SAND2009-3265C

Status of USA's Solar Hydrogen Generation Research (SHGR) Project

Greg Kolb
Sandia National Laboratories

June 4, 2009

SHGR Project Began in 2004

(a.k.a. STCH project)

- Argonne National Laboratory
- General Atomics
- National Renewable Energy Laboratory
- Florida Solar Energy Center
- Sandia National Laboratories
- Savannah River National Laboratory
- University of Colorado, Boulder
- University of Nevada, Las Vegas

- The USA has screened more than 200 thermochemical cycles
- If solar-to-H_2 η >18%, there is a chance of significantly beating solar electrolysis
- Sandia's solar screening method is proposed for IEA Task 25

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Screening Analysis of Solar Thermochemical Hydrogen Concepts

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Sandia National Laboratories

IEA/HIA TASK 25: HIGH TEMPERATURE HYDROGEN PRODUCTION PROCESS

Screening Analysis of Solar Thermochemical Hydrogen Concepts

Goals of Screening

The goal of screening analysis is to identify solar thermochemical plant concepts that have a high likelihood of producing hydrogen at a much lower cost than with a low temperature electrolysis plant [1].

There are 2 qualities which make it likely that thermochemical plant can beat the economics of low temperature electrolysis plant:

- Since efficiency is directly proportional to the cost of a solar hydrogen plant, if the annual solar-to-hydrogen efficiency is at least 30% higher, there is a chance
  - Thermochemical plant approaches are immature relative to low temperature electrolysis plant and are typically more complex. To justify the R&D of thermochemical plant, the efficiency should be at least 30% better
  - For towers, the low temperature electrolysis plant η is 14% (HHV). Thus thermochemical plant > 1.3*14% = 18%
- If the thermochemical plant can be scaled-up to a size similar to the largest low temperature electrolysis plant, there is a chance
  - Using a molten salt technology, a single 1400 MWt tower and storage system could power a low temperature electrolysis cycle with a 75% capacity factor
  - This tower was studied by Sargent & Lundy [10] for electricity application : this low temperature electrolysis solar plant would produce 83 000 kg/day in the Mojave Desert

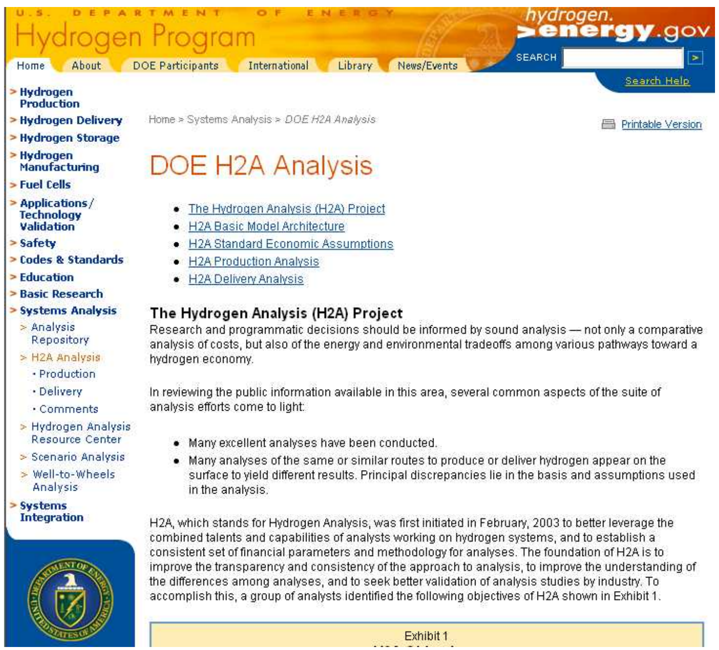
Concentrating solar Approaches

Tower

Dish

Trough

More detailed screening performed with DOE's H2A economic methodology



- Design commercial-scale plants that produce 100,000 kg/day
- Perform case studies for year 2015 and 2025
- Assess ability to achieve ~$3/kg in 2025
- H2A analysis confirmed Sandia's screening method
  - Sandia screened out ZnO early in the project
  - Subsequent H2A analysis of ZnO predicts $5.58/kg in 2015 and $4.14/kg in 2025
- H2A includes cost screening
  - Sandia screen includes SI cycle
  - H2A screen could exclude SI cycle
    - HI decomposition step is very expensive
    - Initial results show $4.46/kg in 2025

Cycles that have survived H2A screening (yr 2025 H2A cost)

- Hybrid sulfur ($3.2/kg)
- Cadmium oxide ($3.5/kg)
- ALD-ferrites ($3 to $4/kg)
- Copper chloride ($3.5/kg)

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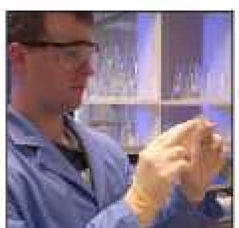
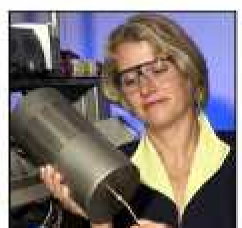
We Put Science To Work

Hybrid Sulfur Cycle Update for Solar Thermochemical Hydrogen (STCH) Working Group Meeting

