

2006 DOE Hydrogen Program Review
Sulfur-Iodine Thermochemical Cycle

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Sulfur-Iodine Thermochemical Cycle Project

Overview

Timeline

- Start - 9/2002
- Finish - 9/2008
- ~ 50% complete

Budget

- Funding
 - DOE – 9.7 M\$
 - CEA In kind
- FY05 Funding – 2.8 M\$
- FY06 Funding – 5.5 M\$

Barriers

- Materials – high temperature, corrosive environments
- Process chemistry, thermodynamic data
- Reactor to process interface

Partners

- INERI Project with CEA
- Process – CEA, SNL, General Atomics
- Supporting Technologies – INL, ORNL, ANL, UNLV, MIT, UCB, Ceramatec

Sulfur-Iodine Thermochemical Cycle

Objectives

- **Determine the potential of the Sulfur-Iodine cycle for Hydrogen production using nuclear energy**
 - Determine process efficiency, operational parameters
 - Evaluate engineering approaches and materials of construction
 - Evaluate reactor –process interface and control technologies
 - Provide basis for cost projections and comparisons
 - Nuclear Hydrogen technology selection decision (FY2011)

Phase 1 Objectives

FY03 – 05 - Evaluate process options, establish baseline flowsheets, construct and demonstrate processes and materials

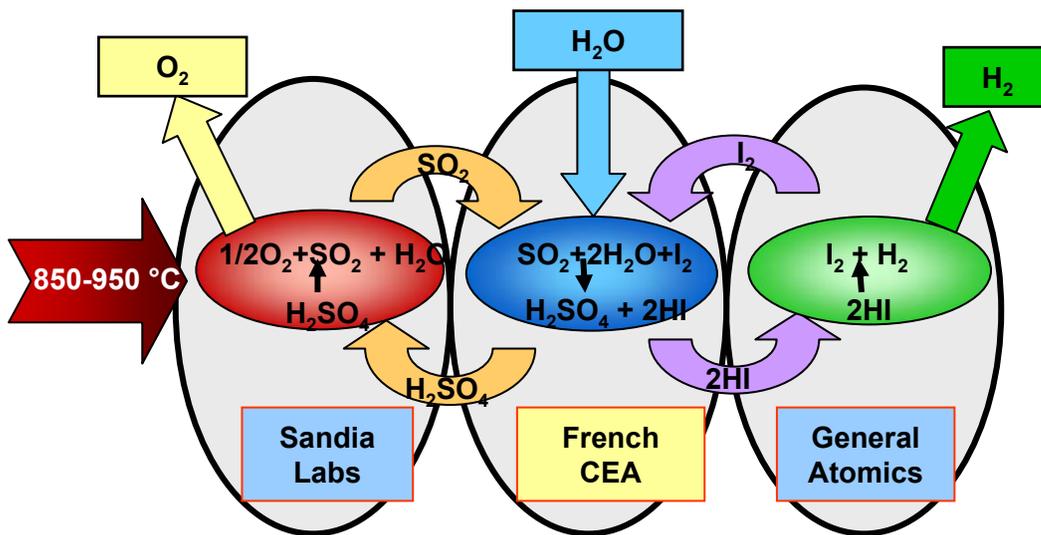
Phase 2 Objectives

FY06 - Complete development of the 3 major reaction sections
FY07 - Assemble integrated, closed loop demonstration experiment
FY08 - Conduct integrated lab scale experiments

NHI Sulfur Based Thermochemical Cycles

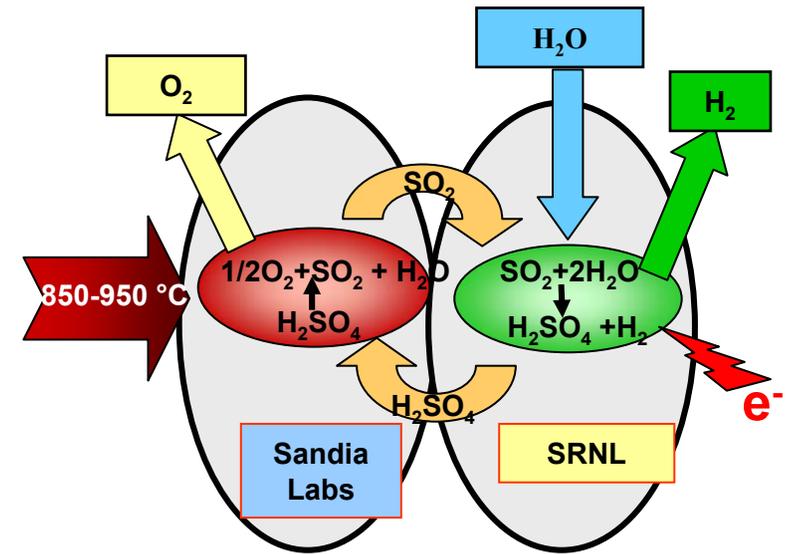
Sulfur-Iodine

Hybrid Sulfur



Sulfur Iodine

- (1) $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$
- (2) $2\text{HI} \rightarrow \text{I}_2 + \text{H}_2$
- (3) $2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$



Hybrid-Sulfur

- (1) $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$
- (2) $2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$

Sulfur-Iodine Integrated Lab Scale Experiment Approach

Flowsheet analysis of process options

- HI decomposition - reactive, extractive
- H_2SO_4 - Direct Contact Heat Exchanger (DCHX)
- Co- or Counter current Bunsen reactor

