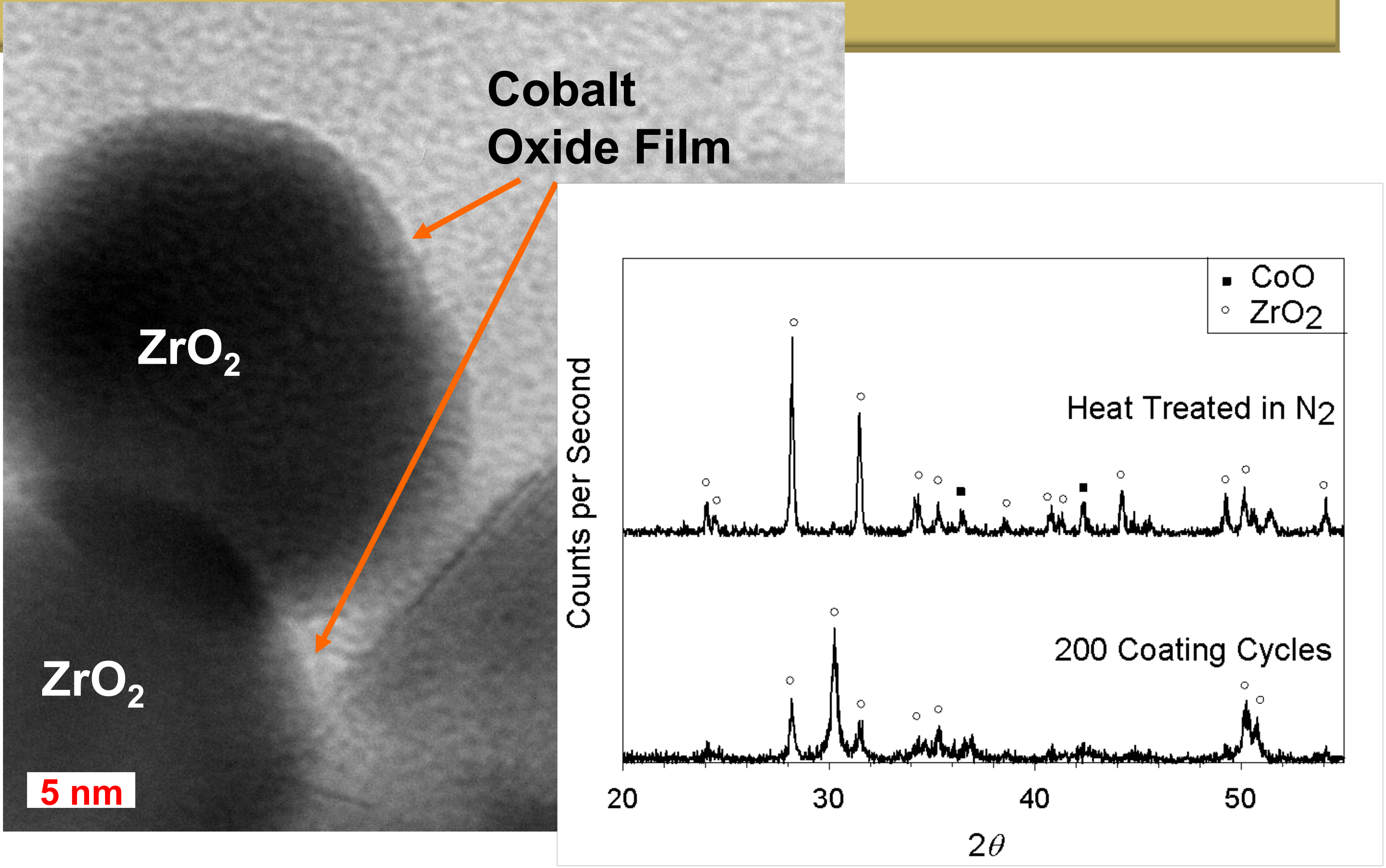
$(CoO)(2FeO)$

$\frac{1}{2}\ O_2$

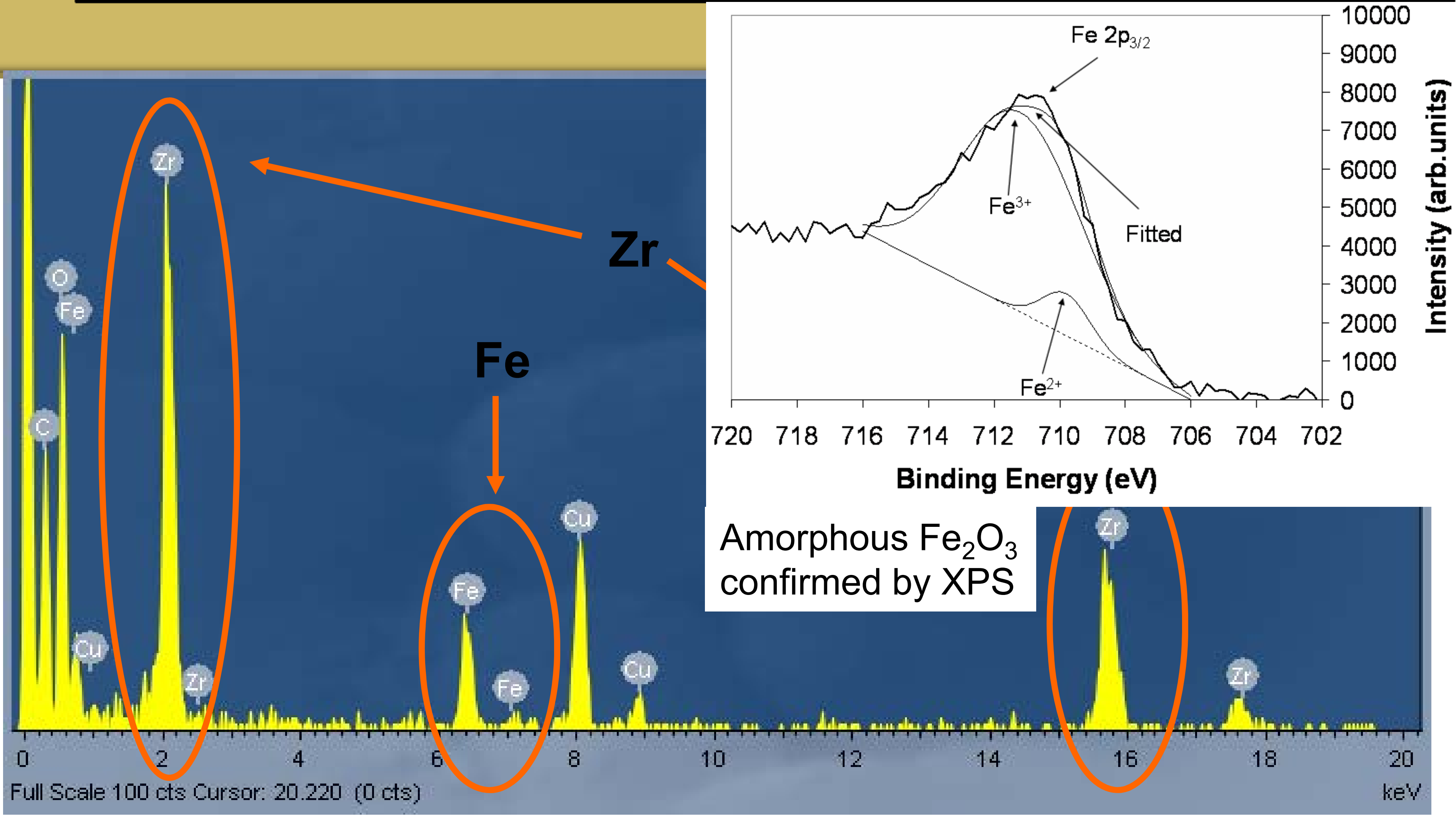
Results - *In Situ* Mass Spectrometry – Particle ALD Synthesis of $CoFe_2O_4$



