2007 DOE Hydrogen Program Review

Sulfur-Iodine Thermochemical Cycle

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Project PD20

Sulfur-Iodine Thermochemical Cycle Project
Overview

Timeline

- Start - 9/2002
- Finish - 9/2008
- ~ 60% complete

Barriers

- Materials – high temperature, corrosive environments
- High temperature process chemistry
- Coupling of reactor to thermochemical process

Budget

- Funding
  - DOE – 14.0 M$
  - CEA In kind
- FY06 Funding – 5.5 M$
- FY07 Funding – 4.3 M$

Partners

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

Sulfur-Iodine Thermochemical Cycle
Objectives

- **Determine the potential of the Sulfur-Iodine cycle for Hydrogen production using nuclear energy**
  - Sulfur cycles - potential for high efficiency and technical maturity
  - Evaluate and test process options, construct integrated lab scale experiment to demonstrate S–I cycle
  - Provide basis for cost projections and comparisons
  - Support Nuclear Hydrogen technology selection decision (FY2011)

Phase 1 Objectives

FY03 – 05 - Evaluate process options, establish baseline flowsheets, conduct experiments on process options and materials

Phase 2 Objective -- (Integrated Lab Scale Experiment - ILS)

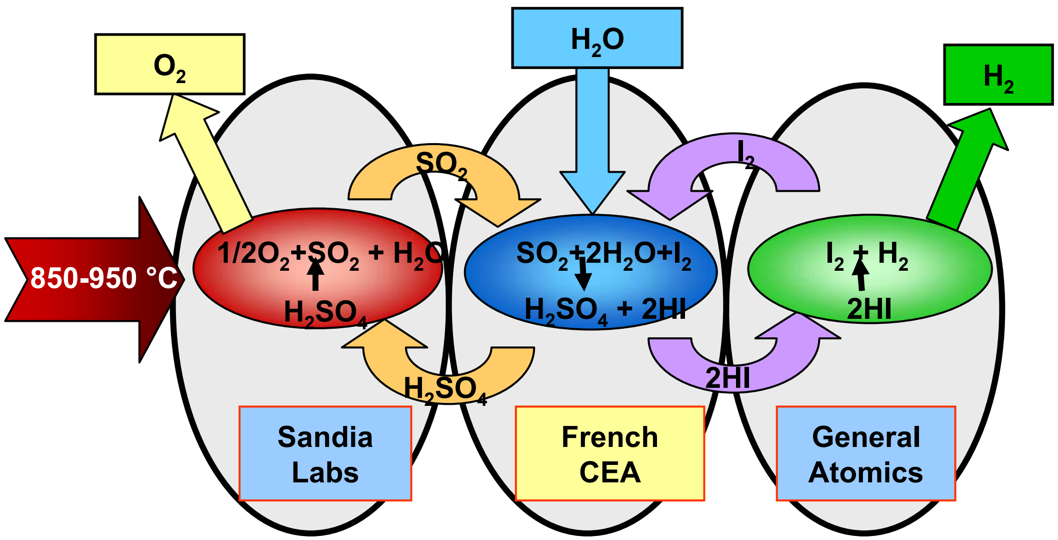
FY06 - Develop and test the 3 major reaction sections for S-I

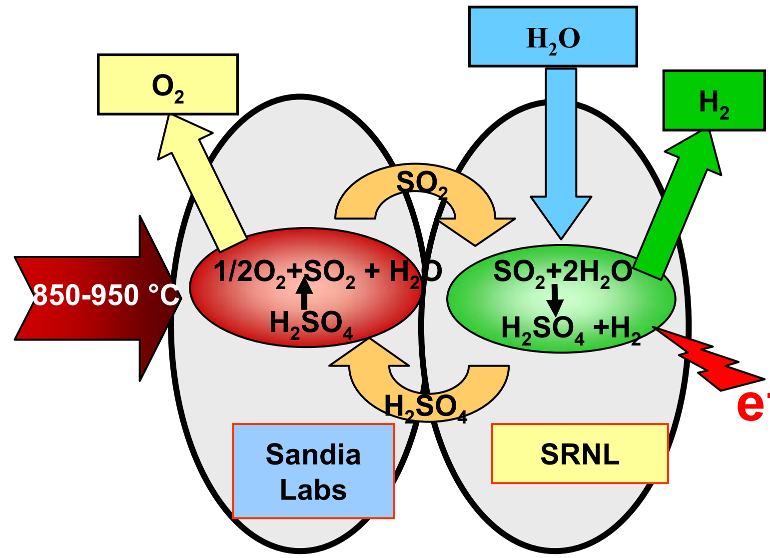
FY07 - Assemble the 3 major reaction sections into an integrated, closed loop demonstration experiment

FY08 - Conduct S-I integrated lab scale experiments program

NHI Sulfur Based Thermochemical Cycles

Sulfur-Iodine *Hybrid Sulfur*





Sulfur Iodine

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$

Hybrid-Sulfur

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$

Sulfur-Iodine Integrated Lab Scale Experiment

ILS Approach

Develop, test 3 reaction sections

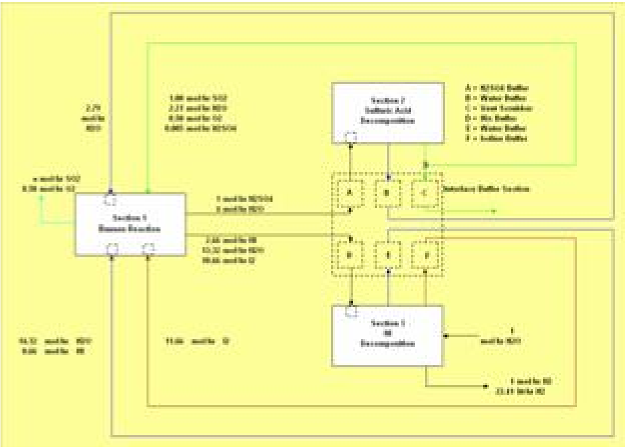
- HI decomposition - extractive distillation (Gen Atomics)
- H_2SO_4 – SiC bayonet decomposer and concentrator (SNL)
- Co-current Bunsen reactor (CEA)

Integrate 3 sections at GA

- Experiment facility at GA completed FY06
- H_2SO_4 section shipped to GA 4/2007
- CEA Bunsen section to be shipped 6/2007
- Connect with interface unit, prelim testing

