2008 DOE Hydrogen Program Review

Sulfur-Iodine Thermochemical Cycle

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Project PD25

Sulfur-Iodine Thermochemical Cycle Project

Overview

Timeline

- Start - 4/2006
- Finish - 4/2009
- ~ 80% complete

Barriers

- Materials – high temperature, corrosive environments
- Process chemistry, catalysts, diagnostics
- Reactor-process coupling

Budget

- Funding
  - FY06- 5.5 M$
  - FY07 - 4.3 M$
  - FY08 - 2.9 M$
  - French CEA – in kind

Partners

- INERI Project with CEA
- Process – CEA, SNL, General Atomics
- Supporting Technologies – INL, UNLV

Sulfur-Iodine Thermochemical Cycle
Objectives

- **Evaluate the potential of the Sulfur-Iodine cycle for hydrogen production using nuclear energy**
  - DOE/NHI - CEA INERI Project (CEA, SNL, General Atomics)
  - Sulfur cycles – potential for high efficiency, relative development level
  - Approach - construct, operate an Integrated Lab Scale (ILS) experiment to investigate the key technical issues
  - Provide basis for nuclear hydrogen technology decisions

Phase 1 (Cycle Evaluation)

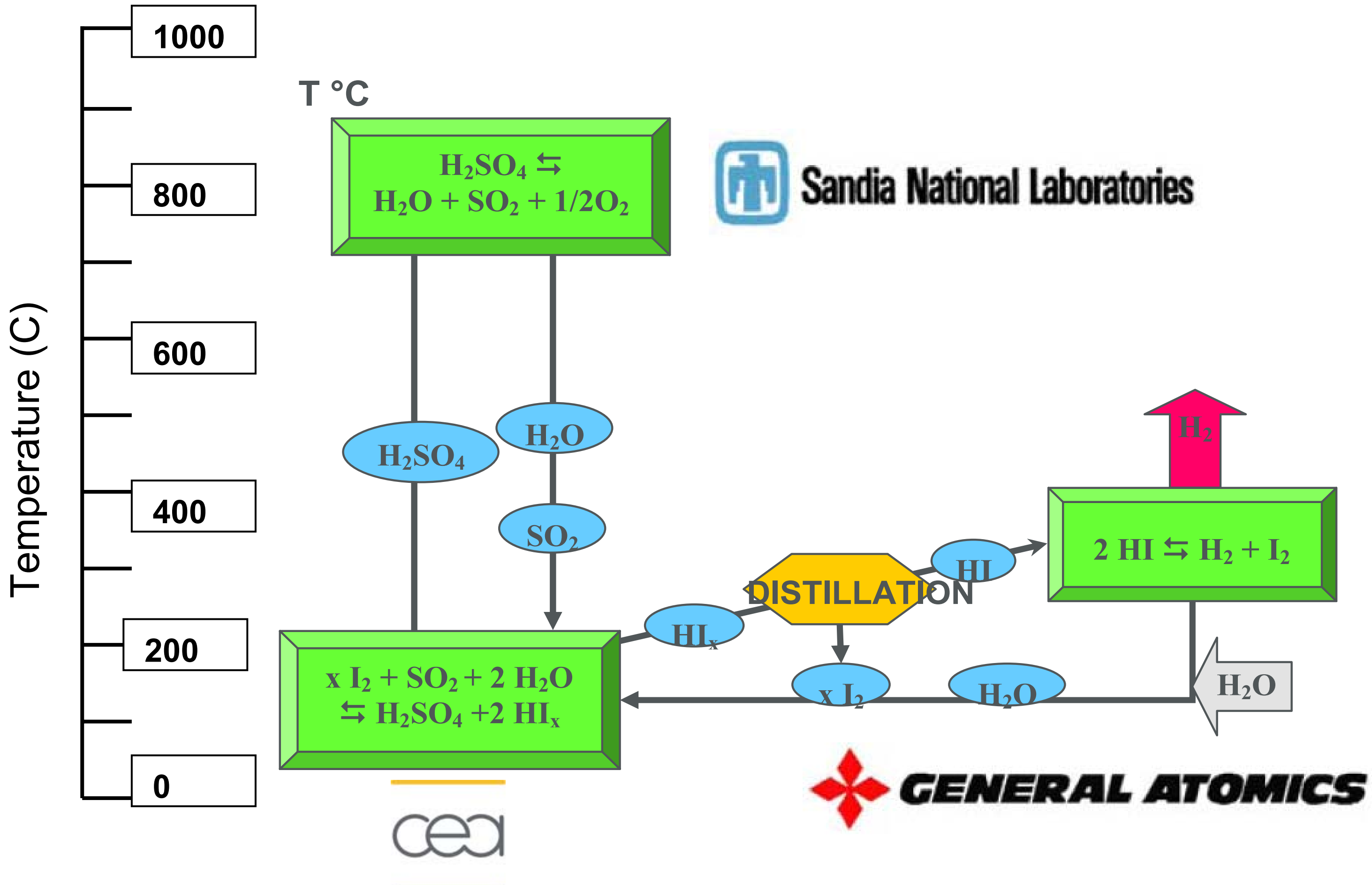
FY03 – 05 - Process chemistry options, flowsheets, materials, small scale experiments

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

FY06 - Develop the 3 major reaction sections for S-I at 3 locations
FY07 - Integrate 3 sections at General Atomics experiment site
FY08 - Conduct integrated lab scale, closed loop experiments

NHI Sulfur Based Thermochemical Cycles

Sulfur-Iodine



Sulfur Iodine

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

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

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

Sulfur-Iodine Integrated Lab Scale Experiment

ILS Approach

Develop, test 3 reaction sections → *Integrate 3 sections at GA* → *Conduct ILS Experiments* → *ILS Exp Improvements*

FY2006

- **HI decomposition - extractive distillation (Gen Atomics)**
- **H_2SO_4 – SiC bayonet decomposer (SNL)**
- **Counter-current Bunsen reactor (CEA)**