Component reaction tests

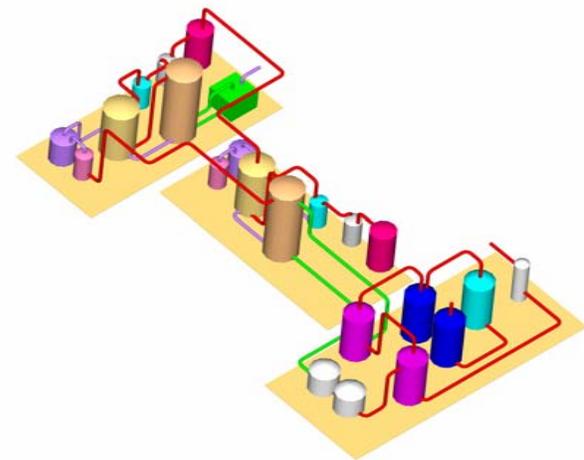
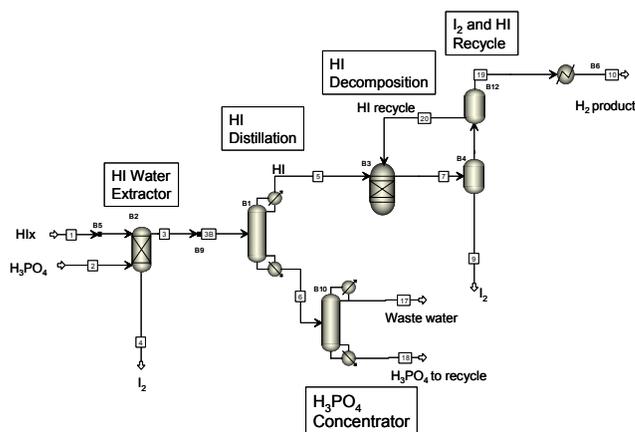
- HI - H_3PO_4 extractive distillation, Ta alloy
- H_2SO_4 - Superalloy, SiC based decomposer
- Co-current Bunsen, thermophysical data

Integrated Lab Scale Experiment

- Closed loop operation
- Nominal 200 l/hr H_2
- Evaluate system controls, contamination
- Longer duration testing, materials, catalysts

Pilot Scale Decision

- Performance, efficiency
- Materials, controls
- Scaling
- Costs



Technical Accomplishments/ Progress Overview

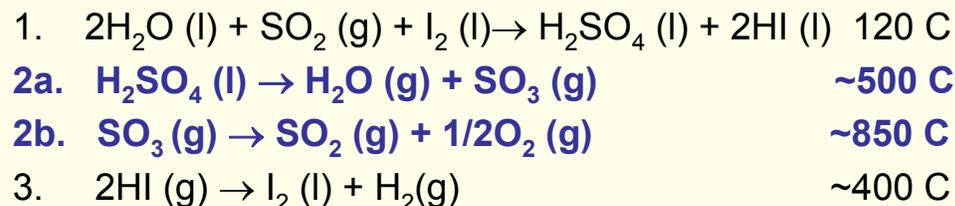
- **Alternative flowsheets for all sections evaluated, selected**
- **H₂SO₄ decomposition experiments**
 - Acid decomposition experiments completed at 850 -875 C, ambient to 11 bar
 - Superalloy decomposer corrosion mitigated,
 - SO₂ generation, diagnostics confirmed
 - Direct Contact Heat Exchanger (DCHX) flowsheet demonstrated
 - SiC integrated decomposer design developed
- **H₂I decomposition**
 - Efficient HI decomposition (H₂ generation) in absence of I₂, H₂ generation reduced in presence of I₂ extractive distillation selected (H₃PO₄)
 - Liquid extraction experiments on I₂ -- define phosphoric acid concentration needed to break HI-Water azeotrope
- **Bunsen reactor section under construction at CEA**
 - Co-current bunsen reactor, reduced recycle I₂, H₂O
 - Glass lined steel reactor
- **Membranes to reduce water recycle and O₂ separation tested**
- **Catalyst experiments completed for Pt and metal oxide materials**
- **Corrosion testing for range of candidate metals, ceramics underway**

Sulfuric Acid Decomposition Section

Status

- **Concentrate dilute acid from Bunsen reaction**

- Vaporize, decompose to form SO_3
- Catalytically decompose SO_3 to SO_2 and O_2
- SO_2 and H_2O output to Bunsen.



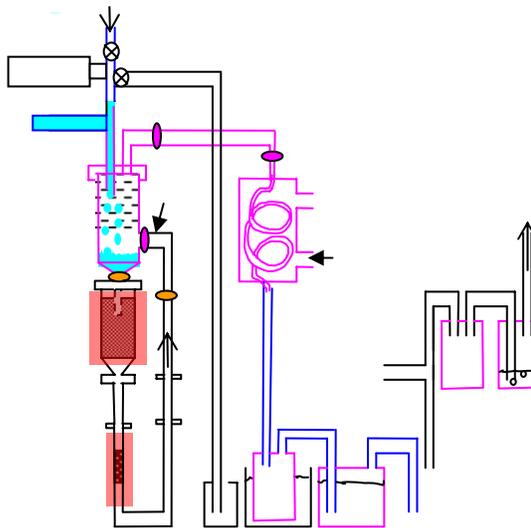
- **Key Issues**

- Materials, interface heat exchangers
- Catalyst activity, stability at temperature
- Energy efficiency - recuperation

- **Status**

- H_2SO_4 decomposition experiments ~850 C, 11 bar
- Direct Contact HX configurations tested

