Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

High temperature reactor catalyst material development for low cost and efficient solar driven sulfur-based processes

Corgnale Claudio (PI)

Organization: Greenway Energy (GWE)

Date: June 13, 2018

GreenWayEnergy®
POWERFUL EXPERTS

Project ID: PD169

NREL | BERKELEY LAB | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

Project Partners

Corgnale C (*co-PI*), Summers W, Ganesan P (*GWE*)

Monnier J (*co-PI*), Regalbuto J, Shimpalee S, Weidner J, Tengco J, Diao W (*USC*)

Ginosar D, Adhikari B (*INL*), Ma Z, Davenport P, Martinek J (*NREL*), Gorensek M (*SRNL*)

Award #	EE0008091
Start Date Yr 1 End Date Project End Date	10/01/2017 12/31/2018 TBD
Total DOE Share Total Cost Share Yr 1 DOE Funding*	$999,998 $267,182 $250,000

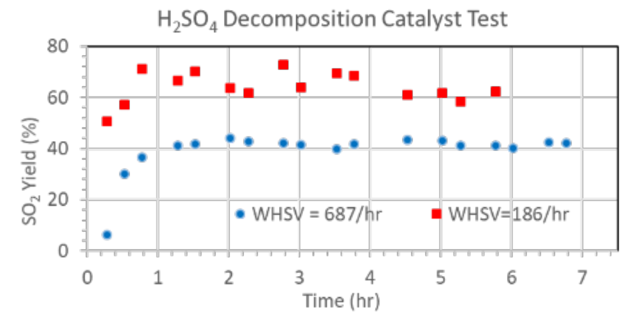
Project Vision

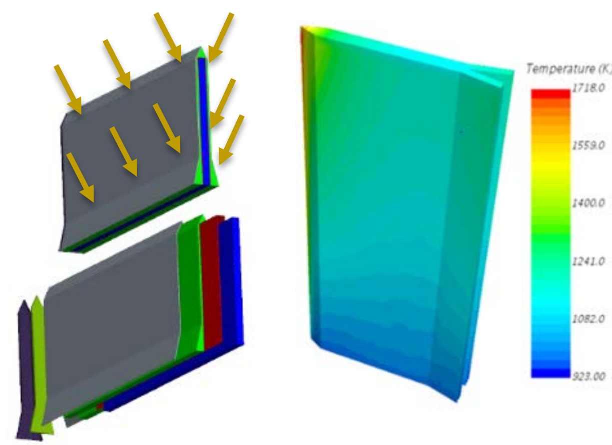
Development of:

- ***New catalyst material*** using our demonstrated surface free energy (SFE) and electro-less deposition technique,
- Novel integrated ***direct solar reactor-receiver***, based on a demonstrated cavity solar reactor,
- New effective ***solar-thermochemical plant process integration***

Objective:

- ***efficient and low cost*** solar thermochemical process





Project Impact

- Increase of the ***energetic and exergetic efficiency*** (solar to H_2 energy efficiency > 20%),
- Projected reduction of the ***H_2 cost to < 2 $/kg***

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project history

- GWE, USC and SRNL have been working together on H_2 and renewable energy based systems
- INL and SRNL were involved in the NHI for sulfur based thermochemical cycles development
- NREL and GWE have common experiences in solar applications (SunShot Initiative)

Initial results

- Initial catalyst formulation identified with promising results
- Novel direct solar receiver-reactor concept for H_2SO_4 decomposition identified and numerically verified
- Novel process flowsheet identified allowing higher efficiency and potential cost reduction

Key Impact – Proposed targets

Metric - Milestones	*State of the Art*	*Proposed*
Catalyst • Activity ($molSO_2/h/g_{Cat}$) • Degradation (%/hour)	0.23 0.030	0.28 0.015
Efficiency • Sun to H_2 (%)	16 % (LHV)	> 20% (LHV)
Cost • H_2 cost ($/kg)	3.6 – 7.6	< 2

Barriers	Solutions
Catalyst activity and lifetime	Bimetallic catalyst - ED technique
Materials of construction and BOP at high temperature	SiC material - Modeling and experimental stress tests
Efficient and cost effective solar- HyS plant integration	Unified intensified solar receiver-reactor
Efficient and cost effective solar HyS plant design	Augmented cross sectional heat recovery – External project results for the electrolysis – Enhanced heat exchangers

Partnerships

GWE – Techno-economic analysis, design solutions and detailed transport phenomena model

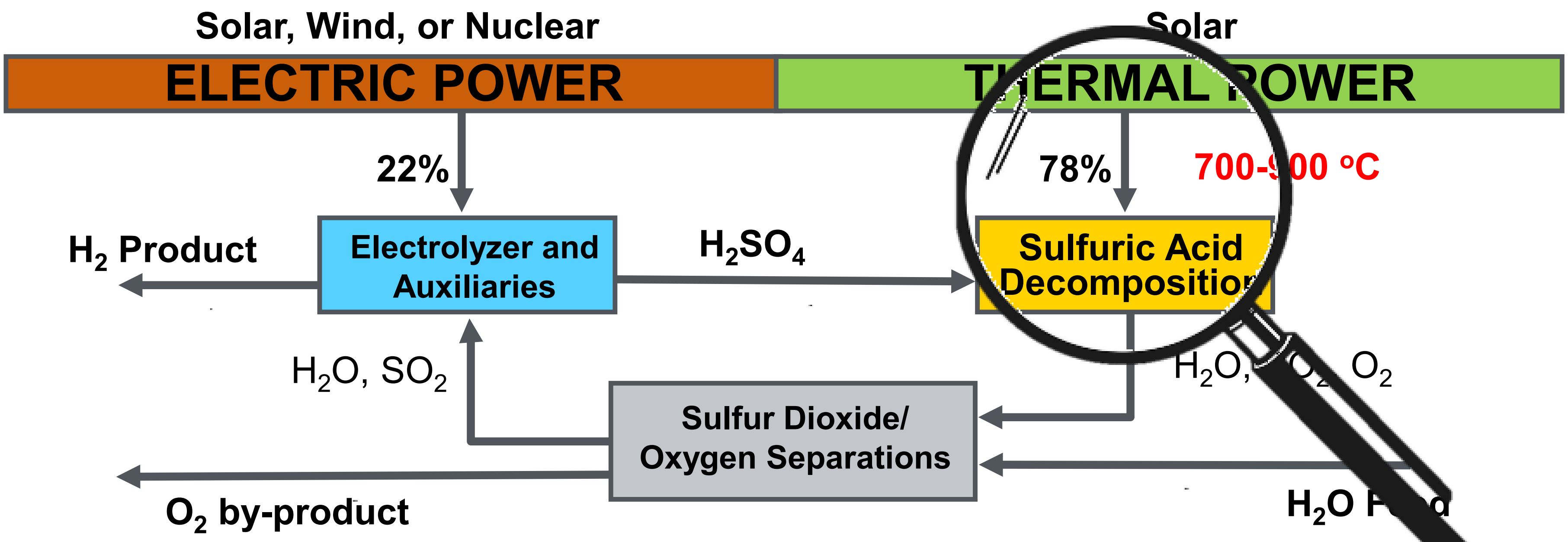
USC – Catalyst development and CFD analysis

INL – Catalyst performance analysis under realistic conditions

SRNL – HyS process modeling and analysis

NREL – Solar plant design and cost assessment

Approach- The HyS process



The high temperature decomposer is the key component for the solar driven process energy efficiency and cost reduction

HyS = Hybrid sulfur

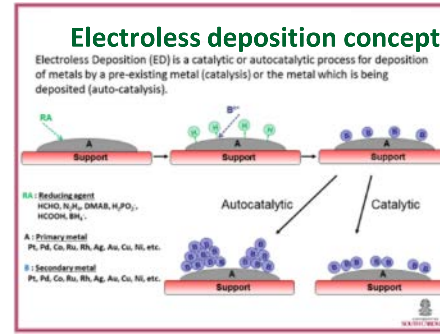
Approach- Innovation

LEVEL 1 – Catalysis fundamentals

H_2SO_4 reaction catalyst understanding and development

- Catalyst performance understanding
- Catalyst development and synthesis
- Catalyst performance experimental tests

Novel Electroless Deposition approach for bi-metallic catalyst formulations based on the Surface Free Energy of the metals



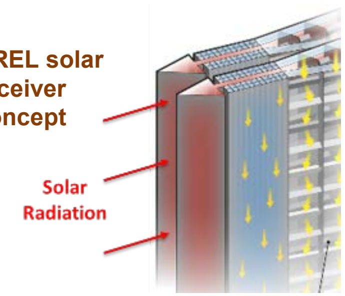
LEVEL 2 – Engineering design

H_2SO_4 reaction solar reactor design

- Novel reactor baseline configuration
- Numerical modeling of the reactor concept
- Reactor fabrication and experimental tests

Novel direct solar cavity receiver-reactor, based on NREL concept

NREL solar receiver concept

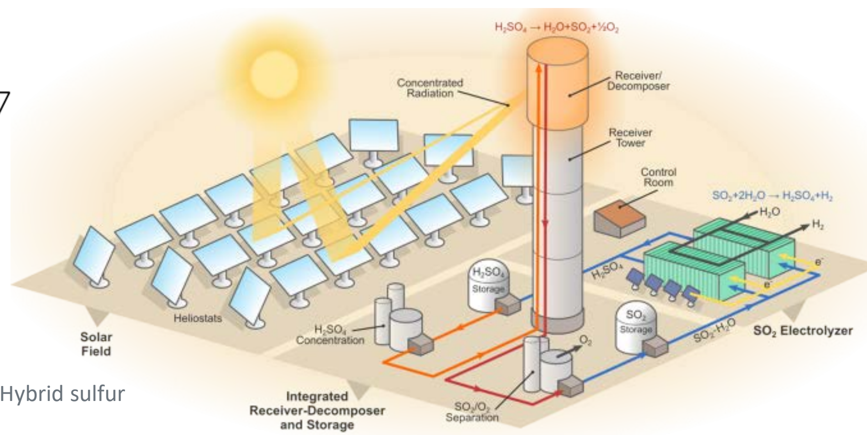


LEVEL 3 – System analysis

Techno-economic analysis of the solar plant

- Novel HyS process flowsheet
- Conceptual design of the overall solar plant
- Economic-financial analysis of the solar plant

