Development of Solar-powered Thermochemical Production of Hydrogen from Water

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UNLV Research Foundation
Las Vegas, Nevada

STCH
SOLAR THERMOCHEMICAL HYDROGEN GENERATION PROJECT
Sponsored by U.S. Department of Energy

Project ID No. PD28

Overview

Timeline

- 6-25-2003
- 12-31-2005
- 40%

Budget

- Total Project Funding
  - $4,869,976 DOE
  - $871,634 Cost share
- Funds received in FY04
  - $2,943,232

Barriers

J. Rate of Hydrogen Production

M. Materials Durability

N. Materials and systems Engineering

P. Diurnal Operation Limitation

Q. Cost

R. System Efficiency

T. Renewable Integration

V. High and Ultrahigh Temperature Thermochemical Technology

W. High Temperature Materials

Y. Solar Capital Cost

Partners

The University of Nevada, Las Vegas   The University of Colorado   The University of Hawaii

Sandia National Laboratories   The National Renewable Energy Laboratory   General Atomics

Arizona Public Service   General Electric   General Motors   ETH-Zurich

Objectives

- Identify a cost competitive solar-powered water splitting process for hydrogen production
- Complete analytical down select to most cost effective cycles and identify and implement experiments needed for quantitative final selection

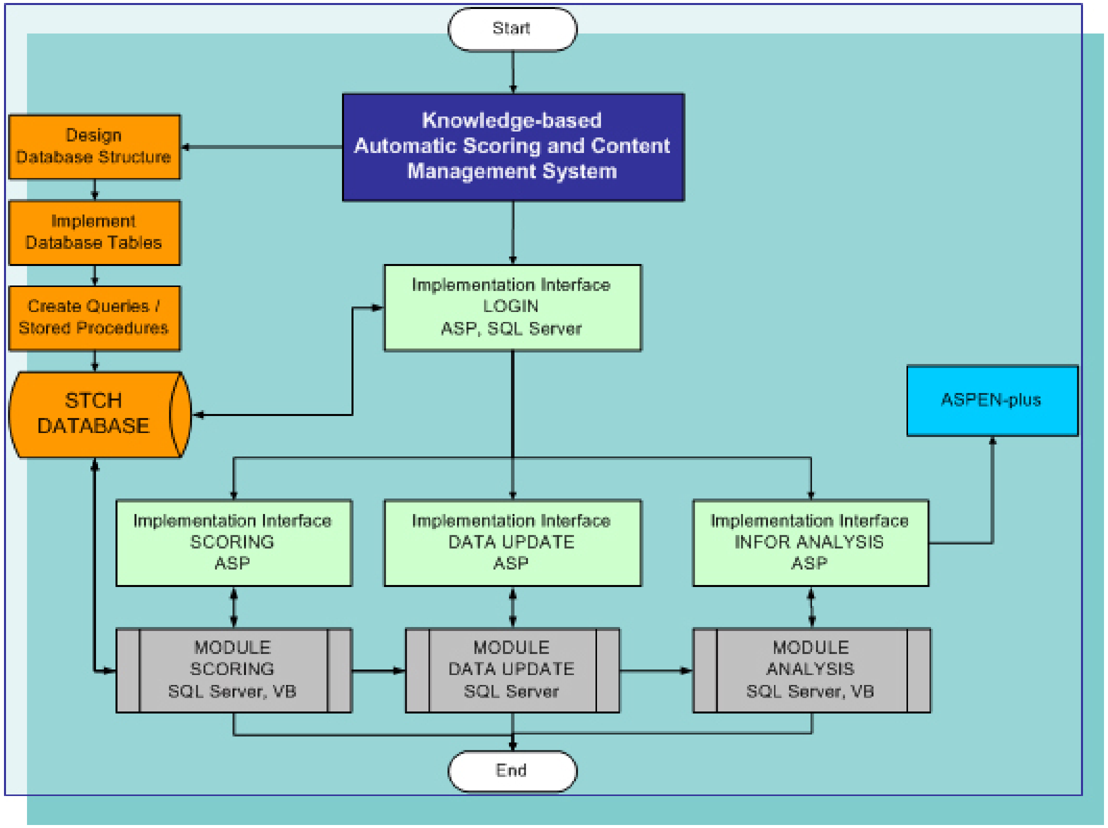
Approach

- Design and implement a quantitative comparative assessment methodology to screen all known thermochemical cycles and select the top several performers
- Perform literature surveys and laboratory experiments to acquire essential evaluation and design data for the top several concepts
- Develop validated designs for collector/receiver/reactor components for integrated system analysis
- Analyze cost and efficiency metrics for integrated cycle performance
- Develop demonstration plant concept design(s) for surviving competitive cycle(s) and provide recommended path forward

Technical Accomplishments/ Progress/Results

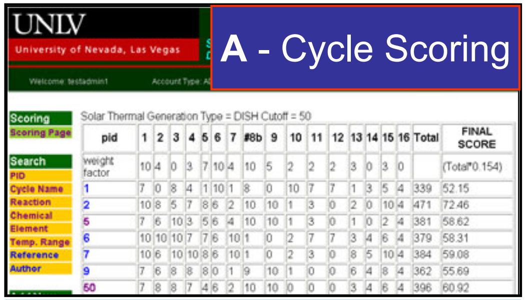
- Cycle database and scoring
- Solar receiver concepts evaluated
- Thermochemical H_2 cycles screened
- Preliminary flowsheets developed for promising cycles
- Preliminary cycle thermal efficiency calculated
- Preliminary heliostat field design
- Experimental work identified & started
- CFD modeling and simulation carried out to develop understanding of reactor transport mechanisms

Database Management and Scoring -1

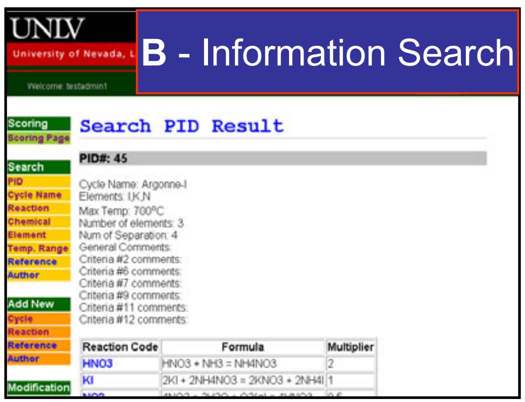


- More than 500 references in database.
- More than 700 authors have been cross-referenced in database.
- Open to the public through the project domain name (shgr.unlv.edu)