**High
Pressure
 H_2SO_4
Decomposer**

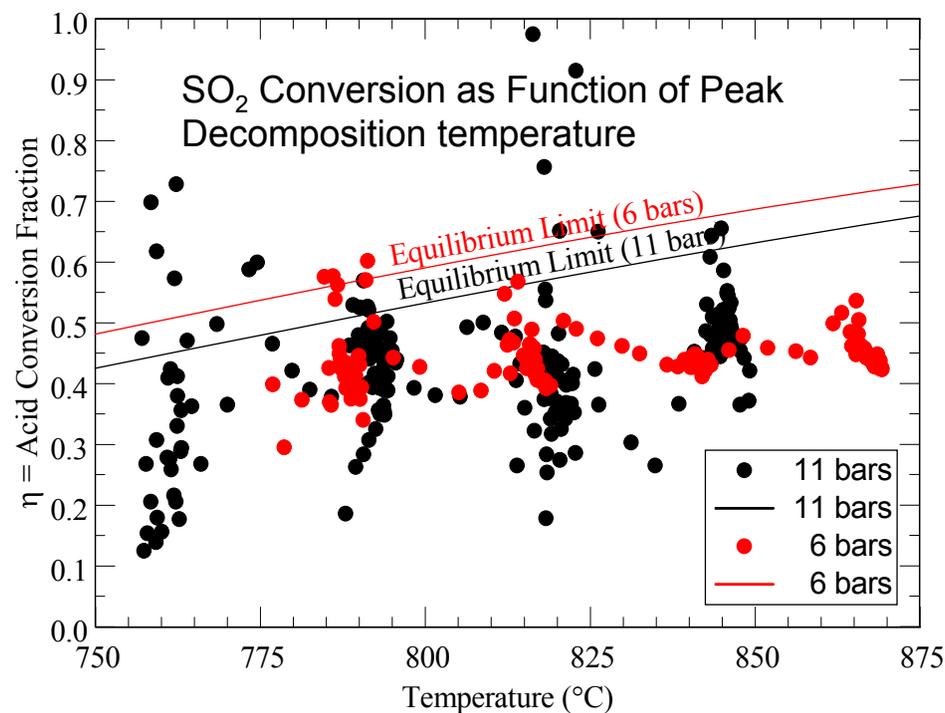


**DCHX
Decomposer**

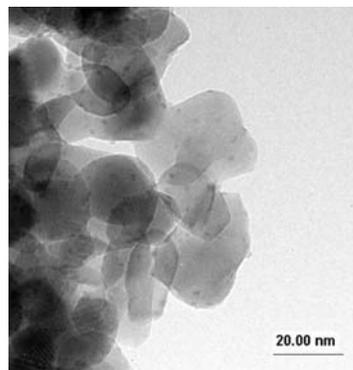
Sulfuric Acid Decomposition Section

Results

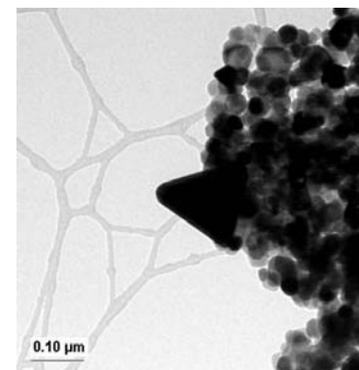
- Completed series of pressurized tests (850 C, 2, to 11 bars), real time diagnostics
 - Conversion fraction ~15% below equilibrium
 - Issues - catalyst degradation, corrosion in liquid and two phase regions
- DCHX experiments demonstrated heat recuperation and SO₃ recovery
- FTIR diagnostics developed for real time SO₂, SO₃ and H₂O measurements
- Developed integrated SiC based integrated boiler, superheater, decomposer



Pt catalyst (ZrO₂)
-before heating

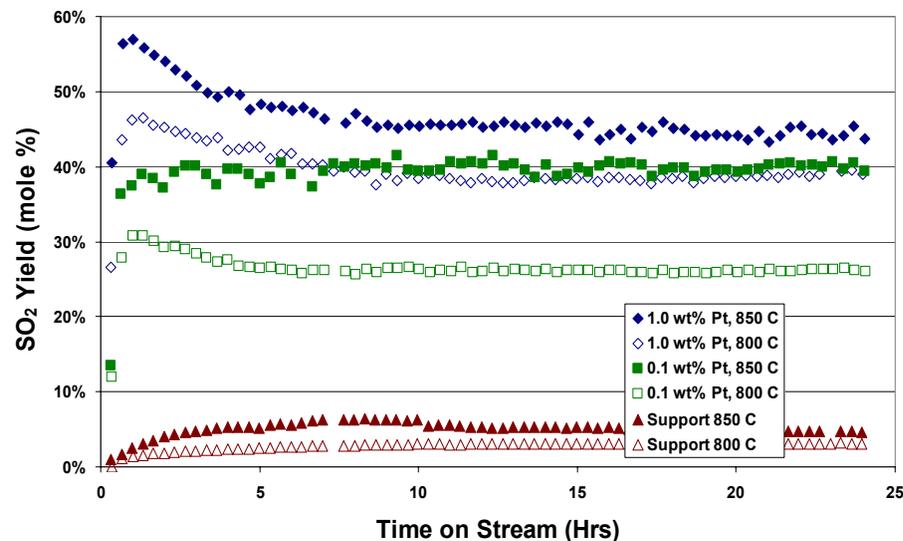


Pt catalyst (ZrO₂)
-after heating



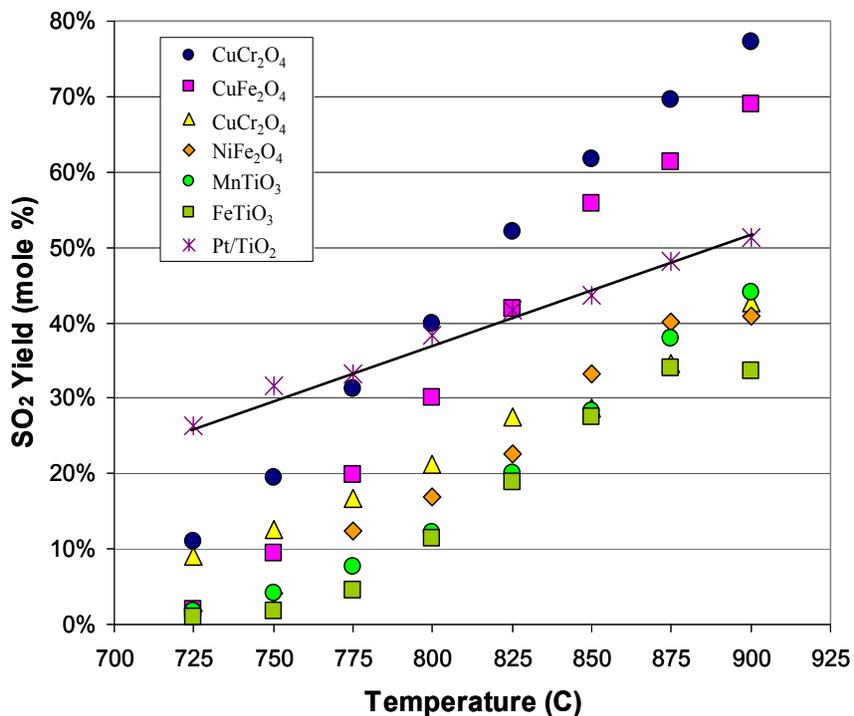
Sulfuric Acid Decomposition Catalysts

- Platinum on porous metal oxides most promising catalyst
- Pt catalysts not stable in high-temperature reaction environment
- Deactivation due to sintering of Pt and supports
- As much as 30% of Pt lost in 10 day tests (sintering and volatility)