Novel HyS flowsheet with chemical storage and direct solar receiver



Final objective

H_2SO_4 decomposition system integrated in a solar HyS

- High energy and exergy efficiency (>20%, DOE target)
- Low hydrogen costs (<2 $/kg, DOE target)

HyS = Hybrid sulfur

Relevance & Impact

Level 1 – Catalyst development

Improved catalyst development and test (100 hours) showing reduced deactivation

Partners: USC - INL

Milestones 1.1 and 1.2 - 45% completed

Level 2 – Reactor design

Design of improved reactor allowing for increased efficiencies and cost reduction

Partners: GWE – USC - NREL

Milestone 1.3 - 70% completed

Level 3 – Solar system analysis

Techno-economic analysis of the overall solar HyS plant, achieving solar to H_2 efficiency > 20% (DOE target) and cost < 2 $/kg (DOE target)

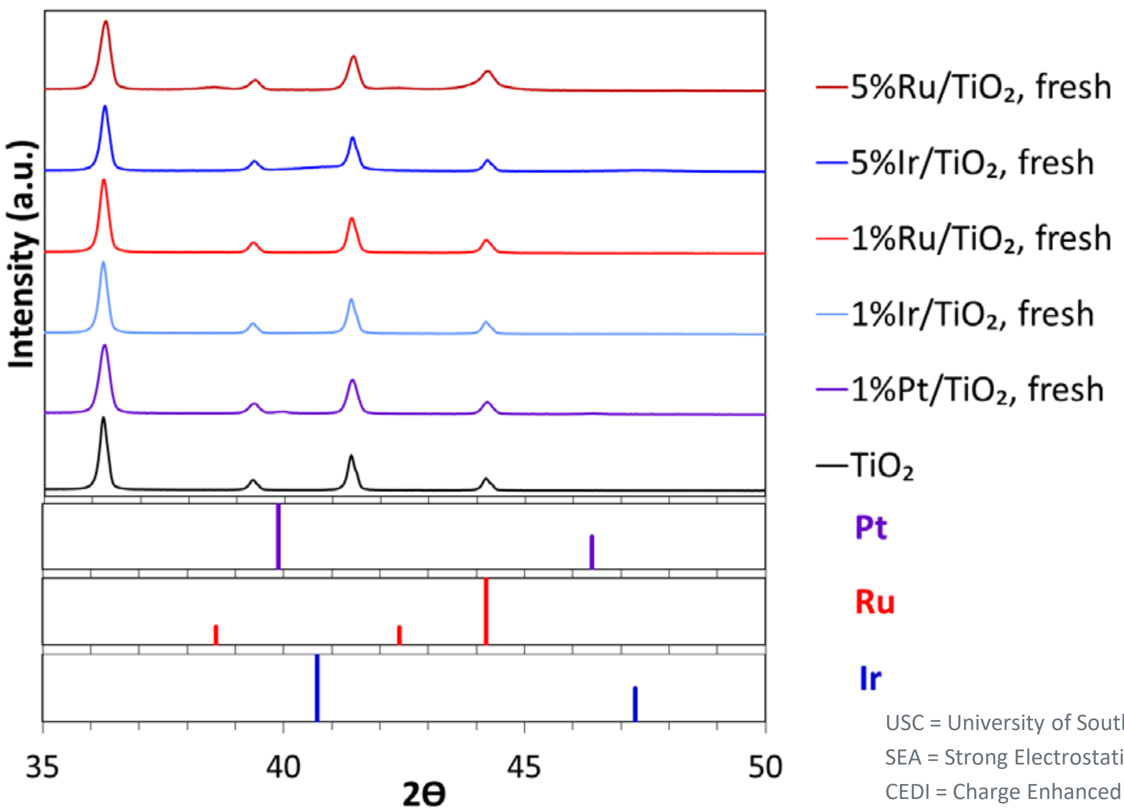
Partners: GWE – SRNL - NREL

Milestone 1.3 – 50% completed)

Metric - Milestones	***State of the Art***	***Proposed***
Catalyst • Activity ($molSO_2/h/g_{Cat}$) • Degradation (%/hour)	 0.23 0.030	 0.28 0.015
Efficiency • Sun to H_2 (%)	16 % (LHV)	> 20% (LHV)
Cost • H_2 cost ($/kg)	3.6 – 7.6	< 2

Accomplishments – Catalyst development
Level 1

Monometallic materials	*Preliminary characterization and status*
1 wt% Pt/TiO_2	Sintering at 800 °C in Ar
1 wt% Ir/SiO_2 1 wt% Ir/Al_2O_3	Sintering of Ir at 800 °C in Ar with supports different than TiO_2
1-5 wt% Ir/TiO_2	No sintering at 800 °C in Ar – bimetallic support
1-5 wt% Ru/TiO_2	No sintering at 800 °C in Ar – bimetallic support



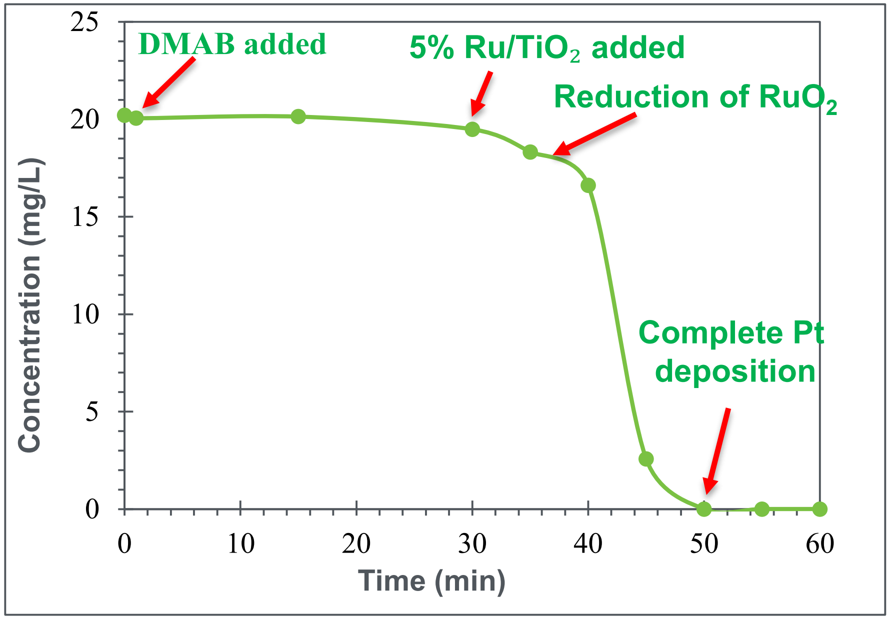
- *Objective: high performance catalyst. Initial material cost is a secondary aspect in the HyS cycle*
- Monometallic Pt sintered
- Bimetallic catalyst using ED of Pt (catalyst) on top of higher SFE core metals (Ru and Ir).
- Best support for bimetallic catalyst is TiO_2 with Ru or Ir.
- Monometallic materials (Ir and Ru) well dispersed using SEA and CEDI.
  - Small peaks and small particles detected in the XRD analysis.
- Catalysts characterized using XRD, STEM, chemisorption, *in-situ* XRD, and TPO.

USC = University of South Carolina
SEA = Strong Electrostatic Deposition
CEDI = Charge Enhanced Dry Impregnation
ED = Electroless Deposition
HyS = Hybrid Sulfur
XRD = X Ray Diffraction
STEM = Scanning Transmission Electron Microscope
TPO = Temperature Programmed Oxidation
SFE = Surface Free Energy

Accomplishments - ED of Pt on 5% Ru/TiO_2 and 5% Ir/TiO_2

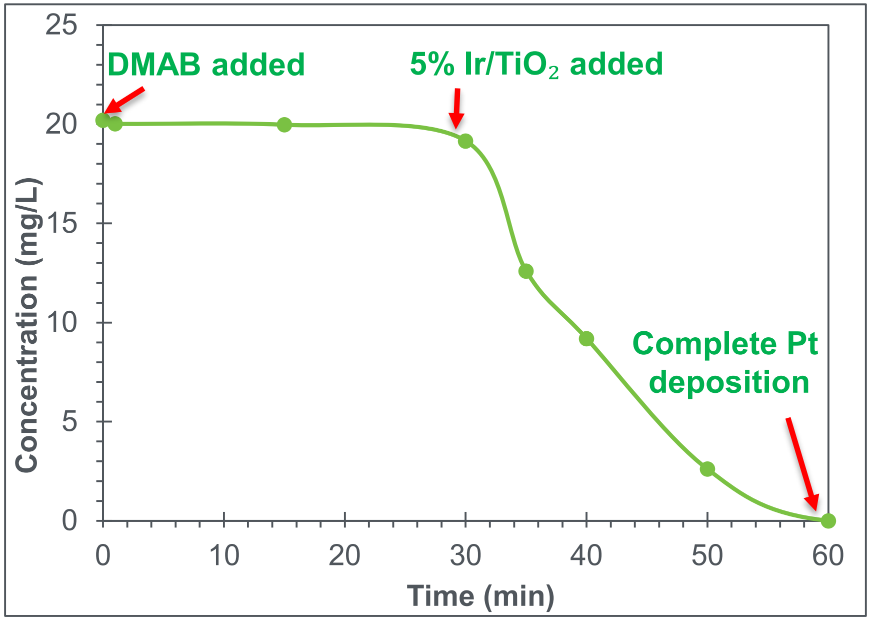
Level 1 (ED kinetics for Pt deposition)

