# 2009 DOE Hydrogen Program Review

# Sulfur-Iodine Thermochemical Cycle

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Project PD_12_Pickard

# Sulfur-Iodine Thermochemical Cycle Project

*Overview*

**Timeline**

- Start - 4/2006
- Finish - 4/2009

**Barriers**

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

**Budget**

- Funding
  - FY08 – 2.7 M$
  - FY09 – 1.06 K$
  - French CEA – in kind

**Partners**

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

# Sulfur-Iodine Thermochemical Cycle
## *Objectives*

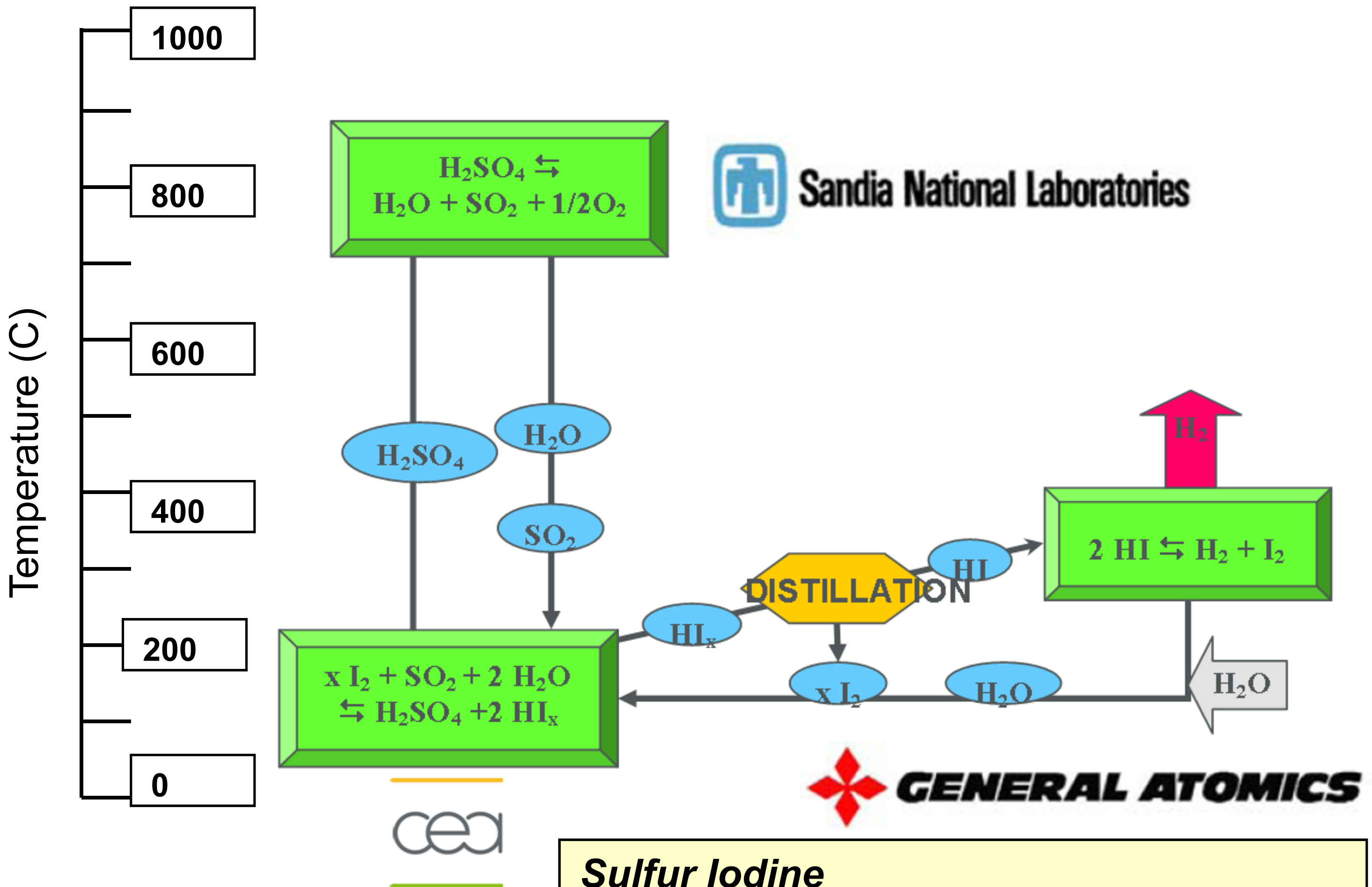
- **Evaluate the potential of the Sulfur-Iodine cycle for hydrogen production using nuclear energy**
  - DOE/NHI - CEA INERI Project (CEA, SNL, General Atomics)
  - Sulfur cycles – potential for high efficiency, relative development level
  - Approach - construct, operate an Integrated Lab Scale (ILS)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