Research Directions

- Increase stability
 - Modify Pt sites with other PGMs,
 - Explore supports with stronger metal/support interactions
- Explore non-PGM catalysts - Spinel (AB_2O_4) and Perovskites (ABO_3). Stability studies in progress

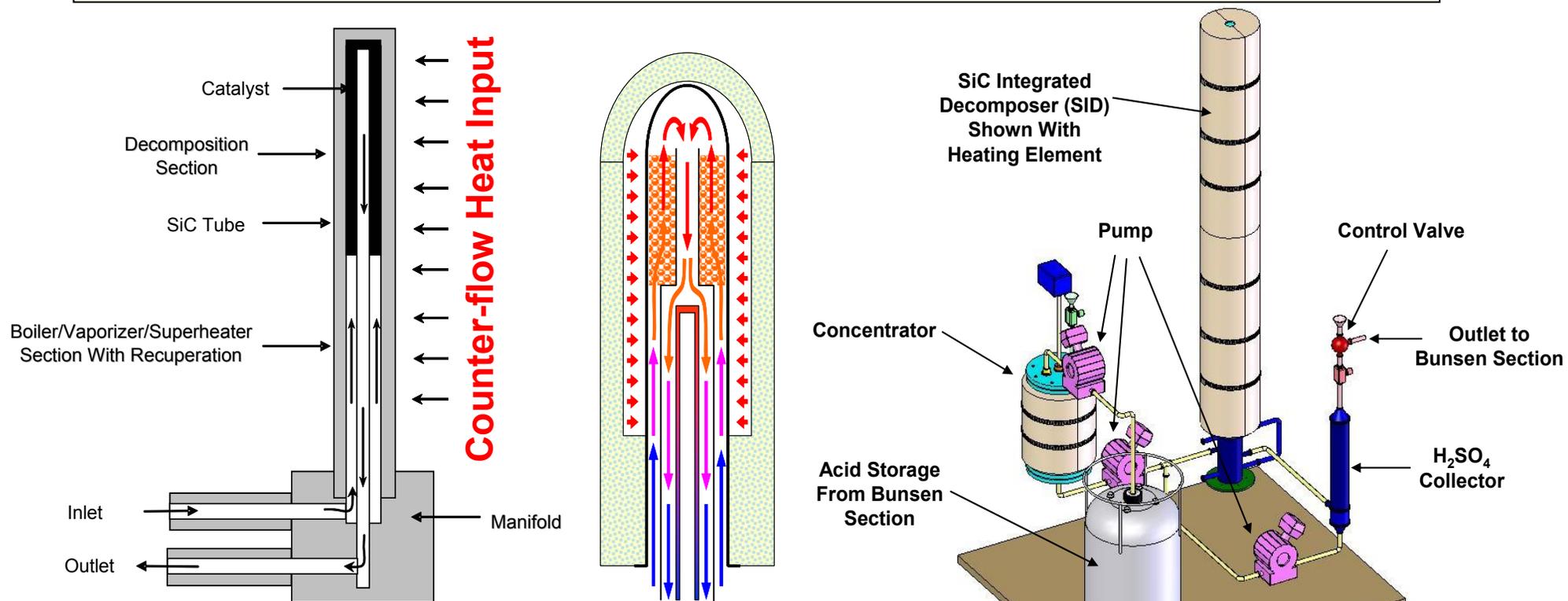


- $CuCr_2O_4$, $NiCr_2O_4$, $FeTiO_3$ - leaching problems
- Activity of $FeTiO_3$ and $NiFe_2O_4$ decreased at the highest temperature
- $CuFe_2O_4$ spinel promising at high temperatures

Sulfuric Acid Decomposition Section

Integrated SiC Based Decomposer

SiC bayonet heat exchanger minimizes connections, seals, corrosion sites



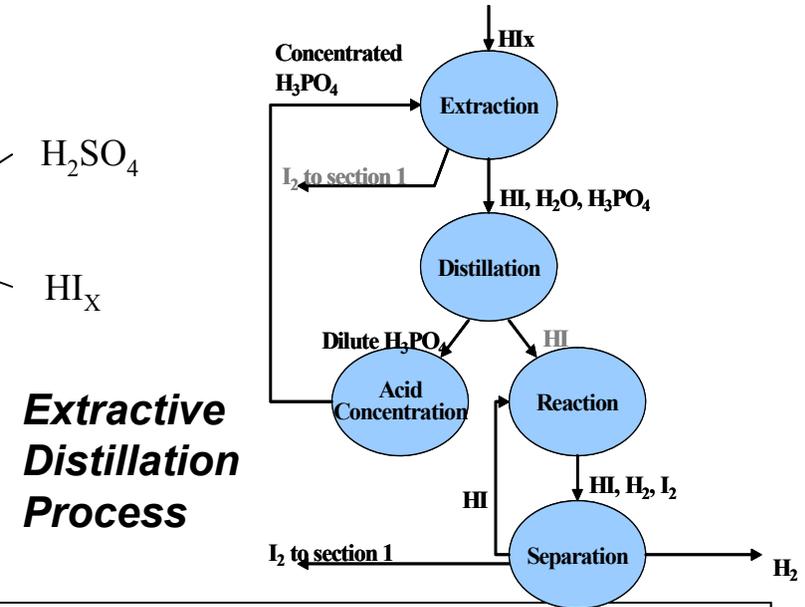
- Full length recuperation of product stream
- Manifold ~ 200 C, SO₃ recombines at cold end
- Allows use of glass/Teflon lined commercial components
- SiC components commercially available

Section 3- HI Decomposition Overview

- Separates I_2 and H_2O from HI,
- Decomposes HI into H_2 and I_2 ,
- Return I_2 and H_2O to Section 1

• Key Issues

- Distillation method
- Uncertainty in HI/ I_2 / H_2O VLE
- High recycle water volumes
- Materials – corrosion, catalysts