Results - Self Limiting Cobalt Oxide Chemistry

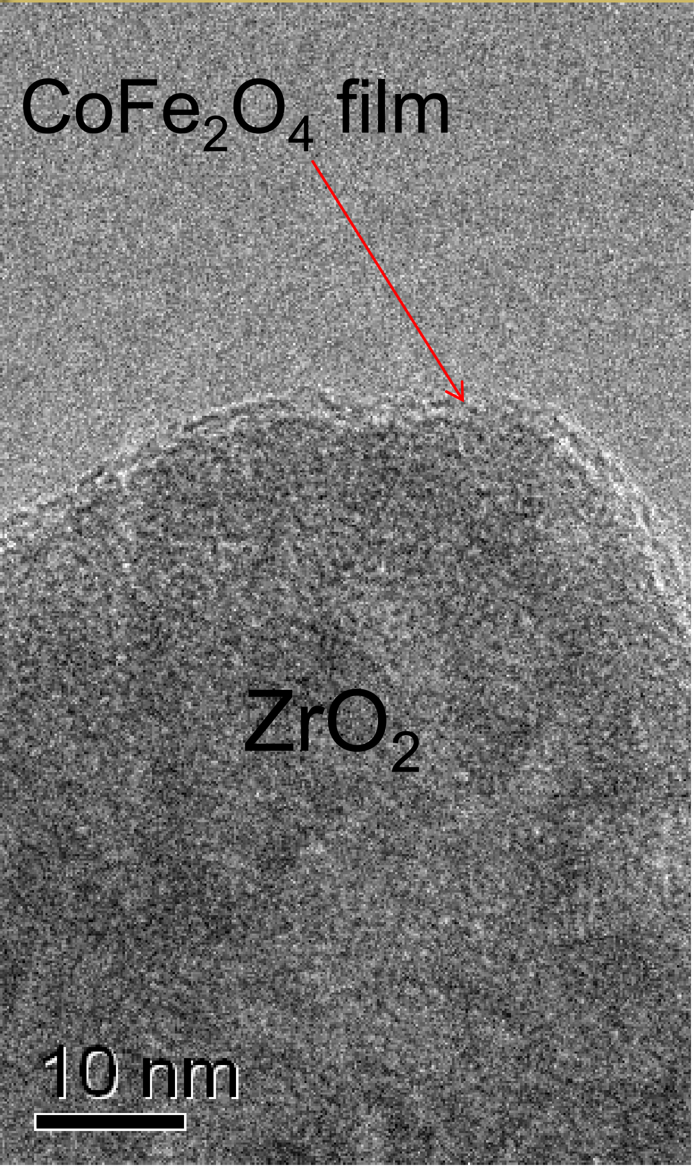


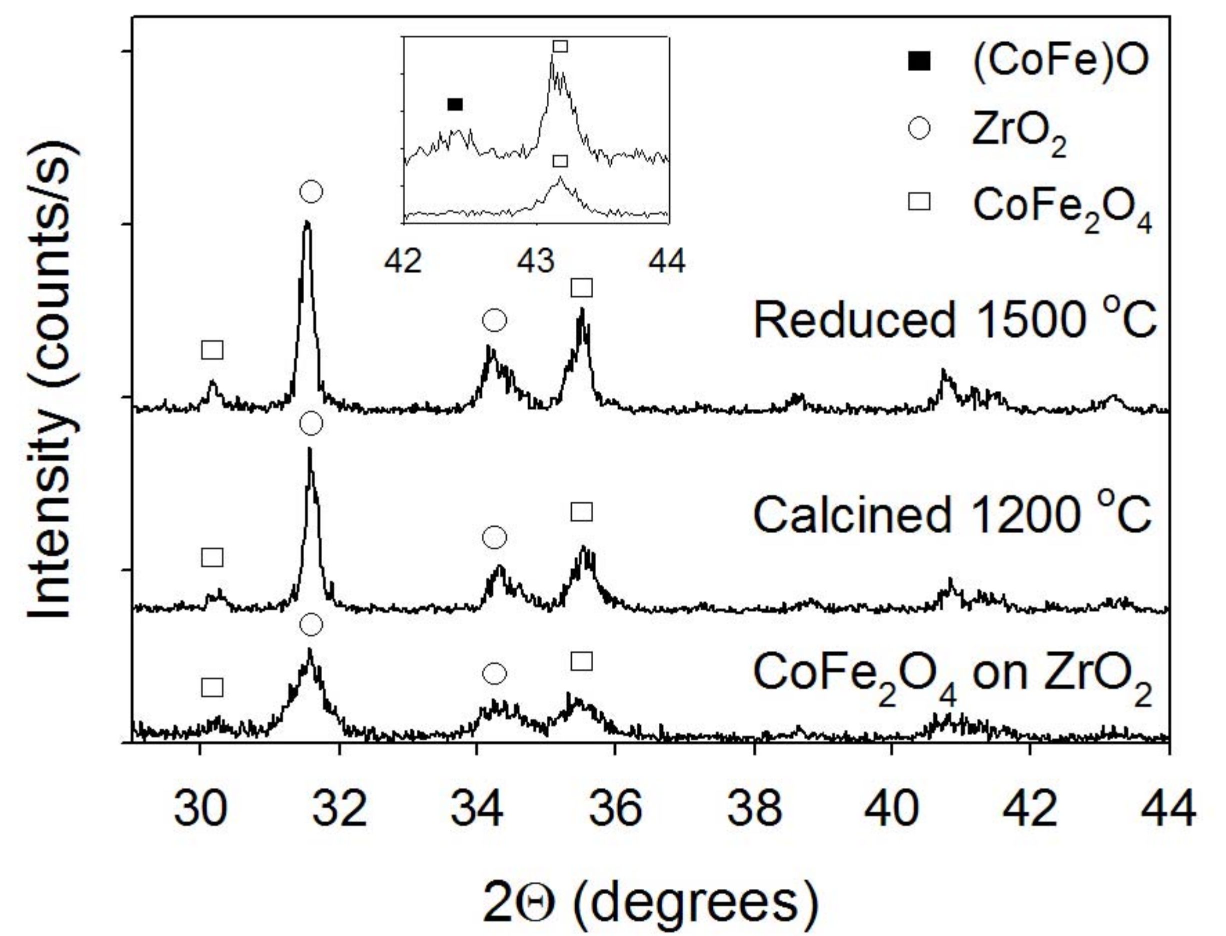
Results – Self-limiting iron oxide ALD; Energy Dispersive Spectroscopy (EDS) Confirms the Presence of Iron