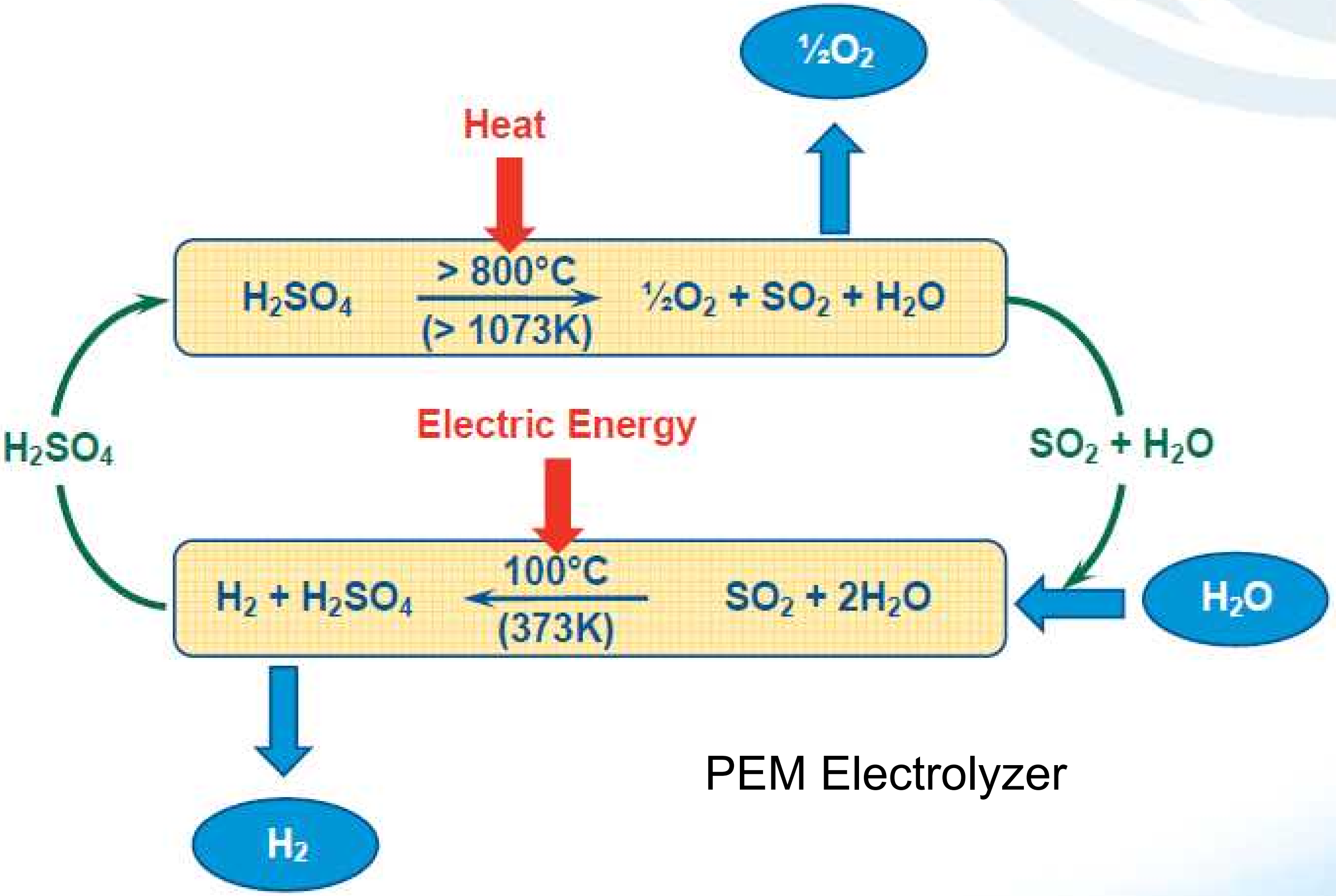
Maximilian B. Gorensek, PE for William A. Summers

May 8, 2009

Hybrid Sulfur (HyS) Cycle

Two-step, all-fluids thermochemical cycle – based on sulfur oxidation and reduction



PEM Electrolyzer

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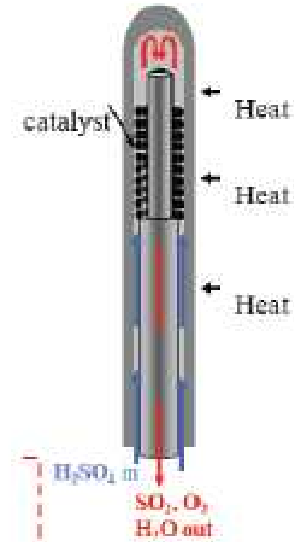
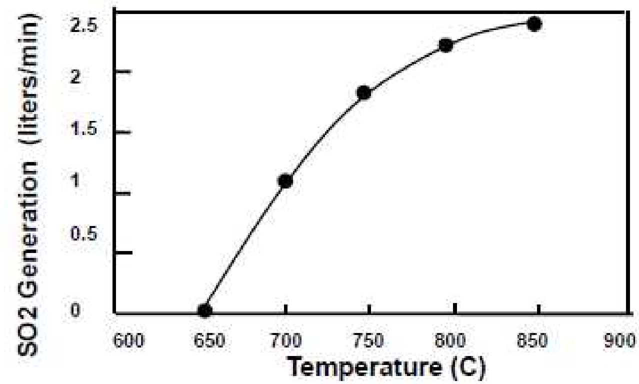
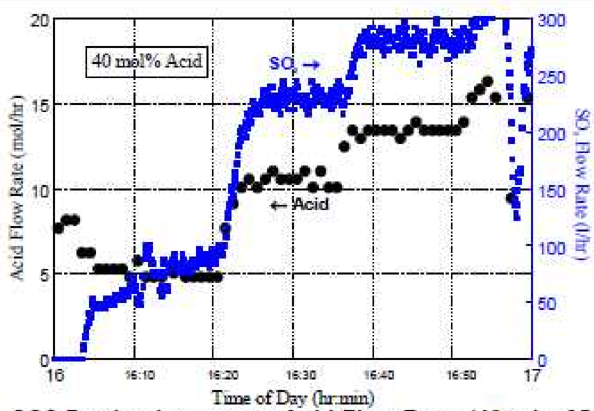
The sulfuric acid skid has produced up to 300 l/hr SO_2

SiC Bayonet Decomposer **(ILS)**

- ~ 300 l/hr SO_2 production rate @ 850 C (10 moles/hr, 40 mole% concentration)
- Conversion rates ~90% of theoretical
- SO_2 production rate limited by heat transfer to catalyst region
- Pressure, flow rate dependence evaluated
- Acid decomposer operation reproducible through ~20 cycles
- Catalyst durability requires further evaluation
- Operations were routine with no significant issues







SO2 Production versus Acid Flow Rate (40 m/o, 850 °C)

GENERAL ATOMICS

Sandia National Laboratories

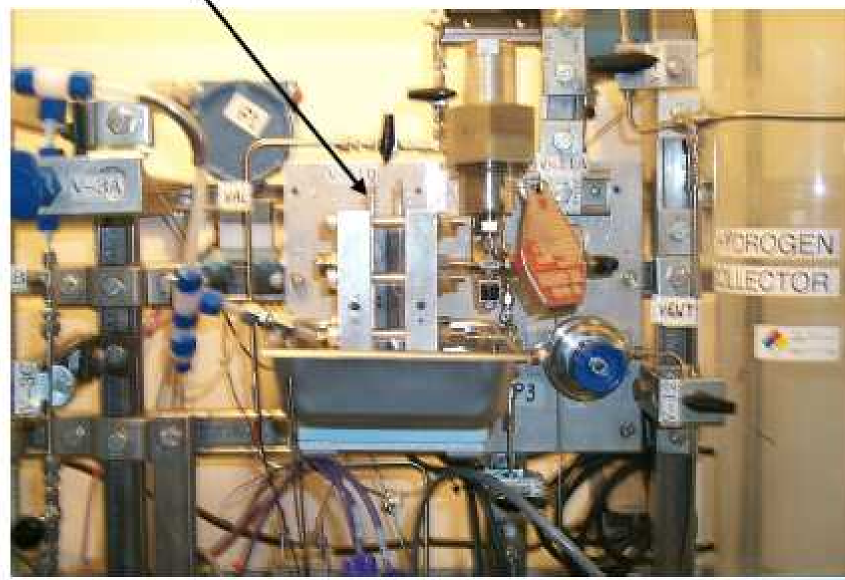
cea

INERI Program concluded in April 2009

Single Cell Testing

31 configurations tested to date
Normal H_2 output = 10-20 Lph
Maximum H_2 output = 86 Lph