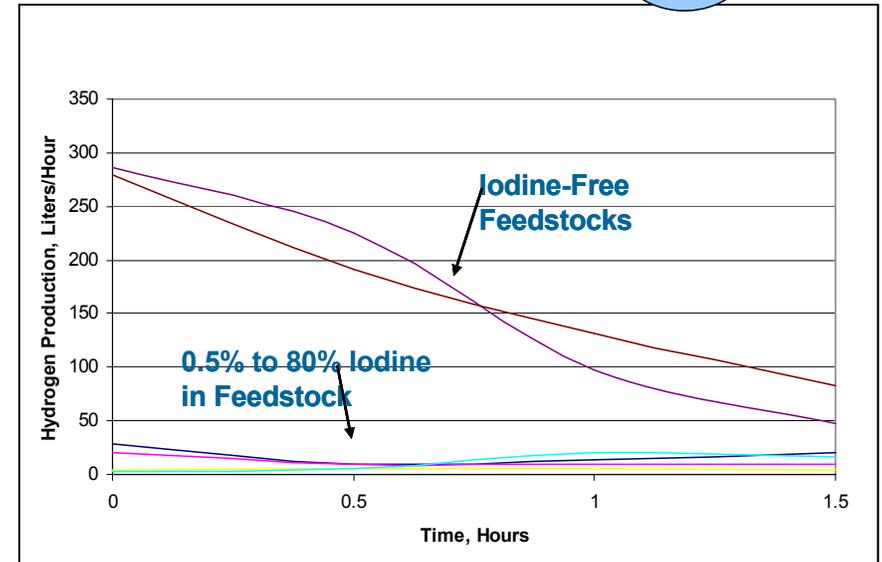


• Process selection

- Reactive distillation- separation and reaction in single vessel --- Poor performance with high I_2 concentration
- Extractive distillation- uses H_3PO_4 to separate I_2 and HI - All steps demonstrated, **selected as baseline**

• Current Experiments

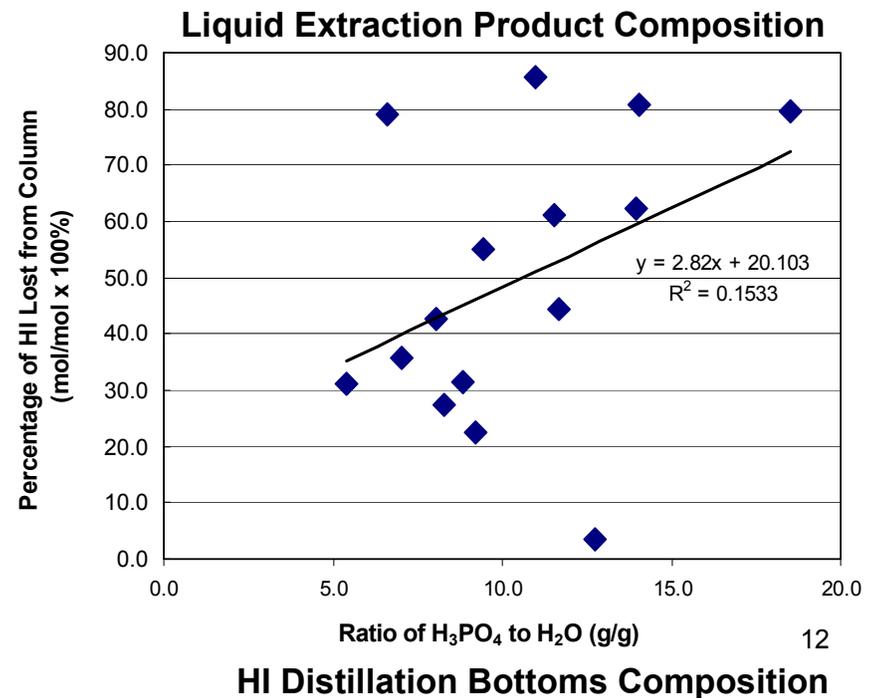
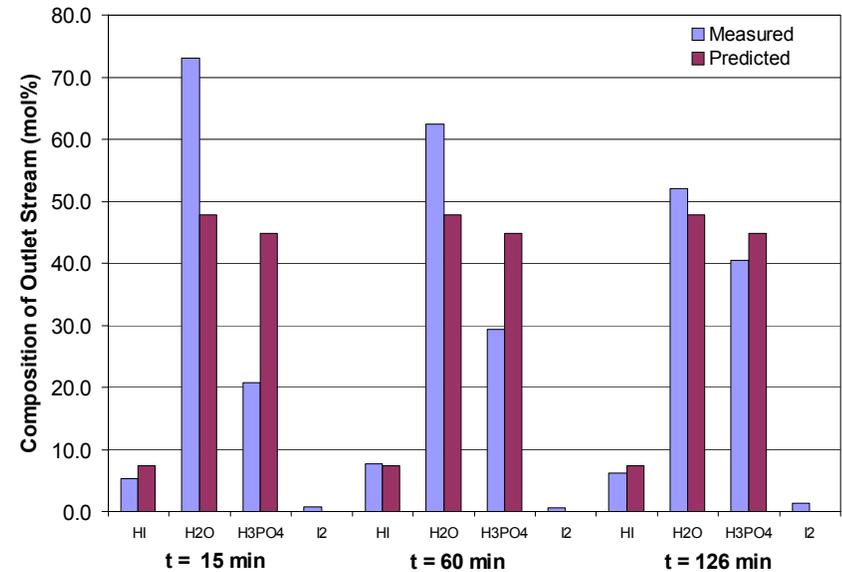
- determine operating regime for H_3PO_4
- Materials for HI, I_2 , H_2O corrosive environment