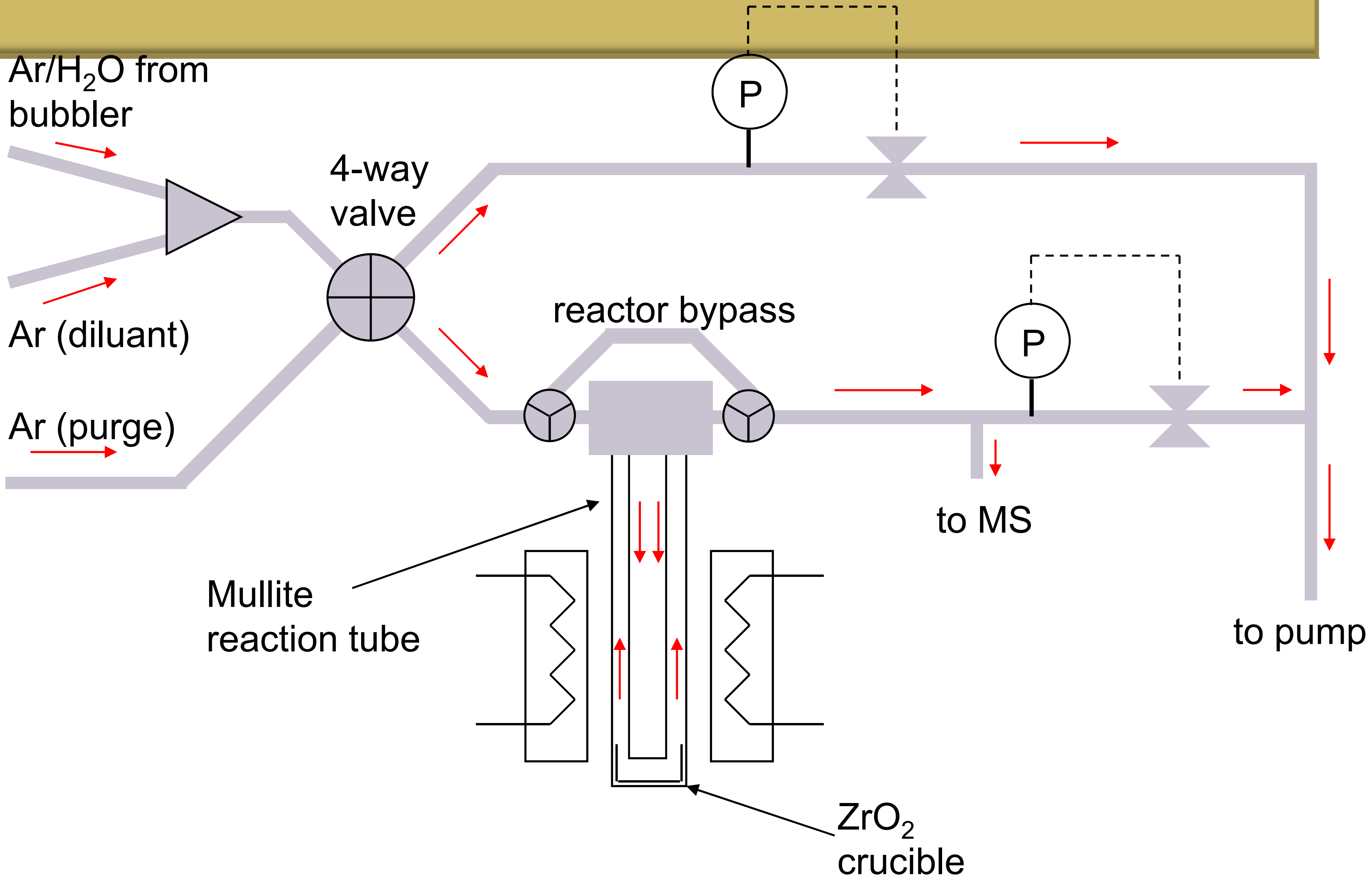
Amorphous Fe_2O_3 confirmed by XPS

TEM Image of $CoFe_2O_4$ on Porous ZrO_2 Support

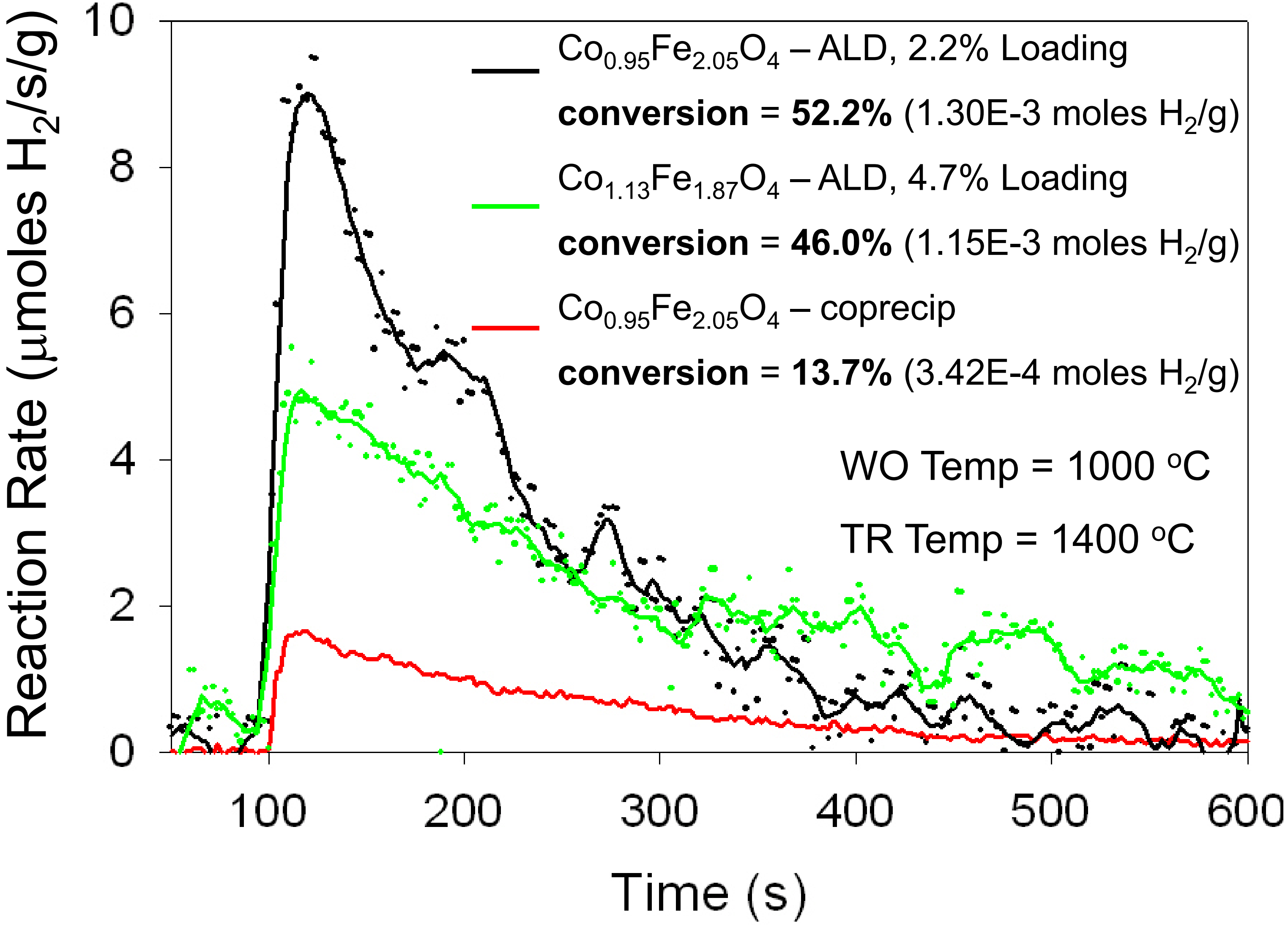




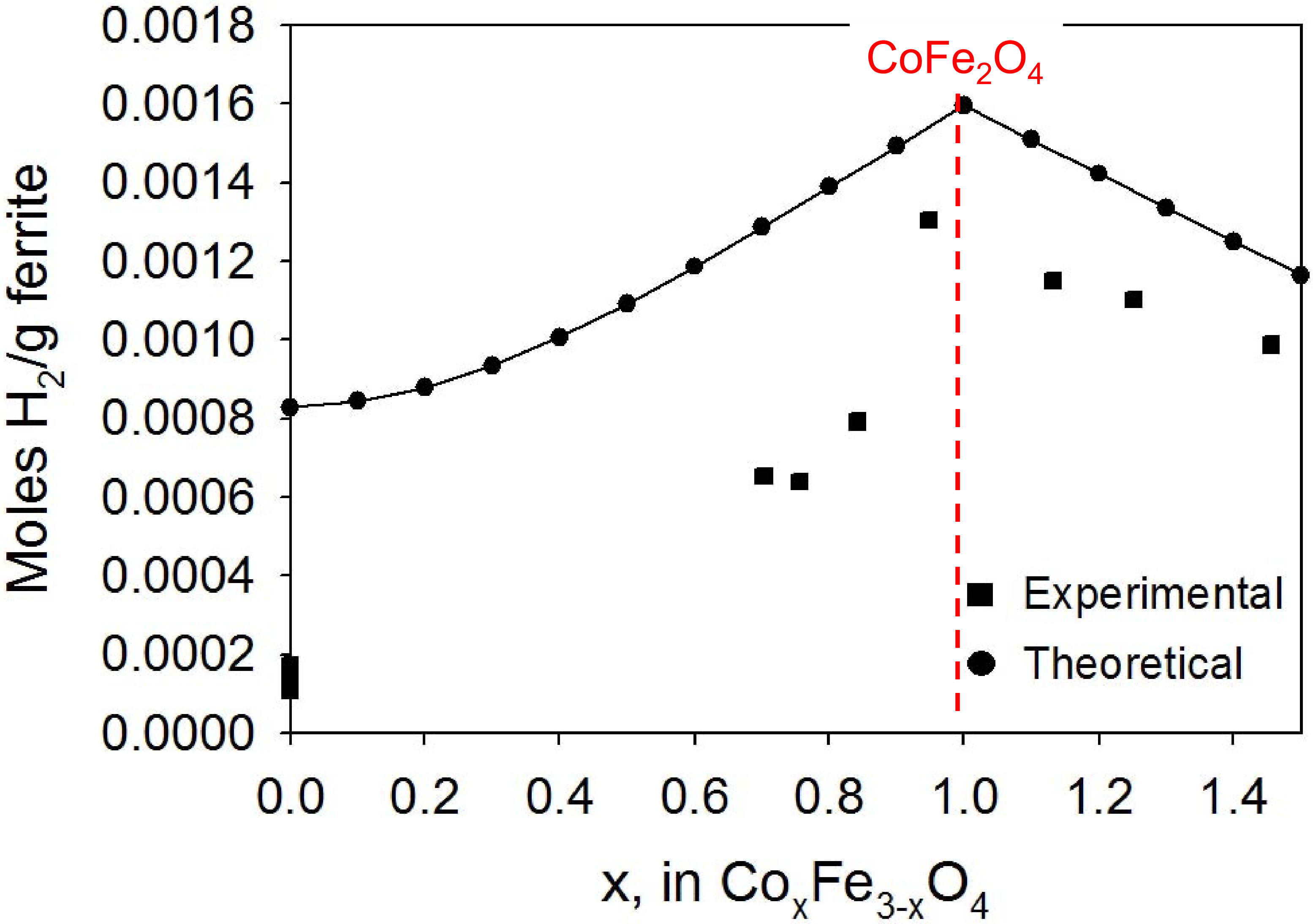
Water Splitting Reactor



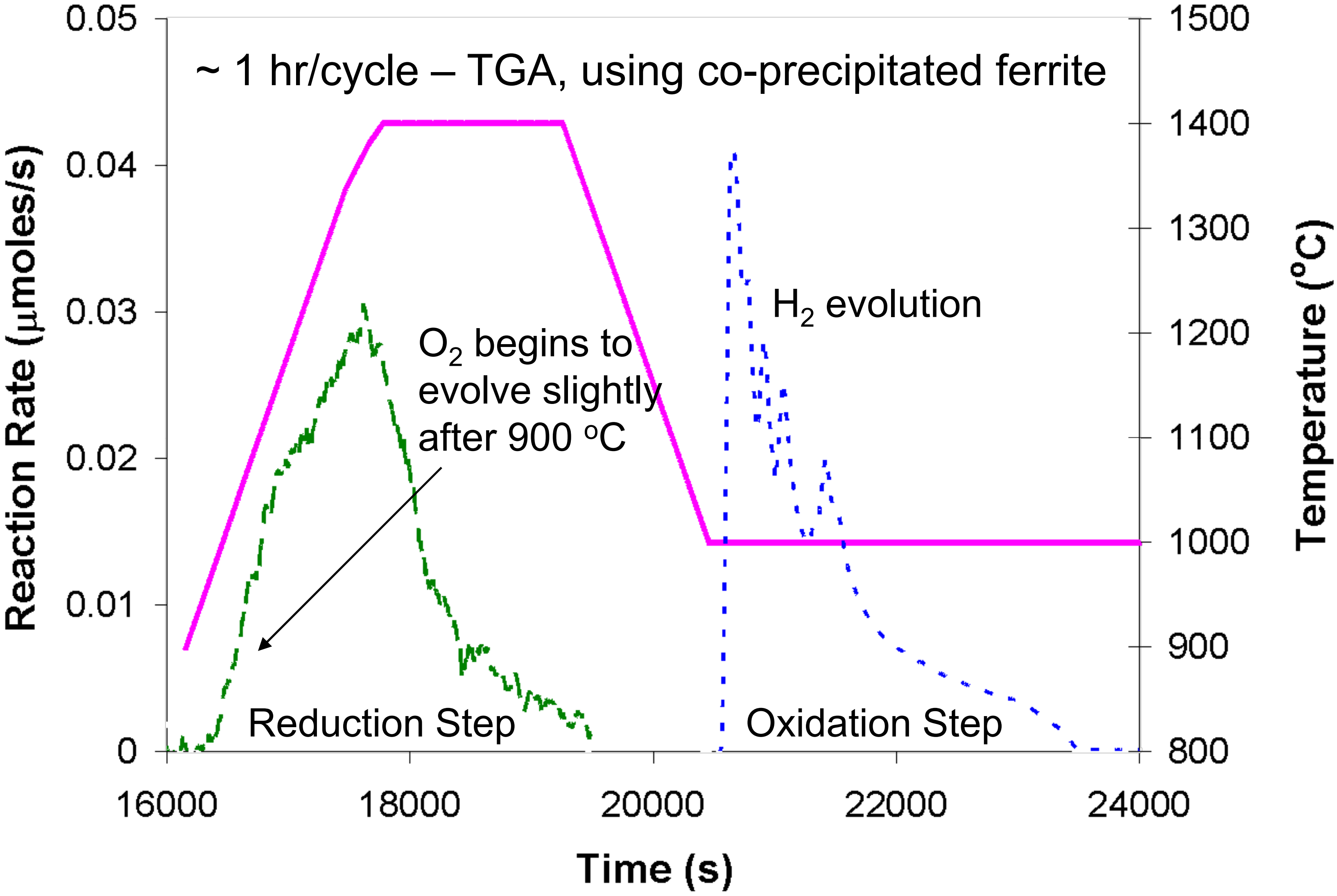
Results - Conversion is Greater for ALD samples