SO_2-depolarized electrolyzer



Single Cell Electrolyzer (60-cm^2 active area)

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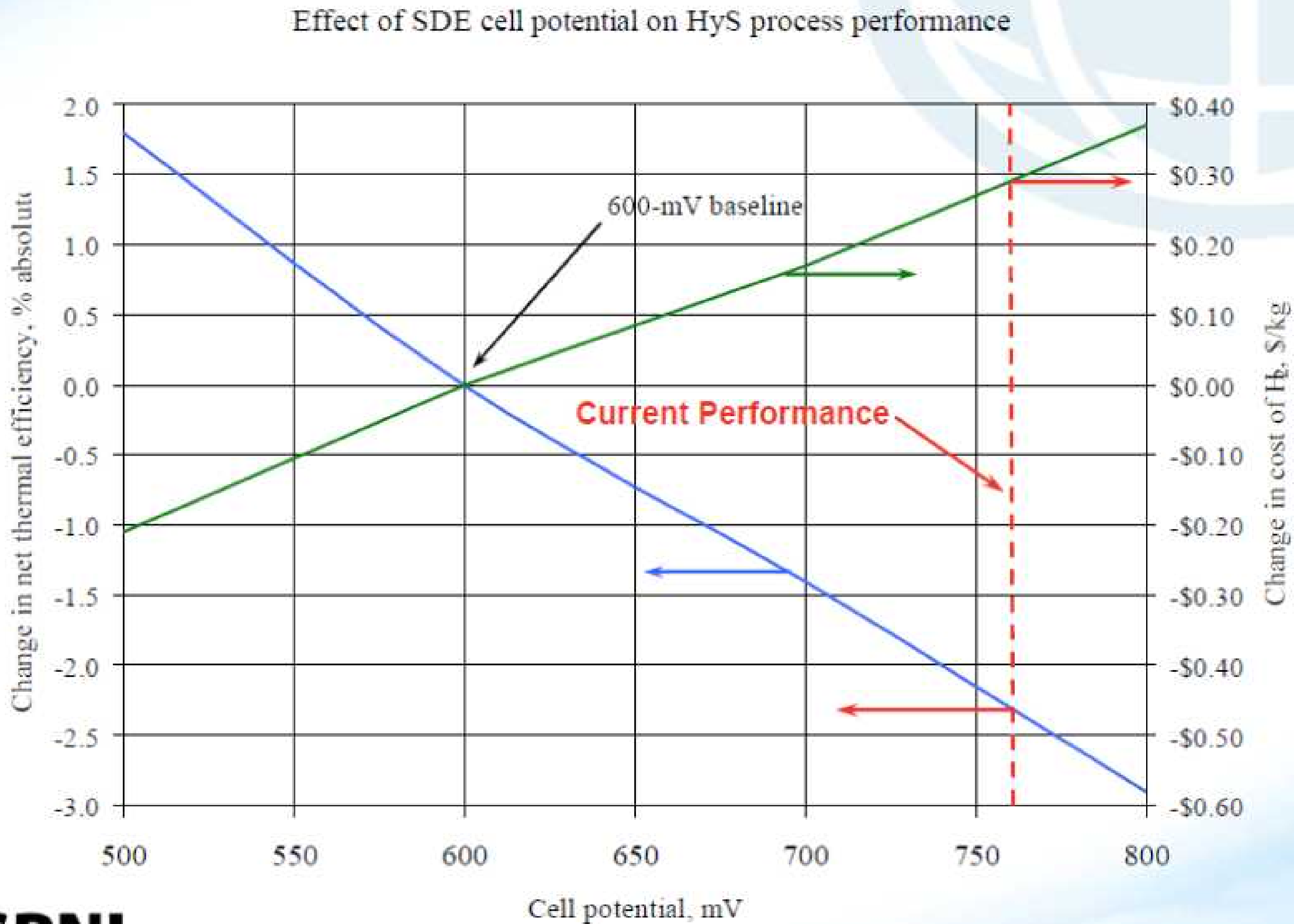
Improved Cell Voltage Increases Plant Efficiency and Lowers Hydrogen Costs, But It Is Not the Major Driver



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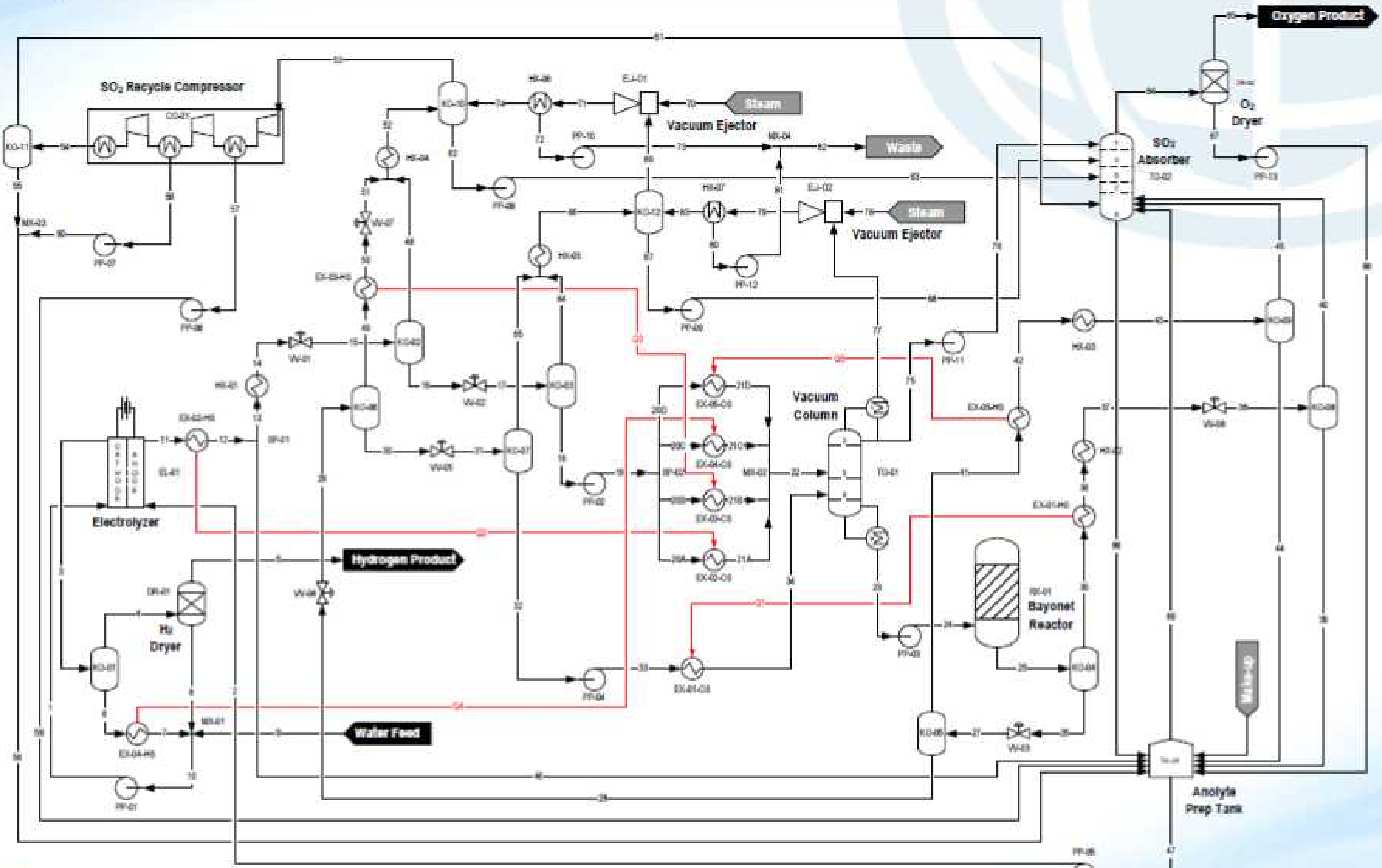
Detailed HyS Flowsheets Have Been Designed*