***(Integrated Lab Scale Experiment - ILS)***

| | |
|---|---|
| FY06 - | Design, construct the 3 major reaction sections |
| FY07 - | Integrate 3 sections at General Atomics experiment site |
| FY08 - | Conduct initial integrated lab scale experiments |
| FY09 - | Complete ILS experiment series (April 2009) |

# NHI Sulfur Based Thermochemical Cycles

## *Sulfur-Iodine*




***Sulfur Iodine***

(1) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$

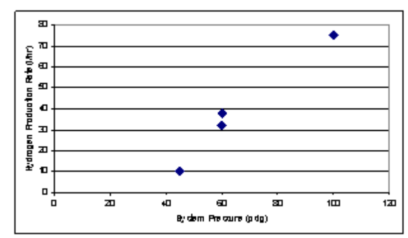
(2) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(3) $2HI \rightarrow I_2 + H_2$

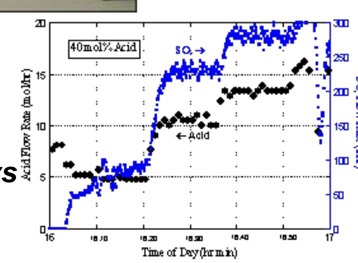
# Sulfur-Iodine Integrated Lab Scale Experiment

## *ILS Approach*

| *Develop, test 3 reaction sections* | *Integrate 3 sections at GA* | *Conduct ILS Experiments* | *ILS Exp Improvements* |
|---|---|---|---|
| **FY2006**<br>• HI decomposition - extractive distillation (Gen Atomics)<br>• $H_2SO_4$ – SiC bayonet decomposer (SNL)<br>• Counter-current Bunsen reactor (CEA) | **FY2007**<br>• $H_2SO_4$ section operational<br>• CEA Bunsen section installed<br>• 3 sections connected with interface unit, prelim testing | **FY2008**<br>• Stand alone section tests<br>• Initial integration (Section 1 & 2) and first full sequence $H_2$ test conducted<br>• Section mods | **FY2009**<br>• Performance improvement mods<br>• Parametric and longer term exps<br>• Provide basis for performance, and cost projections |