Conduct ILS Experiments

- Closed loop operation with integrated unit
- Initial tests 100 - 200 l/hr H_2 production rate
- Steady state, startup, shutdown, crosstalk
- Longer duration testing, materials, catalysts



Pilot Scale Decision

- Performance, materials, catalysts controls
- Basis for efficiency and cost estimate
- Scaling

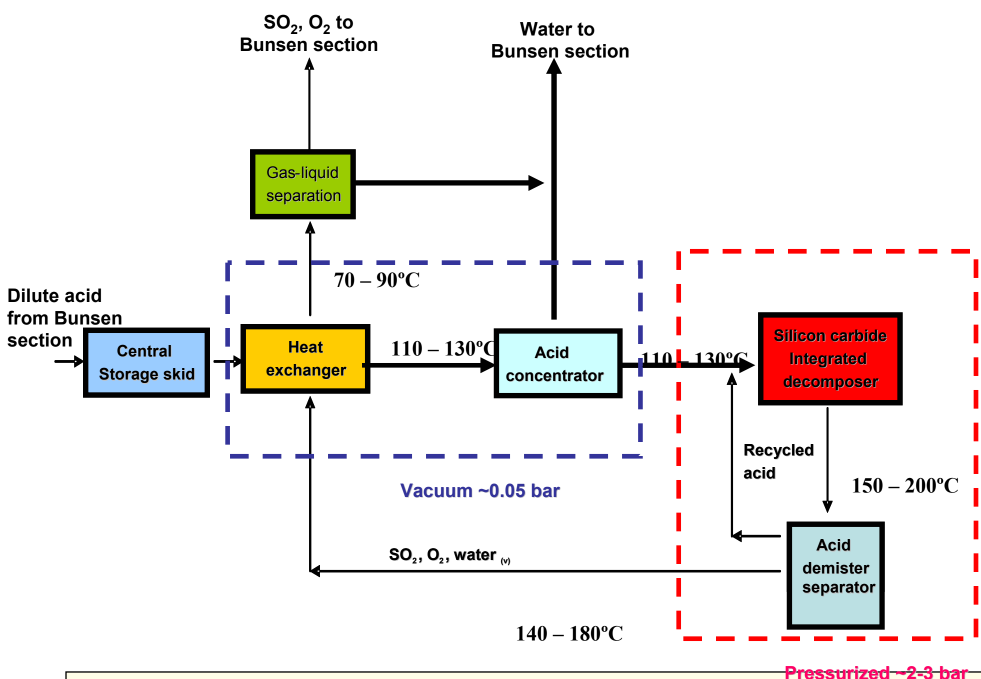
Technical Accomplishments/ Progress
Overview

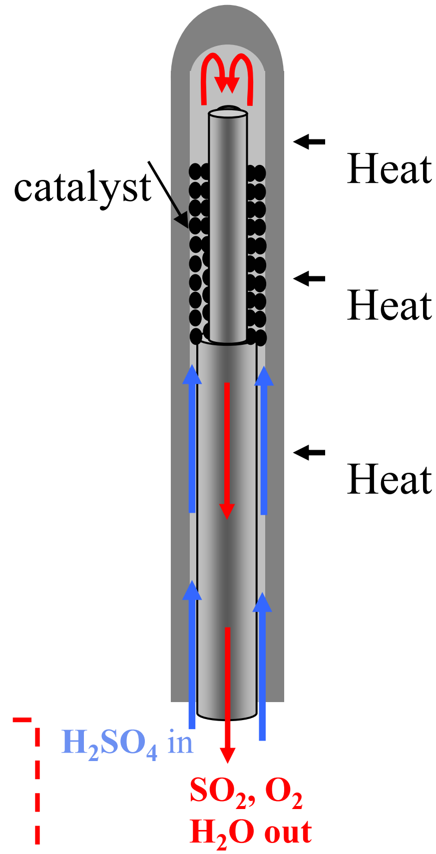
- **H_2SO_4 decomposition experiments**
  - New SiC bayonet acid decomposer unit developed and tested, acid vaporization, decomposition, and recuperation in one integrated ceramic unit
  - Acid decomposition exps completed at 850 C, ambient to 5 bar, 150 - 250 l/hr SO_2 at 40 mole % , SO_2 conversion at ILS flowrates ~90% of theoretical
  - No corrosion issues identified in multiple test series
  - SNL ILS acid decomposer shipped to GA 4/2007
- **HIx decomposition**
  - Efficient HI decomposition (H_2 generation) in absence of I_2 demonstrated
  - Liquid extraction experiments on I_2 -- phosphoric acid feed concentration of 85% needed to break HI-Water azeotrope
  - ILS HI decomposer initial testing underway
- **Bunsen reactor section testing at CEA**
  - Co-current Bunsen reactor, reduced recycle I_2, H_20
  - I_2, SO_2 tests underway, ship date 6/15/2007
- **Catalyst materials** (Pt and metal oxides) and alternate substrates tested
- **Corrosion testing** for candidate HI section metals identified materials of construction for HI section

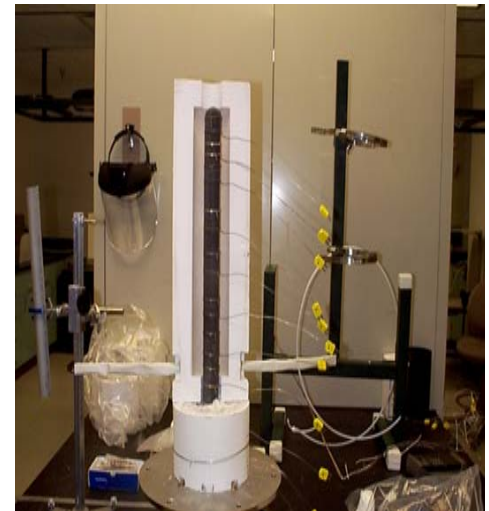
Sulfuric Acid Decomposition Section
SiC Integrated Decomposer Status

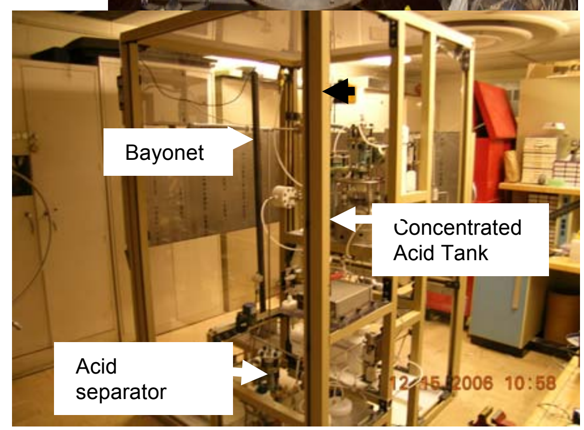
Key Issues

- Materials, corrosion, seals, connections
- Output stream heat recuperation
- Heat transfer to catalyst region
- Catalyst stability