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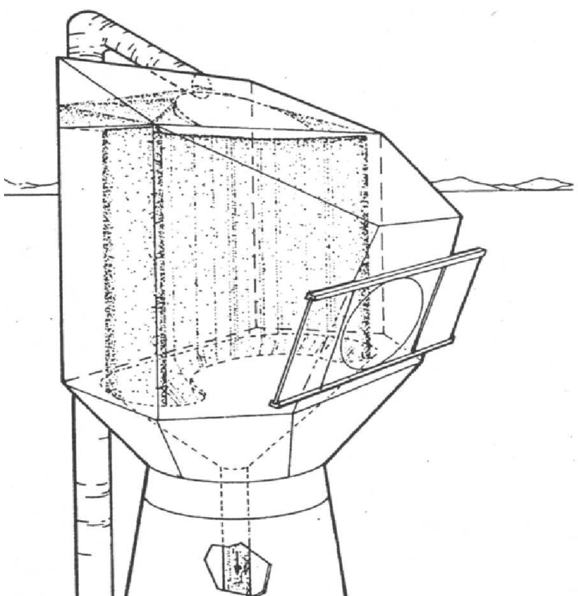
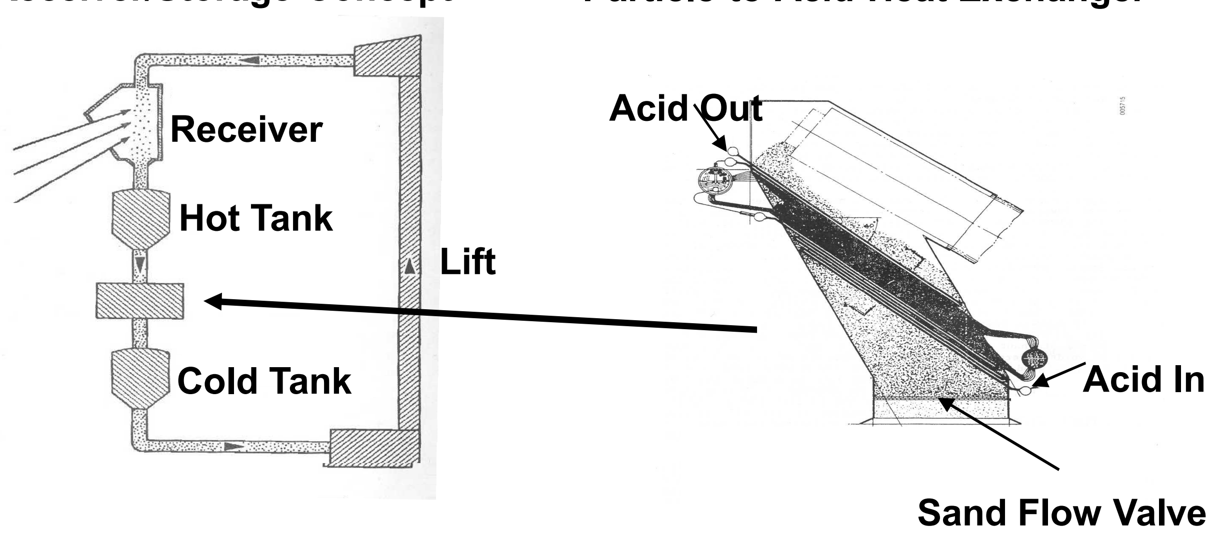
* e.g. Gorensek MB, Summers WA. Hybrid Sulfur flowsheets using PEM electrolysis and a bayonet decomposition reactor. *Int. J. Hydrogen Energy* (doi:10.1016/j.ijhydene.2008.06.049)

Solid Particle Receiver is Proposed Interface for S-Hy Cycle

- Sandia performed early R&D in mid 1980’s and initial on-sun test in 2008
- Falling curtain of “sand” within a windowless cavity
- Low-cost energy storage allows “around-the-clock” operation
  - A requirement to interface solar with complex chemical plant