*H2 production vs HI section pressure*

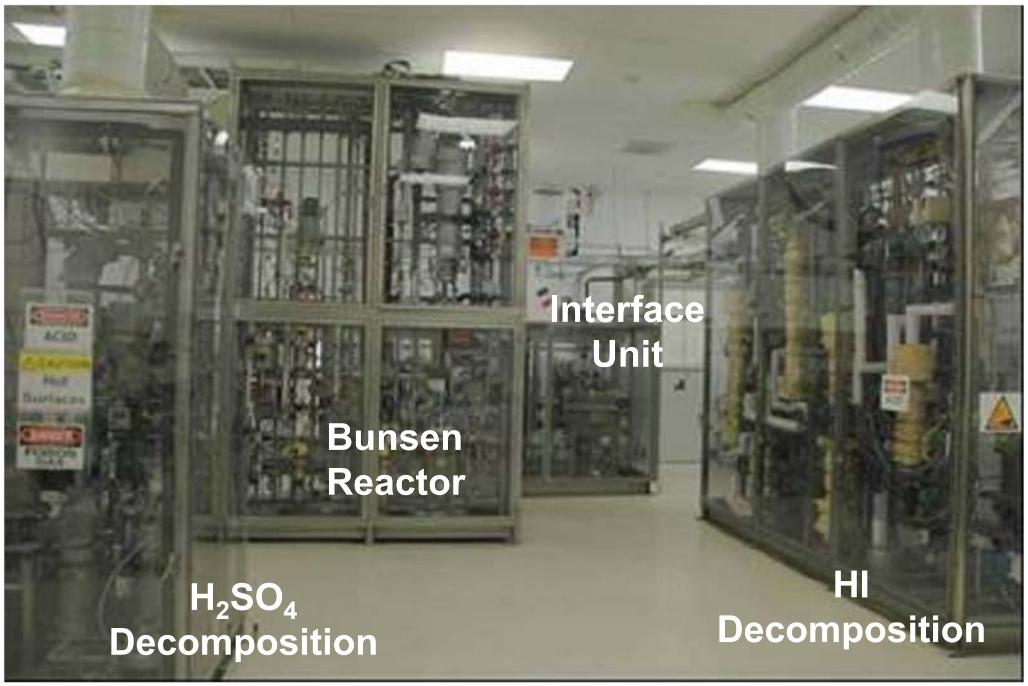


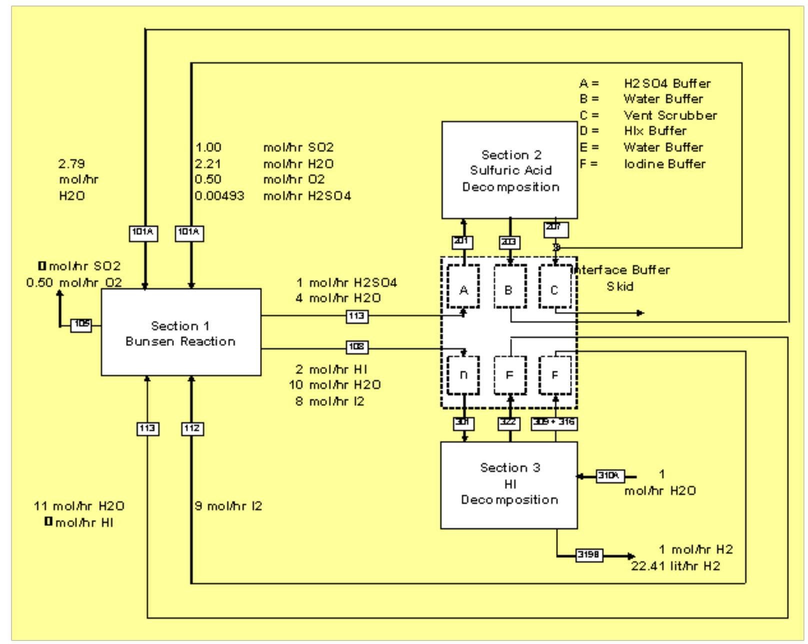

*SO2 production vs H2SO4 flow rate*

# 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*
- *Separate ventilation system for each section*
- *Partially integrated operations since 3/08*

# Technical Accomplishments/ Progress
## *Overview*

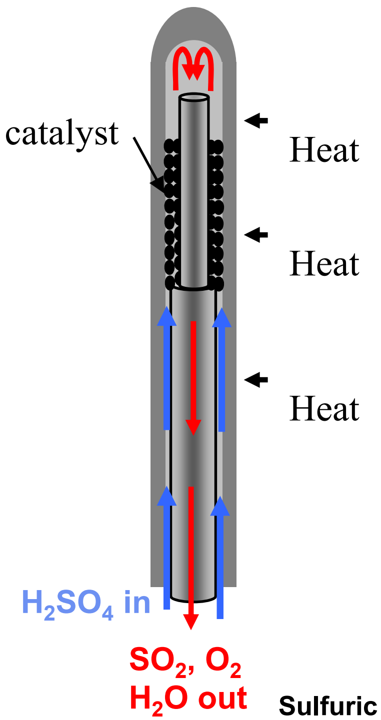
- ***HI decomposition (GA)***
  - Diagnostics, control, flow systems developed and tested, reliable
  - Multiple stand-alone operations, to examine pressure dependence of $H_2$ production and materials behavior
  - Hydrogen production experiment using CEA Bunsen section feed material ~75 liters/hr - 12/08

- ***Bunsen reactor section testing (CEA)***
  - Iodine flow control and monitoring improved in FY09 with HIx (heavy) phase and $H_2SO_4$ (light) phase acid composition near expected values
  - $SO_2/O_2$ separation section operated reliably in multiple operations
  - On spec HIx (heavy) phase produced 12/08

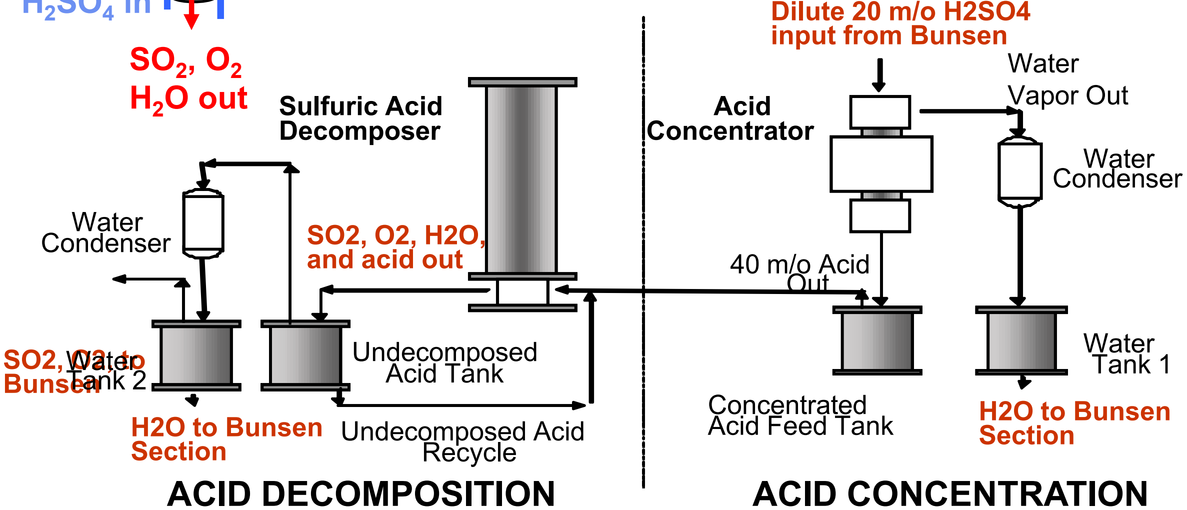
- ***$H_2SO_4$ decomposition experiments (SNL)***
  - Experiments completed up to 900 C, to explore temperature, pressure, and flow rate dependencies.
  - Operated in integrated mode with CEA section ($SO_2$ section)
  - Multiple operations with no corrosion issues identified.