5% Ru/TiO_2



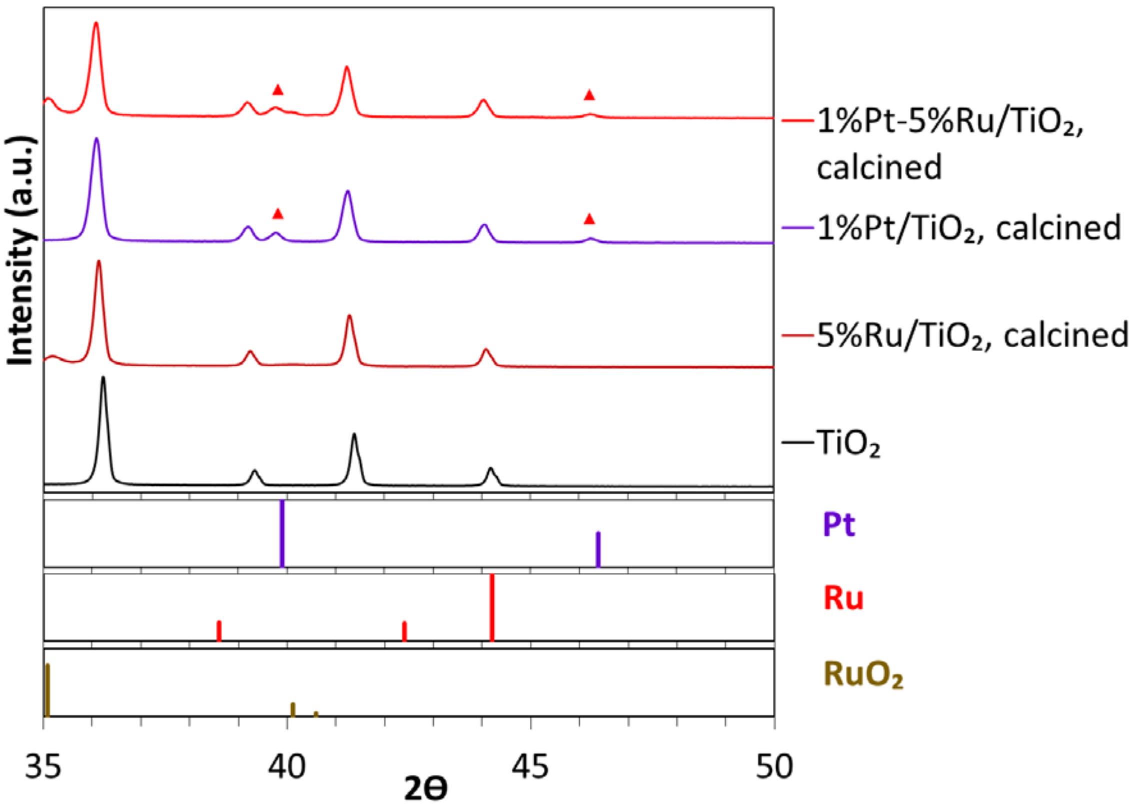
Temperature	50^0C
$[PtCl_6^{2-}]$: [EN] : [DMAB]	1 : 4 : 5
Volume	500 mL
wt of catalyst (5%Ru/TiO_2)	1.0 g
Wt% Pt	1.0 %
pH	10

5% Ir/TiO_2



Temperature	50^0C
$[PtCl_6^{2-}]$: [EN] : [DMAB]	1 : 4 : 5
Volume	500 mL
wt of catalyst (5%Ir/TiO_2)	1 g
Wt% of Pt	1%
pH	10

Accomplishments – Pt deposited on Ru/TiO_2
Level 1

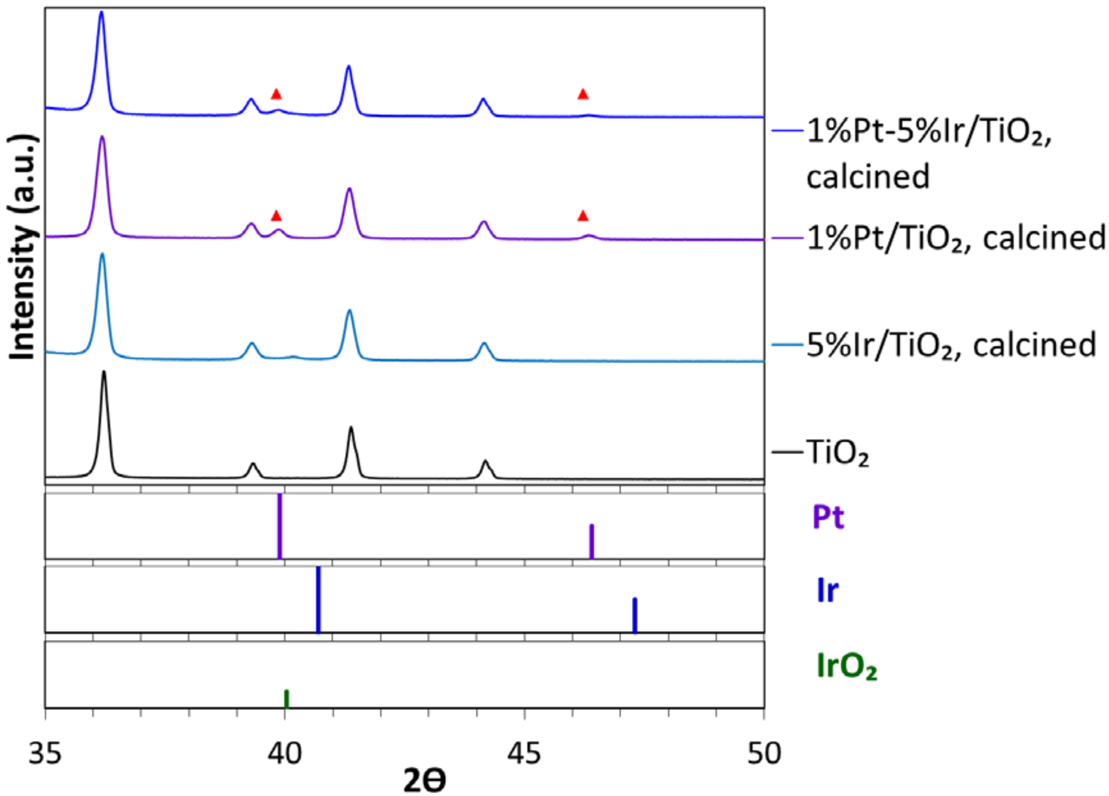


- Visible peaks (red triangles) indicate presence of Pt^o on surface but less intensity than monometallic Pt catalyst.
- Presence of RuO_2 on the surface.
- Initial results showed need for 5% Ru/TiO_2.
- Complete Pt deposition on Ru surface in 20 min.
- Induction period of 10 min to reduce $RuO_2 \rightarrow Ru^o$.

ED = Electroless Deposition

Accomplishments – Pt deposited on Ir/TiO_2

Level 1



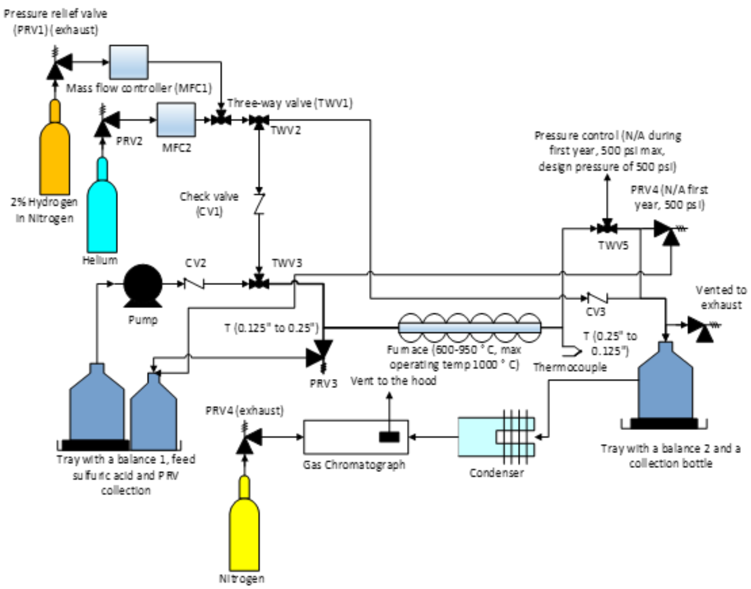
- Red triangles denote Pt^o
- Pt peaks have lower intensity than Pt-Ru bimetallic and monometallic Pt catalyst.

1%Pt/TiO_2 Fresh	Intensity: 0.0078
1%Pt/TiO_2 Calcined	Intensity: 0.0418
1%Pt on 5%Ir/TiO_2 Calcined	**Intensity: 0.0185**
1%Pt on 5%Ru/TiO_2 Calcined	Intensity: 0.0418

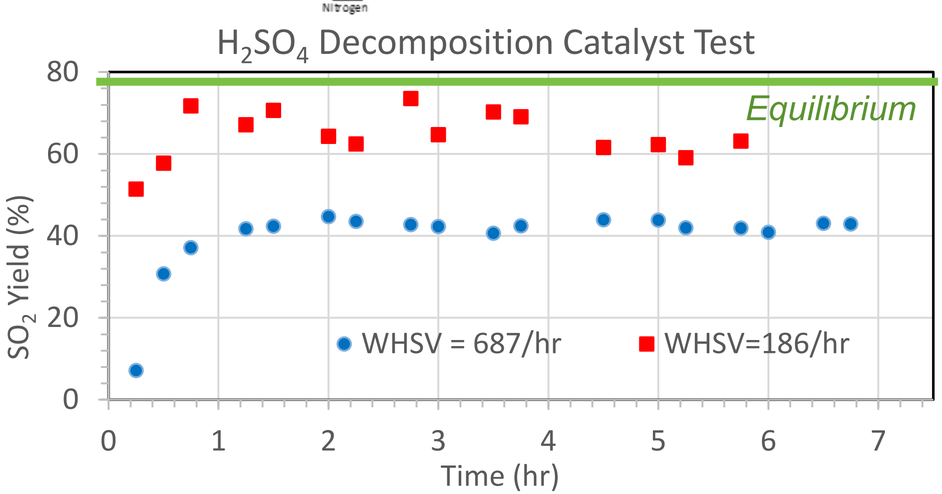
- Initial results showed need for 5% Ir/TiO_2.
- Complete Pt deposition onto Ir surface in 30 min.
- Absence of metal oxides.