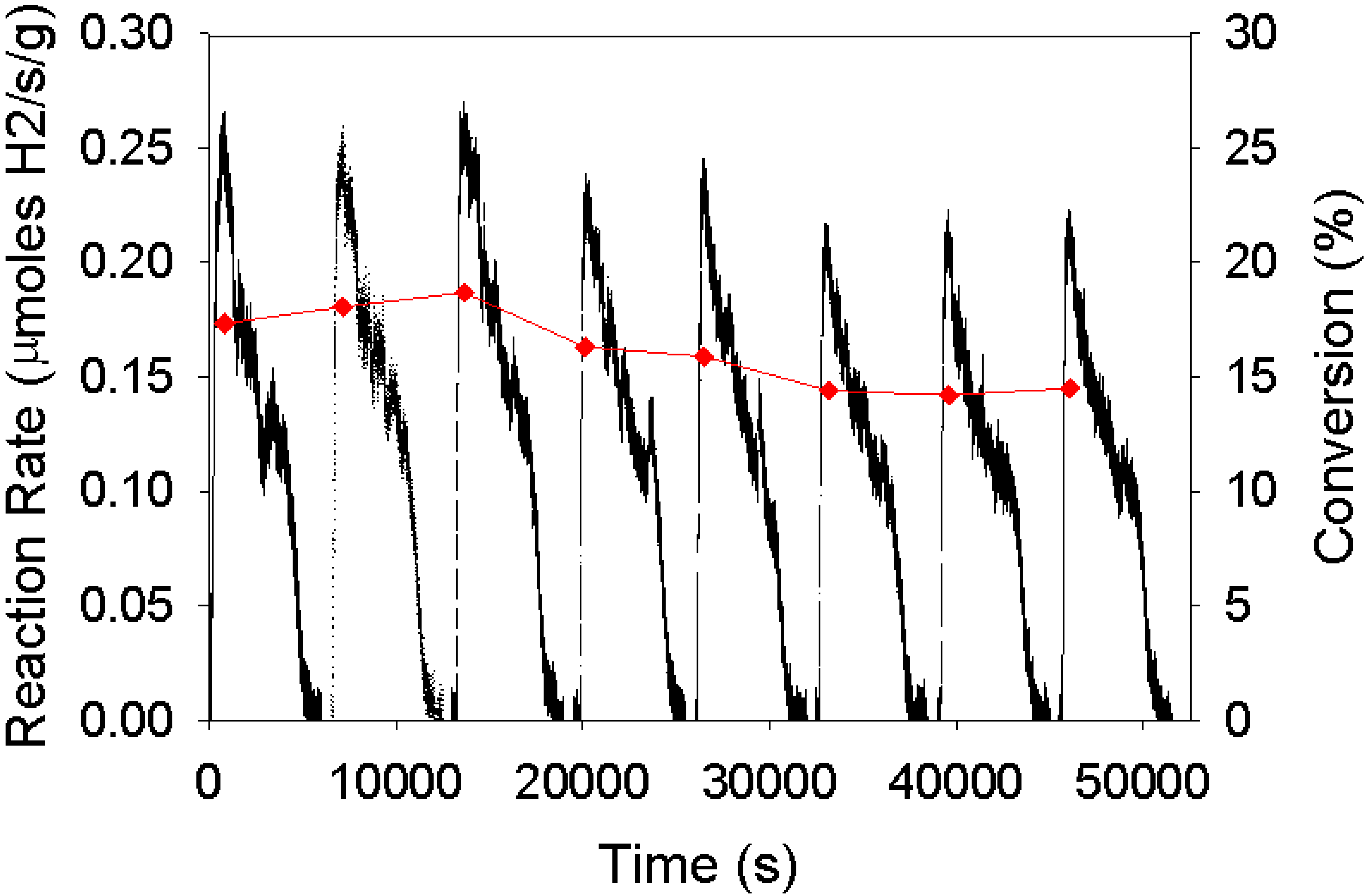
Results - Maximum Conversion Observed with a Co Stoichiometry Near 1.0



Approach - Demonstrate One Low-T Redox Cycle for $CoFe_2O_4$ (alumina support)



Results - Samples are Stable After 8 Cycles



Approach – General Economics

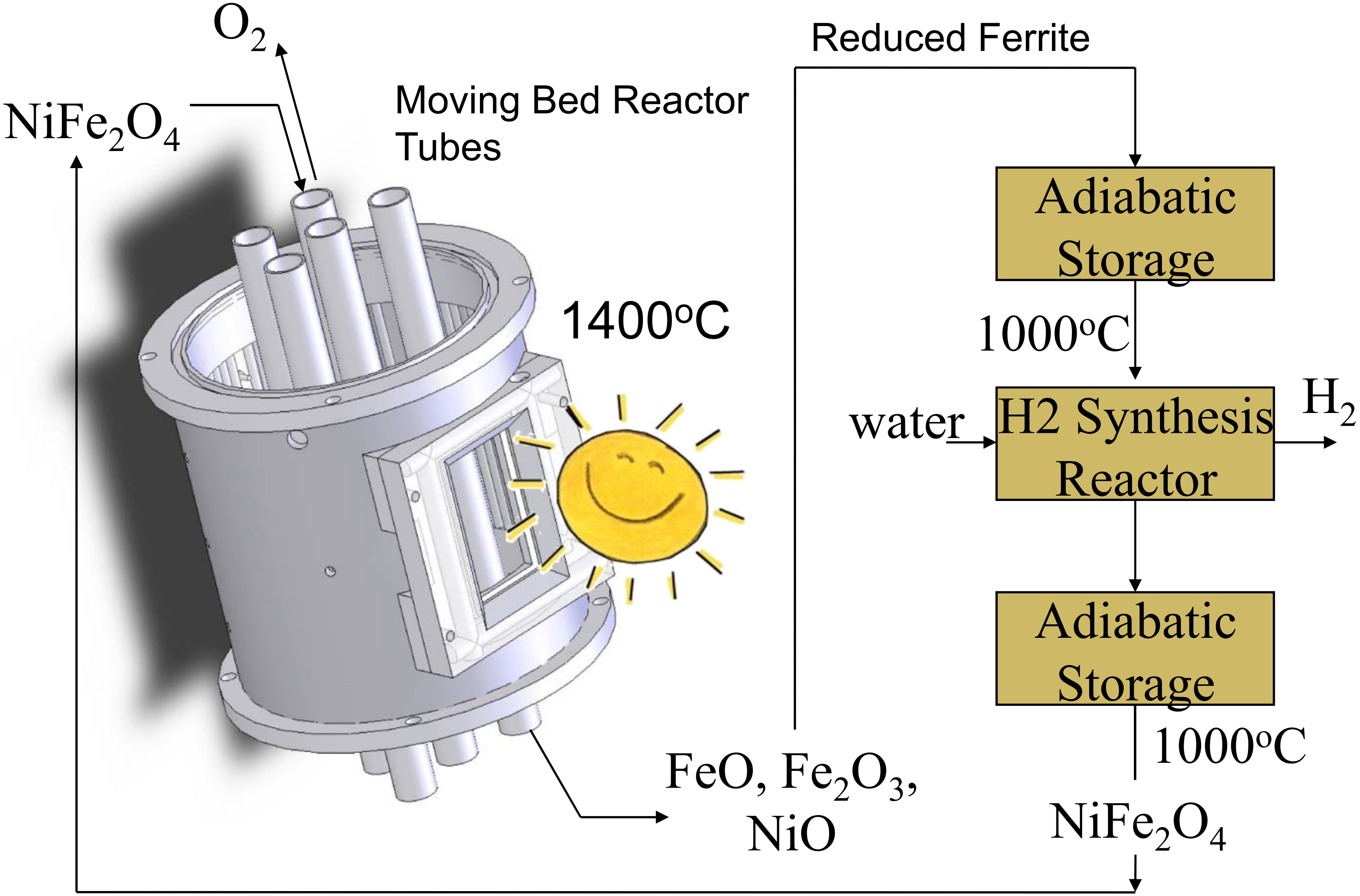
- Central Production Facility supplying H_2 at 300psig
- Produce 100,000 kg H_2/day, operating 8 hours/day, 365 days/yr.
- Calculate the necessary solar field requirements using Soltrace based on AspenPlus™ simulations and measured irradiance data for Daggett, CA (annual average).
- Evaluate a base case and byproduct case for 35%, 70%, and 100% theoretical maximum conversions of $NiFe_2O_4$ in the solar reduction step.
- Size and cost all capital items for variable production rates; Estimate operating costs in line with the general H2A assumptions
- Base case provides for no byproducts and no carbon avoidance credits
- O2 and electricity are produced in the byproduct case and will be sold for allowable H2A credit; no carbon avoidance credits
- Back-calculate the allowable capital cost of $NiFe_2O_4$ for all cases to produce H_2 having an H2A selling price of targeted \$4, \$7 and \$11/kg H_2

Major Operating Assumptions

- 2008 Case
  - $\$180/m^2$ heliostat cost
- 2012 Case
  - $\$140/m^2$ heliostat cost
- 2017 Case
  - $\$80/m^2$ heliostat cost
- No heat recovery between redox steps

- By-product cases
  - O_2 sold for $0.02/kg (H2A)
  - Electricity (heat removal) sold for $0.07/kWhr (H2A)
  - No carbon avoidance credits
- Solar Reactor
  - 1400˚C
  - O_2 removed with vacuum pump system
  - moving bed of ferrite within Silicon Carbide tubes
  - 8 cycles per day