Receiver/Storage Concept **Particle-to-Acid Heat Exchanger**



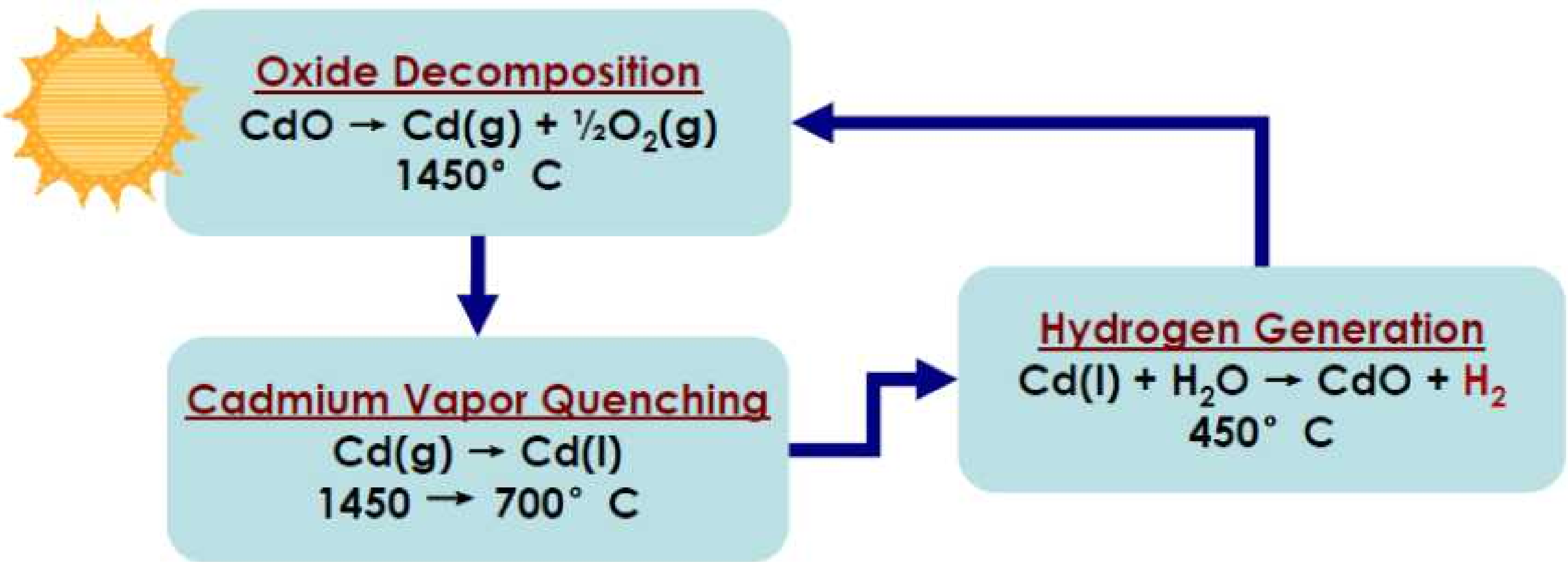
	Molten-Salt Tower, Electrolysis	Particle Tower, Sulfur-Hybrid T/C
Heliostat Mirror Area	1.3 km^2	1.3 km^2
Receiver Peak Power	700 MWt	700 MWt
Receiver Temperature	550 ^oC	1000 ^oC
Process Plant Power	255 MWt	255 MWt
Solar Multiple	2.7	2.7
Storage Size	***13 hrs***	***13 hrs***
Annual capacity factor	***76%***	***76%***
Electrolyzer size	100 MWe	34 MWe
Electrolyzer process-power fraction	***100%***	***12%***
Solar plant installed cost	380 $M	290 $M
H_2 plant installed cost	40 $M	80 $M
Annual Electricity Purchases (@8.7 cents/kWh)	0	25.9 $M
Annual Solar-to-Hydrogen Efficiency	***14%***	***20%***
Annual H_2 production	14 Mkg	28 Mkg
Levelized H_2 Cost	***4.7 $/kg***	***3.0 $/kg***

Reference: *Journal of Solar Energy Engineering,* Vol 129, May 2007, pp. 179-183

Solar Cadmium Hydrogen Production Cycle

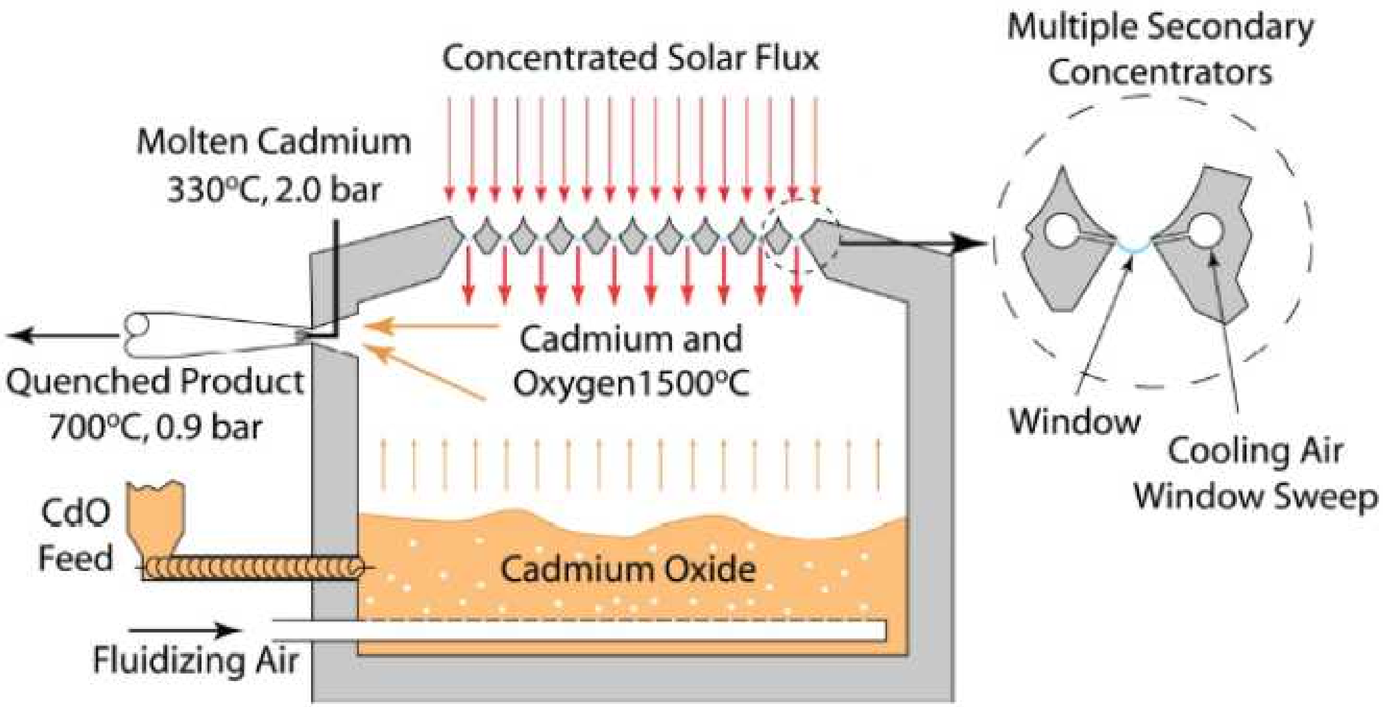
Bunsen Wong, Lloyd Brown and Bob Buckingham
(General Atomics)
Yitung Chen (UNLV)

The solar cadmium-hydrogen cycle consists of only three process steps



- LHV efficiency ~59%
- Quench needed to avoid recombination
- If He used during decomposition, reaction temperature may lower to 1250 °C

CdO baseline decomposer design utilizes a fluidized bed design



- This design concept fits with a beam down solar tower
- Secondary concentrators and windows are employed
- Atm. air is used as carrier gas to fluidize the particles

Prototypes are needed for design concepts verification

FY09

- Quench rate effect measurements
- Multi droplets quench process modeling
- Flowsheet and economics using He as carrier gas

FY10

- Decomposition data under a simulated solar environment using a prototype fluidized bed decomposer
- Molten Cd hydrolysis data under pressure and materials handling concepts and safety studies