2a. H_2SO_4 (l) → H_2O (g) + SO_3 (g) ~500 C

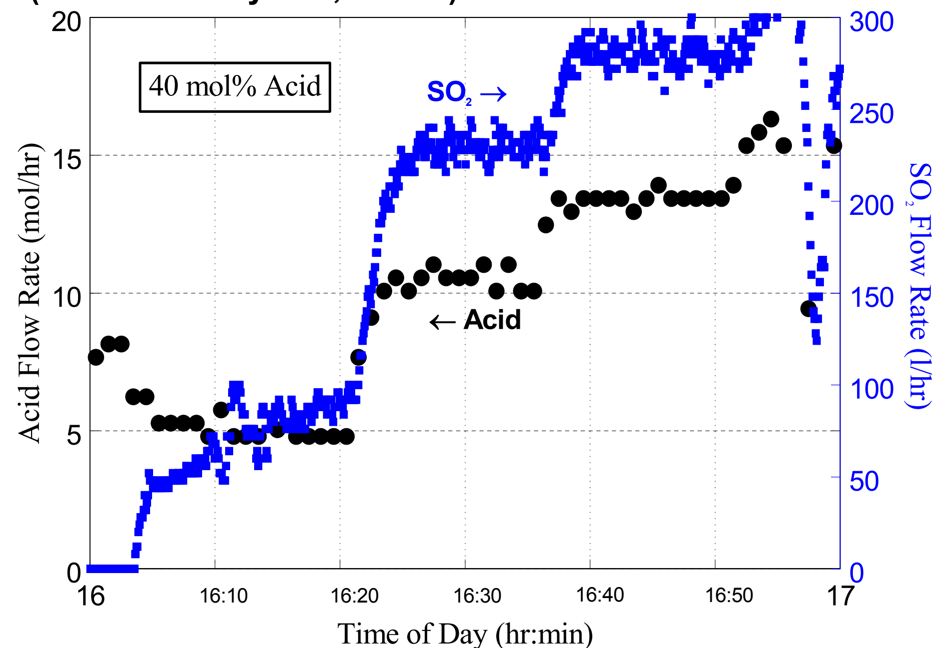
2b. SO_3 (g) → SO_2 (g) + 1/2O_2 (g) ~850 C

Advantages

- *Eliminates most corrosion issues*
- *Simplifies decomposer apparatus*
- *Near complete recuperation*
- *SiC, Glass, Teflon components commercially available*

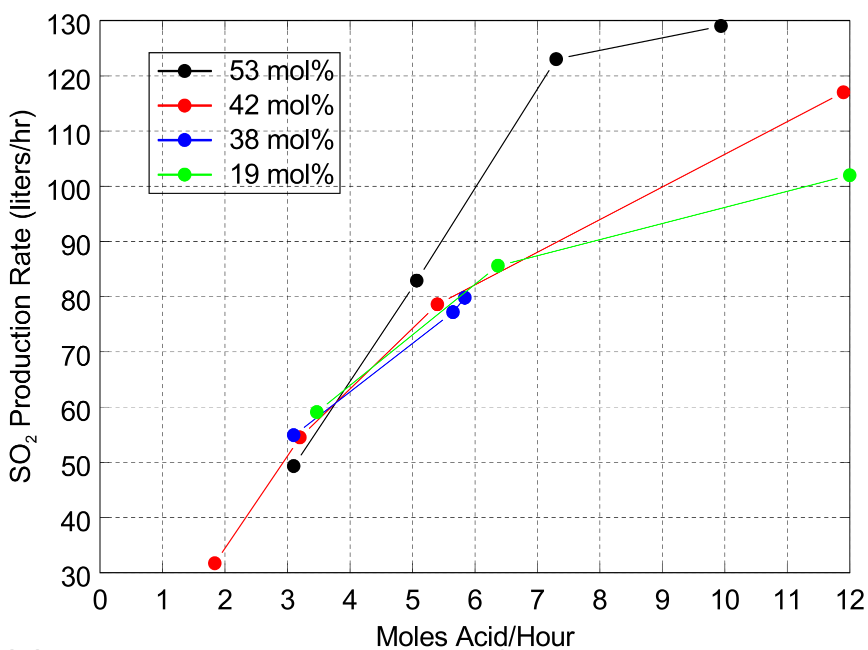
Sulfuric Acid Decomposition Section
Results

SO2 Production versus Concentrated Acid Flow Rate (1.37 meter Bayonet, 850 °C)



ILS (1.37 m) Bayonet Decomposer

- > 200 l/hr SO_2 production rate at 850 C (10 moles/hr, 40 mole% conc)
- Production rate depends on heat transfer to catalyst region
- Increased heat transfer and flow path improvements planned

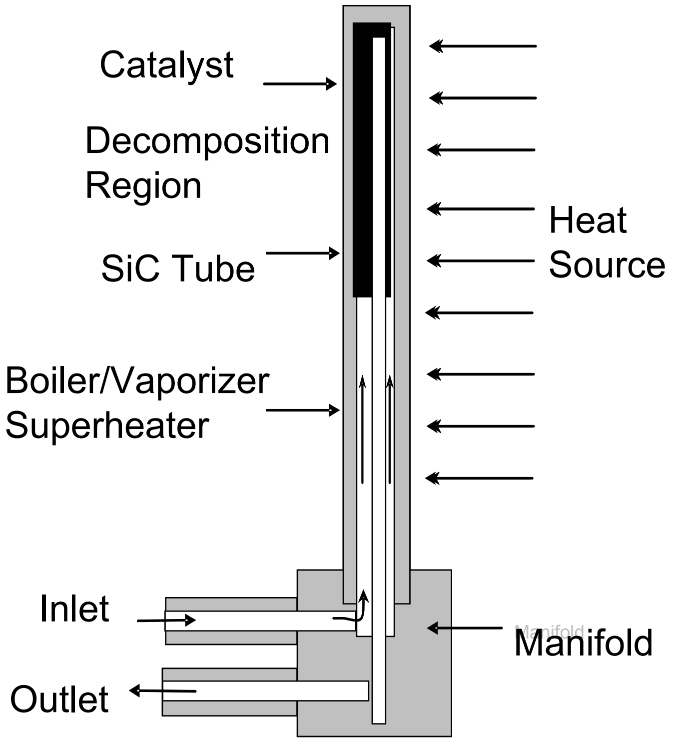


SO_2 Production as Function of Acid Flow Rate and Concentration (0.69 meter Bayonet, 850 °C)