Approach - Base Case Process Flow Diagram



O_2

$NiFe_2O_4$

Moving Bed Reactor Tubes

1400°C

Reduced Ferrite

Adiabatic Storage

1000°C

water

H2 Synthesis Reactor

H_2

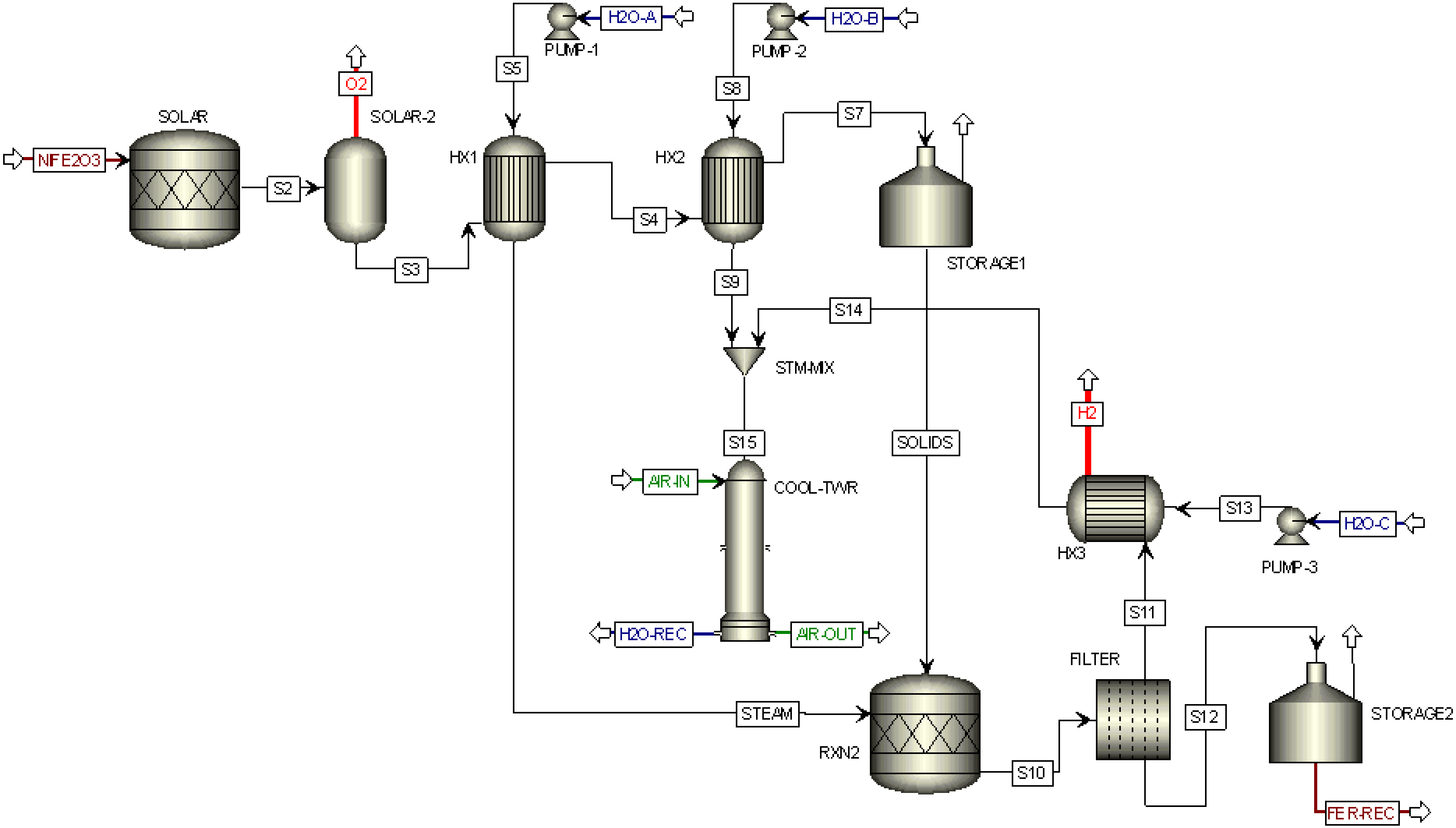
Adiabatic Storage

1000°C

FeO, Fe_2O_3, NiO

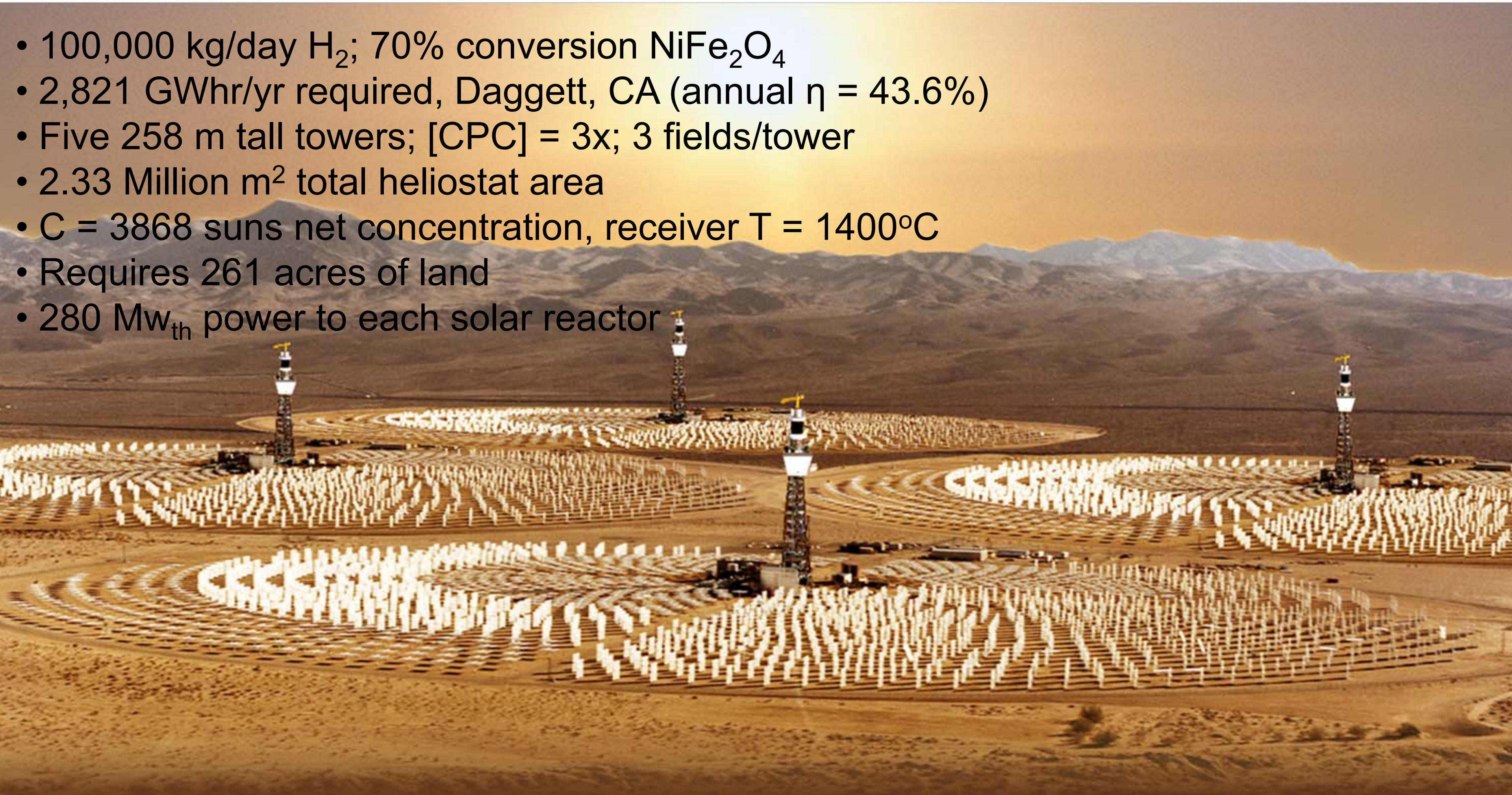
$NiFe_2O_4$

Results - AspenPlus™ Base Case



Results – Solar field design

Solar field design by Mr. Allan Lewandowski



- 100,000 kg/day H_2; 70% conversion $NiFe_2O_4$
- 2,821 GWhr/yr required, Daggett, CA (annual η = 43.6%)
- Five 258 m tall towers; [CPC] = 3x; 3 fields/tower
- 2.33 Million m^2 total heliostat area
- C = 3868 suns net concentration, receiver T = 1400^{o}C
- Requires 261 acres of land
- 280 Mw_{th} power to each solar reactor

2017 Capital Cost Breakdown

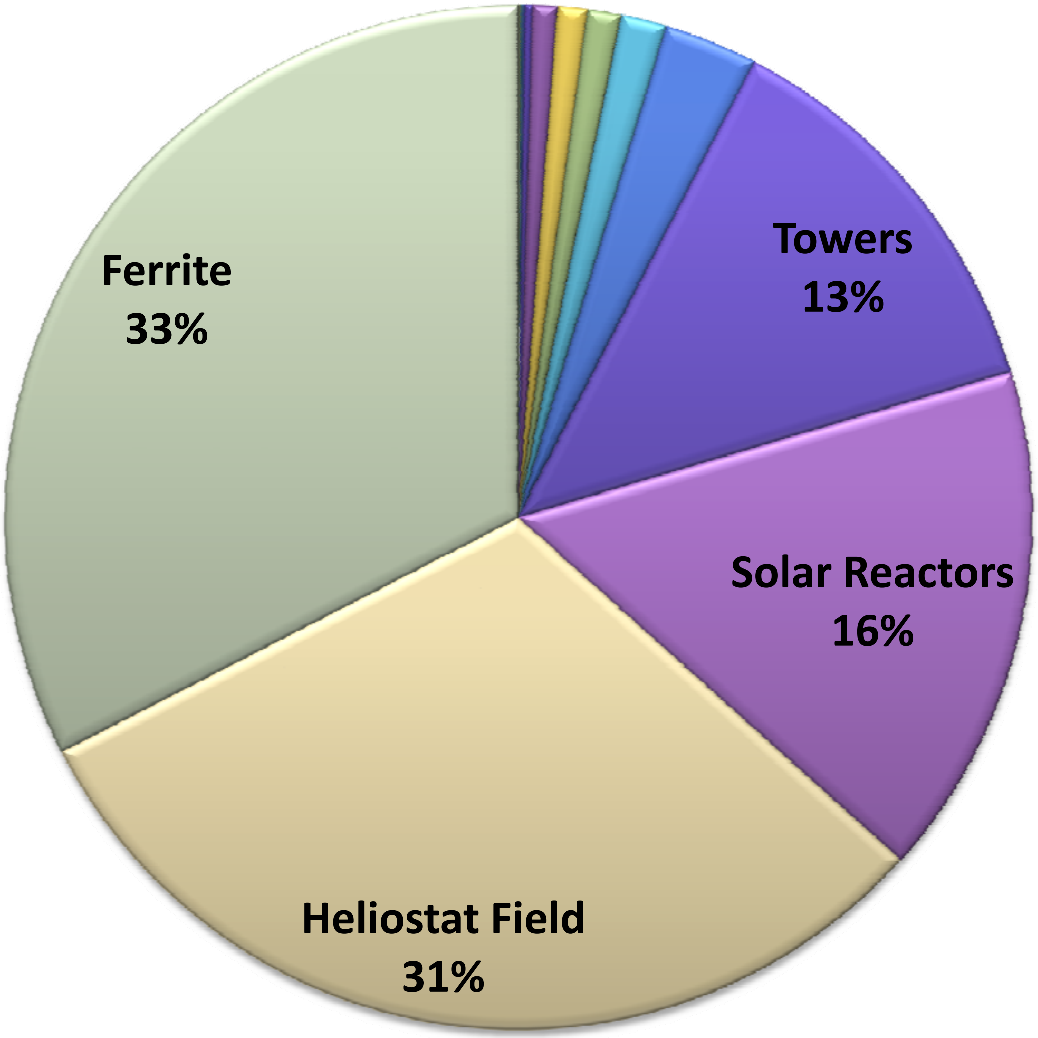
Base Case

TCI \$605M

70% Conversion

H2 \$4/kg

Allowed Ferrite Cost: \$57/kg



Current Material Costs:

NiO \$22/kg

Fe_2O_3 \$2/kg

Then, $NiFe_2O_4$ \$8.67/kg

2017 Capital Cost Breakdown

By-product Case

TCI $654M

70% Conversion

H_2 $4/kg

Allowed Ferrite Cost: $69/kg

Annual Revenue:

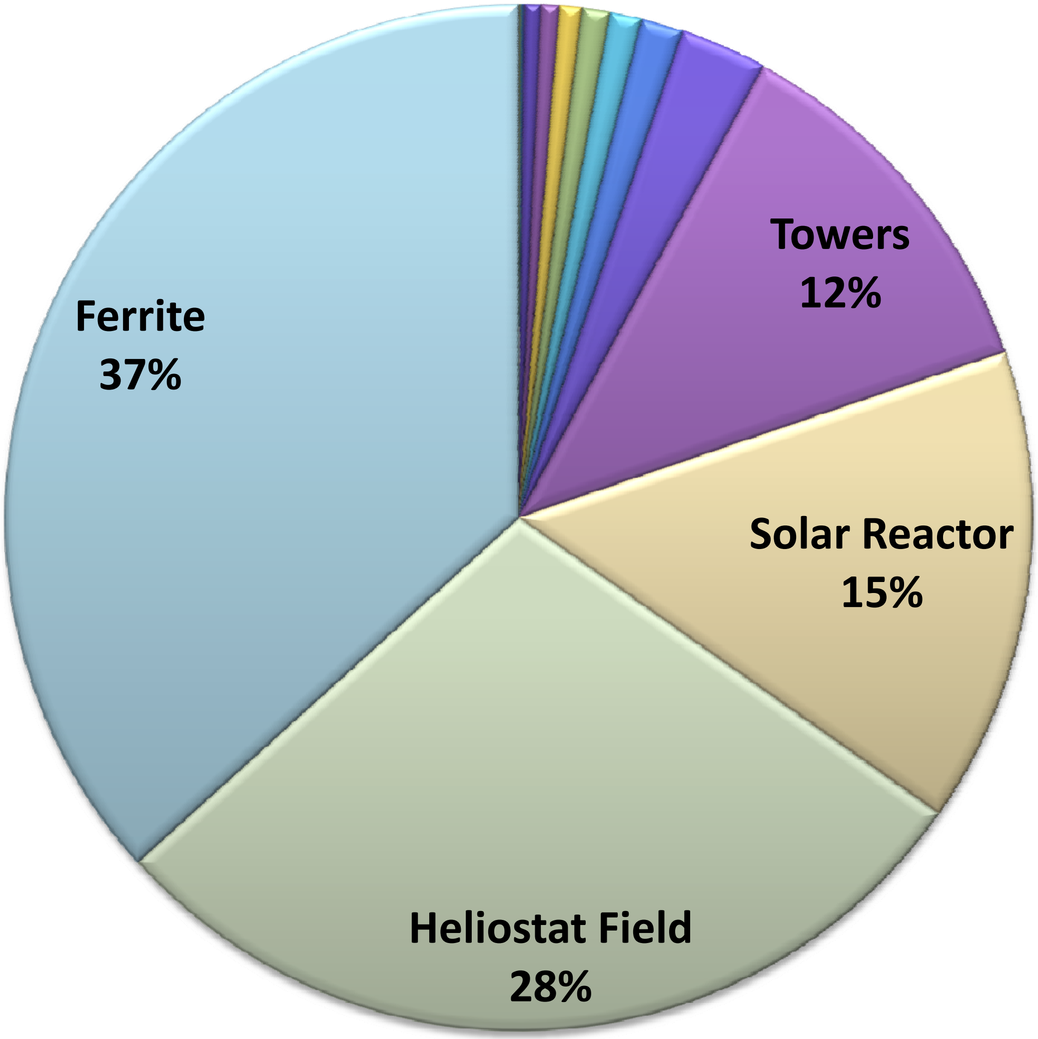
H_2: $146M (93%)

O_2: $5.8M (4%)

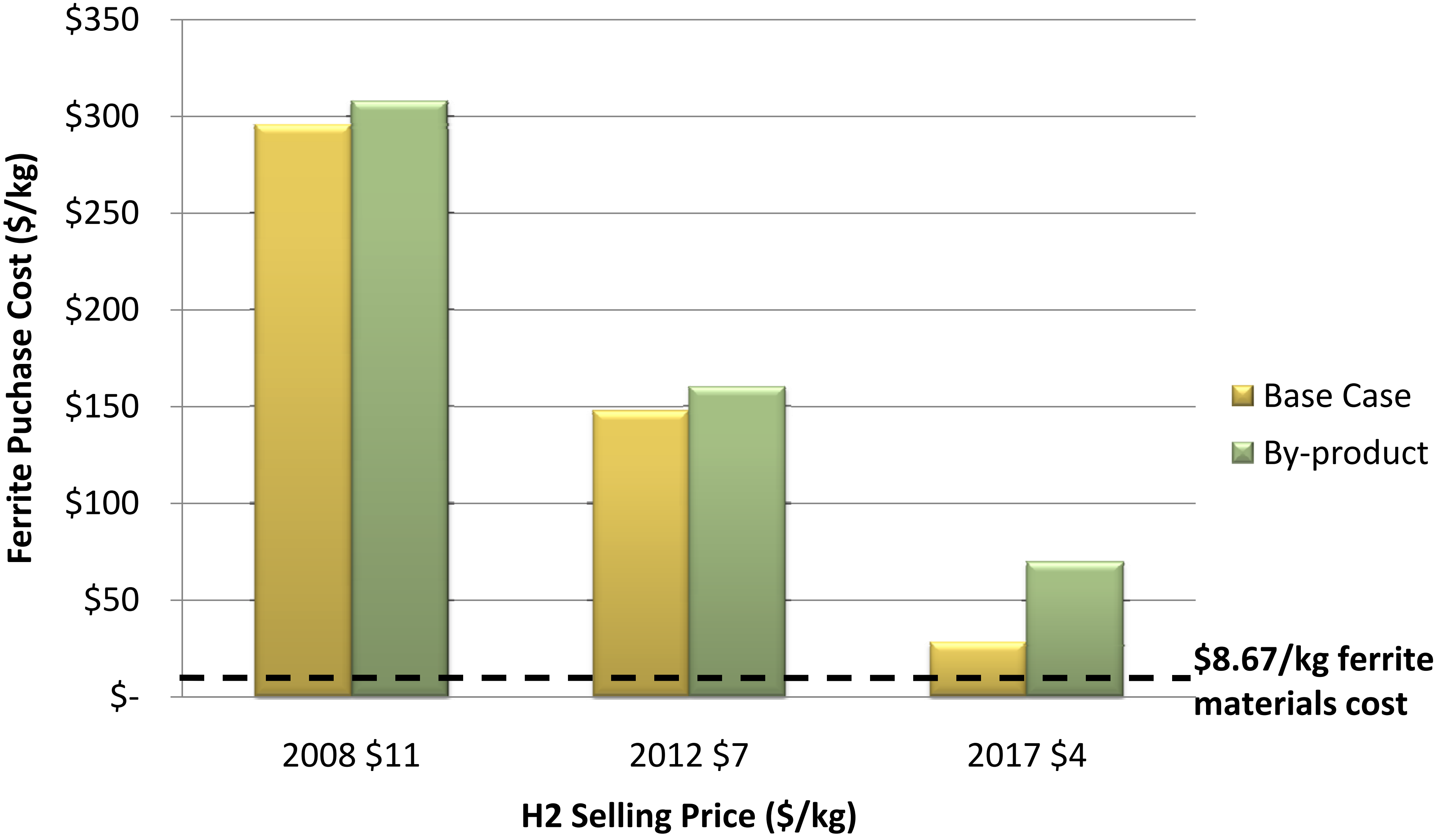
7.94 kg/kg H_2

Electricity: $5.2M (3%)

1.99 kWhr/kg H_2



70% Conversion Ferrite Purchase Cost



Results - Ferrite Cost ($/kg)

		H2 Selling Price ($/kg)	Allowable Ferrite Purchase Cost ($/kg)		
			35% Reduction Conversion	70% Reduction Conversion	100% Reduction Conversion
Base Case	2008	$11	$107	$296	$459
	2012	$7	$37	$148	$244
	2017	$4	$5	$57	$107
By-product Case	2008	$11	$116	$308	$474
	2012	$7	$47	$160	$258
	2017	$4	$14	$69	$122
Byproducts	Electricity (kWhr/kg H2)		4.42	1.99	1.27
	O2 (kg/kg H2)		7.94		

Results – Cycle Efficiencies

		Reduction Conversion		
		35%	70%	100%
Base Case	LHV	31.7%	43.1%	48.4%
	HHV	37.4%	50.9%	57.1%
By-product Case	LHV	35.8%	45.8%	50.2%
	HHV	41.5%	53.5%	58.9%

Summary

- The nickel ferrite water-splitting cycle appears to meet the 2017 \$4/kg H_2 plant gate DOE solar thermochemical target and is potentially the most economical solar process evaluated to date.
- Ferrite materials based on Particle-ALD react faster and at lower temperatures (most likely due to a reduction in diffusional resistances), reducing materials of construction concerns and cycle times
- More experimental work needs to be completed to verify the reactions and conversions.