ED = Electroless Deposition

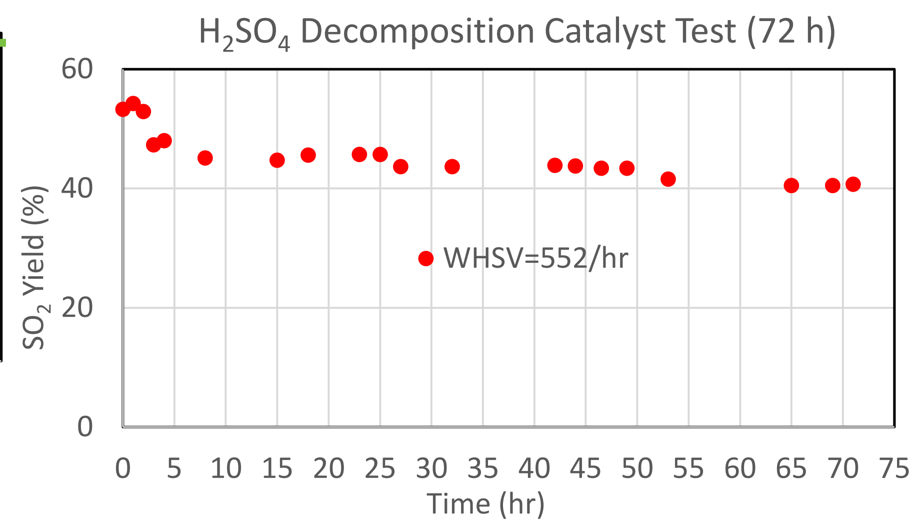
Accomplishments – Monometallic catalyst test
Level 1



- INL test facility – needed for H_2SO_4 decomposition tests at realistic conditions.
  - Temperature up to 1000 °C
  - Pressure ≥ 1 bar
  - H_2SO_4 concentrations up to 90 wt%
  - Realistic flowrates for acceptable GHSV
  - Data acquisition enabling extended testing
- Results for 1% Pt/TiO_2 gave H_2SO_4 conversion up to 70-75% at 100% selectivity to SO_2 (equilibrium at 78%)
- Limited deactivation after 72 hours online.



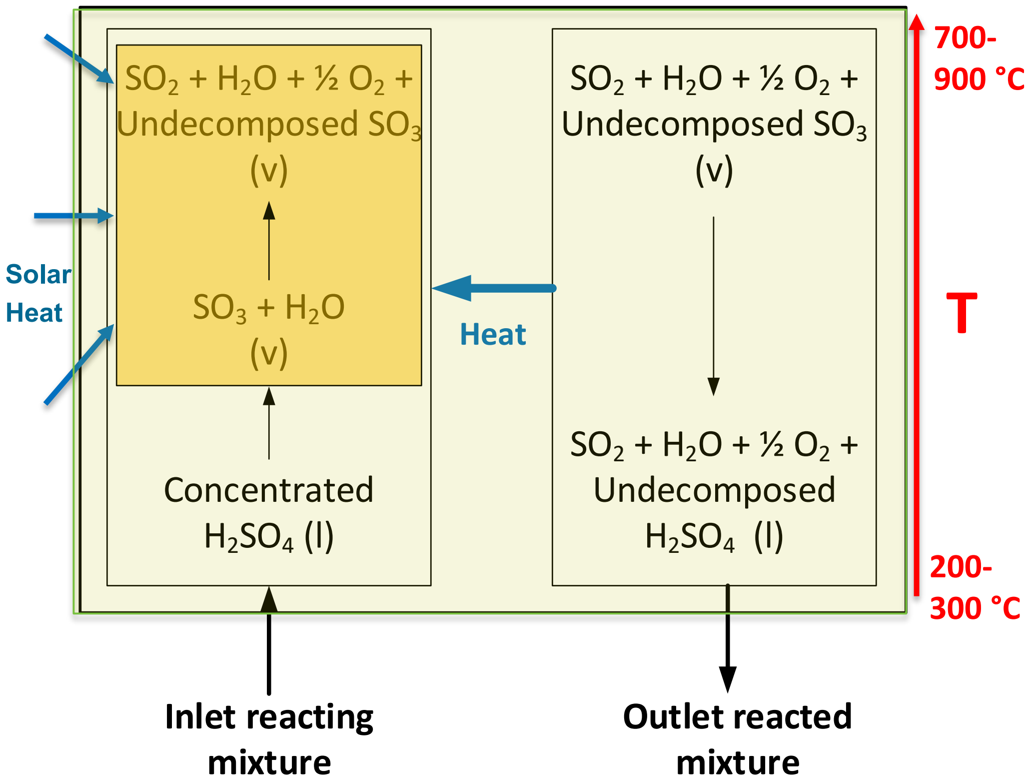
T= 800 °C, P= 1 bar and H_2SO_4 concentration = 85 wt %.
Catalyst: 0.18 g of 1% Pt/TiO_2



ED = Electroless Deposition
GHSV = Gas hourly space velocity
WHSV = Weight hourly space velocity

Accomplishments – H_2SO_4 decomposition

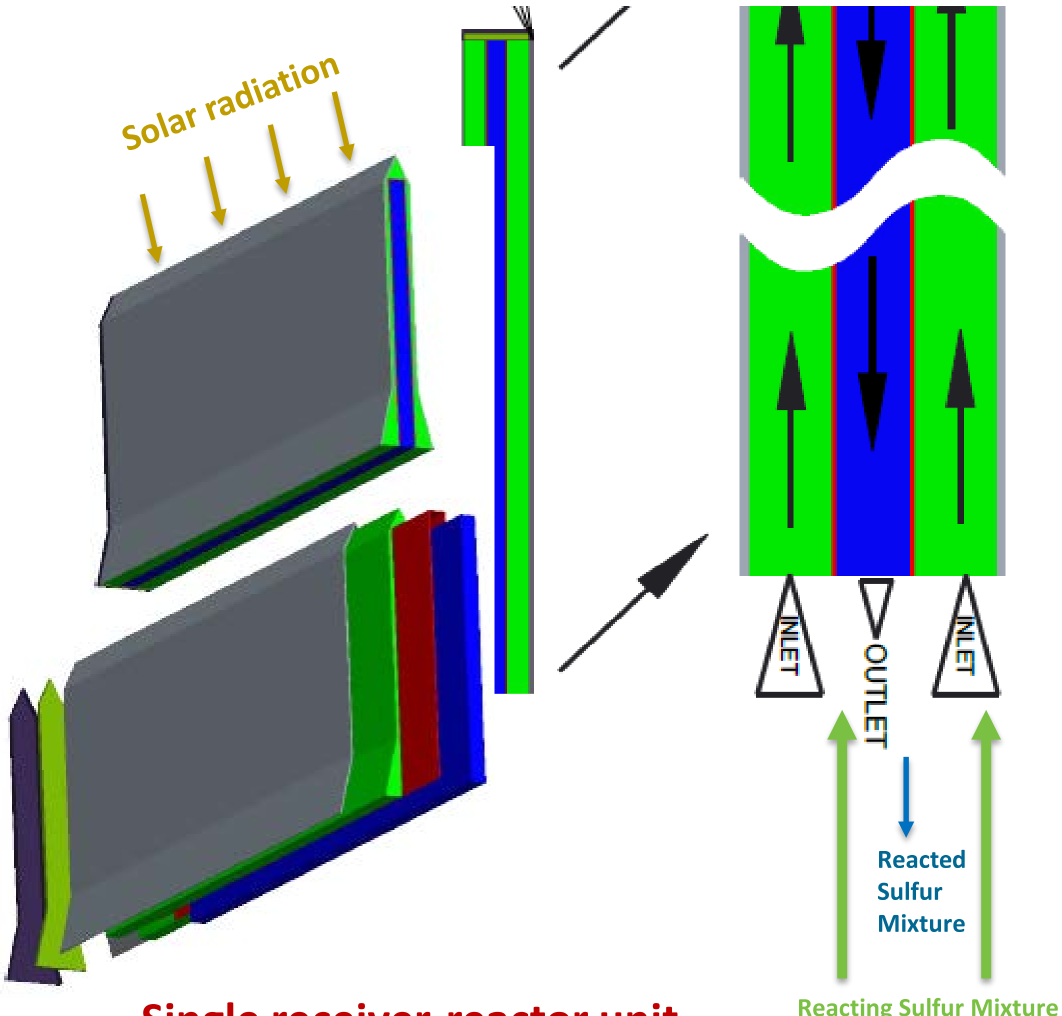
Level 2



- Sulfuric acid decomposition steps
  - Vaporization of concentrated H_2SO_4 and Decomposition into SO_3
  - Catalytic decomposition (yellow box) into SO_2
- Catalyst development
  - High activity at T on the order of 800 °C and higher
  - Low performance degradation
- Reactor analysis and design
  - Need for effective internal heat recovery and solar heat exchange