FY2007

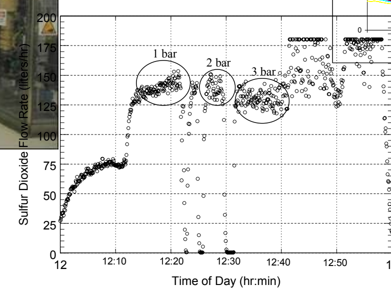
- **H_2SO_4 section operational FY07**
- **CEA Bunsen section installed 6/2007**
- **3 sections connected with interface unit, prelim testing**

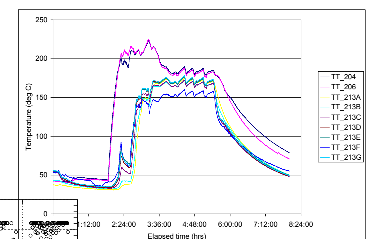
FY2008

- **Stand alone section tests completed**
- **Initial integration (Section 1 & 2) and first full sequence H_2 test conducted**
- **FY08 integrated exps**

FY2009

- **Performance improvement mods**
- **Longer term exps**
- **Provide basis for performance, and cost projections**
- **Pilot scale design**

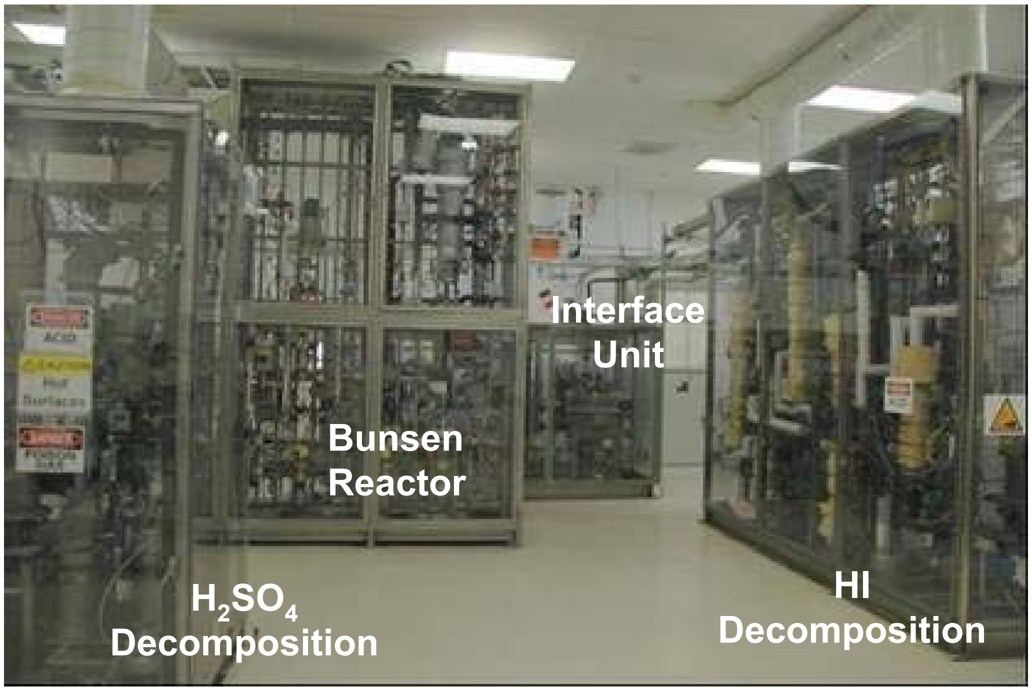


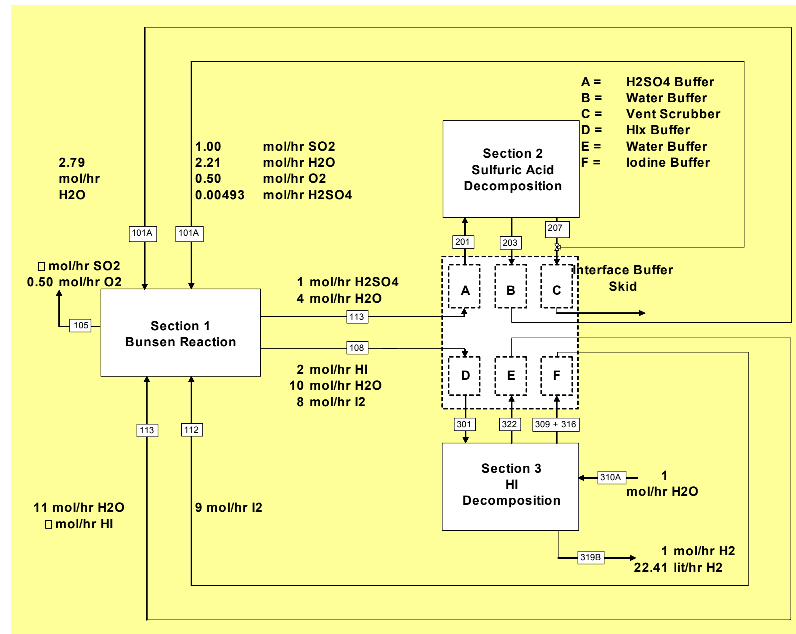


Sulfur-Iodine ILS Experiment

Status

S-I Integrated Lab Scale Experiment at GA Site





- *Interface skid - allows independent operation of each section, facilitates startup, shutdown*
- *Lexan enclosures, separate ventilation system for each section*
- *Initial integrated operations underway - March 2008*

Technical Accomplishments/ Progress
Overview

- ***HI decomposition (GA)***
  - First hydrogen production experiment using CEA Bunsen section feed material ~50 liters/hr - April 2008
  - Iodine extraction, HI distillation, decomposition, recycle demonstrated
  - Diagnostics, control, flow systems developed and tested, reliable