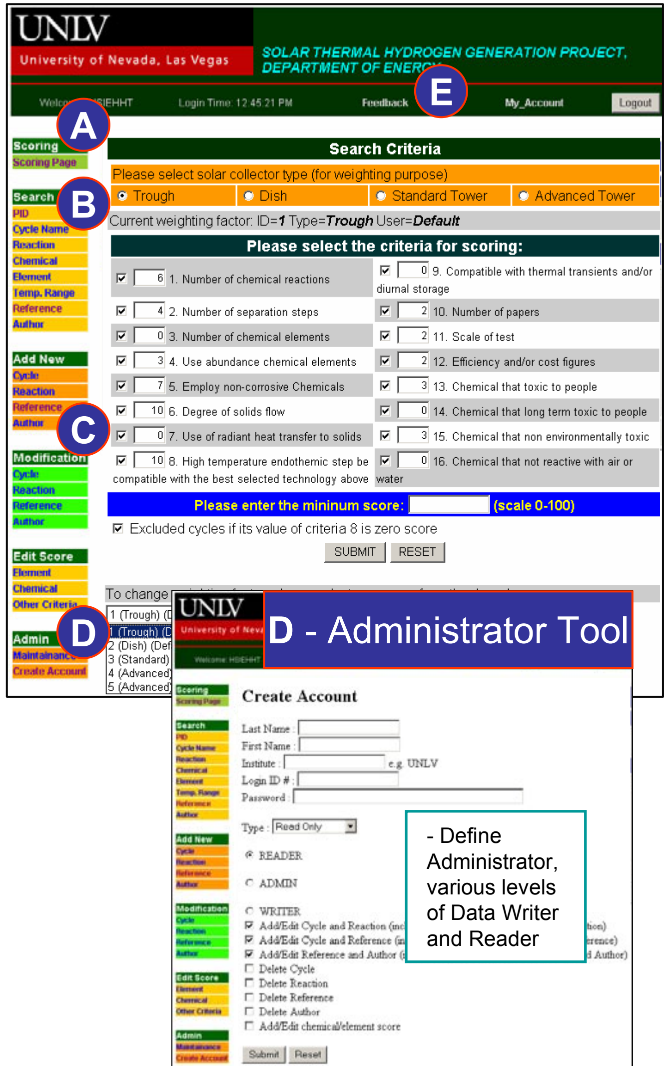
Database Management and Scoring -2



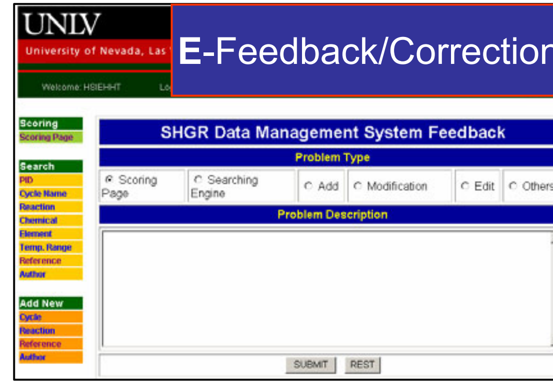
- 16 criteria with corresponding weighting factor, based on solar collector type
- Flexible threshold option
- weighting factor can be customized and saved for each individual user



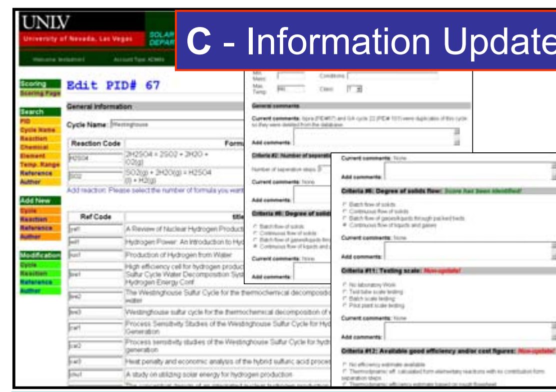
- Search and cross reference PID, cycle name, reaction, chemical, element, reaction temperature range, reference, and author.
- PID search function provides hyperlinked references and reaction codes.



- Define Administrator, various levels of Data Writer and Reader



Feedback and correction processing can be used to
- Assign Chair / Member
- Select committee members
- Feedback search engine
- web-based decision making system



- The module can be used for addition of new cycles.
- The module can be used to modify all the entered data, from cycle, and reaction to references and authors.

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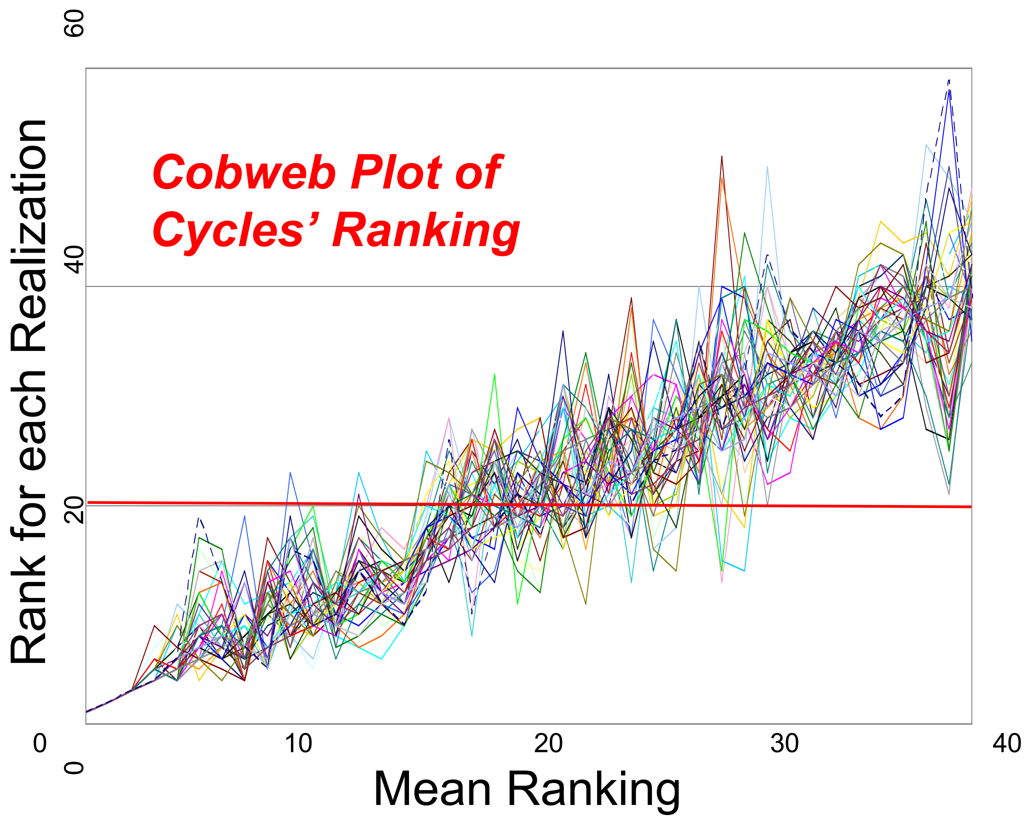
Cycle Screening Sensitivity Analysis