Proposed Future Work

- Compare ALD produced $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ ferrites experimentally
- Demonstrate ability to cycle ALD-based ferrites through multiple redox reactions
- Evaluate methods for producing low cost ALD ferrite materials using non-ZrO2 high surface area substrates
- Development of stationary processing methods with superior heat integration and simplicity suitable for large-scale processing

Collaborations

- ETH-Zurich (Swiss Federal Research Institute)

  - ETH students & facilities involved

- Sandia / NSF

  - PhD student spent two summers working in their lab ($25M Grand Challenge – interested in ALD ferrites)

- ALD NanoSolutions, Inc. (Broomfield, CO)

  - agreed to produce larger quantities of ALD ferrite materials for the project

- Sundrop Fuels (Louisville, CO)

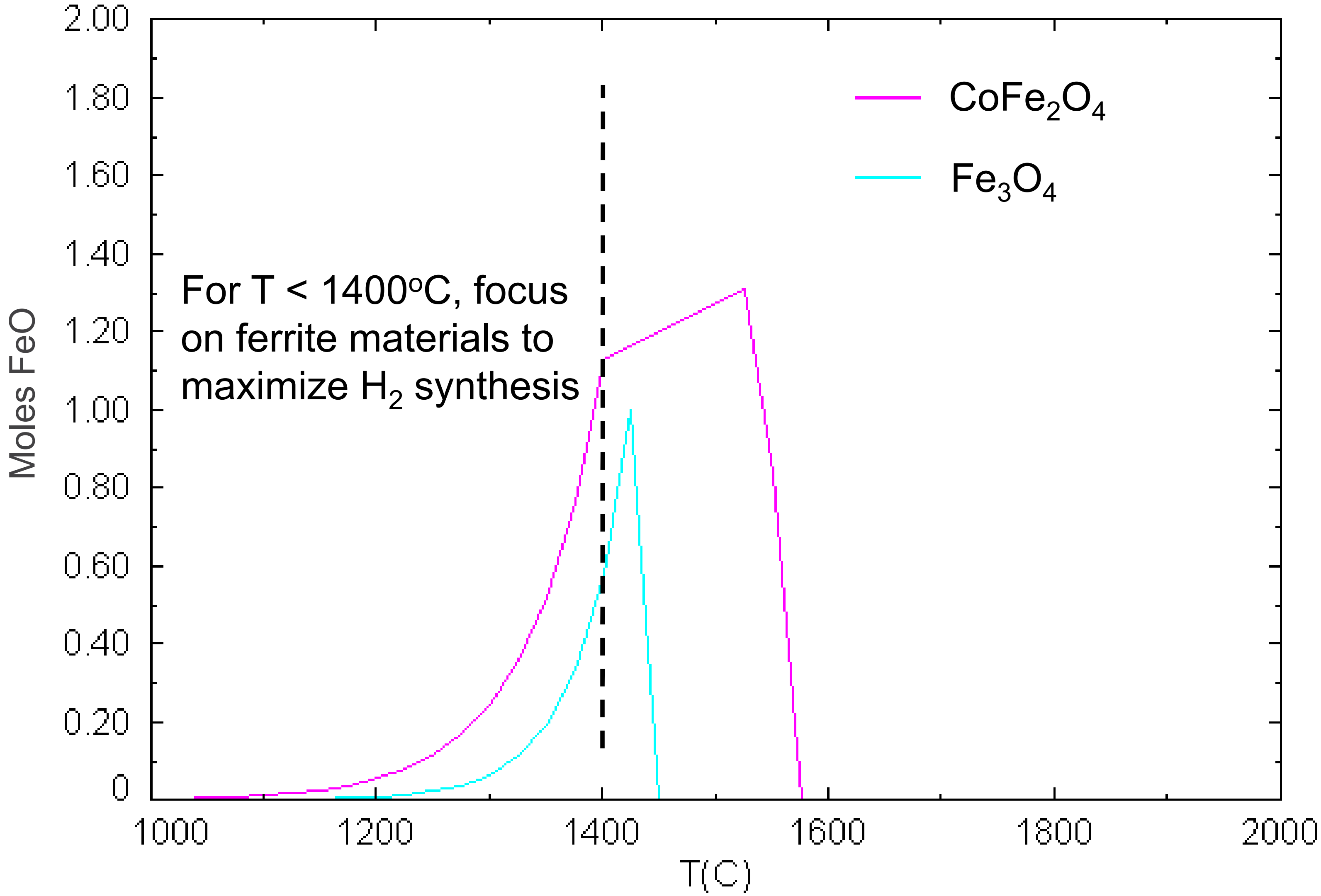
  - interested in on-sun demonstration at their solar pilot facility

Acknowledgements

- DOE Hydrogen Production Program
- Dr. Mark Allendorf and Dr. Tony McDaniel, SNL
- Mr. Carl Bingham, NREL
- Mr. Allan Lewandowski, consultant
- Prof. Aldo Steinfeld, ETH Zurich