# Sulfuric Acid Decomposition Section

## *SiC Integrated Decomposer*




- *Boiler, catalytic decomposer, heat recuperator in single unit*
- *Minimizes high T corrosion issues*
- *Glass or Teflon® lined materials used for low T components*
- *Scales as tube and shell HX*





*$H_2SO_4$ decomposer unit installed at GA ILS experiment site*

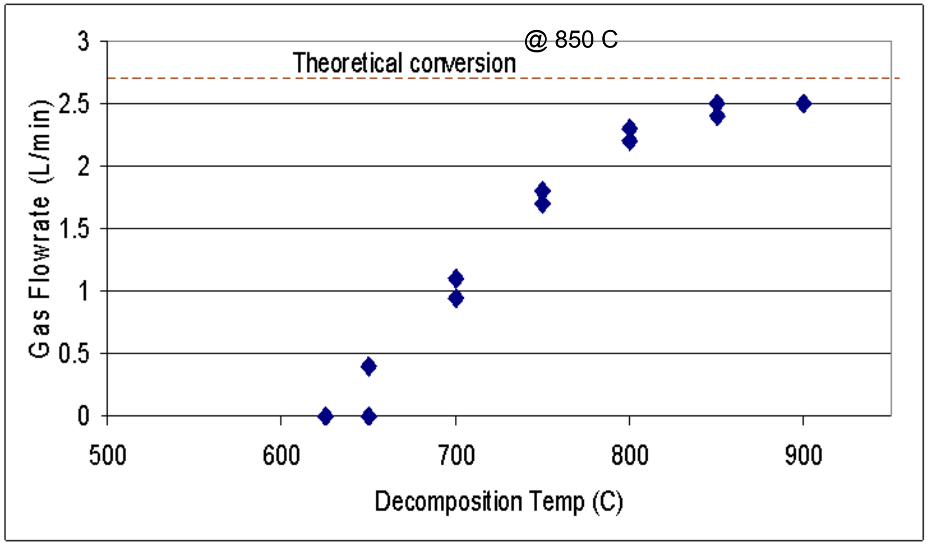
| | |
|---|---|
| $H_2SO_4$ (l) $\rightarrow$ $H_2O$ (g) + $SO_3$ (g) | ~ 500 C |
| $SO_3$ (g) $\rightarrow$ $SO_2$ (g) + 1/2$O_2$ (g) | ~ 800 C |

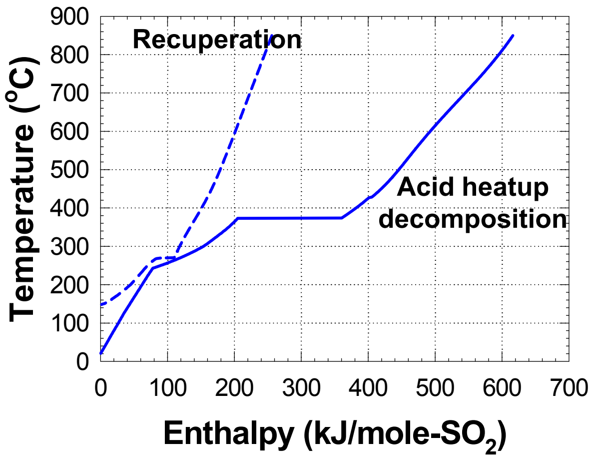
# Sulfuric Acid Decomposition Section

## *Results*

## Additional parametric studies were performed

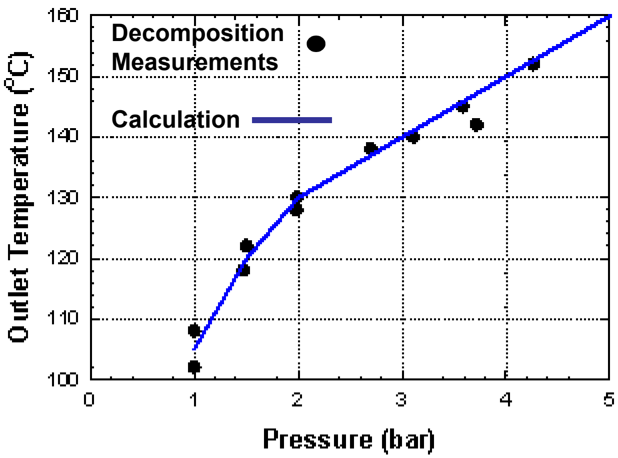
- Acid decomposer operation reproducible through ~30 cycles
- SO2 production controlled by inlet flow rate (up to 300 l/hr @ 850 C)
- Near theoretical conversion at design flow rates
- Significant SO2 conversion at 700 deg C (ext. bayonet temperature)
- $SO_2$ production rate limited by heat transfer to catalyst region
- Catalyst durability requires further evaluation