Solar-Thermal Hydrogen Generation using Ferrite- Based Water Splitting Cycles

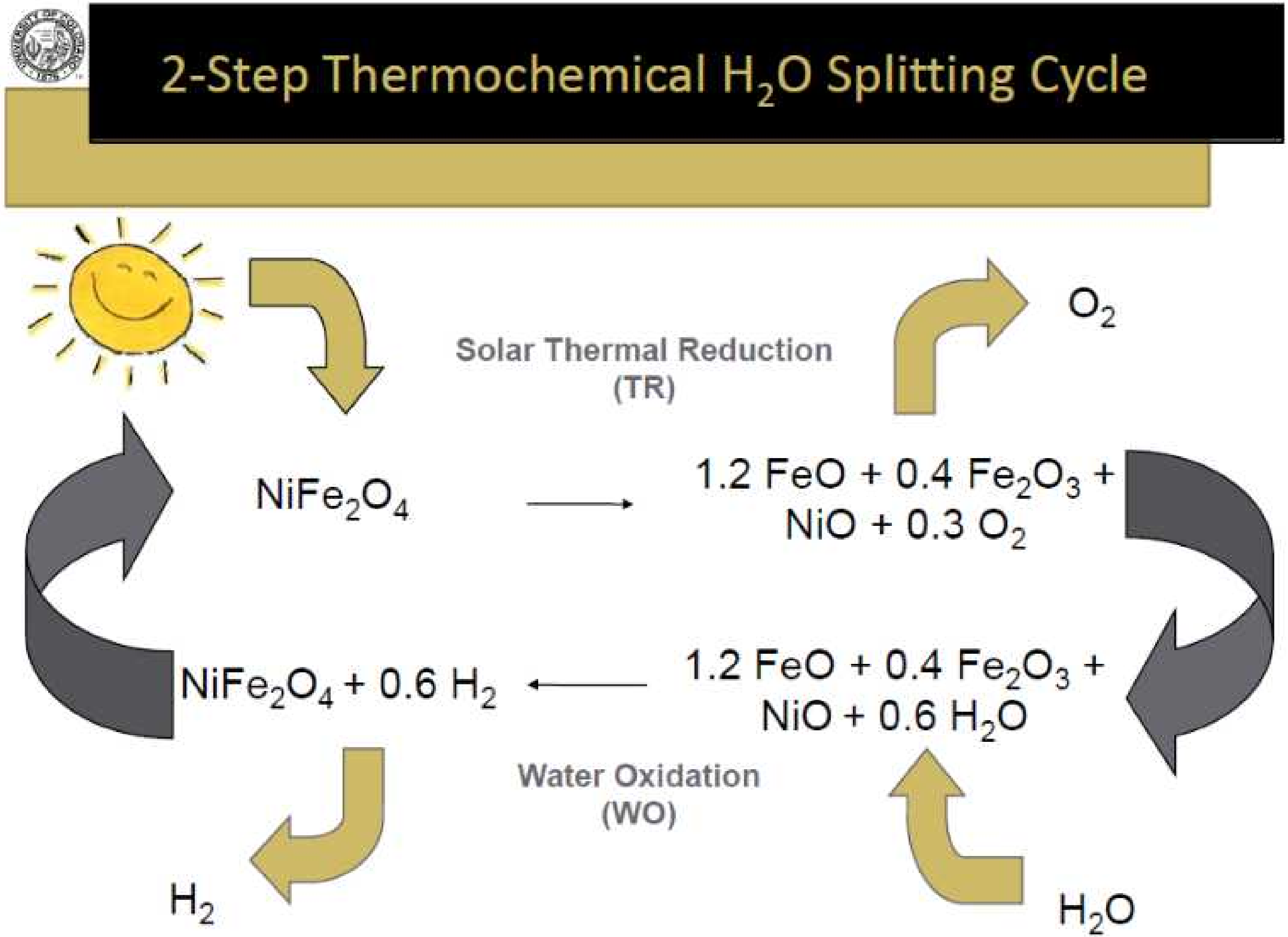
STCH Meeting, May 7-8

Jonathan Scheffe, Anthony McDaniel,* Mark Allendorf *, Jianhua Li, Hans Funke, and Alan Weimer

Chemical and Biological Engineering
University of Colorado

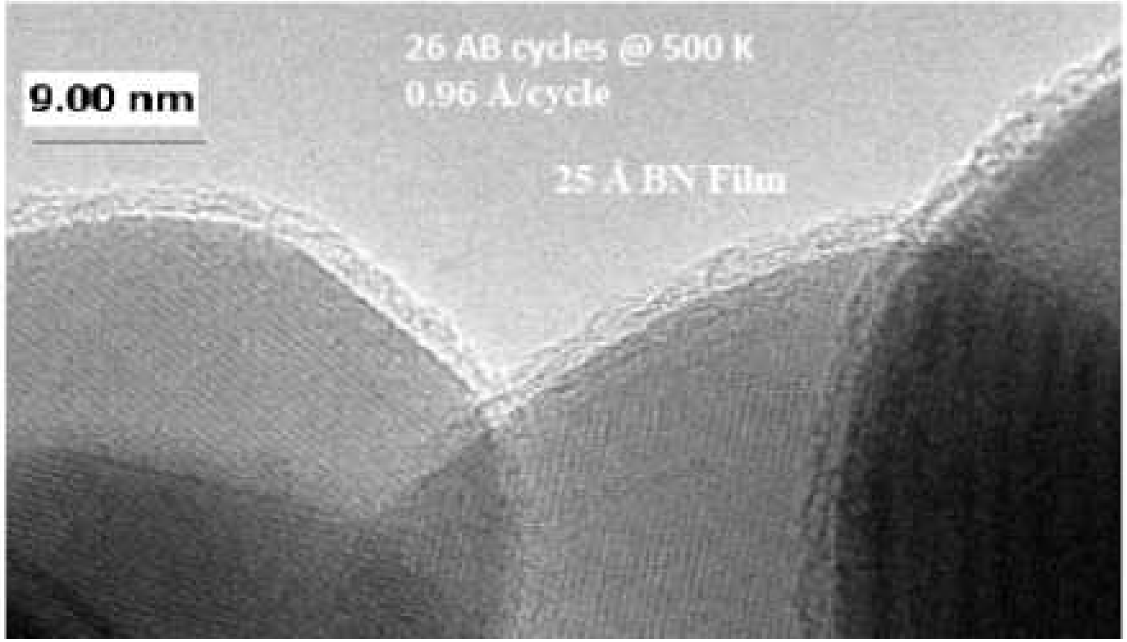
*SNL (Livermore, CA)

Ferrite Cycles



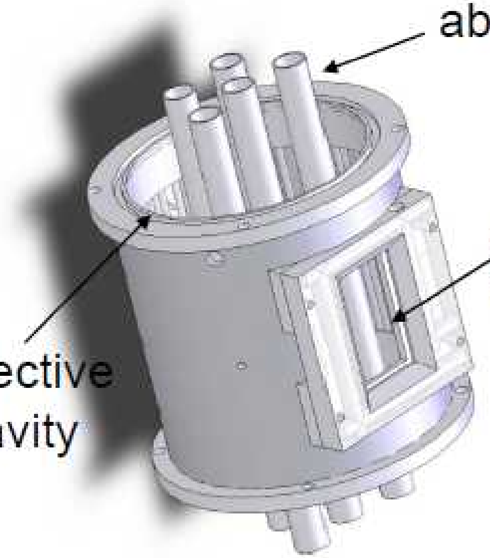
Atomic Layer Deposition (ALD) Ferrite Cycle