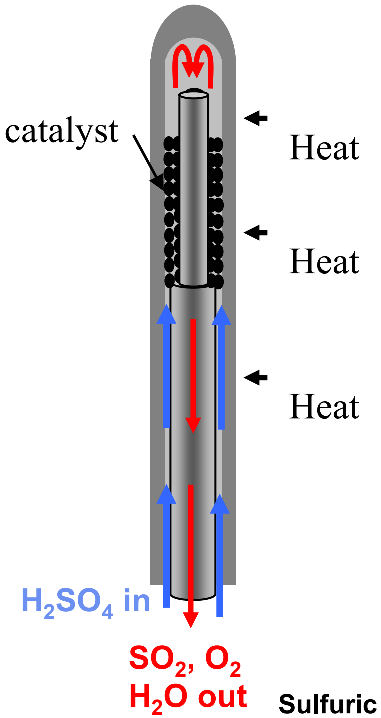
- ***Bunsen reactor section testing (CEA)***
  - First Bunsen reaction test completed - produced and separated HIx (heavy) phase and H_2SO_4 (light) phase acids
  - Subsequently processed by HI section to produce H_2
  - SO_2/O_2 separation section operated reliably in multiple operations

- ***H_2SO_4 decomposition experiments (SNL)***
  - Acid vaporization, decomposition, and recuperation in one integrated SiC bayonet unit, no corrosion issues identified in multiple test series
  - Experiments completed at 850 C, ambient to 5 bar, ~300 l/hr SO_2 at 40 mole %, SO_2 conversion at ILS flow rates ~90% of theoretical
  - Operated in integrated mode with CEA Bunsen section March, 2008

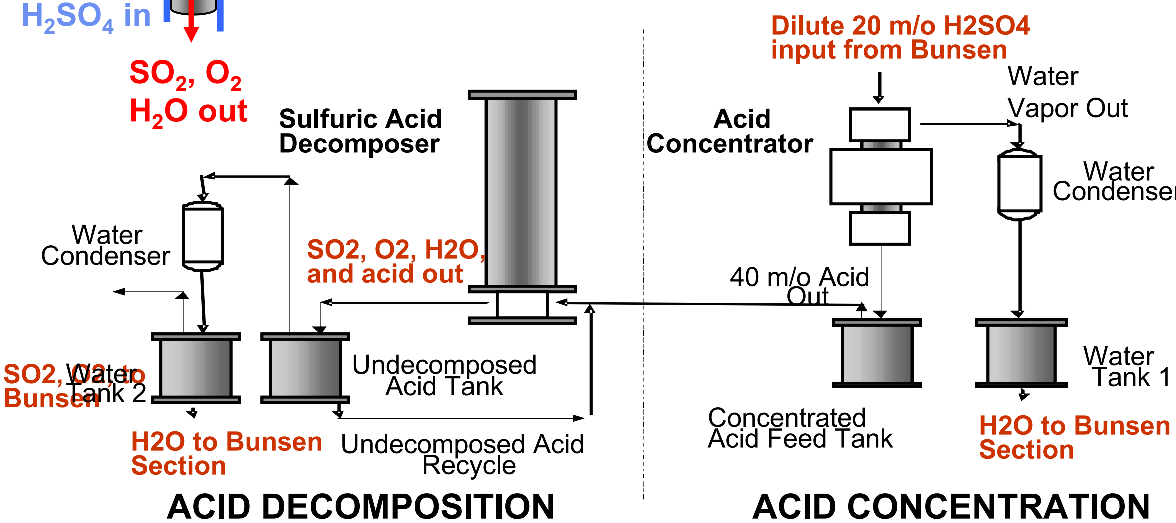
- ***Next steps – diagnostics and equipment modifications, and complete FY08 testing program***

Sulfuric Acid Decomposition Section

SiC Integrated Decomposer



- *Minimizes high T corrosion and connections*
- *Heat recuperation*
- *Commercially available materials for low T systems*
- *Scales as tube and shell HX*



H_2SO_4 decomposer unit installed at GA ILS experiment site

$$H_2SO_4\,(l) \rightarrow H_2O\,(g) + SO_3\,(g) \qquad \sim 500\ C$$

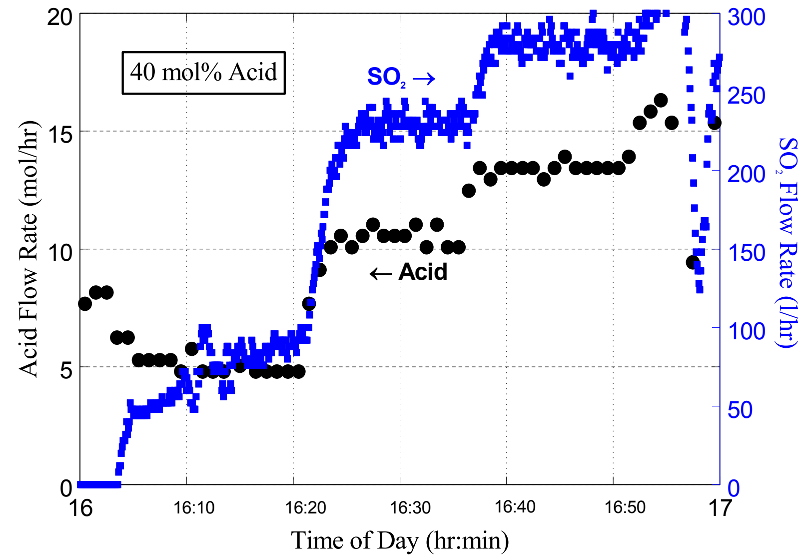
$$SO_3\,(g) \rightarrow SO_2\,(g) + 1/2O_2\,(g) \qquad \sim 800\ C$$