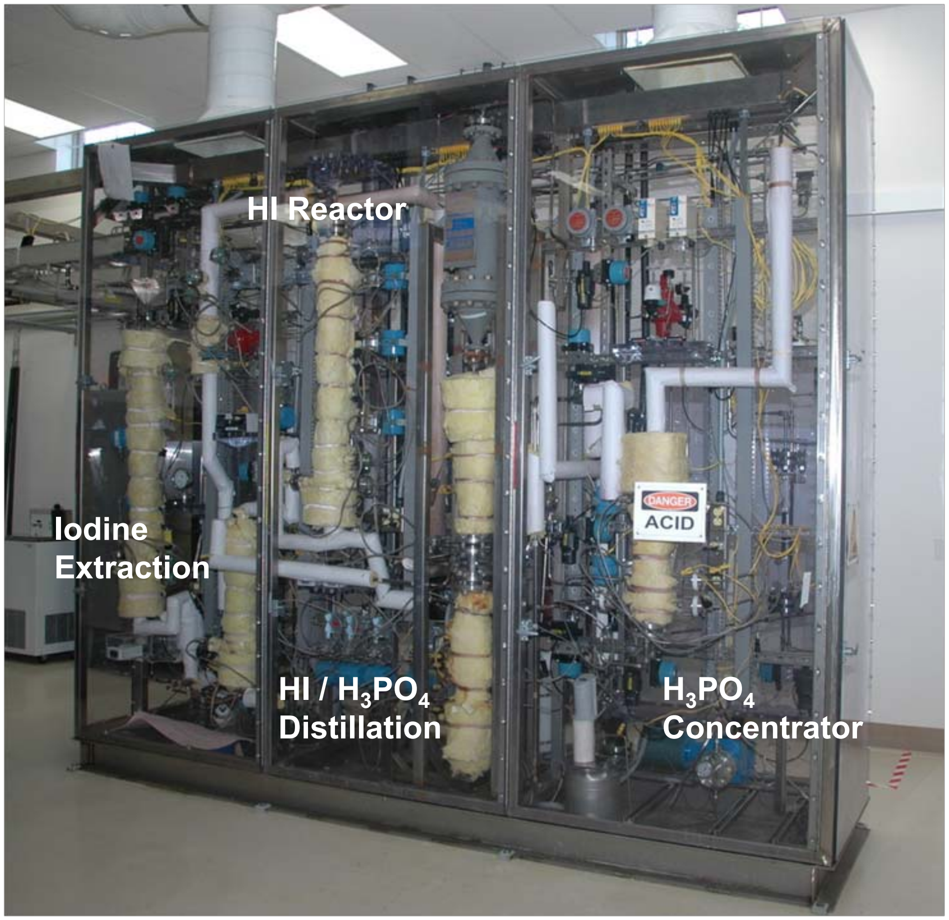




Bayonet decomposer pinch point analysis

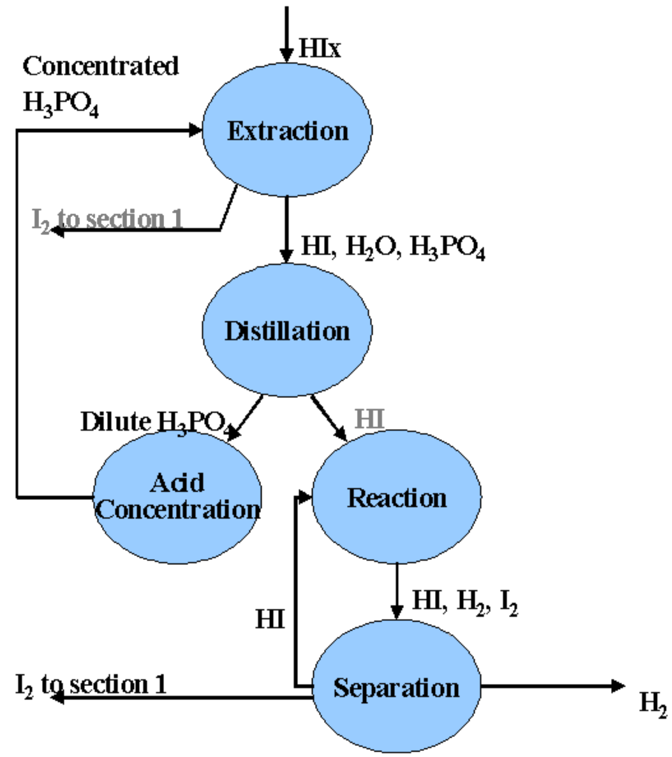
- Product outlet temperature dependent on system pressure
- Parametric studies performed to provide data for validation of models
- Bayonet design can be tailored to adjust outlet temperature