- Analyzed Phase One screening methodology
  - Wanted to avoid omitting "good" cycles
  - Created probability density function for all weights
  - Used Monte Carlo, stepwise regression and rank correlation



- Result: selected cycles are not highly dependant on criteria weights. Hence,
  - Process is robust
  - Generally accurate in determining best cycles for further analysis

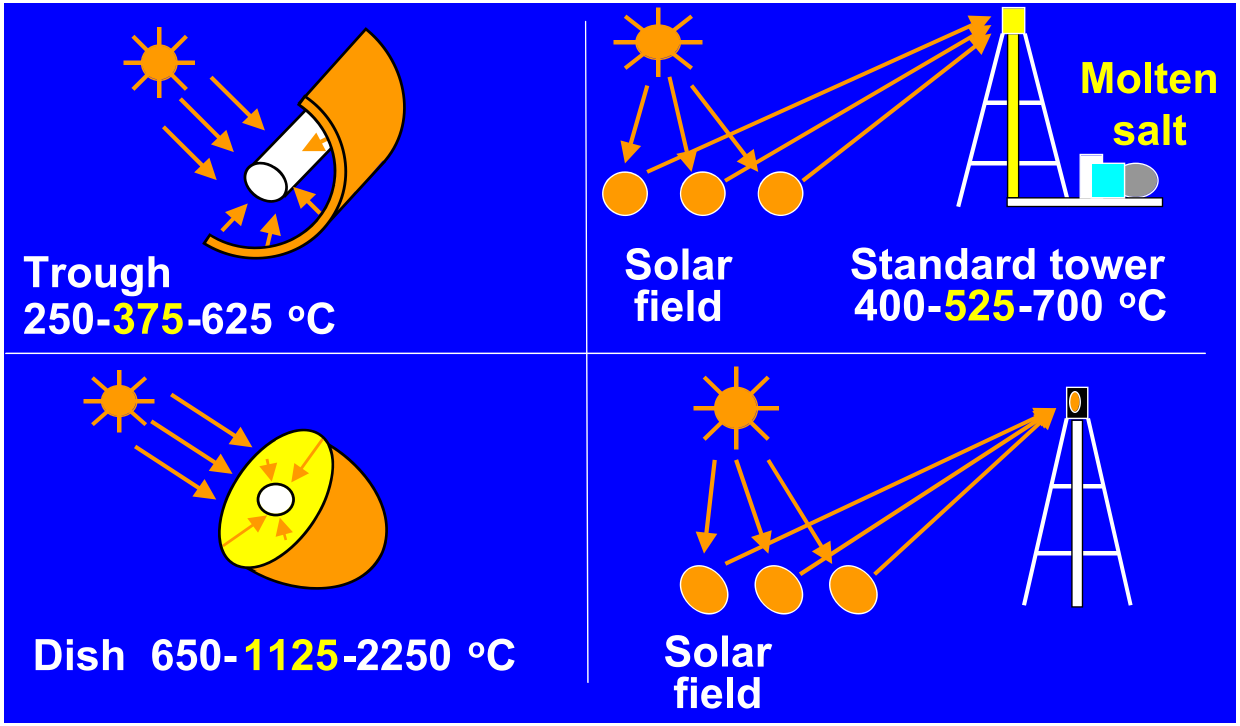
Solar Receiver Concepts for the Top Cycles

- Receiver concepts recommended for the top cycles

  - None of the top cycles were compatible with parabolic troughs
  - Sandia invented Rotating Disk Reactor - only concept suitable for dishes
  - Only ANL Copper Chloride cycle compatible with conventional molten salt power towers
  - Numerous concepts evaluated for high temp power tower cycles
  - Solid Particle Receiver and Fluid Wall Reactor selected for most power tower cycles

Thermochemical Hydrogen Cycles were Screened

- 182 cycles were subjected to a “practicality screening” relative to 4 solar energy collector technologies, each with an applicable temperature range and “sweet spot”