Accomplishments – Solar receiver/reactor

Level 2



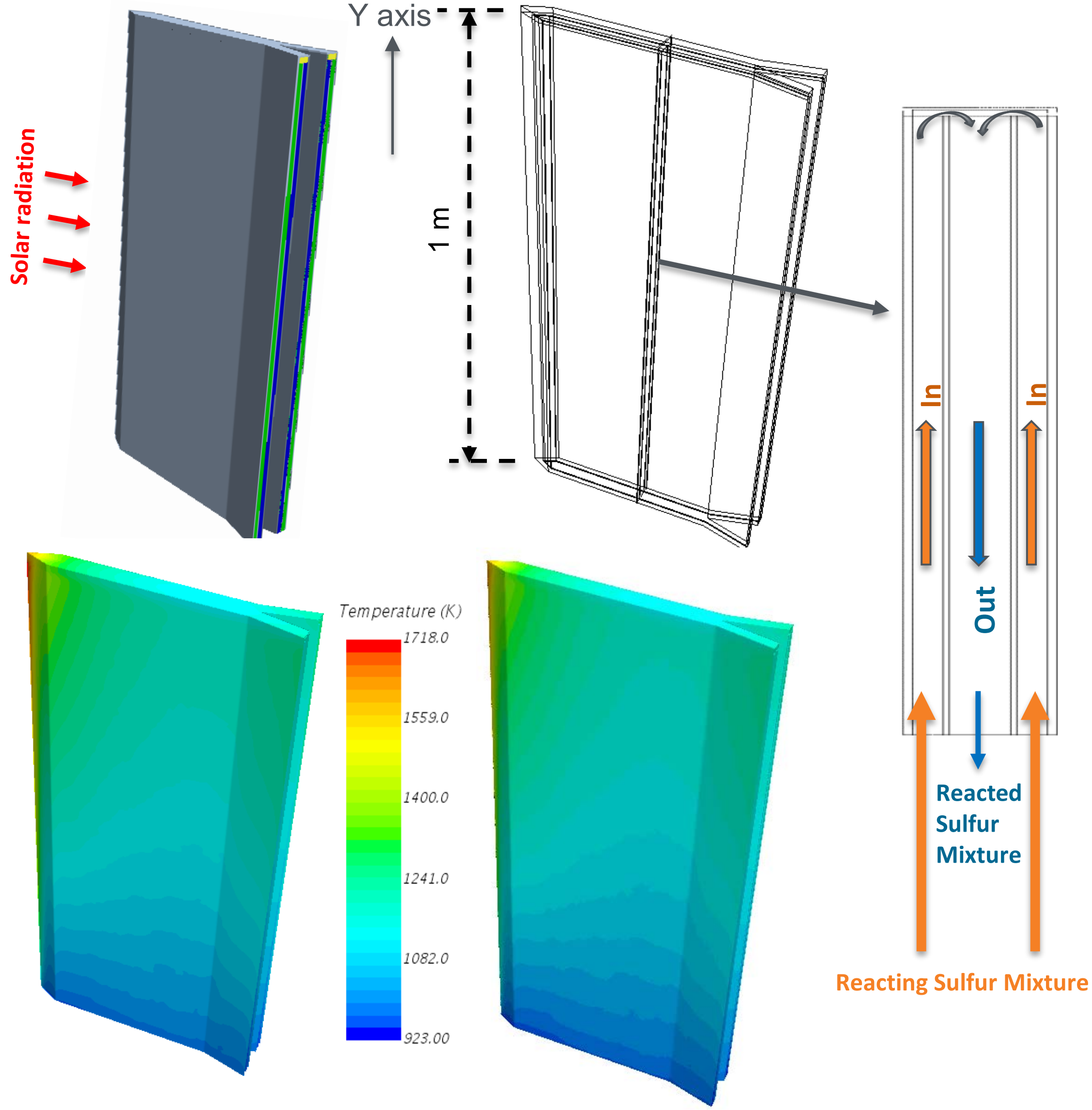
Single receiver-reactor unit

Novel GWE-NREL H_2SO_4 decomposition reactor configuration (ROI filled)

- Compact and intensified design
- External solar heating and internal heat recovery accomplished in a single SiC unit
- Technical feasibility demonstrated with detailed transport phenomena modeling results
- Projected strong cost reduction and overall increase of exergetic efficiency vs 'traditional' bayonet reactor

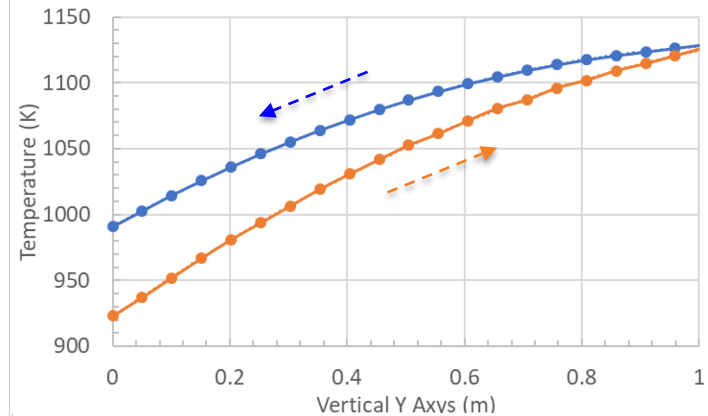
ROI = Record of Invention

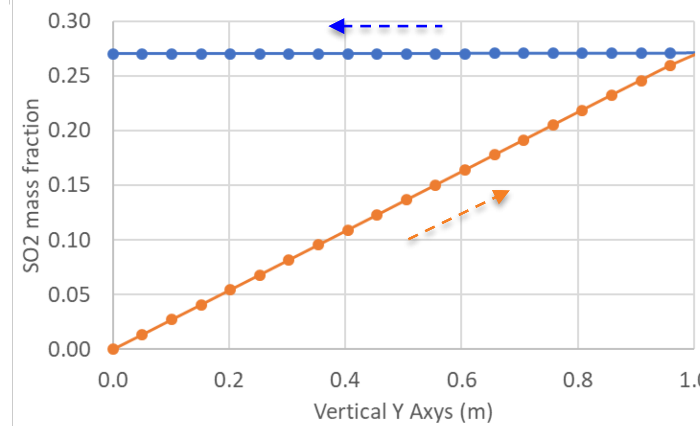
Accomplishments – Catalytic reactor simulation
Level 2



Temperature of housing

Temperature of gases



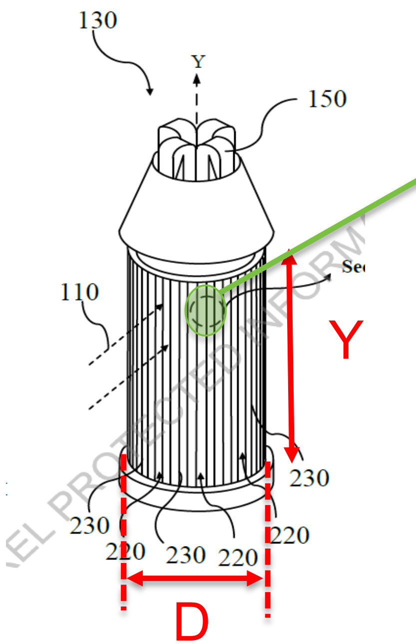


Excellent internal heat recovery without temperature decrease of the reactive mixture (as for the traditional bayonet system)

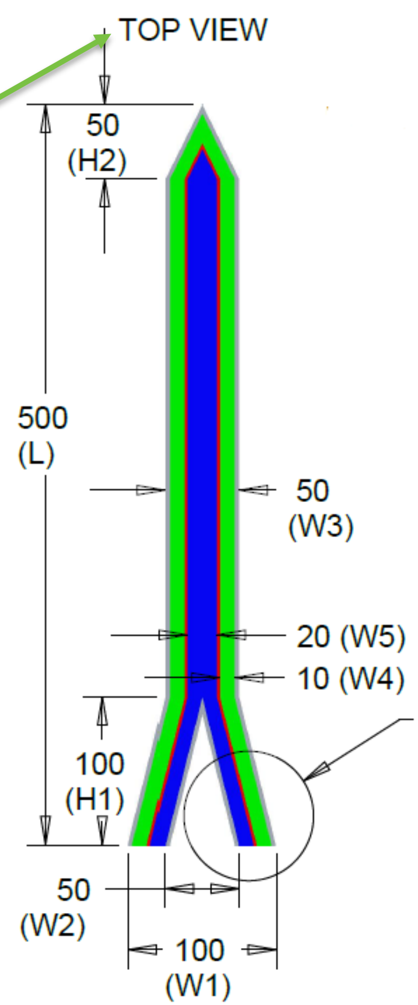
Effective SO_3 decomposition achieving almost the equilibrium SO_2 concentration