# Section 3- HI Decomposition
## *Overview*




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




***Extractive distillation method***

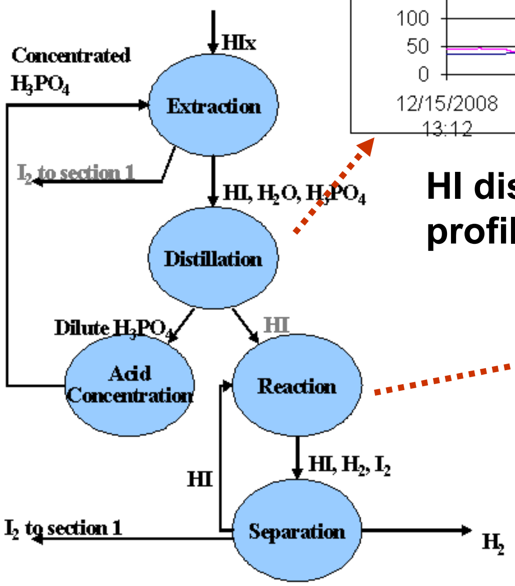
- $H_3PO_4$ – separates $HI/H_2O$ from $I_2$
- HI distilled from $H_3PO_4$,
- HI decomposed at ~ 400 C to $H_2$ and $I_2$
- Undecomposed HI recycled to HI reactor
- $I_2$ returned to Bunsen reactor section

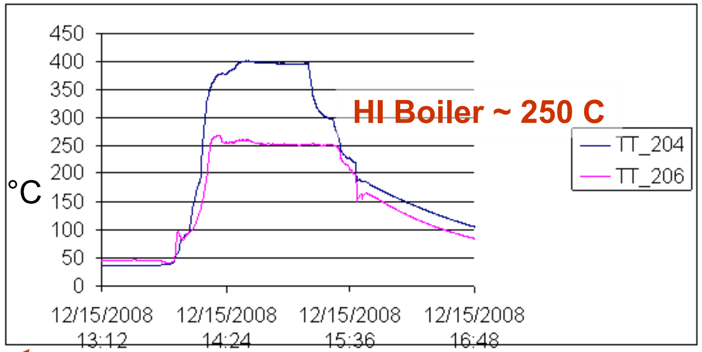
**Key Issues**

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

# Section 3- HI Decomposition Section

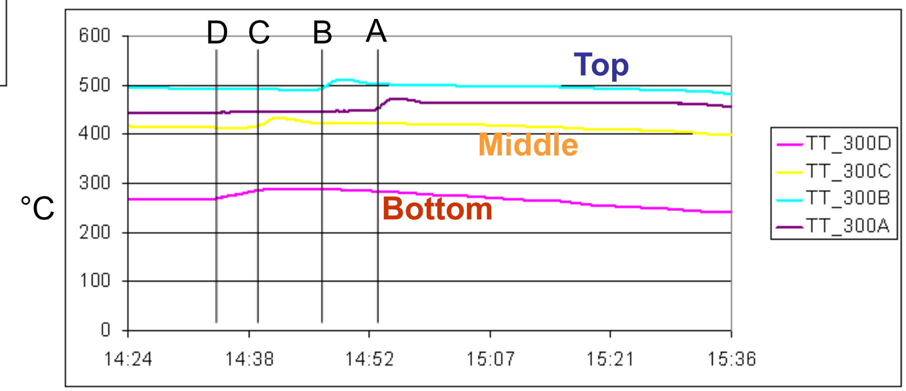
*HI section H2 run with Bunsen section feed 12/08*