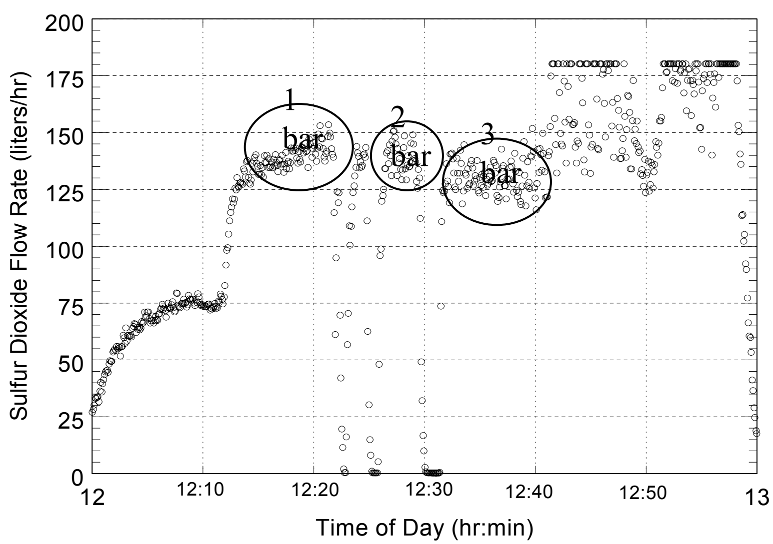
Sulfuric Acid Decomposition Section
Results

SiC Bayonet Decomposer (ILS)

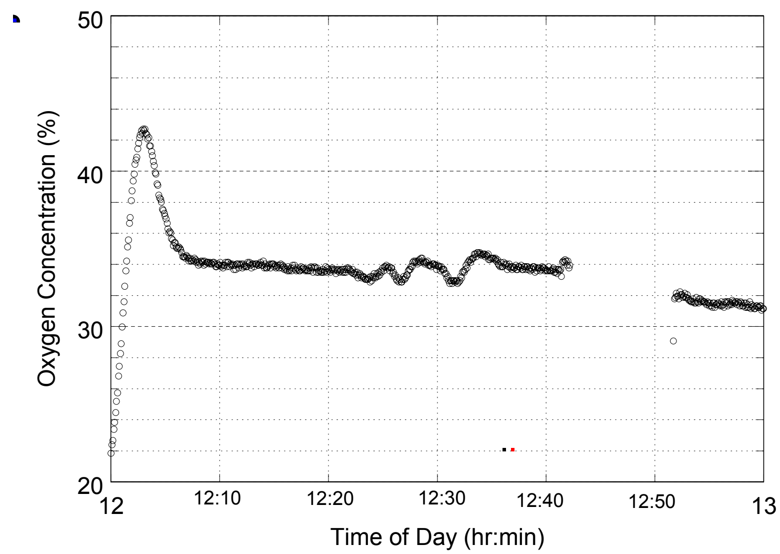
- ~ 300 l/hr SO_2 production rate @ 850 C (10 moles/hr, 40 mole% concentration)
- Conversion rates ~90% of theoretical
- SO_2 production rate limited by heat transfer to catalyst region
- Pressure, flow rate dependence evaluated
- Acid decomposer operation reproducible through ~20 cycles
- Catalyst durability requires further development

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





Pressure dependence of SO_2 production rate. (1, 2, and 3 bar pressure, 7.1 m/hr)

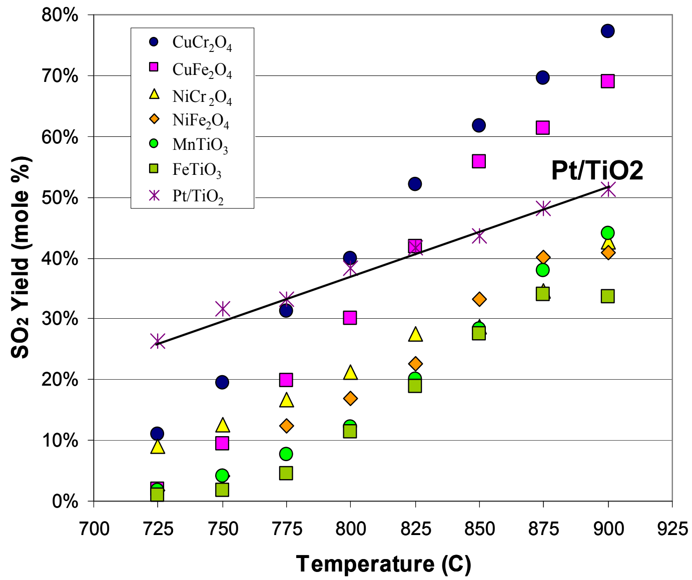


Oxygen concentration in product gas stream - 67% SO_2 and 33% O_2

Sulfuric Acid Decomposition Catalysts

INL H_2SO_4 Catalyst Studies

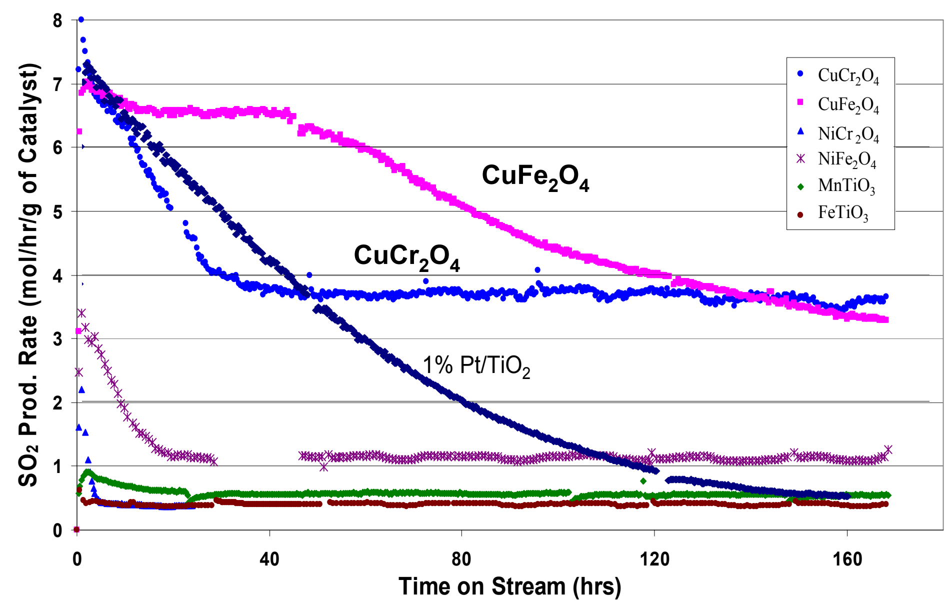
- Catalyst stability for extended operation remains a key issue
- Supports studied: SiO_2, γ-Al_2O_3, ZrO_2, α-Al_2O_3 and TiO_2. Pt/TiO_2 most stable in short term tests
- Some complex metal oxides show high activity above 825°C
- Stability of some complex metal oxides appeared promising
- Further investigation of complex metal oxides anticipated in FY09