- Ferrite conversion rates are relatively low
- To increase surface area for reaction, use ALD to coat particles with ferrites

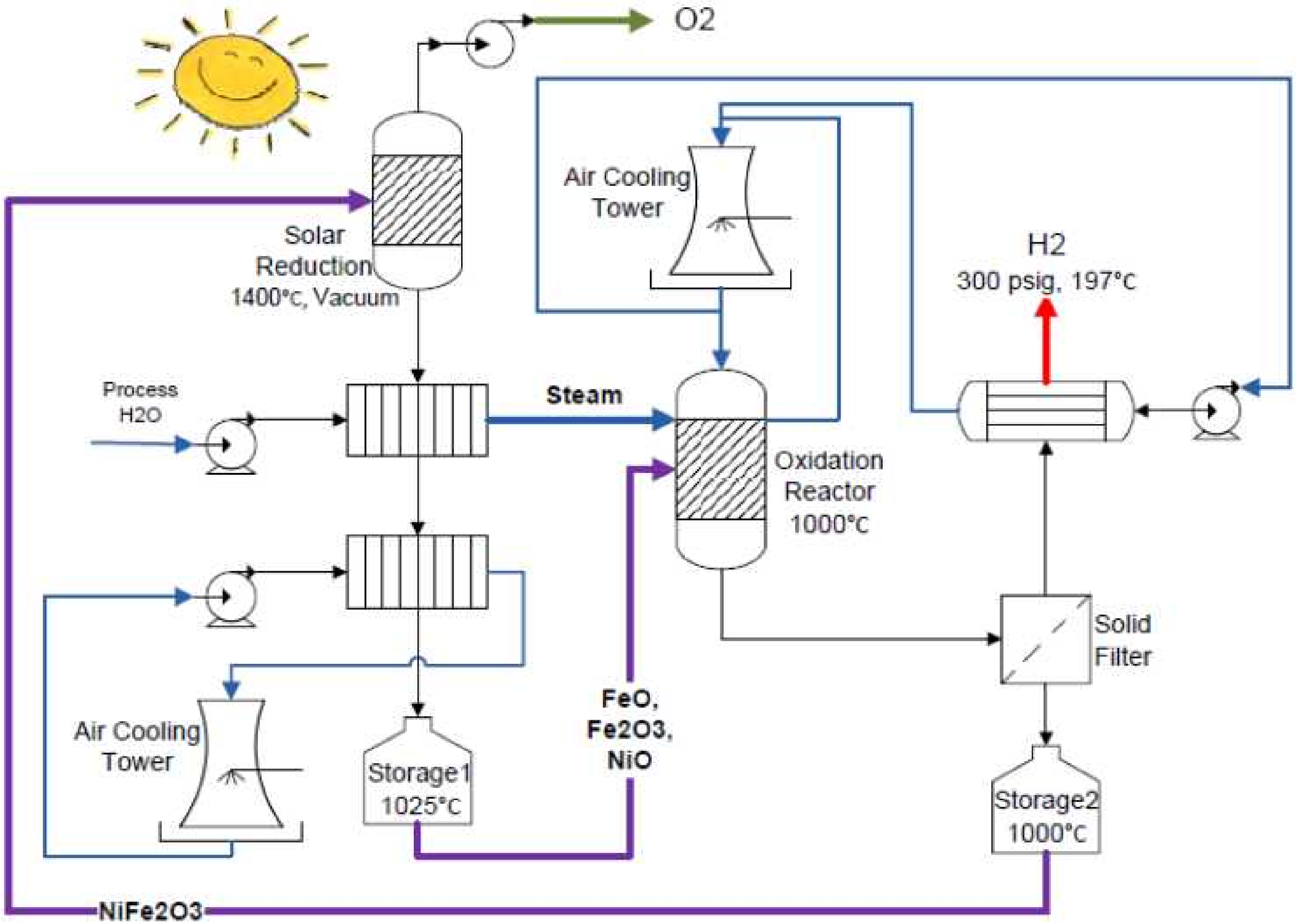


Reactor Design

- 5 aerosol flow tubes
- Reflective closed cavity with window
- Closed cavity design limits re-radiation losses



Ferrite Base Case PFD



ALD-Ferrites

- Key to ~\$3/kg is low cost (<\$10/kg) and durable ferrites given multiple thermal cycles
- Must also demonstrate ~70% conversion within solar reactor

		H2 Selling Price (\$/kg)		
		35% Reduction Conversion	70% Reduction Conversion	100% Reduction Conversion
Base Case	2008	\$6.52	\$4.44	\$3.79
	2012	\$5.68	\$3.82	\$3.24
	2017	\$4.43	\$2.90	\$2.42

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An overview of R&D activities for the Cu-Cl cycle with emphasis on the thermal reactions