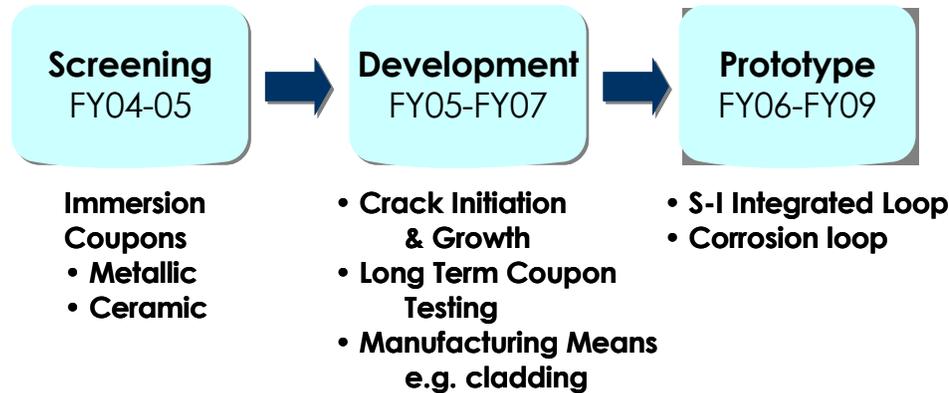
Reactive Distillation Results

HIx Decomposition (Section 3) Chemistry Results

- Current Experiments:
 - liquid extraction
 - HI distillation & H₂ Production
- *Extraction efficiency expts* provide operating bounds for phosphoric acid concentration to extract HI and water from I₂
- *HI Distillation composition expts* determine phosphoric acid concentration needed to break HI-Water azeotrope
- *Improved diagnostics* needed to reduce scatter. Several candidates being developed



HI Section Process Materials Development



- **Testing to identify candidates for:**
 - I₂ separation (HI_x + H₃PO₄ at 140°C)
 - HI gaseous decomposition (HI + H₂ + I₂ at 450°C)
 - H₃PO₄ concentration (boiling acid at 450°C)
- **Ta-2.5W shown to be compatible with the HI_x + H₃PO₄ acid complex**
- **Stress corrosion effects will need to be studied**

• Test system for HI gaseous decomposition is online (3/30/06)

- Boiling phosphoric acid has been found to be extremely corrosive
- Ta alloys and Ag have acceptable corrosion resistance

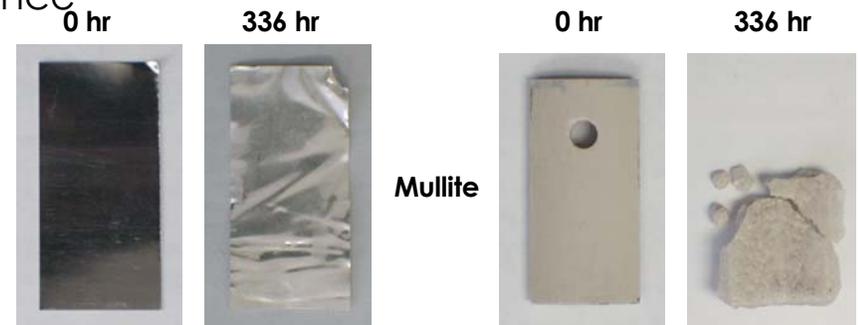
Materials to test

Hastelloy B-2 (Ni-Mo)
Ti and alloys
Ta and alloys
C-SiC
Mullite

Hastelloy C-276
W and alloys
SiC
Alumina

Ag

Mullite



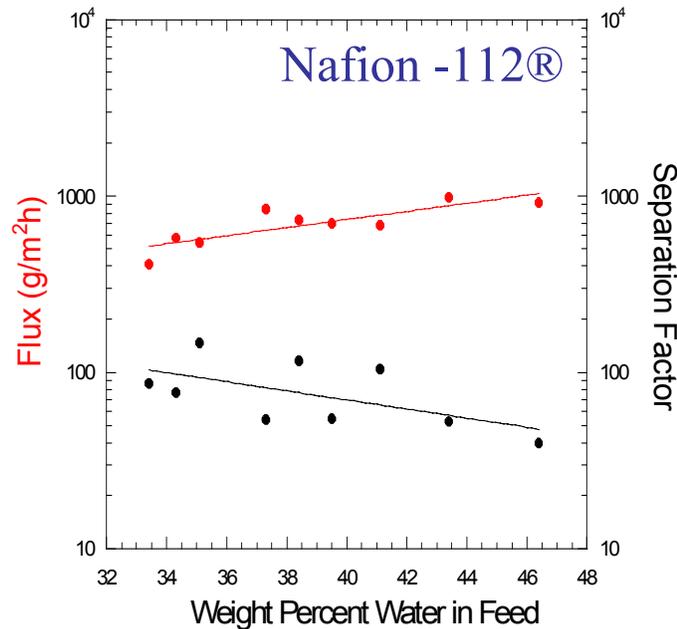
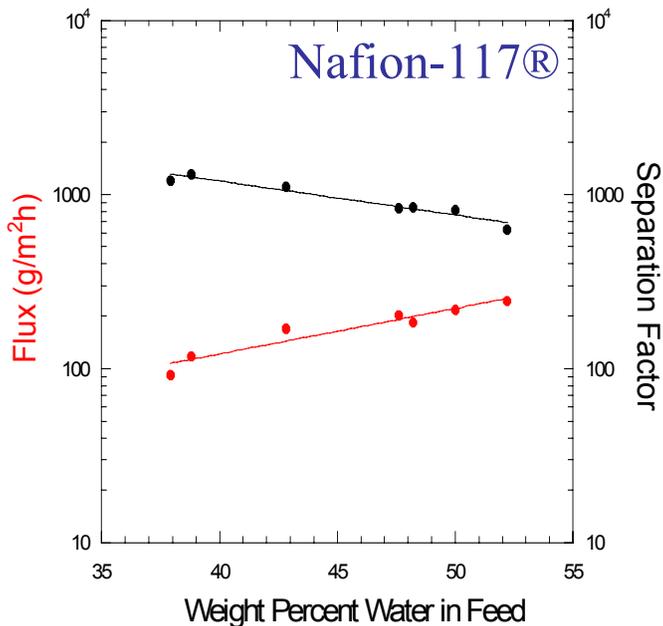
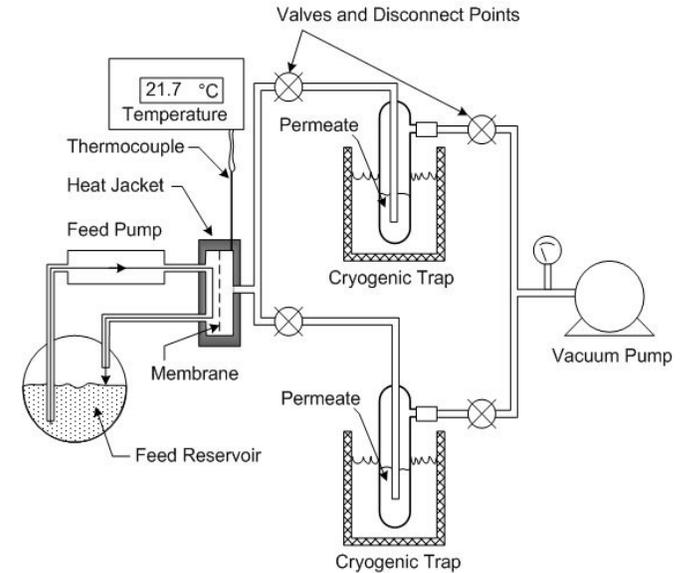
HI Section Process Improvements