WHSV = 50 g acid/g cat./hr

SO_2 yields with temperature

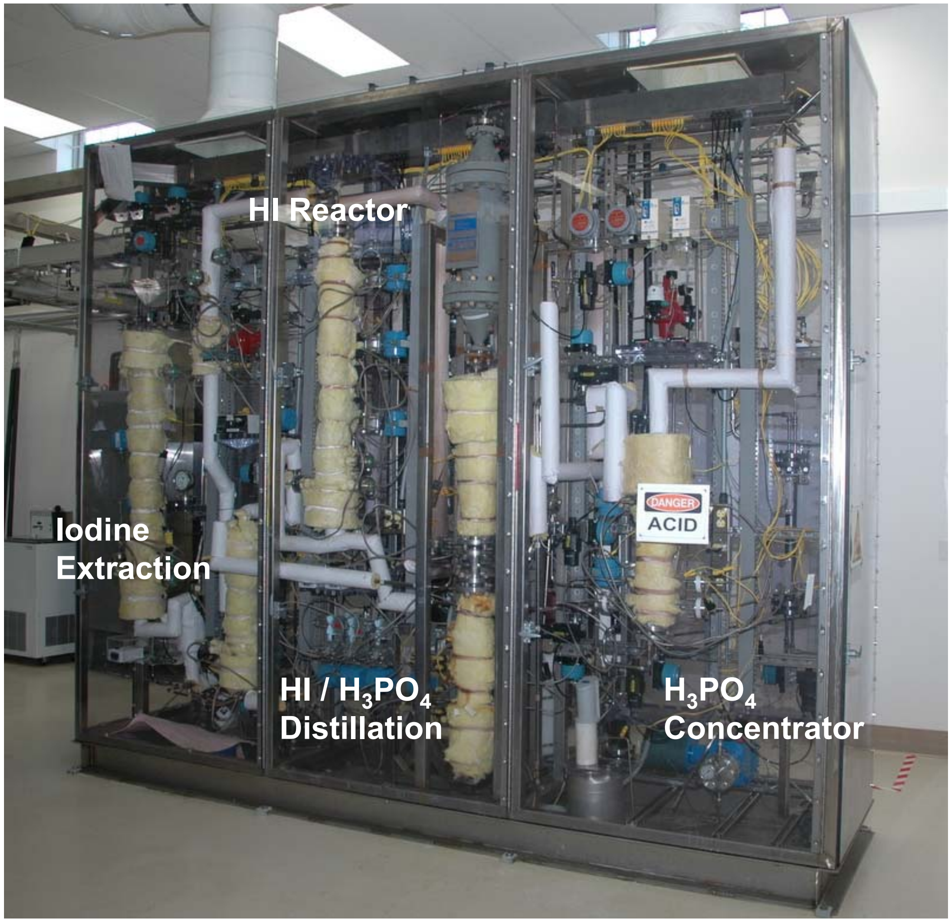
- ***$CuCr_2O_4$, $NiCr_2O_4$, $FeTiO_3$ - leaching problems***
- ***Activity of $FeTiO_3$ and $NiFe_2O_4$ decreased at the highest temperature***
- ***Cu Fe_2O_4 spinel promising at high temperatures***