Accomplishments – Solar reactor tower sizing

Level 2



Solar receiver-reactor assembled units on top of the solar tower



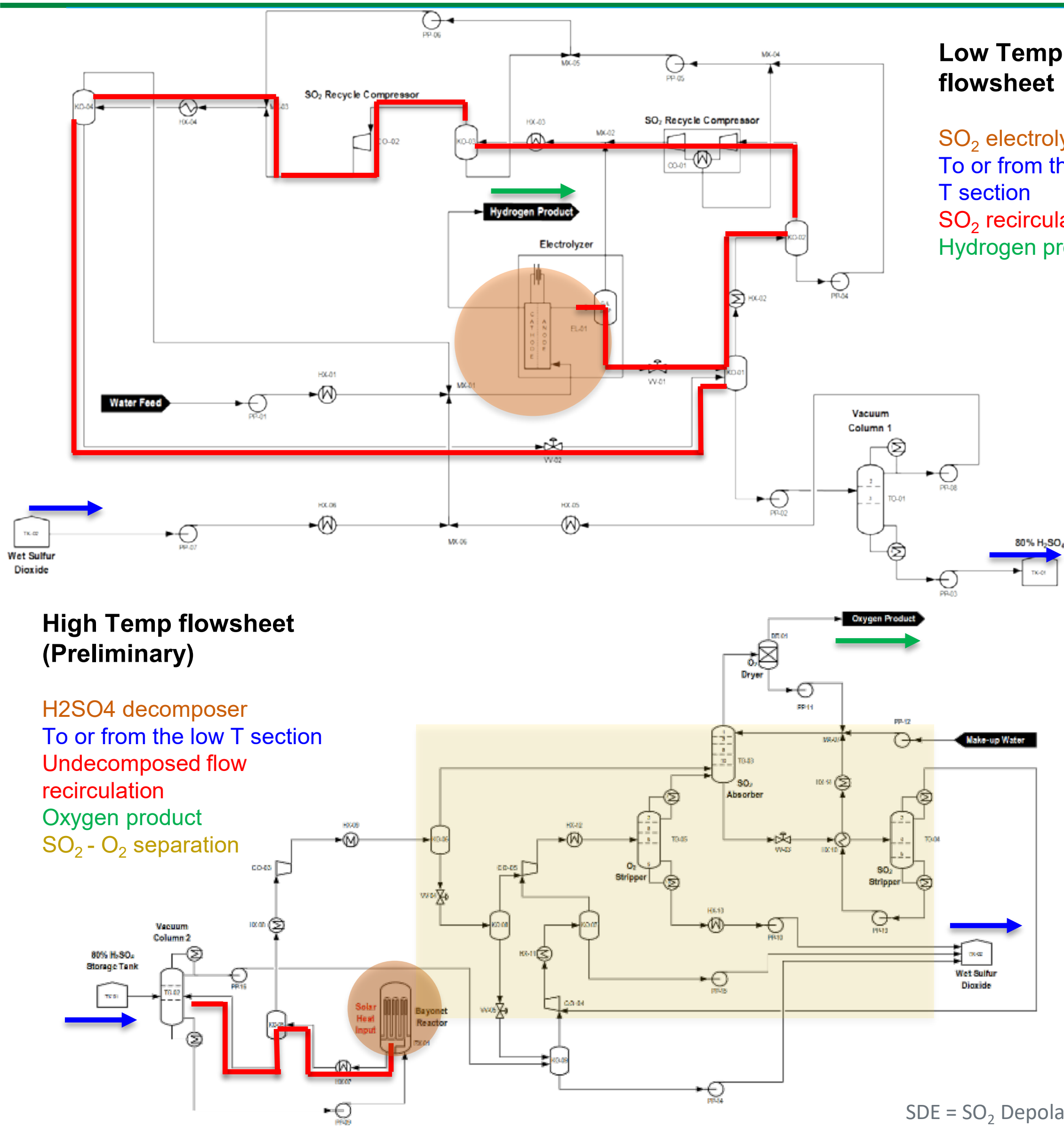
Single receiver-reactor

Sizing of the solar receiver-reactor

- Initial configuration achieved
  - Matching between heat exchange power requirements and geometry constraints

Single unit receiver/reactor	
L (m)	0.5
W1 (m)	0.1
H_2SO_4 flow rate (kg/s)	0.285
Assembled units for 50 TPD H_2 production	
D (m)	16.5 (single tower)
Y (m)	2 (projected total length) 1 (SO_3 catalytic decomposition section length)
Number of reactor units	516

Accomplishments – Novel HyS flowsheet
Level 3

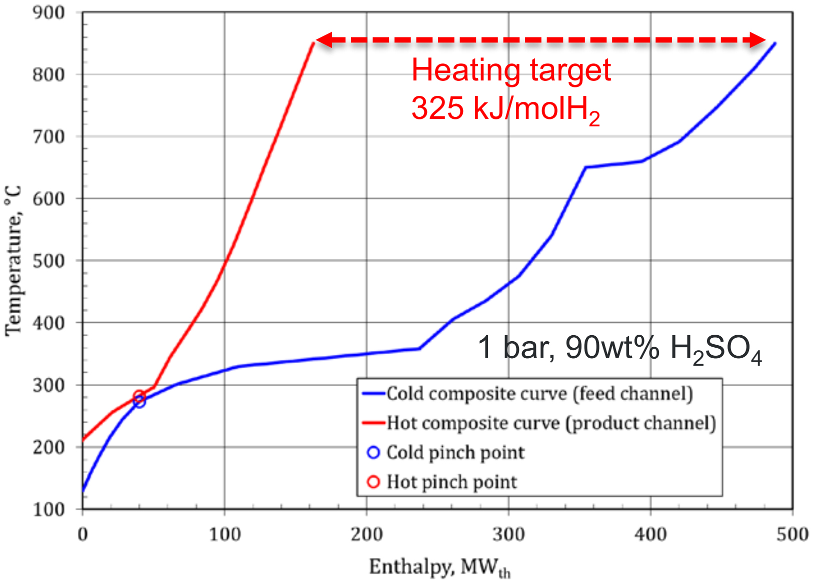


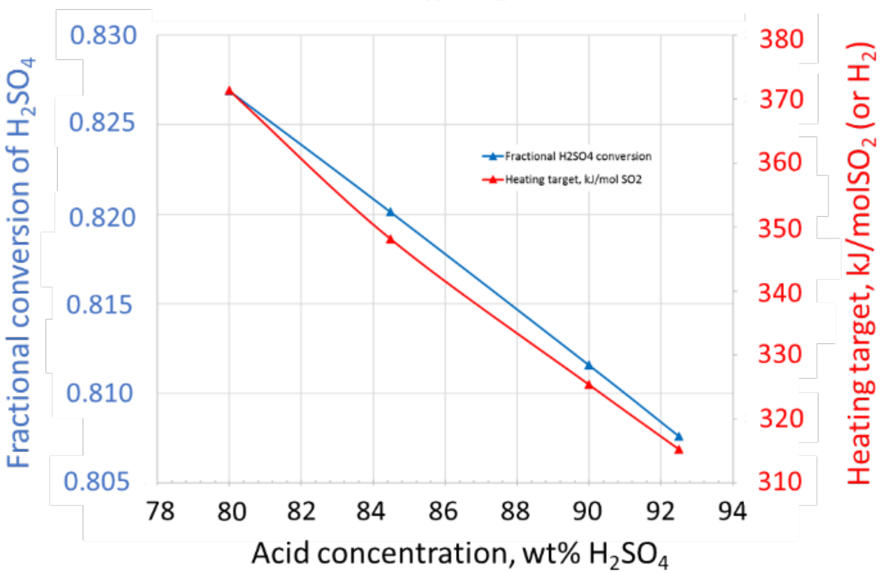
Novel HyS cycle flowsheet based on the vapor fed SDE section

- SDE section
  - Increase of SDE efficiency *(externally financed USC work)*
    - V= 545 mV, I= 500 mA/cm^2
    - W_{el} = 105.2 kJ/molH_2
  - Production of high concentration sulfuric acid
  - Higher temperature waste heat (140 °C) internally recoverable to concentrate H_2SO_4 up to 80wt%
- High T section (preliminary version)
  - Decrease of the decomposer heat duty
  - Total internal heat recovery from undecomposed flow recirculation to concentrate H_2SO_4 up to 90wt%
  - Increase of the overall efficiency – no need for external low T

SDE = SO_2 Depolarized Electrolyzer

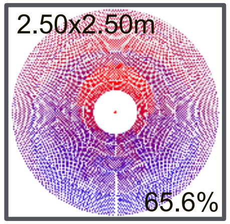
Accomplishments – H_2SO_4 decomposer process
Level 3



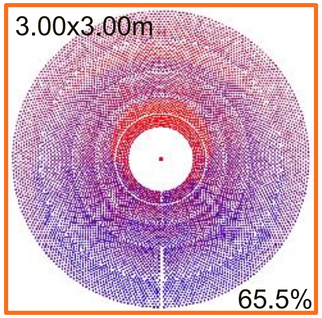


- Pinch analysis of the high temperature decomposition unit
  - Different scenarios analyzed (pressures, temperatures, concentrations)
  - Heating target duty = 325 kJ/molH_2 at 1 bar, 90wt% H_2SO_4, 850 °C
  - Reduction of about 10-12% compared to previous baseline configuration
  - Available waste heat at about 200°C recoverable to concentrate H_2SO_4
- Initial sensitivity analyses
  - P = 1 bar, T = 850 °C (so far)
  - High fractional conversion of H_2SO_4 achieved (81-83%)
  - Reduced heating target values, with baseline value of about 325 kJ/molH_2 for 90wt% H_2SO_4

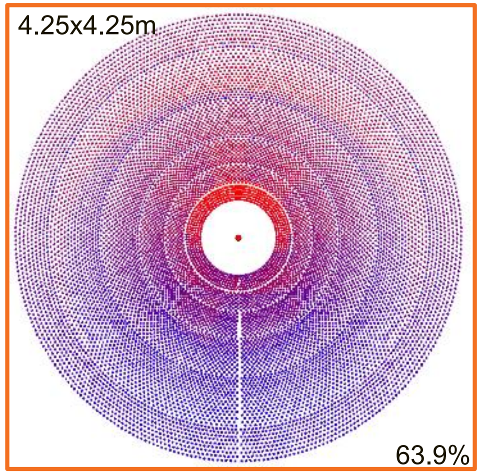
Accomplishments – Solar field design
Level 3