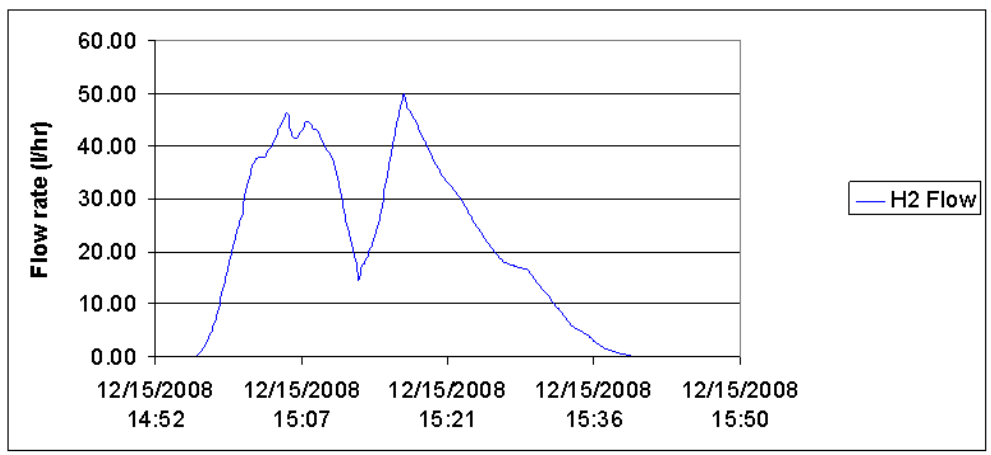



**HI distillation column temperature profile at 5 bar, integrated run**

**HI adsorption/reaction temperature front moving through HI reactor**



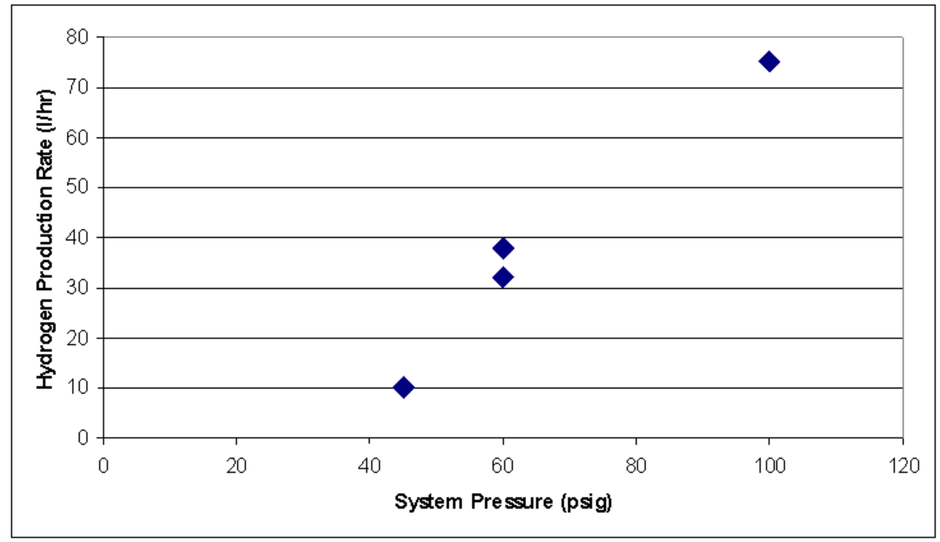



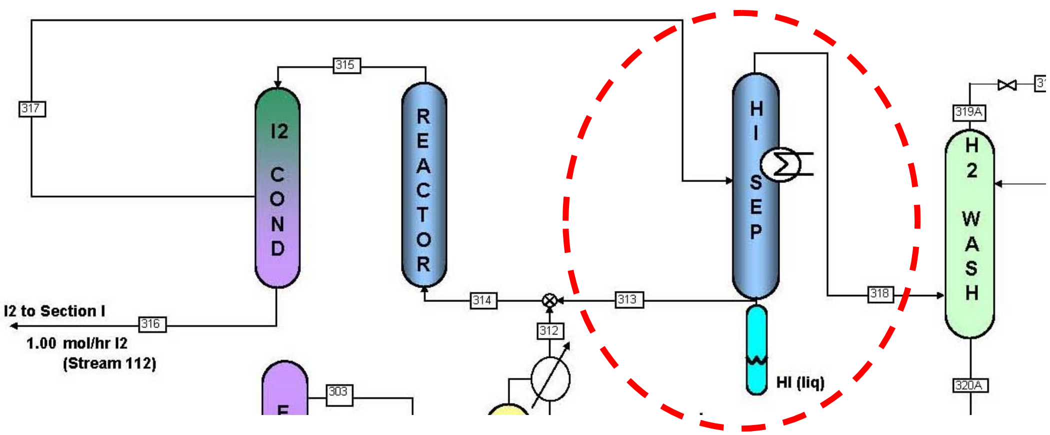

**$H_2$ integrated production run ~50 l/hr with partial recycle**

# Section 3- HI Decomposition Section

- Hydrogen runs at various pressures
  - Validates the HI recycle system
    - Unreacted HI is condensed at 0-5 °C
    - Recycled back to the reactor
  - Produced 75 l/hr $H_2$
  - Design pressure 200 psi (150 l/hr)