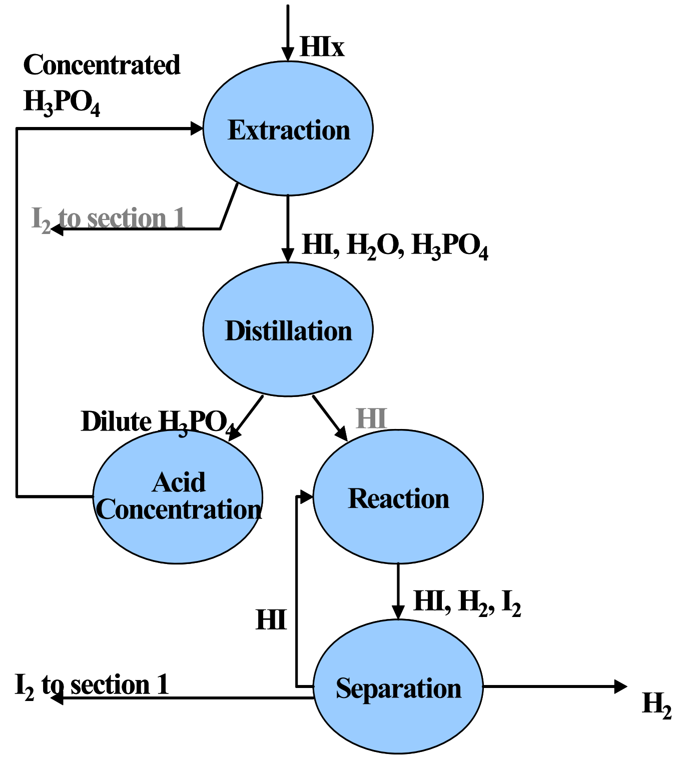
WHSV = 2,000 g acid/g cat./hr, 850°C

SO_2 production rate, 850°C

Section 3- HI Decomposition
Overview



HI Decomposition section (section 3) installed at GA ILS site



Extractive distillation method

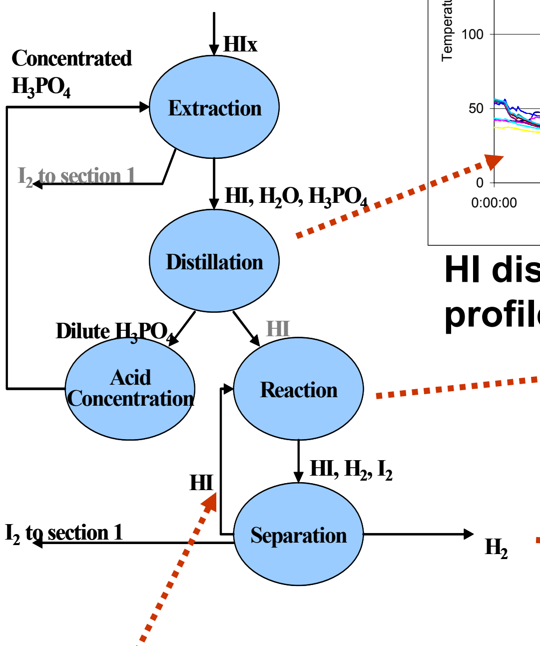
- H_3PO_4 – separates HI/H_2O from I_2
- HI distilled from H_3PO_4,
- HI decomposed at ~ 400 C to H_2 and I_2
- Undecomposed HI recycled to HI reactor
- I_2 returned to Bunsen reactor section

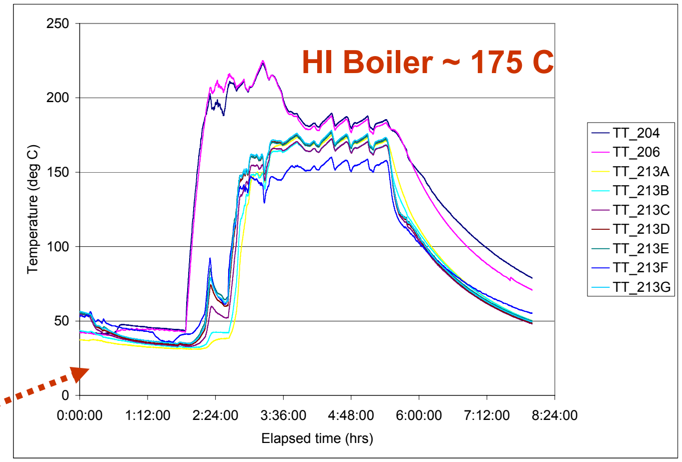
Key Issues

- Uncertainty in HI/I_2/H_2O VLE
- Materials – corrosion, catalysts

Section 3- HI Decomposition Section

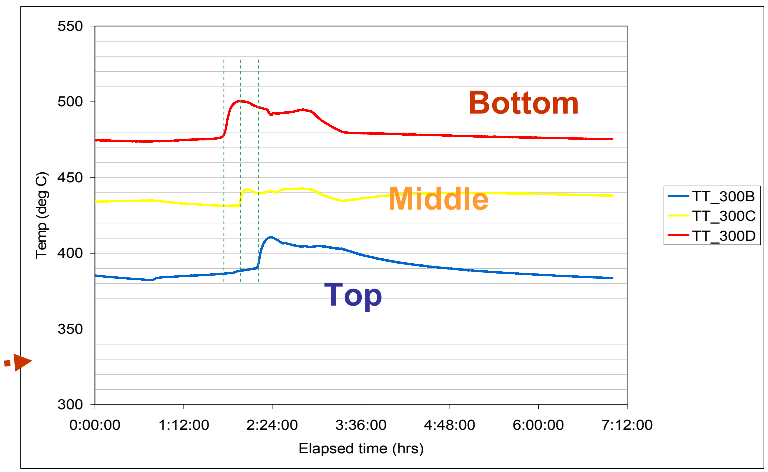
First HI section H2 run with Bunsen section feed





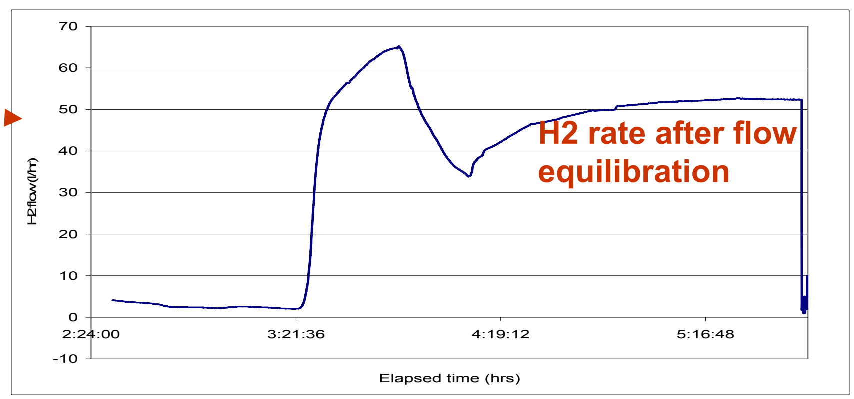
HI distillation column temperature profile at 5 bar, integrated run