Several potential process modifications are being investigated to improve efficiency or simplify process

- **Water recycle reduction membrane development (INL, ORNL)**
 - Reduction of 10-20% water could improve efficiency, reduce some hardware requirements
 - Reduction of > 20% water could dramatically change the process, may simplify Section 3, eliminate need for H_3PO_4
- **Liquid phase decomposition (GA)**
 - Decompose HI in the liquid phase - allows for greater conversion, easier separation of H_2 product, reduced temperature and improved efficiency
- **Supporting Analysis**
 - Flowsheet development to determine efficiency
 - Equipment and plant capital cost estimates

Membranes for Reduction of Recycle Water Volumes in HI Section

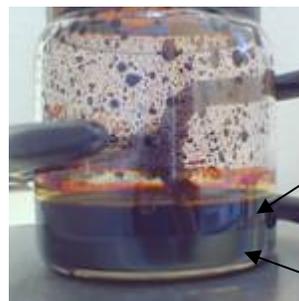
- HI_x concentration (H_2O , I_2 , HI) of Bunsen output 120 °C – 350 °C
- H_2 separation from HI and I_2 membranes identified, high selectivity polymeric membranes are being studied.
- H_2O removal membranes for H_2SO_4 section also being evaluated (~150 to 200 C)



- HI /water concentrated above 57% HI azeotrope
- No significant degradation in HI/I_2 /water or sulfuric acid membranes.
- Pervaporation systems for HI/I_2 concentration being incorporated into the S-I flowsheet

Bunsen Reaction Section- Status

- Primary reaction making the HI and H₂SO₄
- Delivers Hlx (HI, H₂O, I₂) to section 3 (lower phase)
- Delivers H₂SO₄ to section 2 (upper phase)



Status

- Hardware design and construction almost complete, testing begins 6/06, completes 3/07. Verify counter-current operation
- Thermophysical properties - VLE data for Hlx solutions

	t °C	FTIR		UV-Vis	Σ P _{partial}	Pressure		FTIR			Prophy simulation		
		P _{partial} HI mbar	P _{partial} H ₂ O mbar	P _{partial} I ₂ mbar	mbar	P measured mbar	% HI molar	% H ₂ O molar	% I ₂ molar	Pressure mbar	% HI molar	% H ₂ O molar	% I ₂ molar
Ternary 9.6% HI 51.3% H ₂ O 39.1% I ₂	111	20.8	678.4	na	699,3	653	3,0	97,0					
	121	21,8	932,0	na	953,8	895	2,3	97,7	856	0,3	91,0	8,5	
	126	12,1	1049,4	na	1061,5	1036	1,1	98,9	980	0,4	90,7	8,7	
	131	18,3	1196,1	na	1214,5	1195	1,5	98,5	1152	0,5	90,4	9,0	
Ternary 11.67% HI 48.58% H ₂ O 39.74% I ₂	102	88,0	238,0	17,9	344,0	287	25,7	69,1	5,2	287	11,7	78,3	10,0
	117	137,0	406,0	34,0	577,0	510	23,7	70,4	5,9	501	16,3	73,2	10,5
	132	236,0	823,0	55,8	1115,0	885	21,2	73,8	5	854	21,2	68,1	10,7
	101	477,5	157,9	20,3	655,7	612	72,9	24,1	3,1	328	43	49	7,6
Ternary 13.11% HI 47.9% H ₂ O 39% I ₂	119	647,8	293,0	40,2	981,0	941	66,1	29,9	4,1	700	49,7	42,9	7,4
	133	881,1	549,0	64,3	1494,4	1380	58,9	36,7	4,1	1174	51,8	40,8	7,5

Hlx VLE partial pressure measurements

Sulfur Cycle Supporting Technology Activities

- **Materials** – high temperature corrosion and mechanical properties – metals, ceramics (UNLV, GA, MIT, ORNL)
- **High temperature systems interface** – innovative heat exchanger designs, analysis (UNLV, UCB, Ceramatec)
- **Membranes** – high temperature inorganic membranes for acid decomposition (ORNL, INL)
- **SO₃ electrolysis** (ANL)

Sulfur Iodine Thermochemical Cycle

Planned Activities (FY06-FY08)

- FY06 – Complete testing of reaction sections for S-I cycle
 - Complete acid decomposer high pressure tests in SiC integrated decomposer
 - Complete Hx section construction (Ta-2.5W) and supporting experiments
 - Complete Bunsen reactor construction and initial tests
- FY07 – Assemble component sections, initiate closed loop testing
- FY08 – Perform S-I Hydrogen test program in integrated lab-scale apparatus

- **End of Presentation Slides**

Comments from FY05 DOE Review (1)

1. **Reviewer Comment:** Proper design protocol calls for a heat exchanger approach temperature of 10 to 20 deg C and a pressure drop through a heat exchanger of 1.5 to 2 psi. This results in a decreased efficiency and could be significant for complicated processes such as this that have a large number of unit operations.

Project Response: The new bayonet HX design (in the H₂SO₄ section) greatly reduces the number of heat exchanger units used in the previous flowsheets. The sulfuric acid boiler, superheater and catalytic decomposer have been integrated into a single, relatively low pressure drop configuration. The system delta P is now derived from liquid pumps (low power requirement), and pinch points have been evaluated – and are generally in the 20°C range for the current (nonoptimized) design.