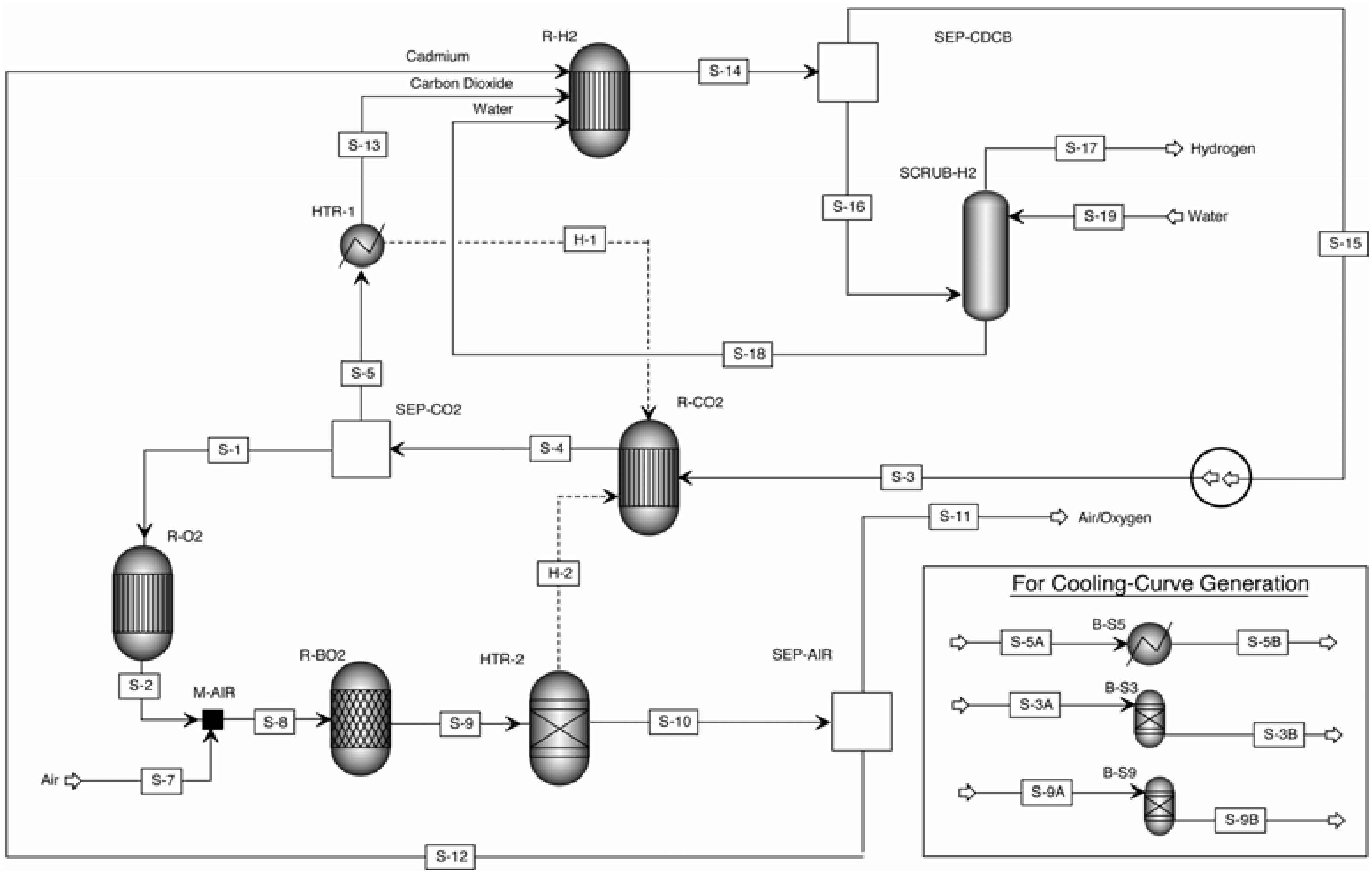


- Retained cycles were combined into a single list of 67 cycles for efficiency analysis

Cycle Screening Sensitivity Analysis

- Phase One screening methodology analyzed
  - Reduce vulnerability of omitting "good" cycles
  - Used stepwise regression and rank correlation methods
- Results indicate the selected cycles are not highly dependant on criteria weights
  - Process is robust
  - Generally accurate in determining best cycles for further analysis

Advanced flowsheet work done on promising cycles



Thermal efficiency of hydrogen production was evaluated for 67 cycles

- Free energy evaluated for each reaction of a cycle
  - Standard free energy evaluated, as a function of temperature, for reaction as written
  - Minimum free energy calculated considering alternative products
  - Carrier flows determined where necessary to shift equilibrium in solid/gas processes
  - Electrochemical step defined free energy is too positive
- Temperature chosen for each reaction based on free energy and processing considerations
- Enthalpy change determined for each step of the cycle
- Process flow diagram developed for the cycle
- Heat recuperation specified where possible
- Shaft work determined when gas compression is involved
- Electrical requirements for electrochemical steps
- Efficiency calculated from mass and energy balance for process

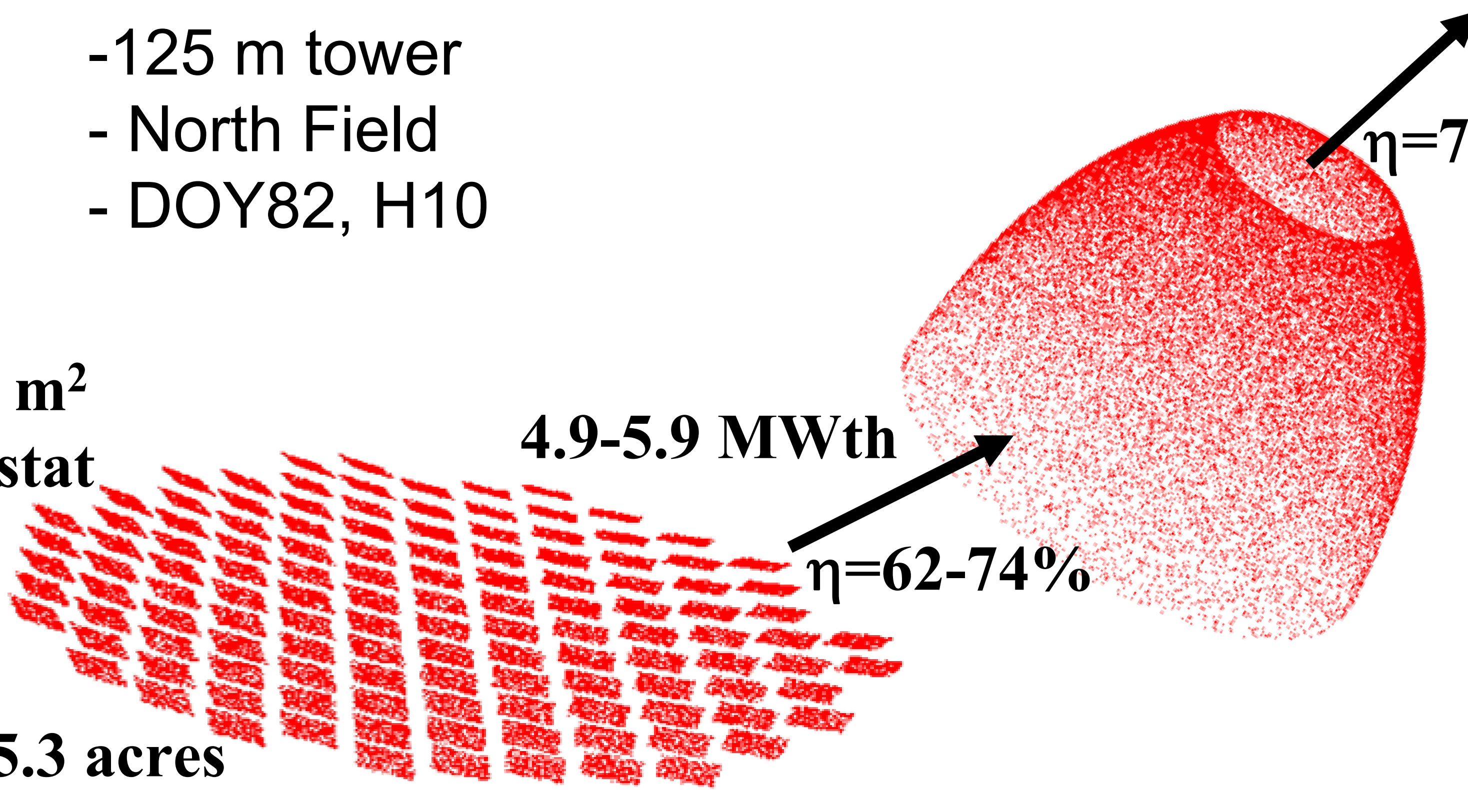
14 Cycles had calculated efficiencies greater than 33%