HI adsorption/reaction temperature front moving through HI reactor



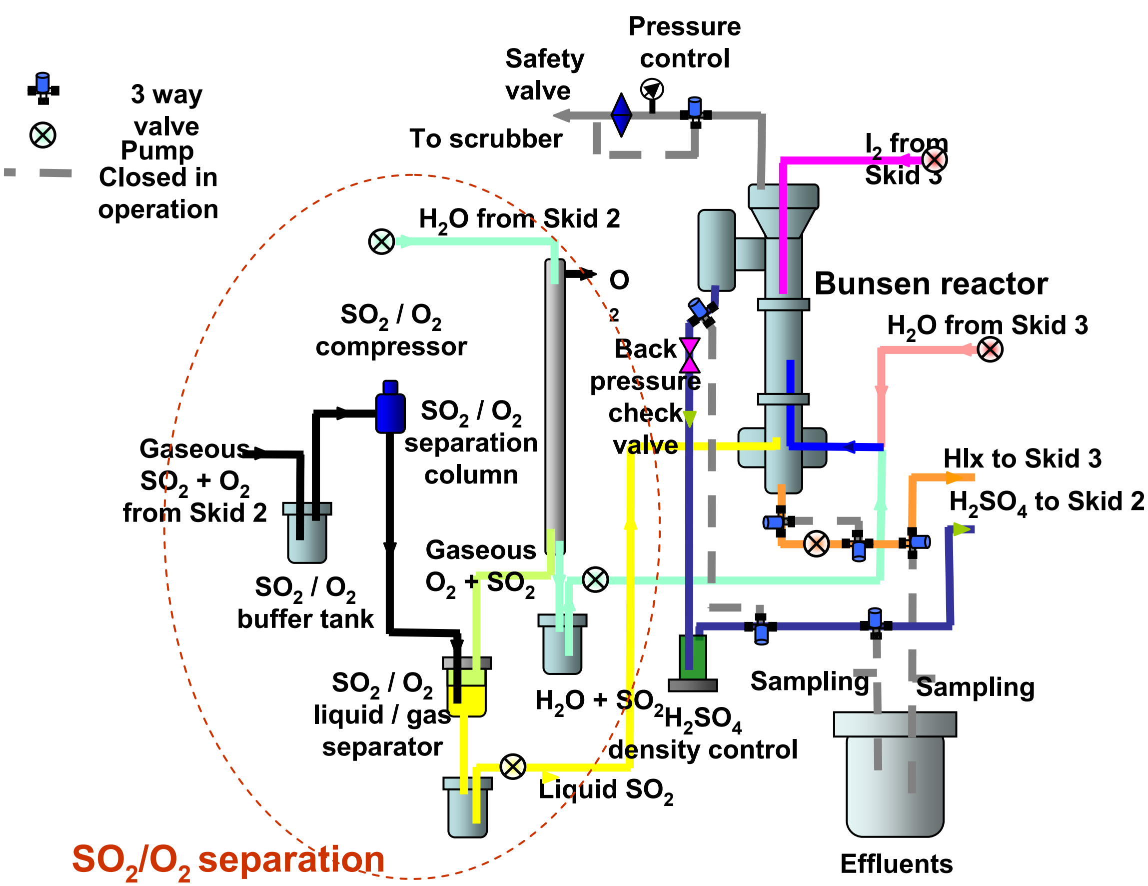
HI feed in HIx	17 mol/hr
HI distilled to reactor	8.5 mol/hr
Predicted H_2 produced with no recycle	0.85 mol/hr (19 l/hr)
H_2 actually produced	2.7 mol/hr (60 l/hr)

HI Recycle Effect (5 bar)



H2 integrated production run ~50 l/hr with partial recycle

Bunsen Section Status (CEA)



CEA Counter-current Bunsen Reactor Section

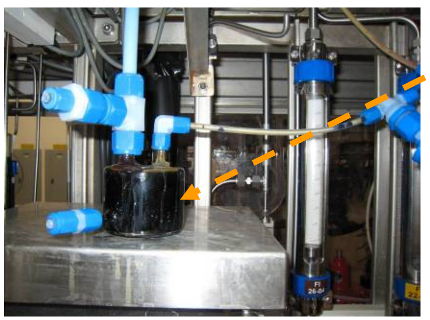
CEA Bunsen Section assembled at GA experiment site.

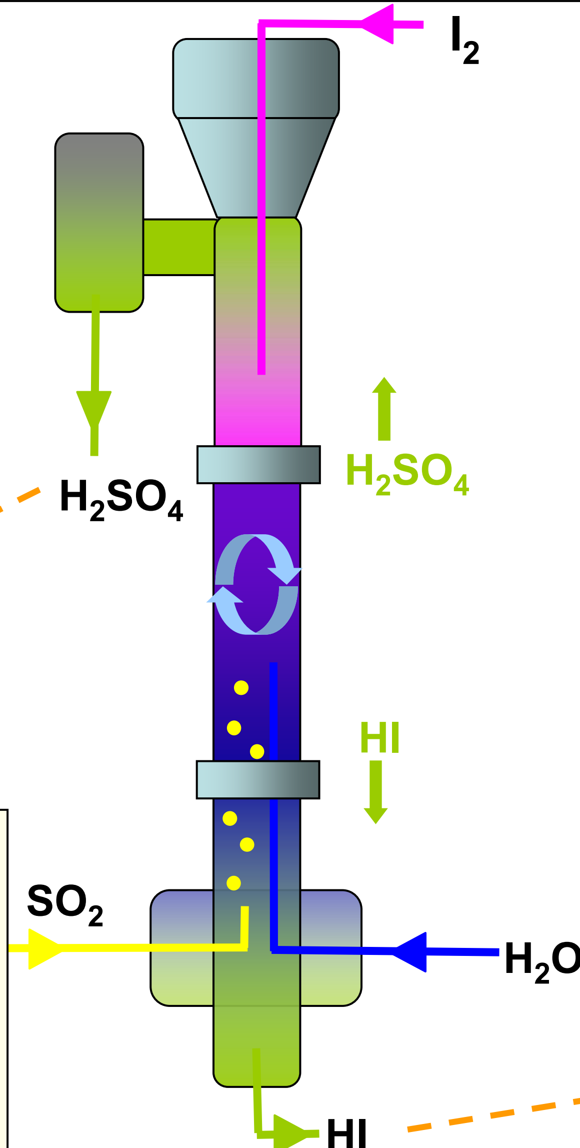
Bunsen Section Status (CEA)