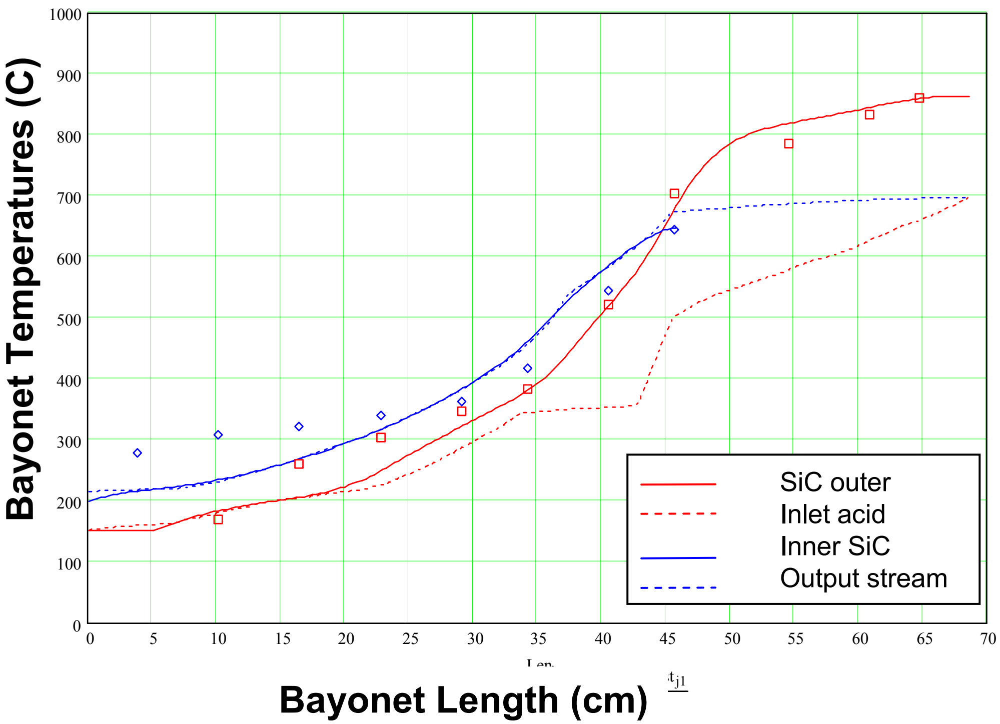
Small (0.69 m) Bayonet Tests

- Flow rate tests at 850 C, 19 to 53 mole%, 1 to 5 bar
- Conversion factors – ~90% of equilibrium at low flow rates.
- High flow rates ~40% due to reduced temperature in catalyst - heat transfer limited conversion
- Catalysts require continued development

Sulfuric Acid Decomposition Section
Heat Transfer



Calculated vs Measured Temperature Distributions (0.69 m SiC bayonet, 42.5 mole% @ 12 mole/hr acid)

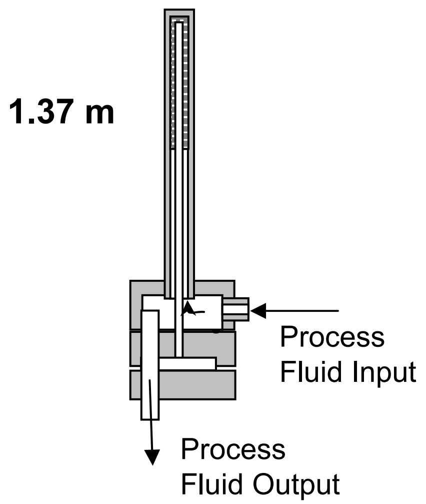


- Recuperation of product stream heat with incoming acid stream
- Product stream output ~ 200 °C, SO_3 recombines at cold end, recycled
- Liquid acid components – commercially available glass, Teflon lined

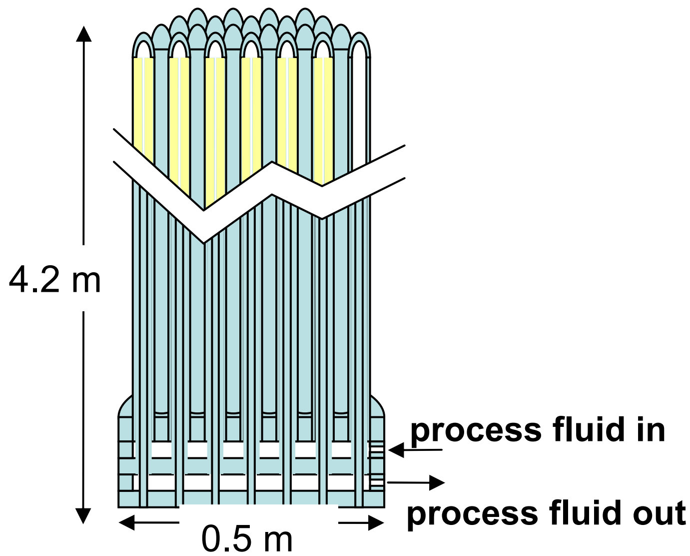
Sulfuric Acid Decomposition Section

Bayonet Decomposer Scale up Approach

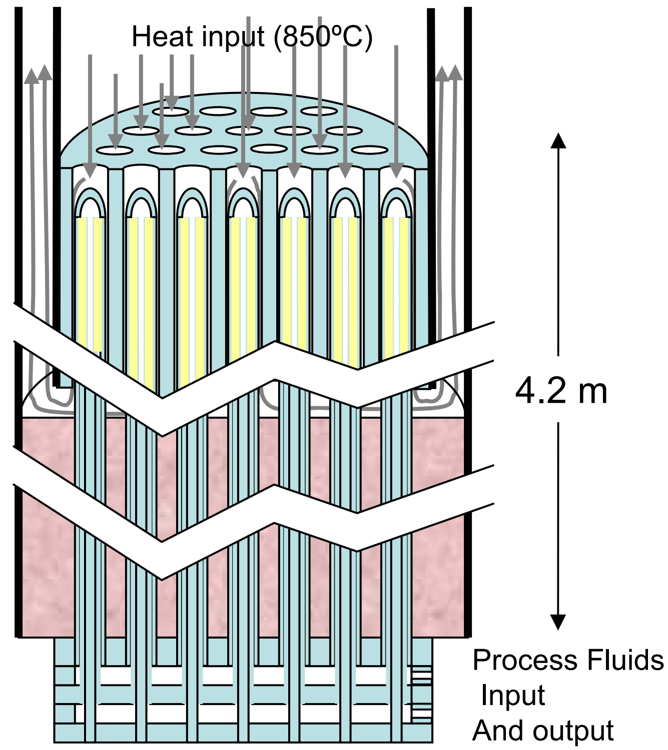
Manifold multiple bayonet units in a tube and shell HX arrangement.