2. **Reviewer Comment:** Did not specifically mention iodine recycle rates and the impact of the kg iodine/kg hydrogen. At one time, this ratio was 6,000 kg iodine/kg hydrogen. Supposedly work by the French partner indicates a 5 fold reduction in iodine flow. Is 1,000 kg iodine handling per 1 kg hydrogen really sufficient? This needs to be a major initiative – continuing to find ways to reduce iodine handling.

Project Response: The current flowsheets and experiments require an iodine flow of 1270 kg I₂ per kg of H₂ (or 10 mol of I₂ per mol of H₂). The weight ratio is high due to the molecular weight difference between the I₂ and the H₂). However, that flow is completely recycled, so the iodine inventory is essentially fixed, so the economically relevant number is the I₂ charge for a given plant size. The ILS experiment will have an I₂ flow rate of 20 kg/hr for 200 L/hr of H₂ (0.0018 kg H₂/hr or 8 moles H₂/hour), with a charge volume in the range of 50-100 kg. So in a 10 hour run, 200 kg of I₂ will have been processed, but it is all the initial 20-50 kg of I₂. While it would be desirable to reduce the I₂ flow, the excess is necessary to create the phase separation in the Bunsen reaction. There may be a new membrane technology that allows for the separation of the H₂SO₄ and HI phases without the excess I₂, but that has yet to be developed. I don't know of any other potential way to reduce I₂ flow or inventory.

Comments from FY05 DOE Review (2)

3. - **Reviewer Comment:** The use of ceramics in large scale hydrogen reactors is questionable. (brittle, fabricability)

Project Response: The SiC bayonet type heat exchangers being used in the S-I design are being in current commercial applications. SiC has been investigated and utilized in industrial heat exchangers, heat recuperators, and heat pipes. The material has high thermal conductivity, excellent corrosion resistance, high durability, excellent thermal shock resistance and can be used in processes operating in excess of 1600 °C. The bayonet design currently being investigated at SNL is based on technology used in heat exchangers and high temperature heating pipes for liquids, gases and liquid metals. (Foster and Patton, Ceramics in Heat Exchangers 1984; Smith, Advances in thermal Design of heat Exchangers, 2005).

Heat exchangers fabricated from commonly used SiC based materials (Hexoloy a boron doped silicon carbide) can be used under pressures exceeding 2,700 psi. (Carborundum Corp. manufacturer of silicon carbide and silicon carbide alloys). Recently, several companies have reported the development of silicon carbide alloys that exhibit very high strength (Ceradyne, Inc; Mitsubishi Gas Chemical Co, Inc: Osake University). These new high-strength silicon carbide materials may be valuable to the future development of the S-I process.

The bayonet design being investigated at SNL utilizes commercial off-the-shelf products that are widely used in industry. The bayonet unit is constructed of Hexoloy heat exchanger tubes manufactured by Saint-Gobain in the United States. The integration of the acid boiler, superheater and catalytic decomposer into a single silicon carbide bayonet unit eliminates many problems in previous designs including materials corrosion, high temperature connections and heat recuperation. Silicon carbide is known not to corrode in sulfuric acid, there are no high temperature connections in the unit and heat is recuperated throughout the entire flow path of the superheater and boiler sections of the apparatus.

Publications and Presentations

Sulfur Iodine Thermochemical Cycle

Presentations

- NHI Semiannual Reviews (November 2005, March 2006)
- UNLVRF High Temperature Heat Exchanger Programs - Quarterly reviews
- July 2005, DARPA Future Fuels Meeting "Synfuel from Nuclear Production of Hydrogen"
- October 2005, Americas Nuclear Energy Symposium, "Nuclear Production of Hydrogen"*
- November 2005, PCS Nitrogen (fertilizer), "Nuclear Production of Hydrogen"
- November 2005, MIT Symposium "Nuclear Production of Hydrogen"
- November 2005, ANS Meeting "Nuclear Production of Hydrogen"
- December 2005, Aker-Kvaerner (Houston) "Synfuel from Nuclear Production of Hydrogen"
- March 2006, The Fertilizer Institute "Nuclear Production of Hydrogen"
- April 2006, National Energy Technology Laboratory "Synfuel from Nuclear Production of Hydrogen"

Publications

- April 2005, AIChE Meeting: "Lab-Scale Catalytic Decomposition of Sulfuric Acid with Scalable Materials"
- Sept 2005, SAND Report: "High Pressure Sulfuric Acid Decomposition Experiments for the Sulfur-Iodine Thermochemical Cycle"
- September 2005, "Metallurgical and Corrosion Characterization of Structural Materials for the National Hydrogen Initiative", Ajit Roy, Radhakrishnan Santhanakrishnan, Ancila Kaiparambil, Bunsen Wong, Gottfried Besenbruch, Lloyd Brown Materials Science & Technology 2005, Symposium: Materials for the Hydrogen Economy
- June 2006, World Hydrogen Energy Conference: "Pressurized Sulfuric Acid Decomposition Experiments"
- Nov 2006, AIChE Meeting: "Sulfuric Acid Decomposition Experiments with Heat and Mass Recovery using a Direct Contact Exchanger"

Critical Assumptions/Problems

Sulfur Iodine Thermochemical Cycle

- **Materials for high temperature corrosive environments:** Materials capable of long term service in the highly corrosive environment of the TC cycles needs to be developed – or innovative heat exchanger designs that use corrosion resistant materials already available (ceramics) must be developed for S-I to succeed. Innovative HX designs have been developed for the high temperature parts of the cycle, and appear to mitigate the requirements for new materials. Data from the next tests will provide significant confirmation of this approach.
- **Interactions between major process sections:** The interaction between the major process sections will introduce the possibility of crosstalk between sections (contamination of one section with another chemical species), as well as control issues introduced for the overall thermochemical system. The implications of these additional systems and associated costs for process viability must be assessed before decisions on scale up for a process can be made. Control issues for balancing the major reactions must also be addressed. The approach being taken is the Integrated Lab Scale Experiment (ILS) which will perform a closed loop experiment based on the integration of the three sections for S-I.
- **Production Process Costs:** Estimating the costs of hydrogen produced from the NHI processes is highly uncertain at this stage of development. A cost framework is being developed to provide a consistent basis for comparison of the nuclear hydrogen process alternatives, and how they fit in to the bigger hydrogen production picture.