Counter-current Bunsen reactor – initial run

$$9\ I_2 + SO_2 + 16\ H_2O\ = 2\ HI + 10\ H_2O + 8\ I_2 + H_2SO_4 + 4\ H_2O$$

- SO_2, H_2O and I_2 react to form HI and H_2SO_4
- HIx (HI, H_2O, I_2) to section 3 (heavy phase)
- H_2SO_4, H_2O to section 2 (light phase)





- Improved I_2 pumping and metering required
- CEA will install new top reactor section to include DP cells for liquid level control (May 2008)

Initial Test Results

- First Bunsen reaction completed in April with H_2SO_4 section
- Heavy phase - 42% HI, 10% I_2 – acceptable for processing in HI section
- Light phase density 1.23, target 1.5
- Testing will resume after installation of modified Bunsen reactor

Sulfur Cycle Supporting Activities

System Analyses

FY07 NHI Baseline Process Cost Projection Update

NHI Baseline Cycle	H2 Cost ($/kg)	Efficiency (H2A Analysis)
Sulfur-Iodine (extractive distillation)	3.41	40
Sulfur-Iodine (reactive distillation)	3.05	39
Hybrid Sulfur	2.94	43
High Temperature Electrolysis	3.22	44

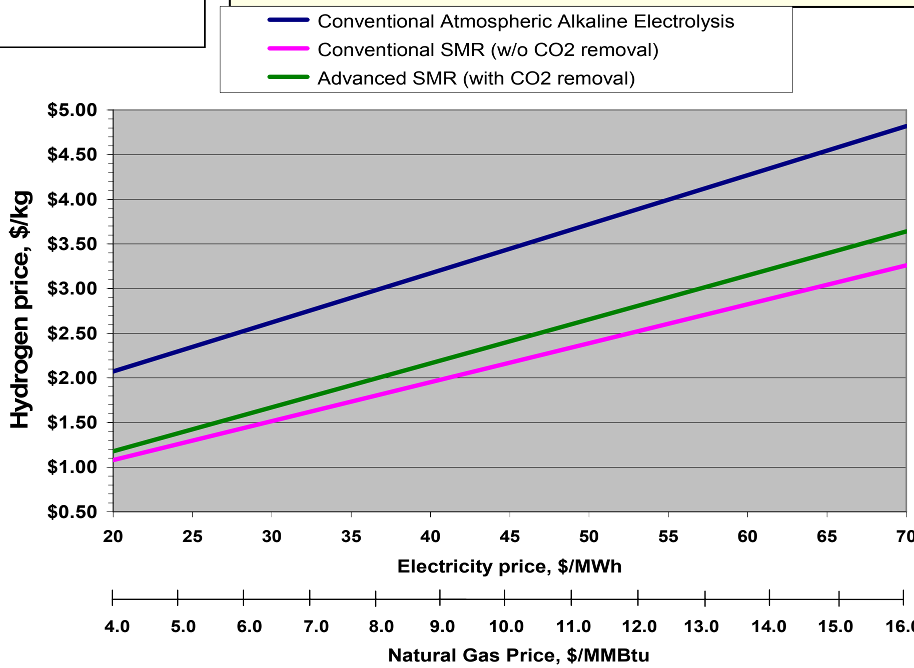
- *Efficiencies based on available flowsheets*
- *Cost of energy*
  - *Electricity = 0.06 $/kWhr*
  - *Thermal = 0.02 $/kWhr*

Other assumptions

- *Low temp electrolysis – 660 $/kWe*
- *High temp electrolysis – 500 $/kWe*

Cost Analyses (H2A)

- *Development of H2A cost framework for NHI processes (TI, MPR)*
- *Update capital, operating cost estimates, performance based on updates from process teams*
- *Consistency, uncertainty review at MPR (FY08), H2A analyses for updated cost estimate*
- *FY07 update (preliminary draft)*



Sulfur Iodine Thermochemical Cycle

Planned Activities - FY08 - FY09 (tbd)

- **FY08 – Complete Phase 2 test program in ILS apparatus**
  - Process improvements, equipment modifications
    - Level diagnostics for Bunsen reactor - achieve flowsheet light and heavy acid phase characteristics,
    - Smaller HI reactor to facilitate section 3 flow control,
    - Interface unit diagnostics for extended operation
  - Establish baseline operational data for integrated operations, HI extractive distillation, and counter current Bunsen reactor

- **FY09 – TBD – examine improved /alternate process options**
    - Complete investigation of operational characteristics and performance for current configuration, extended operations
    - Consider reactive or co-current options
    - Complete assessment of S-I for nuclear hydrogen

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: *Flowsheet analysis identified process options for the S-I cycle. Laboratory experiments evaluated process options and provided the basis for the design and testing of the 3 major reaction sections of the S-I cycle.*

Technical Accomplishments: *The 3 major reaction sections of the S-I cycle have been assembled at the integrated lab scale experiment site and initial testing has been initiated. SNL has completed testing of a SiC bayonet sulfuric acid decomposer section at the GA site and conducted initial integrated operations with the CEA. The CEA has completed the first Bunsen reactor test, producing and separating the heavy (HI) and light (H2SO4) phase acids for subsequent processing. GA has completed the initial H2 production runs on the HI extractive distillation and decomposition section.*

Tech Transfer/Collaboration: *The S-I cycle research is conducted as an INERI project with the French CEA. There is also collaboration with Universities (chemical analyses, materials). The DOE sponsored work will be a major component in the Generation IV International Forum (GIF) nuclear hydrogen collaboration signed in March FY2008.*

Future Research: *The focus in FY08 will be to complete the initial series of ILS test in the current configuration. FY09 is TBD but the possibility of examining advanced process options is a primary consideration. Research on improved catalysts will also be conducted.*