	LHV Efficiency	T(°C)	Device
Sulfuric Acid cycles			
Hybrid Sulfur	43%	900	Dish/Advanced Tower
Sulfur Iodine	38%	900	Dish/Advanced Tower
Multivalent sulfur	35%	1570	Dish/Advanced Tower
Metal Sulfate cycles			
Cadmium sulfate	46%	1000	Dish/Advanced Tower
Barium sulfate	39%	1000	Dish/Advanced Tower
Manganese sulfate	35%	1100	Dish/Advanced Tower
Volatile Metal Oxide cycles			
Zinc Oxide	44%	2000	Dish/Advanced Tower
Hybrid Cadmium	42%	1600	Dish/Advanced Tower
Cadmium Carbonate	43%	1600	Dish/Advanced Tower
Non-volatile Metal Oxide Cycles			
Iron Oxide	42%	2200	Dish
Sodium Manganese	49%	1560	Dish/Advanced Tower
Nickel Manganese Ferrite	43%	1800	Dish/Advanced Tower
Zinc Manganese Ferrite	43%	1800	Dish/Advanced Tower
Other			
Hybrid Copper Chloride	41%	550	Trough/Standard Tower

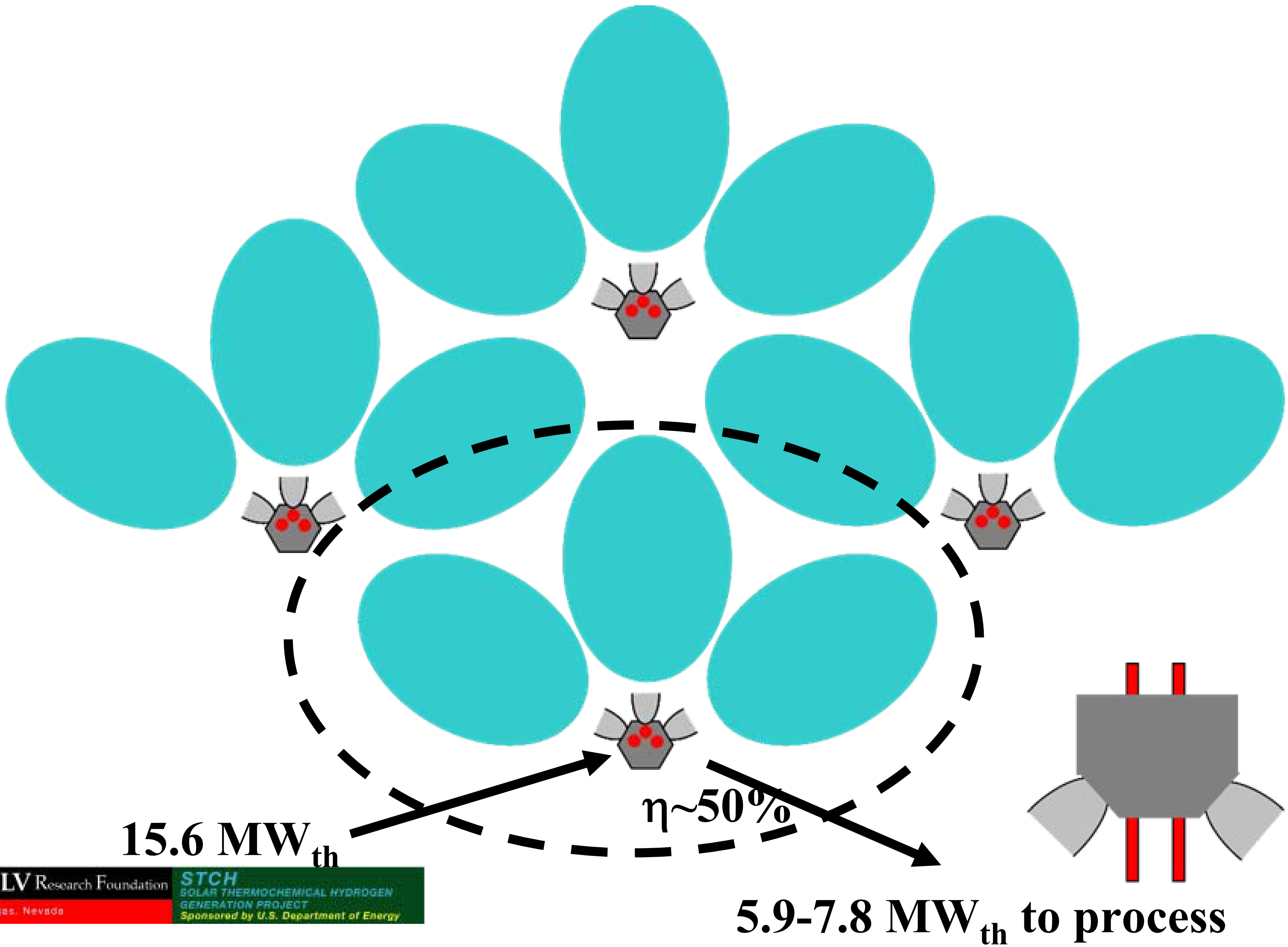
Preliminary Field Design Concepts Investigated

Ray Trace Images (SolTrace)

-125 m tower
- North Field
- DOY82, H10



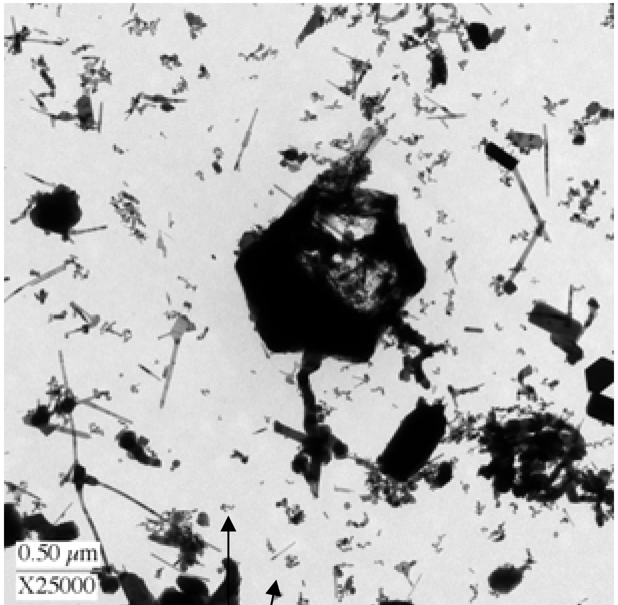
Multiple Field, Single Reactor Concept



Experimental studies have begun for some cycles

- Basic feasibility is an issue for some potentially efficient cycles
- Metal sulfate cycles may not produce hydrogen
  - Sulfur or sulfide will be formed in aqueous systems unless rate of hydrogen generation is fast. Studies underway to investigate interaction of hydrogen and SO_2 in aqueous solutions
  - Flow system assembled to study elevated temperature gas-solid hydrogen production
- The hydrogen generation step of the cadmium carbonate cycle was reported to be slow
  - Study of hydrogen generation at high pressure in the presence of mechanical abrasion of the cadmium metal surface has begun
  - Flow system assembled to study elevated temperature gas-solid hydrogen production