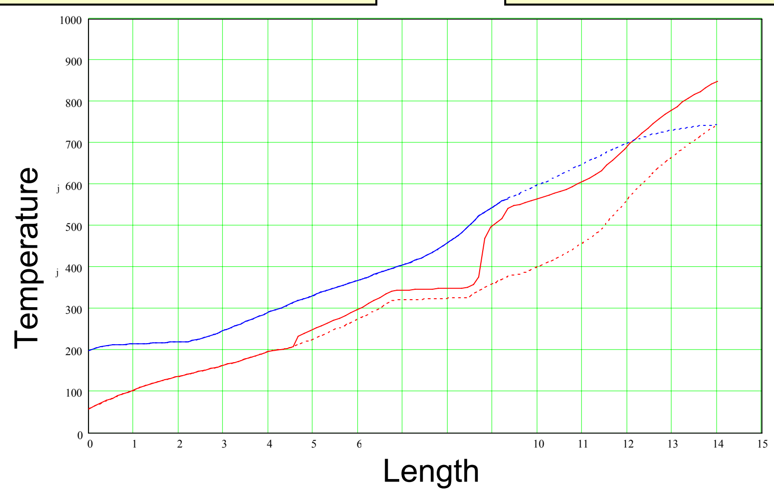
Laboratory Scale (kW)
Single Tube



Pilot Scale (~MW)
Multiple (33) Tube Unit



Large Scale (>100 MW)



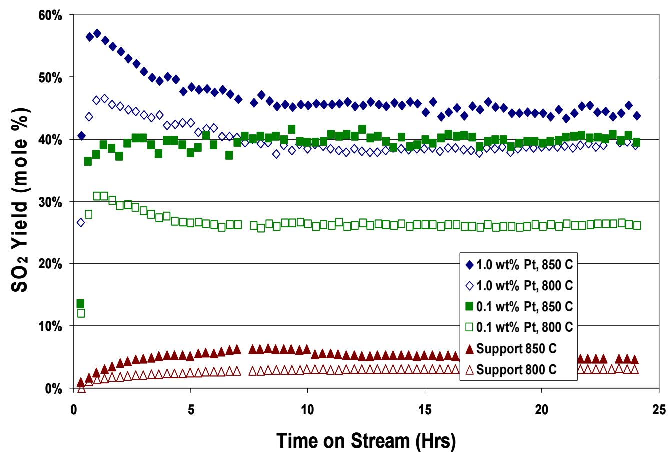
Increased area heat transfer model (fluted tubes), 27 kW/tube, turbulent flow

- *1 MW decomposer ~ 33 tube array, 0.5 m dia*
- *100 MW - 3300 tube array, 5.5 m dia*

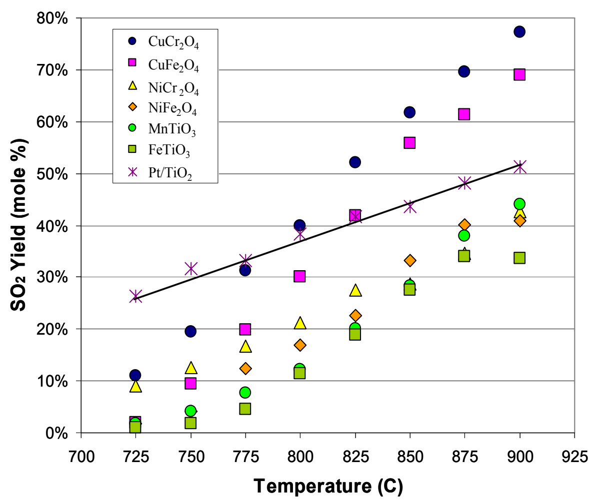
Sulfuric Acid Decomposition Catalysts

INL Catalyst Evaluation

SO_2 yields over Pt/TiO_2 (left) and $Pt/\alpha Al_2O_3$ (right) at 800 and 850 ºC.



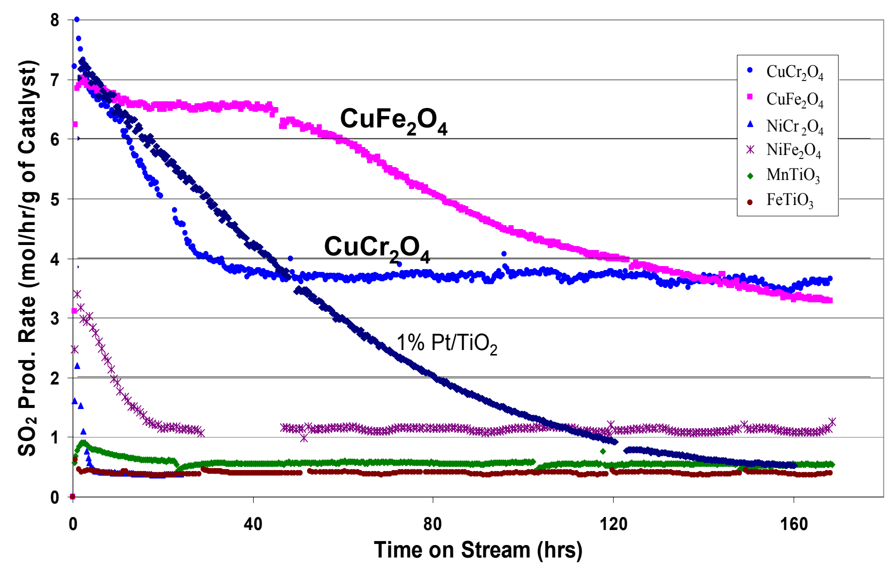
- **Catalyst stability for extended operation remains a key issue**
- **Supports studied: SiO_2, γ-Al_2O_3, ZrO_2, α-Al_2O_3 and TiO_2, Pt/TiO_2 most stable in short term tests**
- **Some complex metal oxides had better activity than Pt above 825°C**
- **Stability of some complex metal oxides appeared promising**
- **Further exploration of complex metal oxides is being pursued**