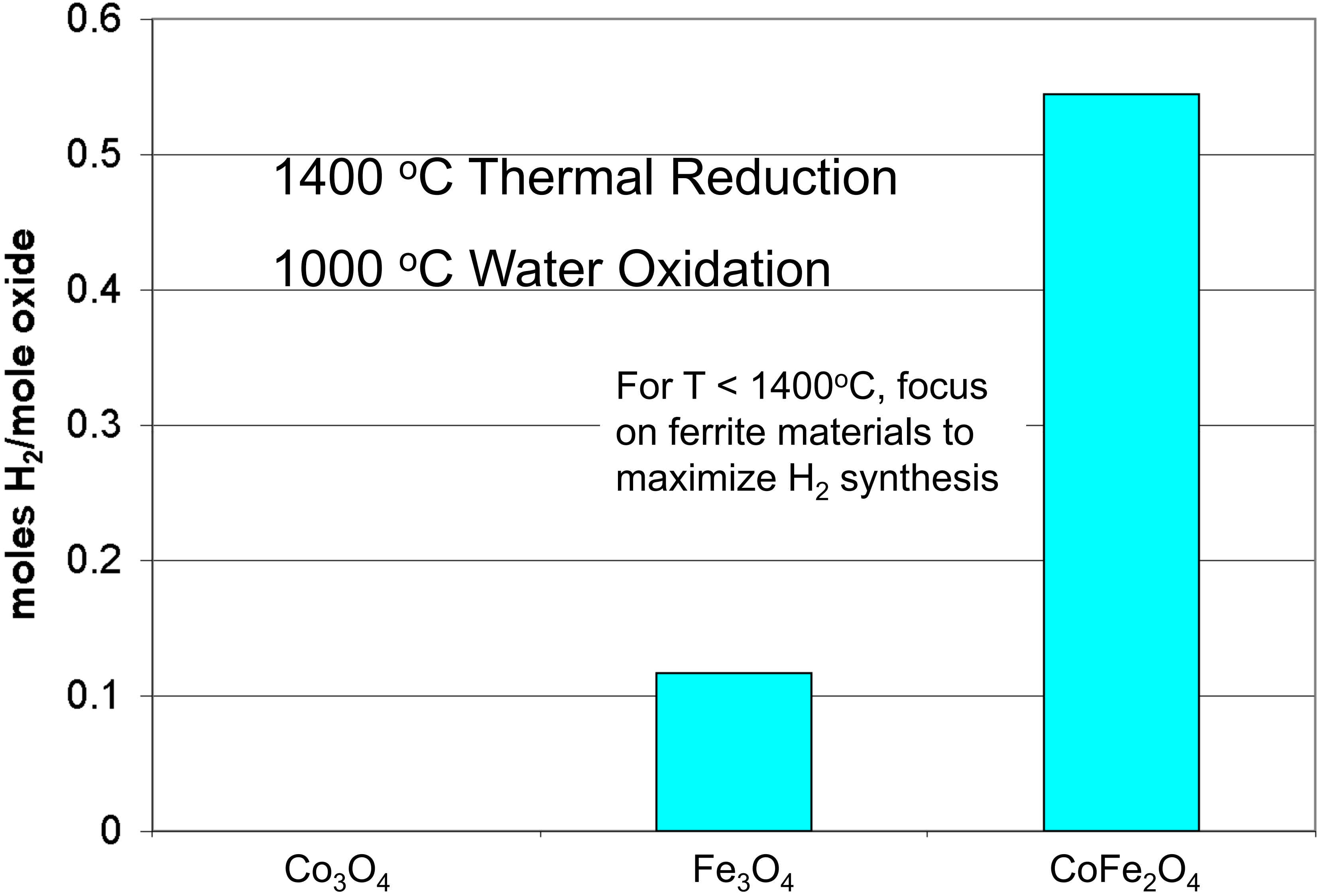
Supplemental Slides

Approach - More FeO generated with $CoFe_2O_4$



For T < 1400°C, focus on ferrite materials to maximize H_2 synthesis

Approach - more H_2 generated with $CoFe_2O_4$

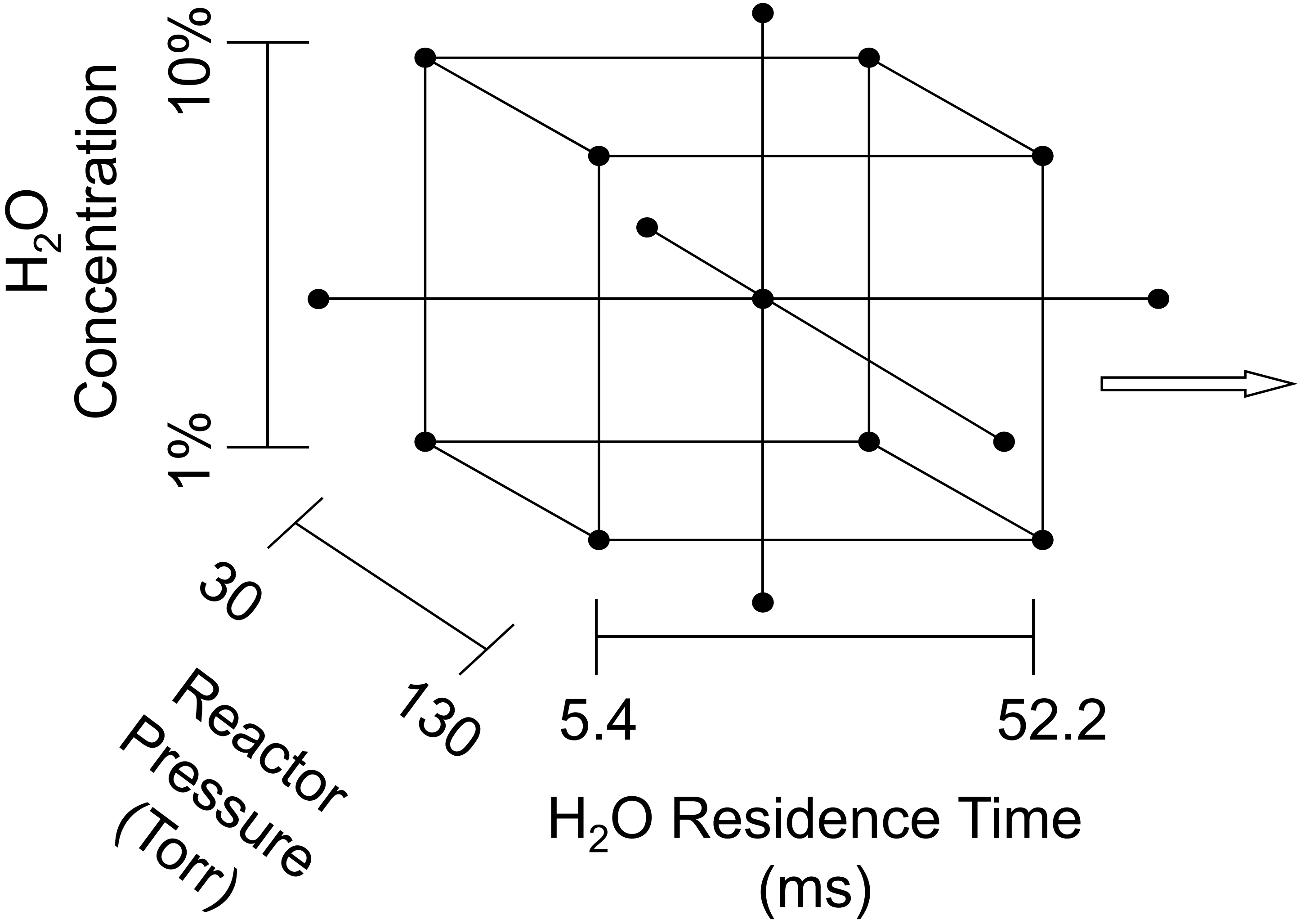


1400 °C Thermal Reduction

1000 °C Water Oxidation

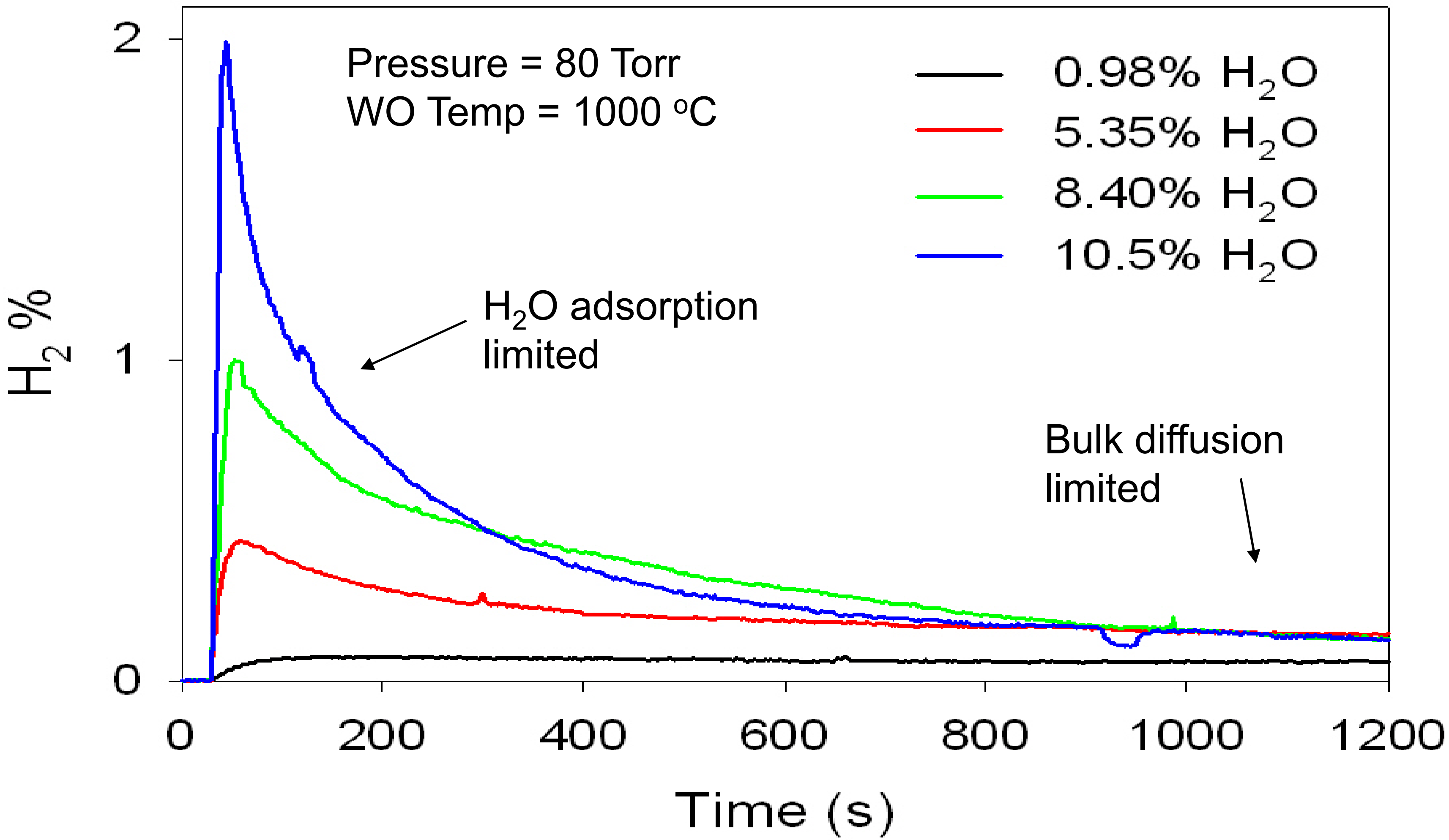
For T < 1400°C, focus on ferrite materials to maximize H_2 synthesis

Results - Optimize H_2O Flow



<u>Response</u>
moles H_2
evolved

Results - [H_2O] Affects Oxidation Rate

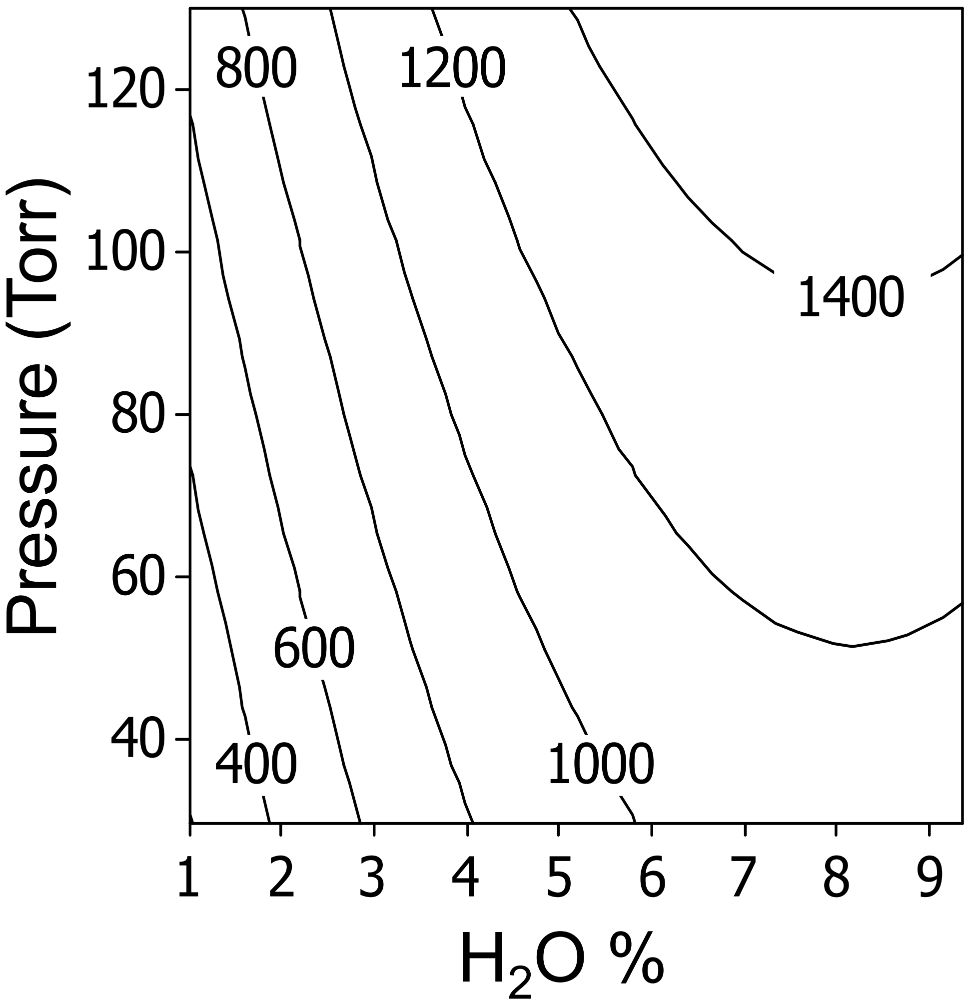


Pressure = 80 Torr
WO Temp = 1000 °C

H_2O adsorption limited

Bulk diffusion limited

Results - Largest H_2 Responses (µmoles H_2) seen at Highest [H_2O]



Factor	P-Value
H_2O %	<<0.001
Pressure	0.001
Residence Time	0.221

Results - 1200°C Reduction/800°C Oxidation

$NiFe_2O_4$ (from SB Han 2007) – Solid state synthesis	1.97 E-5 moles H_2/gram ferrite
$CoFe_2O_4$(9% loading) on Al_2O_3 - ALD	1.89 E-4 moles H_2/gram ferrite
Completely achieving thermodynamic limit for $CoFe_2O_4$ reduction	2.5 E-3 moles H_2/gram ferrite

~10X H_2 generation relative to solid state synthesis

Results - Annual Reduction Energy Requirements

$$NiFe_2O_4 \rightarrow 1.2\ FeO + 0.4\ Fe_2O_3 + NiO + 0.3\ O_2$$

$\Delta H_{rxn} = 214{,}612.9$ J/mol (FactSage™ results at 0.1 MPa & 1400°C)

Solar Reactor (GWhr/yr)	**Reduction Conversion**		
	35%	**70%**	**100%**
Heat of Reaction	1,799	1,799	1,799
Sensible Heat	2,044	1,022	715
Total Energy Required	3,843	2,821	2,514

Cavity operates at ~3,800 suns, losses are primarily radiative.