ZnO Dissociation Demonstration and Kinetics Experimentation

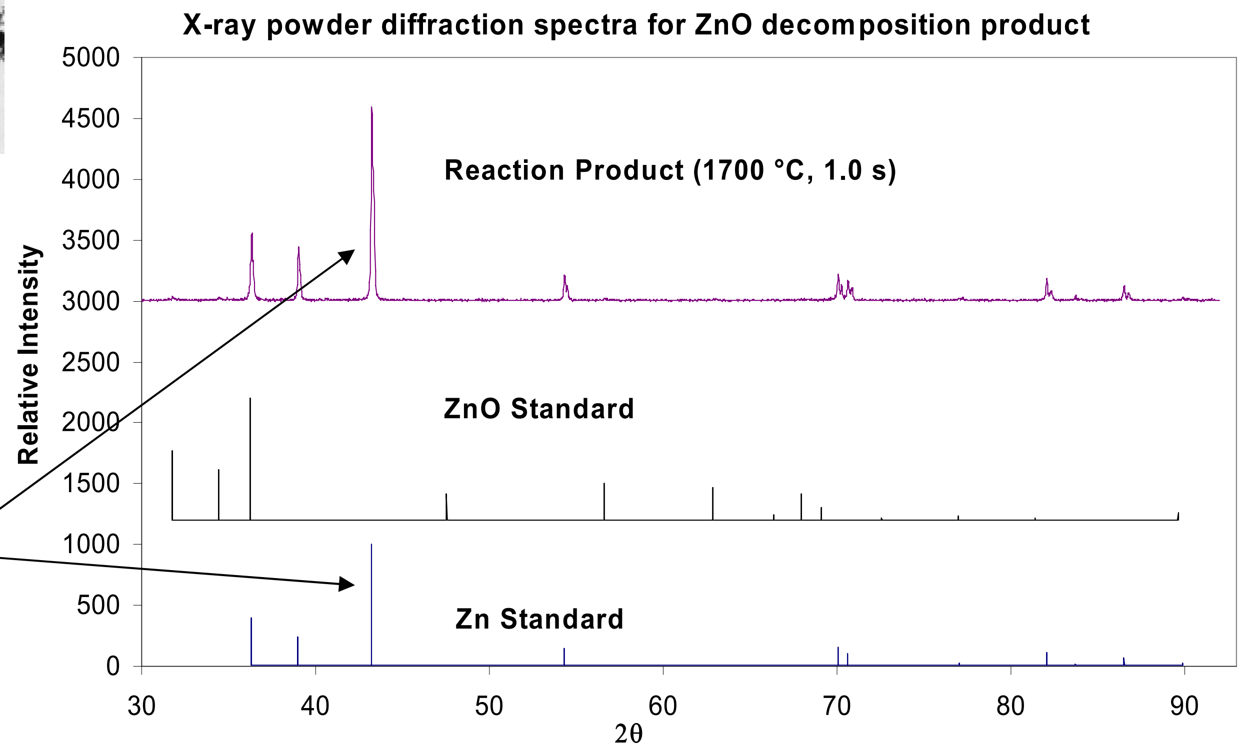


500 nm

40 nm Zn particles

Collected product spectrum matches Zn standard spectrum almost exactly (+/- 5%)

- Demonstration of efficacy of rapid aerosol metal oxide (ZnO and Mn_2O_3) decomposition
- High conversion (70-85%) to small particles (20-400 nm) observed
- Experimentation to determine kinetic rate law for MO_x thermal dissociation in progress