WHSV = 50 g acid/g cat./hr

SO_2 yields with temperature

- ***$CuCr_2O_4$, $NiCr_2O_4$, $FeTiO_3$ - leaching problems***
- ***Activity of $FeTiO_3$ and $NiFe_2O_4$ decreased at the highest temperature***
- ***Cu Fe_2O_4 spinel promising at high temperatures***



WHSV = 2,000 g acid/g cat./hr, 850°C

SO_2 production rate, 850°C

Section 3- HI Decomposition
Overview

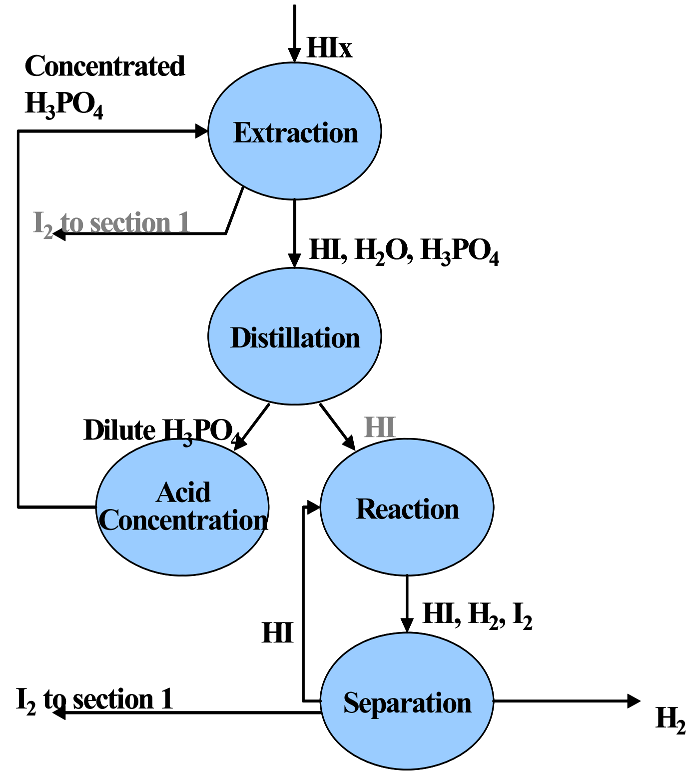
Extractive distillation method selected for HI decomposition

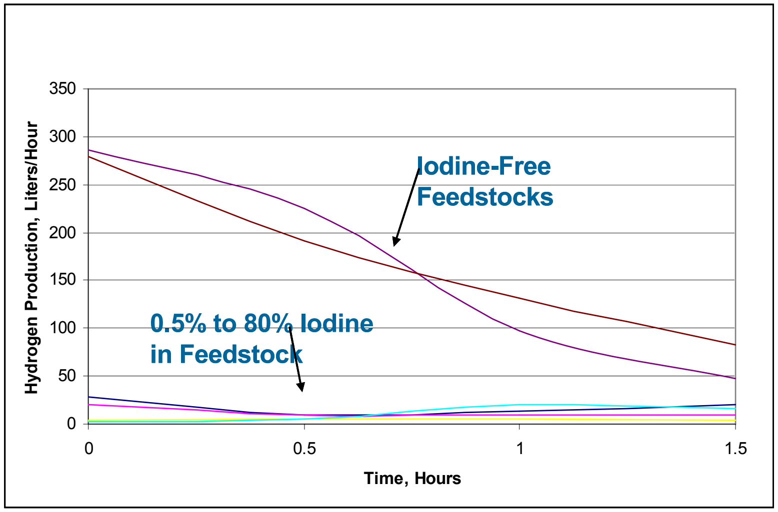
- Separates I_2 and H_2O from HI,
- Decomposes HI into H_2 and I_2,
- Return I_2 and H_2O to Section 1

Key Issues

- Uncertainty in $HI/I_2/H_2O$ VLE
- High recycle water volumes
- H_3PO_4 concentrations to extract HIx
- Materials – corrosion, catalysts

Extractive Distillation Process





Reactive Distillation Results

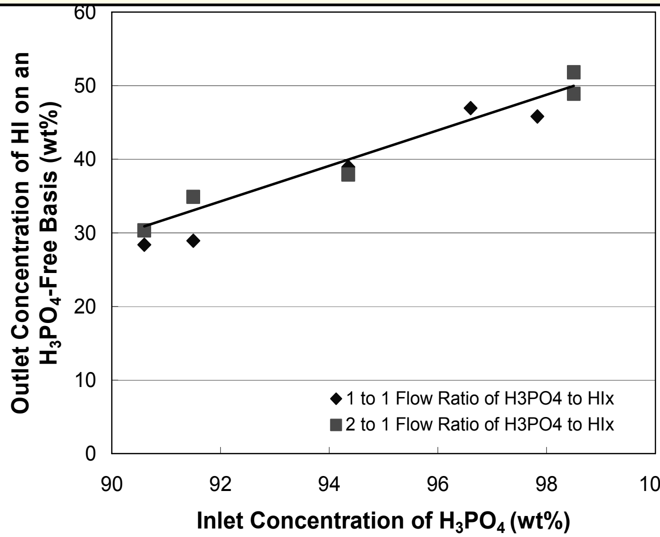
Recent Experiments

- Determine operating regime for H_3PO_4
- Determine effect of H_3PO_4 concentration and flow ratio on $HI-H_2O$ extraction efficiency
- Corrosion testing for HI, I_2, H_2O environment