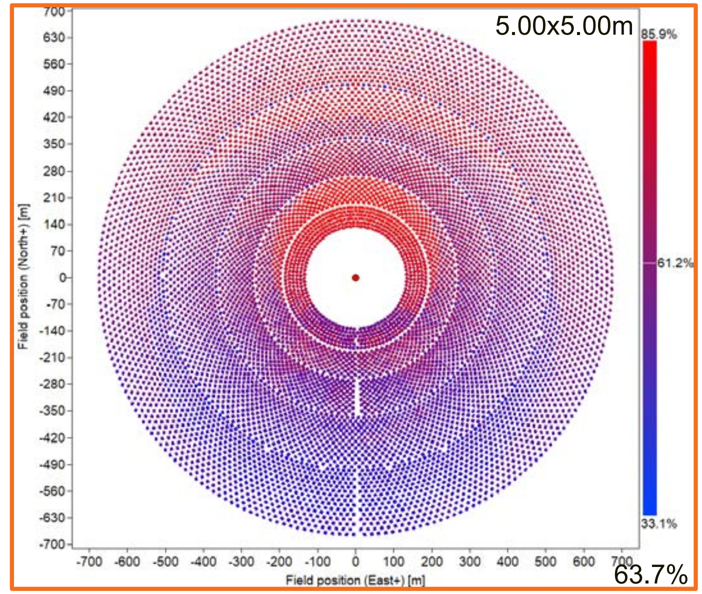
70MWt, 80m



100MWt, 100m

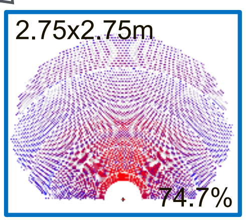


200MWt, 130m



300MWt, 160m

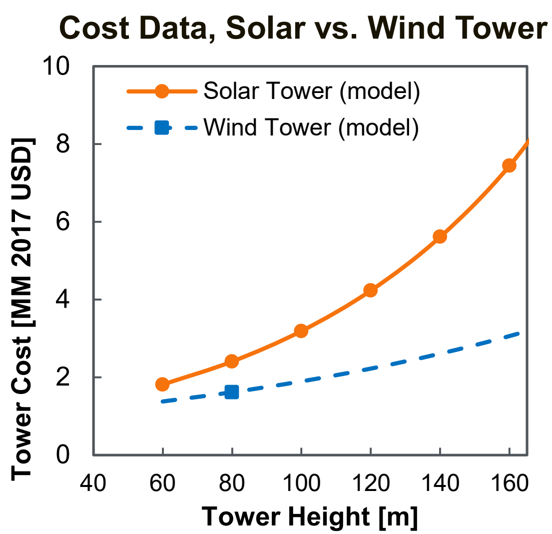
Focused extent and reduced circularity - wind tower

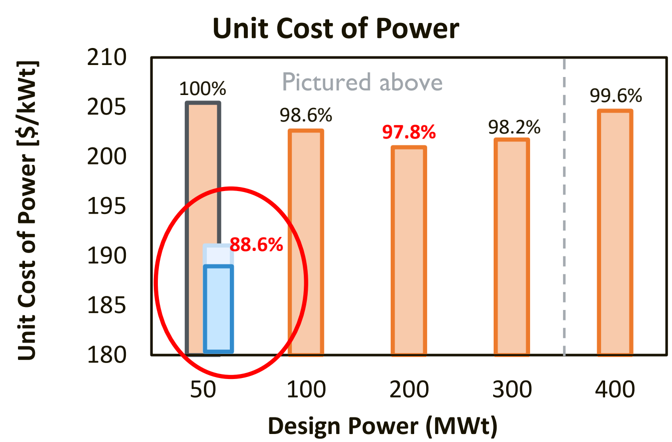


45MWt, 80m

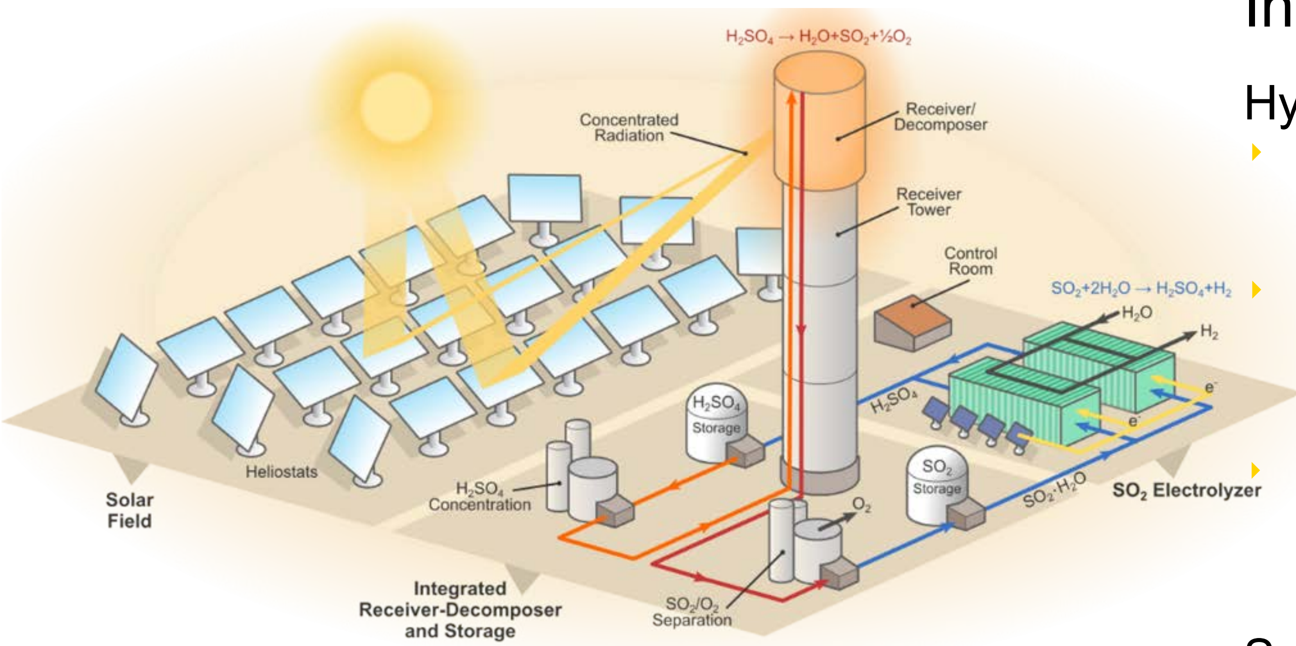
Selected options

- Centralized single solar tower
- Multiple towers (possible distributed H_2 production)
  - Solar towers
  - Wind towers





Accomplishments – Initial solar system analysis
Level 3



Solar HyS plant system

- Integrated direct H_2SO_4 decomposition receiver-reactor unit
- Solar or wind tower
  - Unitized vs distributed approach
- Chemical storage
  - Liquid SO_2 storage (P = 1-5 bar)
  - Liquid H_2SO_4 storage

Initial efficiency analysis

HyS thermochemical process

- Low T section
  - W_{el} = 107.5 kJ/molH_2 (98% for the SDE)
- High T section (preliminary)
  - W_{th} = 325 kJ/molH_2 (100%for the decomposer)
  - W_{el} = 2 kJ/molH_2
- Overall HyS thermochemical efficiency (preliminary)
  - Electric power plant η = 40%
  - ***HyS efficiency = 40.4% (LHV)***

Solar plant (preliminary)

- Heliostat η = 65%
- Receiver η (projected) = 85%
- Additional losses (e.g. storage, tubing) = 1%
- Overall solar η = 54.7%

Overall solar HyS process (preliminary)

- ***Solar to H_2 efficiency = 22% (LHV)***

HyS = hybrid Sulfur
SDE = SO_2 Depolarized Electrolyzer

Collaboration: Effectiveness

Level 1 Action	Institution	Need for the AWSM
Catalyst development and synthesis	USC	- ***INL*** → run of H_2SO_4 decomposition tests at the required T, P and concentration – *Milestone 1.2*
Catalyst tests under realistic conditions	*INL*	

Level 2 Action	Institution	Need for the AWSM
Identification of novel solar reactor	GWE – *NREL*	- ***NREL*** has been critical to identify and optimize the novel direct solar reactor (concept being patented, ROI filled) – *Milestone 1.3*
Detailed model of the new reactor	GWE – USC	
Lab scale reactor demonstration	GWE – *NREL*	

Level 3 Action	Institution	Need for the AWSM
HyS Flowsheet	GWE – *SRNL*	- ***NREL*** → design of solar tower plants - *Milestone 1.3* - ***SRNL*** → development of HyS process flowsheeting – *Milestone 1.3*
Solar plant design	GWE – *NREL*	
Plant techno-economic analysis	GWE – *SRNL* - *NREL*	

ROI = Record Of Invention

Collaboration: Interactions

- Meetings and data sharing
  - By-weekly meetings between recipients (GWE and USC) and capable labs (INL, NREL, SRNL) → presentations uploaded in the NREL Sharepoint
  - Face to Face meetings
    - Meeting 1 in SRNL (December 2017) with GWE, USC, SRNL → identification of the baseline flowsheet concept for the low T section (electrolysis)
    - Meeting 2 in NREL (March 2018) with GWE, USC, NREL → discussion about the solar field design and optimization, CFD analysis of the solar reactor, conditions for the SDE section
  - Reports uploaded in the NREL Sharepoint
- DataHub data
  - Flowsheeting data
    - High T equilibrium data for sulfuric mixtures (based on new process model from SRNL)
  - Solar plant design data (solar flux data, efficiencies, optimization and design data for solar tower and mirrors)
  - High temperature catalysis test data being updated

CFD = Computational Fluid Dynamics
SDE = SO_2 Depolarized Electrolyzer

Proposed Future Work

- Catalyst development and tests (USC – INL)
  - Complete the development of bimetallic catalysts, with lower content of Ir/Ru and in-situ XRD tests
  - Long time tests (100 hours) on the monometallic and bimetallic Pt catalysts
  - Optimization of the bimetallic formulations
  - Continuous longer time tests (400-500 hours) on the optimized formulations
- Receiver reactor design (GWE – USC – NREL)
  - Optimized configuration of the receiver-reactor concept
  - Transport model analysis of the enhanced configuration
  - Modeling of the two-phase region of the decomposer
  - Use of realistic solar flux profiles
  - Fabrication of a receiver-reactor prototype
  - Experimental tests under electric heating conditions
- HyS process flowsheet (GWE – SRNL)
  - Finalization of the high temperature decomposition flowsheet
  - Mass and energy balance assessment (i.e. thermochemical efficiency)
  - Chemical storage design and optimization
  - Sensitivity analyses (pressure, temperature, concentrations)
  - Optimization of the HyS flowsheet
- Solar plant system design and analysis (GWE – NREL – SRNL)
  - Conceptual design and installed cost assessment of the HyS process equipment
  - Conceptual design and cost assessment of the solar plant (heliostat field, tower, BOP, etc)
  - Sensitivity analyses for different configurations and scenarios (e.g. centralized vs distributed)
  - Overall efficiency and cost assessment (H2A)
  - Analysis of optimized configurations
  - Assessment of alternative solutions (HyS equipment and solar components)