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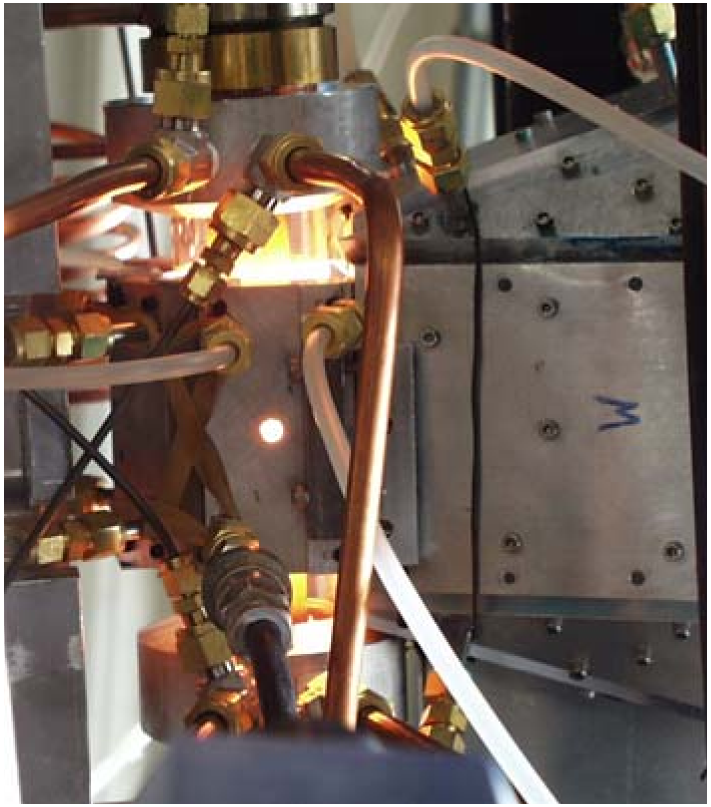
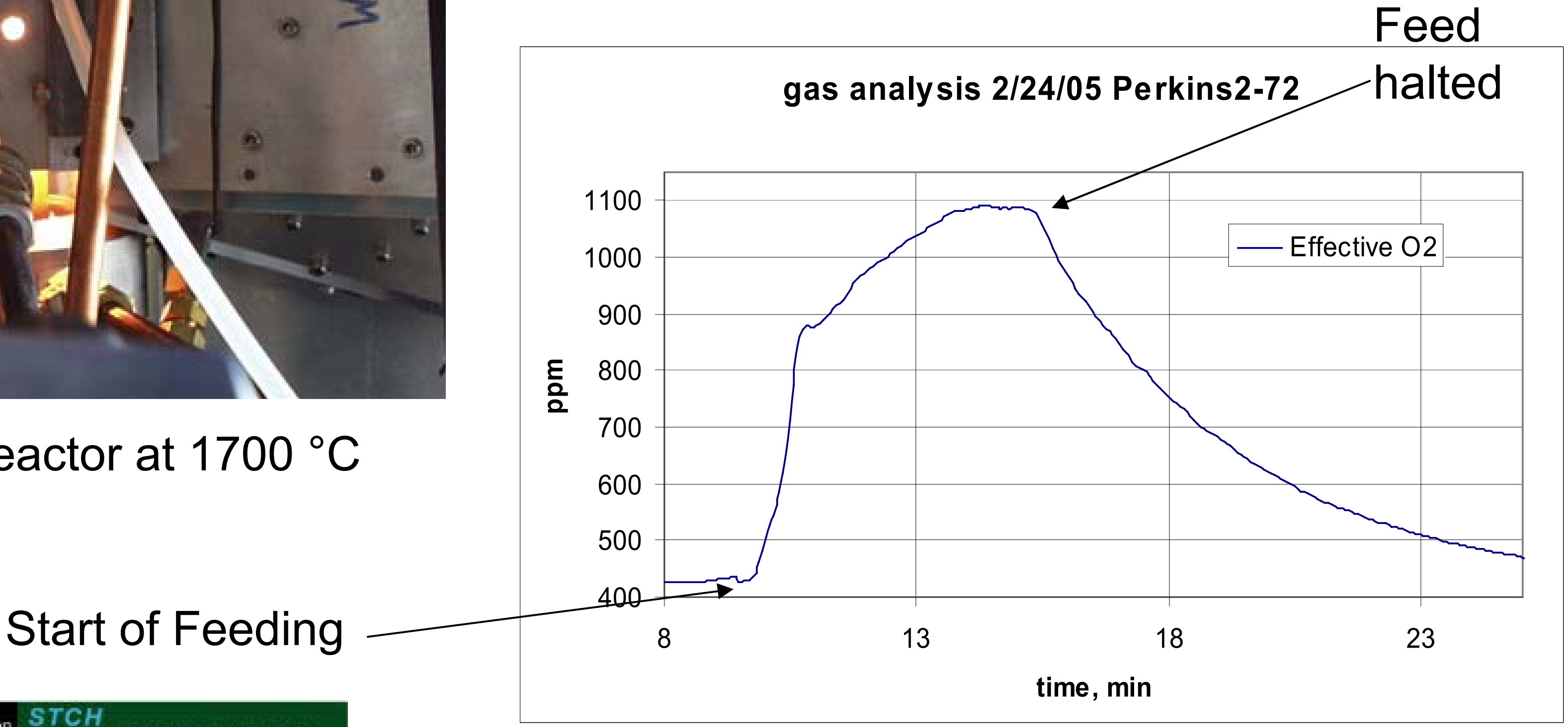
ZnO Dissociation Experiments in High Flux Solar Furnace



Solar Reactor at 1700 °C

- Reaction demonstrated at temperatures as low as 1700 °C
- Thermal dissociation demonstrated at short residence time (20 ms -200 ms)
- Reactor temperatures as high as 2050 °C reached



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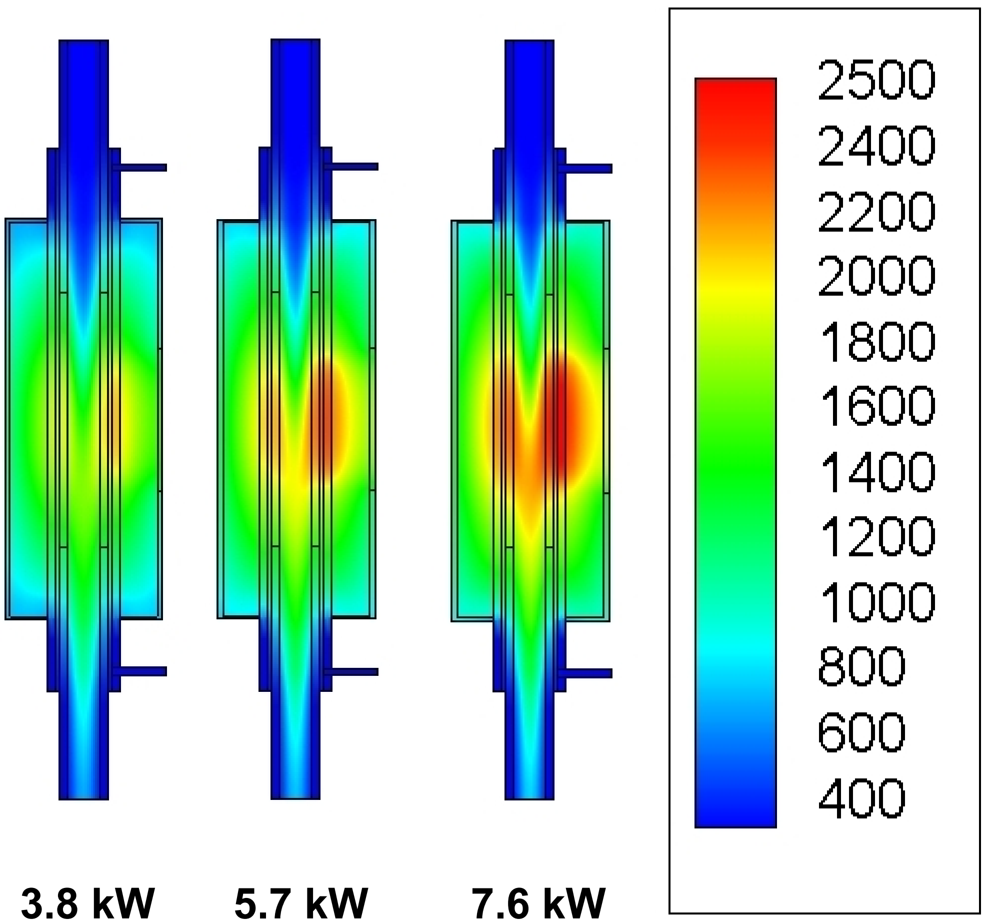
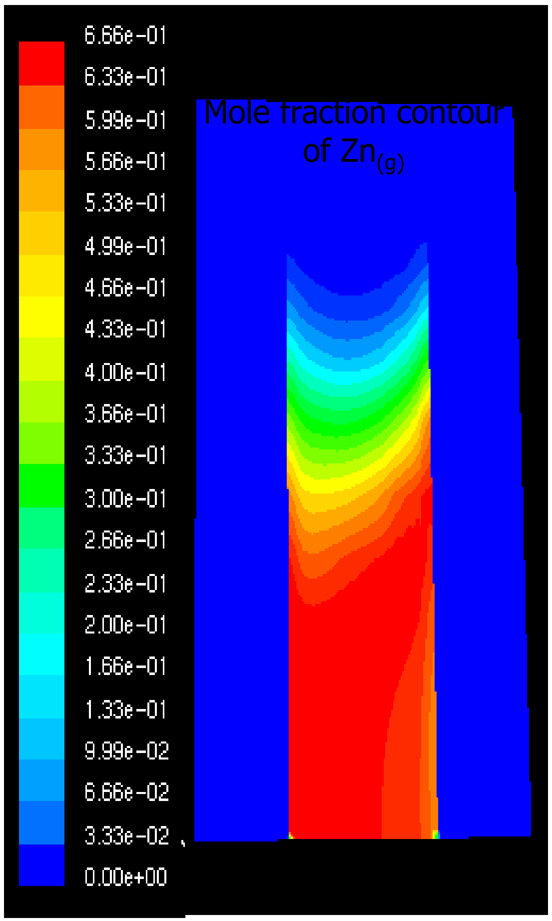
CFD Fluid Wall Reactor Simulation