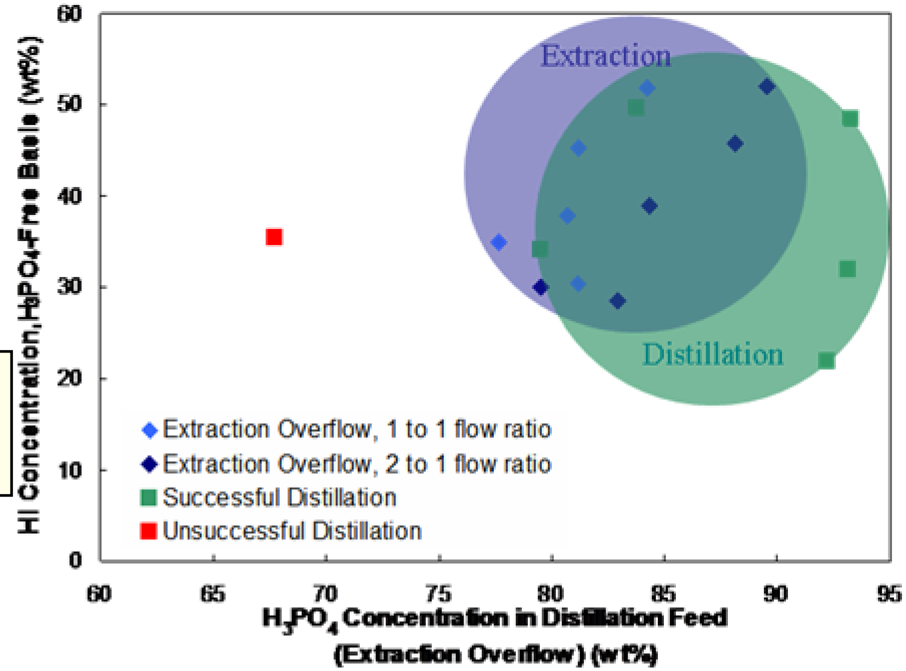
Section 3- HI Decomposition

HI Decomposition Parameter Experiments

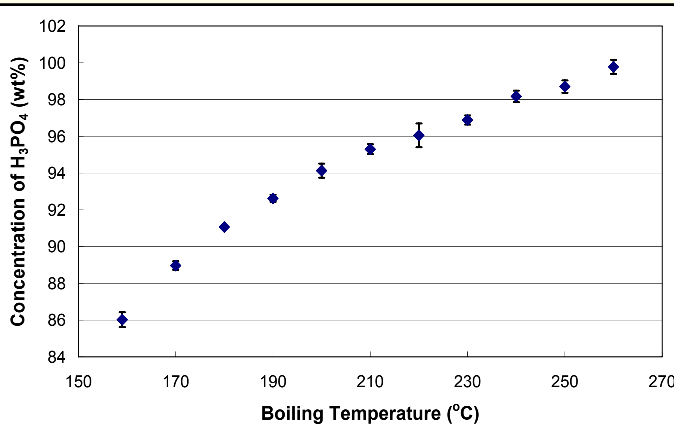
- Effect of H_3PO_4 concentration and flow ratio on the HI-H_2O extraction efficiency



- H_3PO_4 operating space for the extraction and distillation sections over lap



Boiling point curve of concentrated H_3PO_4 concentrations up to 99 wt %



Section 3- HI Decomposition Section

ILS Skid Conditions and Assembly Status

Conditions for high HI recovery and successful HI distillation

- *H_3PO_4 extraction feed composition*
  - 96-98 wt%
- *H_3PO_4 concentrator temperature*
  - 220-240 C
- *H_3PO_4:HIx flow rate ratio*
  - 2:1 to 4:1

- HI Section assembly completed
- Ta/10%W vessels and process lines
- Ta coated fittings and valves
  - Delay in delivery of coated fittings and valves has delayed chemical shakedown
- Water testing underway

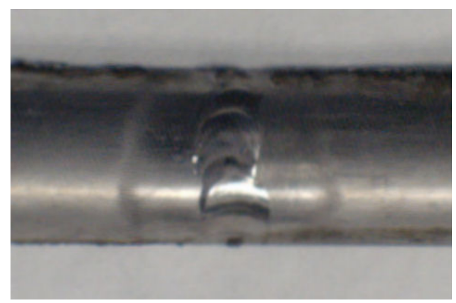
HI Decomposition Section

Materials Testing for the HI Section

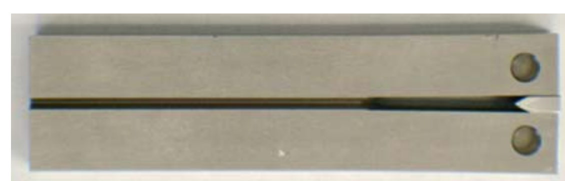
Previous testing has qualified Ta alloys (HI_x; $HI_x + H_3PO_4$; conc. H_3PO_4) and Hastelloys ($HI + I_2 + H_2$) for Section III use

- **Testing of processed Ta alloy parts in Iodine Separation ($HI_x + H_3PO_4$) and conc. H_3PO_4 environments has been completed**
- **Testing of Ta-10W stress corrosion and tensile samples under the same settings is on going**
- **Testing of parts and components with Ta cladding in an Iodine Separation flow system is continuing**
- **Chemical contaminations in conc. H_3PO_4 lead to corrosion in some candidates**
- **Stress corrosion testing of C-22 and C-276 in HI Decomposition ($HI + I_2 + H_2$) showed no crack initiation; crack growth testing is on going**

Ta coated fitting and Ta-10W tubing w/ weld tested in HI_x+ H_3PO_4



Ta-10W tubing tested in conc. H_3PO_4 w/HI & I_2



C-276 DCB crack growth specimen for HI Decomp. Environment

HI Decomposition Section
Process Improvements

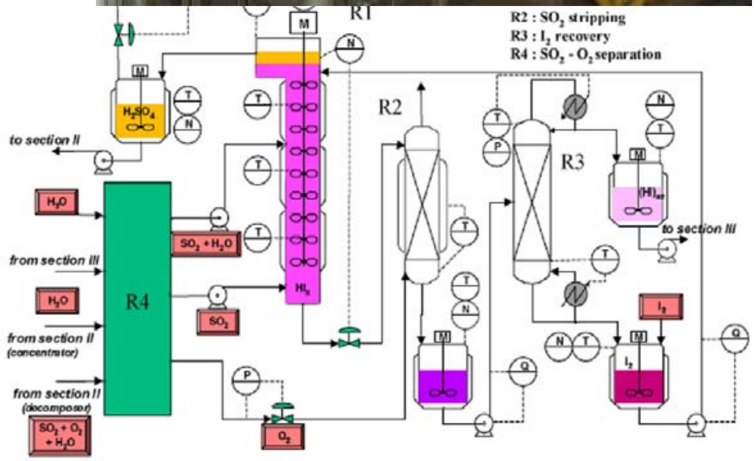
Several potential process modifications are being investigated to improve efficiency or simplify process