Michele Lewis, Magali Ferrandon and Dave Tatterson

STCH Workshop

May 7, 2009

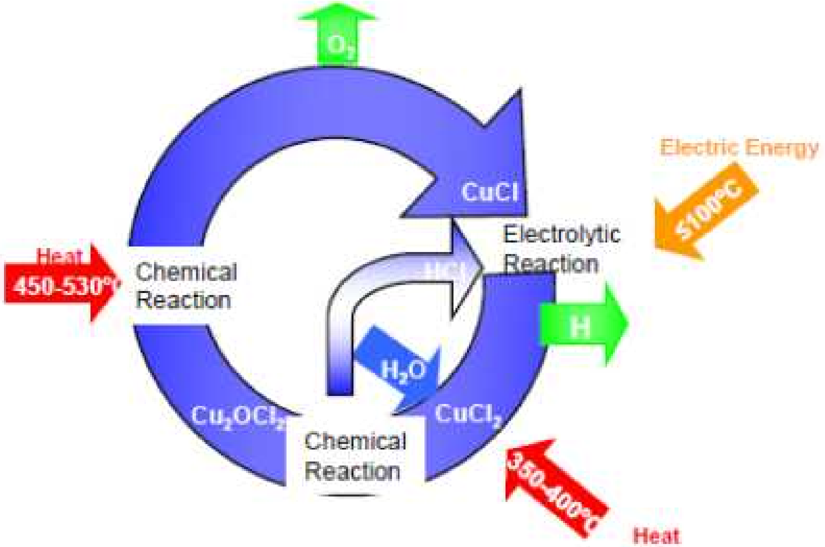
U.S. Department of Energy

UChicago Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

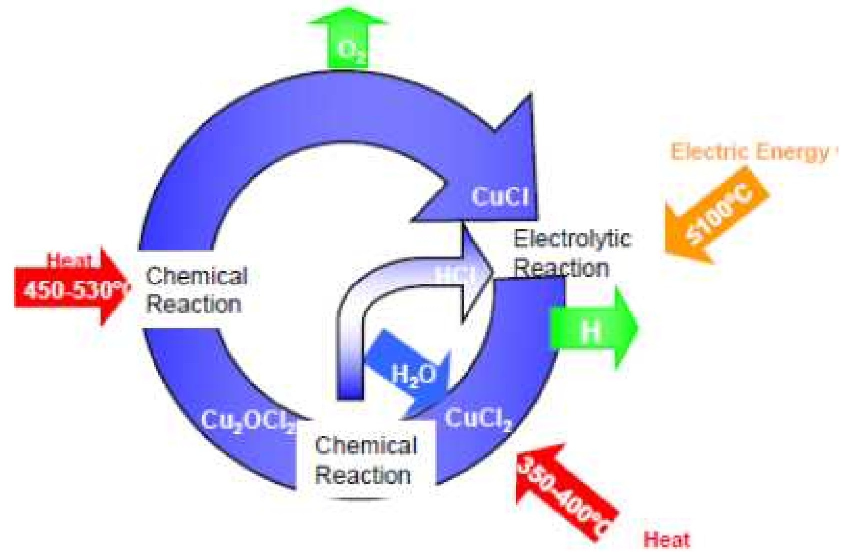
Cycle chemistry

- **Hydrolysis reaction**
  - $2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$
  - Optimize conditions for high yields and free flowing powders
- **Oxychloride decomposition**
  - $Cu_2OCl_2 \Leftrightarrow 2CuCl + \frac{1}{2}O_2$
  - Maximum temperature reaction
- **Electrolysis (simplified)**
  - $2CuCl + 2HCl \Leftrightarrow 2CuCl_2 + H_2$
    - *Anode:* $2Cu^{+} \Leftrightarrow 2Cu^{2+} + 2e^{-}$
    - *Cathode:* $2H^{+} \Leftrightarrow H_2$



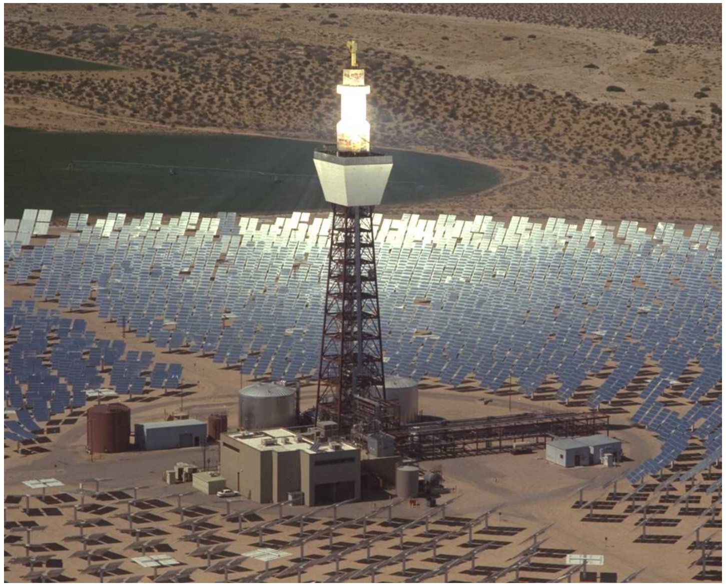
Development of Cu-Cl cycle is a team effort

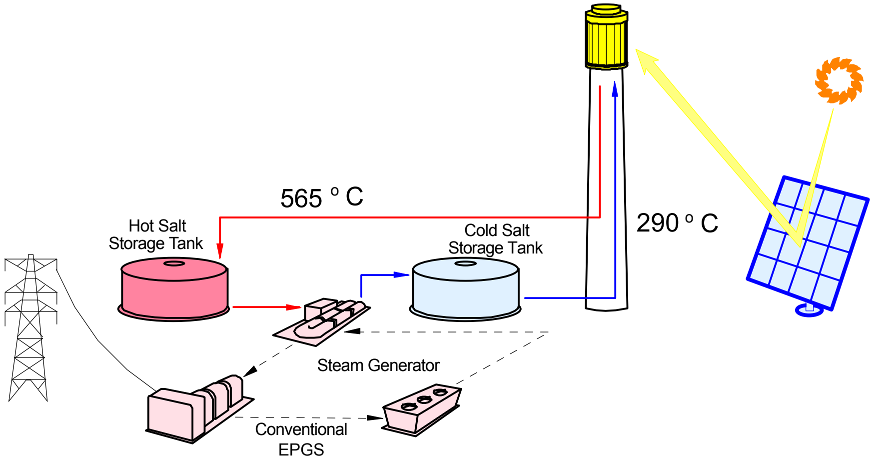
- **Hydrolysis reaction**
  - *Argonne National Laboratory*
  - *University of Ontario Institute of Technology and other Canadian universities (G. Naterer)*
  - *NERI-C universities (S. Lvov)*
  - *CEA (D. Doizi)*
- **Oxychloride decomposition**
  - *Argonne National Laboratory*
  - *University of Ontario Institute of Technology*
- **Electrolysis**
  - Atomic Energy of Canada Ltd
  - *Canadian universities*
  - *NERI-C universities*



Solar Two technology can be used to provide heat to CuCl cycle

- Solar Two operated from 1996 to 1999
  - 40 MWt molten salt receiver with 2-tank molten salt storage system
- Solar Reserve is commercializing this technology
  - 540 MWt receiver with large 2-tank salt storage
  - 13 hours of salt storage can provide “around-the-clock” 550 ^{o}C heat to the CuCl cycle (~70% annual capacity factor)





Summary

- Spray reactor provides necessary heat and mass transfer and product powders are free flowing
- Maximum process temperature of 550 C confirmed with Cu_2OCl_2 powders produced with ultrasonic nozzle
- Conceptual process design based on commercially practiced operations to reduce development costs
- Based on current Aspen model, it should be possible to meet hydrogen production cost target for 2025
  - Assumptions on operability of crystallizer and electrolyzer to be proven
- AECL has promising results for the electrolyzer's operation-work is continuing
- NERI-C partners are focused on advanced electrochemical technologies, e.g. membrane development, electrolyzer model development, etc

Conclusions and Future Prospects

- More than 200 cycles reduced to 4 with potential to produce H_2 in the \$3 to \$4/kg range
  - A possible 5th, FSECs sulfur ammonia cycle, requires H2A scrutiny
- Several technical issues must be resolved for all 4 approaches
- CuCl may be the near-term solar-hydrogen approach
  - Existing 565 ^{o}C solar technology can be used
  - S-Hy, Cadmium Oxide, and Ferrites also require development of hi-T (900 to 1400 ^{o}C) solar technology
- Obama's budget recommends \$0 for H_2-generation R&D
  - Obama wants to give primary focus to plug-in hybrids rather than H_2
- US Congress can make changes to Obama budget