Beyond Budget Period 1 depending on funding availability

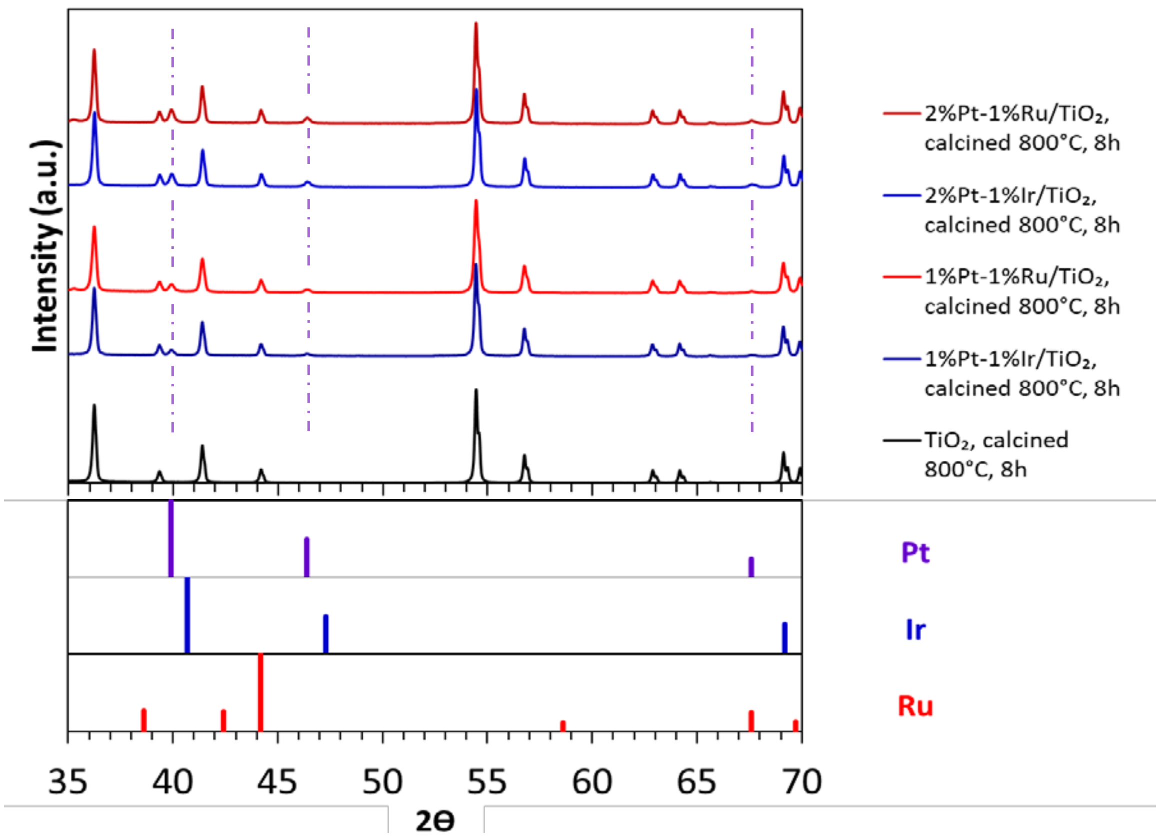
Project Summary

- Catalyst development and tests (USC – INL)
  - Identified baseline monometallic configuration
  - Identified initial bimetallic formulations (1% Pt on 5% Ir-TiO_2)
  - Initial successful tests for monometallic catalyst at INL
- Receiver reactor design (GWE – USC – NREL)
  - Identified an integrated solar receiver-reactor configuration
  - Configuration demonstrated through detailed transport modeling
  - Conceptual design of a scaled up reactor achieved
- HyS process flowsheet (GWE – SRNL)
  - Novel vapor fed electrolyzer flowsheet developed
  - Initial development of a high temperature section flowsheet
  - Projected reduction of the electric and thermal power requirements
- Solar plant system design and analysis (GWE – NREL)
  - Initial solar field layout optimization carried out
  - Different configuration analyzed
  - Initial efficiency projections exceeding the initial targets

Technical Back-Up Slides

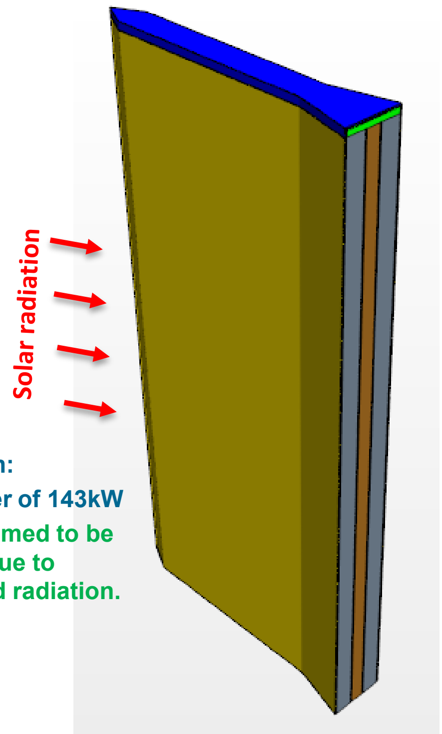
Calcined Samples of Pt (ED) on Ir/TiO_2 and Ru/TiO_2

Lower Pt concentration on 1% Ru or Ir support shows better behavior

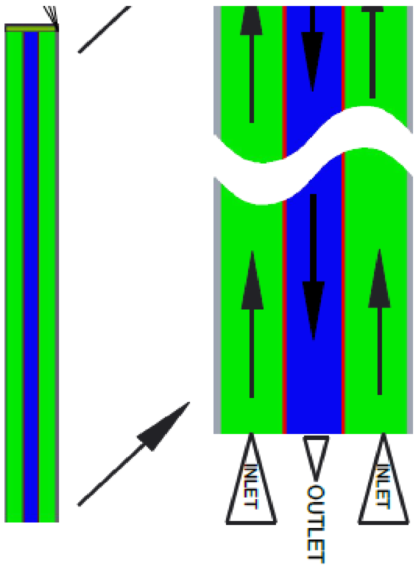


- Calcination was done in a muffle furnace, with static air.
- Temperature was ramped up at 5 °C/min from RT to 800°C and then holding at that temperature for 8 h.
- Calcined samples showed formation of significantly sharp peaks corresponding to Pt.
- Sharper peaks were observed for higher Pt loading.

Boundary Conditions for CFD simulation of the receiver/reactor



Solar Radiation:
Constant power of 143kW
Note: it is assumed to be NO heat loss due to convection and radiation.



Inlet:
Mass flow rate = 0.2835 kg/s
Temp. = 923.15K (650C)
Species mass fraction:
SO_3 = 0.69
H_2O = 0.31
System pressure = 14e5 Pa

Porous Material Properties

Catalyst:
Porosity = 0.5
Solid thermal conductivity = 8.0W/m-K
Isotropic permeability ~ 2E-9 m^2

End Cap and outlet tube:
Porosity = 0.5
Solid thermal conductivity = 34.8 W/m-K
Isotropic permeability ~ 2E-9 m^2

Reaction

$$R_j = R_{i,kin} = -A_j T^{\beta_j} \prod_{all\ reactants} \left(\frac{\rho Y_i}{M_i}\right)^{P_{ij}} e^{-E_{aj}/R_u T} \qquad \text{kmol}/\left(\text{sm}^3\right)$$

A_j = pre-exponential factor (0.16*)
β_j = temperature exponent (0.0)
E_{aj} = activation energy

* V. Nagarajan, Intl. J. of Hydrogen Energy, 33 (2008), 6445-6455.

Accomplishments – SDE section flowsheet
Level 3

SDE section flowsheet balance

H_2 Production Rate (kmol/sec)	1		
Electric power requirements (MW_e):			
EL-01, SO_2-Depolarized Electrolyzer	105.244		
CO-01, Low-Pressure SO_2 Recycle Compressor, First Stage	0.087		
CO-01, Low-Pressure SO_2 Recycle Compressor, Second Stage	0.024		
CO-02, High-Pressure SO2 Recycle Compressor	2.130		
PP-01, Water Feed Pump	0.003		
PP-02, Acid Flash Condensate Pump	0.000		
PP-03, LP SO_2 Recycle Compressor Intercooler Condensate Pump	0.001		
PP-04, Total Condensate Recycle Pump	0.003		
Total electric power requirement:	107.490	MW_e	
Cooling requirements (MW_{th}):		Temperatures (°C)	
HX-02, Acid Flash Vapor Condenser	7.034	98.7	40.0
HX-03, SO_2 Recycle Condenser	39.594	140.1	40.0
CO-01, low-pressure SO_2 recycle compressor stage 1-2 intercooler	0.701	170.2	40.0
EL-01, SO_2-Depolarized Electrolyzer	296.306	140.0	139.0
Total cooling requirement:	343.635	MW_{th}	
HX-01, Water Feed Vaporizer	47.116	25.0	120.0
HX-04, Water Recycle Vaporizer	43.682	55.5	120.0
Total heating requirement:	90.798	MW_{th}	
SDE performance			
SO_2 conversion, mol%	50		
H_2O/SO_2 feed mole ratio	2.75		
Reversible cell potential, mV	411.0		
MEA iR loss, mV	25.0		
Anodic overpotential, mV	109.4		
Total cell potential, mV	545.4		
Current density, A	0.5		
Total cell area, m^2	38.6		
SDE product acid concentration, wt% H_2SO_4	66.96		
Acid concentration exiting SDE flowsheet section, wt% H_2SO_4	68.38		