Temperature Distribution (K)



Mole fraction contours

Responses to Previous Year Reviewers’ Comments

<u>Questions 2 and 5</u>

- ”appears to be very high-cost paper study with limited experimental effort”
- “too much paper study and not enough experimental verification”

- Nearly 200 identified TCH cycles warrants paper study to reduce competitive options to manageable number of experimental efforts
- Feasibility experiments are proceeding for four reaction classes identified as most competitive

Responses to Previous Year Reviewers' Comments

- Weaknesses
  - "Why the analysis study if ZnO and Mn_2O_3 already chosen?"
- ZnO and Mn_2O_3 not already chosen
  - ZnO work already underway and STCH volunteered to continue that effort according to its plan; ZnO project capabilities enable feasibility work for the other competitive metal oxides with resource savings
  - Mn_2O_3 study undertaken at the request of the Department of Energy

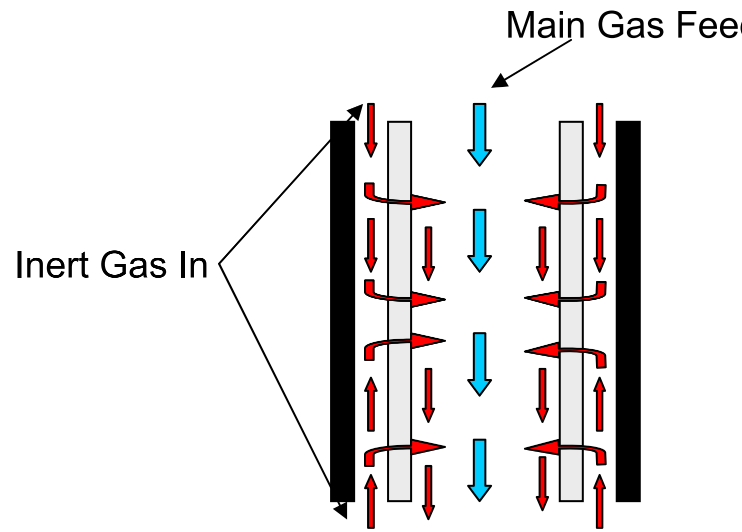
Future Work

- Experimentally resolve the uncertainties of the down selected cycles
- Update the process thermal efficiency
- Develop and validate the transport mechanisms and the design of the solid particle receiver
- Update the system efficiency and H_2 gate costs
- Design bench scale/pilot model for selected cycle(s)

ZnO/Mn_2O_3 Cycles

•Completion of kinetic experimentation for ZnO and Mn_2O_3 aerosol dissociation in SiC tubes
•Allows enhanced reactor design and improves cycle efficiency estimates

•Porous material qualification and permeability determination
•Enables design, modeling, and optimization of fluid-wall for material protection and product cooling



Fluid wall concept

•On-sun demonstration of high temperature, high efficiency solar reactor
•Ultra-high temperature reactor material qualification with and without fluid-wall (C, SiC, Hf)

Experimental studies have begun for some other cycles

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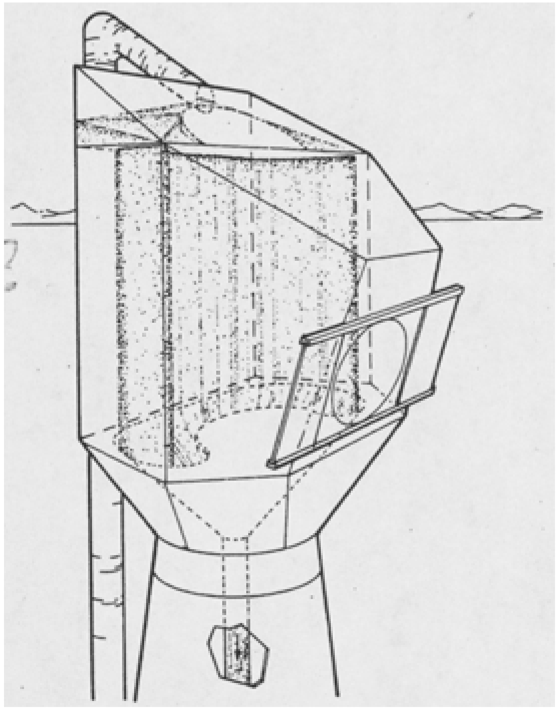
  - Study of hydrogen generation at high pressure in the presence of mechanical abrasion of the cadmium metal surface has begun
  - Flow system assembled to study elevated temperature gas-solid hydrogen production
- Cyclic thermal reduction/water oxidation (redox) studies of candidate mixed-metal ferrites to assess reactivity and kinetics initiated

Solid Particle Receiver

- Solid particle receiver uses sintered bauxite proppants for heat collection and storage
  - Directly illuminated curtain of falling particles
  - Low cost thermal storage
  - Non-corrosive
  - High heat flux capability
- Extensive development by Sandia Livermore in mid 1980s
  - Sintered bauxite suitable to 1000^{o}C
  - Zircon suitable to 1200^{o}C
  - Flow stability is a potential issue
- Analytical/experimental investigations proposed



Hydrogen Safety

- At this stage of the project, H_2 quantities involved in the experiments are so minimal as to pose no H_2 safety risks
- The most significant current hazard is associated with ultra-high temperature (> 1500^{o}C) operations
- Hazards mitigated with personnel training, well documented SOPs, and internal safety reviews at each institution