- **Gas phase membrane reactor development -** improve conversion of HI, increases efficiency 2-5%
- **Enhanced Bunsen reaction development - i**ncrease HI concentration in lower phase, increases efficiency 3-6%
- **Liquid phase decomposition -** decompose HI in the liquid phase – potential for greater conversion, easier separation of H_2 product, possible 2-5% improved efficiency
- **Water recycle reduction membrane development -** Reduction of 10-20% water could improve efficiency, reduce some hardware requirements. 20% reduction would simplify Section 3, potentially eliminate need for H_3PO_4

Bunsen Section Status (CEA)

9I2 + SO2 + 16H2O → (2HI + 10H2O + 8HI) + (H2SO4 + 4H2O)

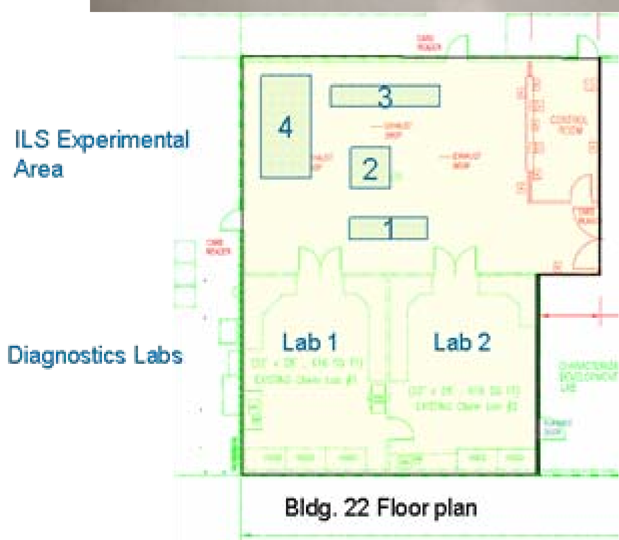
- Primary reaction of SO_2, H_2O and I_2 to form HI and H_2SO_4
- Delivers HIx (HI, H_2O, I_2) to section 3 (lower phase)
- Delivers H_2SO_4 to section 2 (upper phase)
- Equipment assembly is complete in Marcoule
- Testing with water and air is complete
- Testing with acids is underway
- Equipment is scheduled to arrive at General Atomics before July 2007



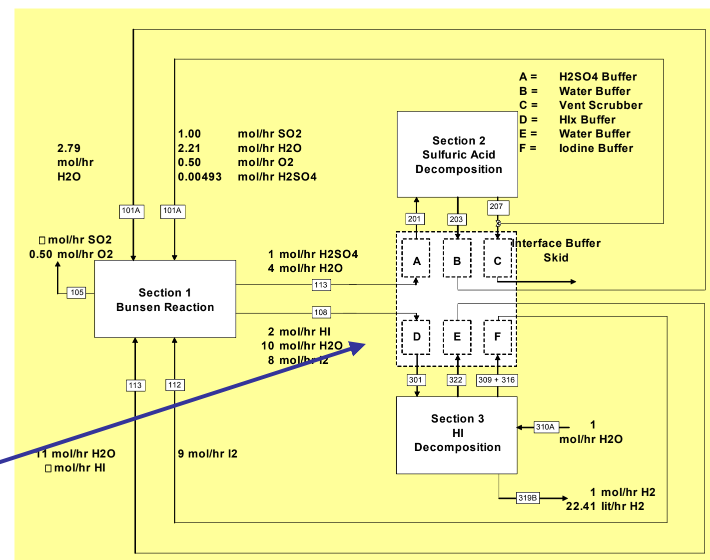
Sulfur-Iodine ILS Experiment

Facility and Schedule

Date		ILS Activity
• *4/2007*	*……….*	*Ship H2SO4 section to GA*
• 6/2007	……….	System diagnostics and controls
• *6/2007*	*……….*	*CEA Bunsen Section to GA*
• 9/2007	………..	Complete shakedown testing
• *9/2007*	*……….*	*Begin integrated experiments*
• 3/2008	………..	Complete first series of S-I exps
• *9/2008*	*……….*	*Complete final series*
• 9/2008	…………	Documentation of ILS exps
• *9/2008*	*…………*	*Pilot scale flowsheet and design*



- 1560 sq ft high bay
- 2 chem labs
- Separate control room
- Dedicated ventilation system
- Chemical detection system
- Interface skid under construction



Sulfur Cycle Supporting Technology Activities

- **Materials** – high temperature corrosion and mechanical properties – metals, ceramics (UNLV, GA, MIT, ORNL)
- **High temperature interface** – innovative heat exchanger designs, analysis (UNLV, UCB, Ceramatec)
- **Membranes** – high temperature inorganic membranes for acid decomposition (ORNL, INL, SNL)
- **SO_3 electrolysis** (ANL)

Sulfur Iodine Thermochemical Cycle

Planned Activities (FY07 - FY08)

- **FY07 – Complete individual section testing, and transport CEA and SNL Sections to GA.**
  - Integrate sections with interface skid, control systems
  - Complete integrated shakedown testing
  - Initiate closed loop testing
- **FY08 – Perform S-I Hydrogen test program in integrated lab-scale apparatus**
  - Operational characteristics and performance
  - Control strategies – startup, shutdown
  - Longer term experiments, materials, catalysts
  - Process improvements, equipment modifications

Sulfur-Iodine ILS Experiment
Project Summary

Relevance: *This project is providing the technical information needed to assess the potential of the Sulfur Iodine thermochemical cycle for large scale production of hydrogen using Generation IV reactors. Results from this project will support the DOE FY2011 technology decision for the NGNP hydrogen production technology.*

Approach: *Perform flowsheet analysis of process options, perform lab experiments to identify suitable materials and process configurations. Based on these results, design and construct the major reaction sections of the S-I cycle. Assemble the 3 sections in an integrated lab scale experiment to demonstrate operational characteristics and performance* of the S-I cycle.

Technical Accomplishments: *SNL has completed construction and testing of a SiC bayonet sulfuric acid decomposer section and shipped this unit to the GA integration site. GA has completed construction and initiated testing on the HI extractive distillation and decomposition section. INL, ORNL and SNL have conducted supporting catalyst, materials corrosion, and membrane studies to support the cycle development.*

Tech Transfer/Collaboration: *The S-I cycle research is conducted as an INERI project with the French CEA. There is also extensive collaboration with Universities (materials HX analysis), and industry (materials and process development). The DOE sponsored work will be a major component in the Generation IV International Forum (GIF) nuclear hydrogen collaboration to be signed in FY2007.*

Future Research: *The focus in FY07 and FY08 will be the conduct of the ILS experiment. Research on improved catalysts and longer term testing of material of construction will also be conducted.*