**H2 Production as a function of Pressure**



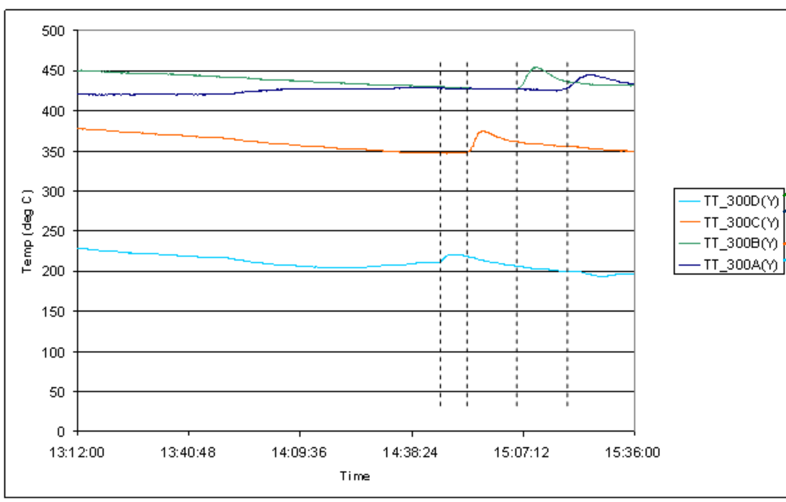

**Predicted vs Experimental H2 production**

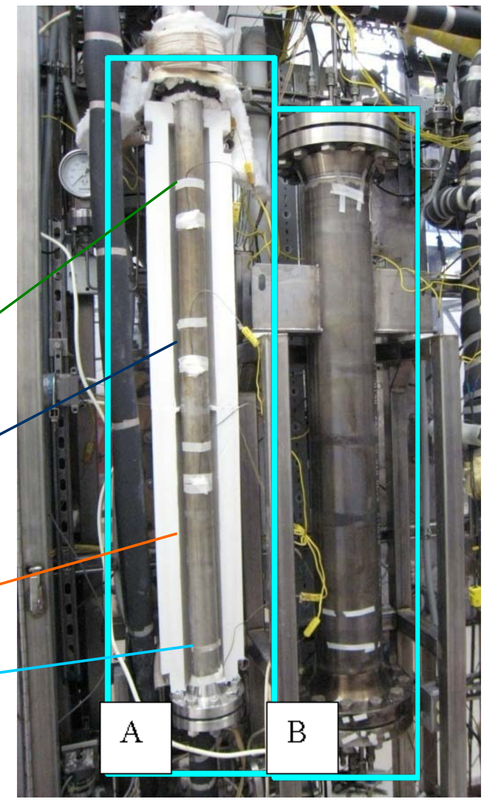
| | |
|---|---|
| HI feed in HIx | 17 mol/hr |
| HI distilled to reactor | 8.5 mol/hr |
| Predicted $H_2$ produced with no recycle | 0.85 mol/hr (19 l/hr) |
| $H_2$ actually produced | 2.7 mol/hr (60 l/hr) |

# Section 3- HI Decomposition Section

- Reactor performance has been improved
  - A new 2” diameter reactor installed
  - Better heating, better response

HI adsorption front- 2” reactor



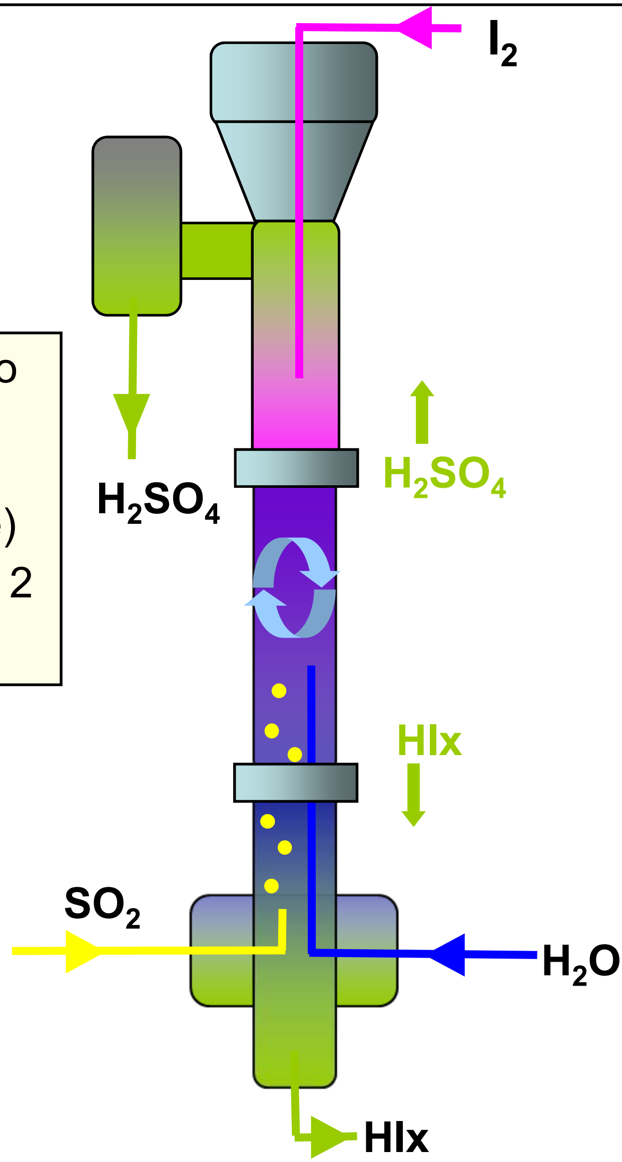

| Reactor diameter | External temp 450°C | Internal temp 450°C |
|---|---|---|
| B 6” | 2:16 | 5:49 |
| A 2” | 0:16 | 0:25 |

# Bunsen Section Status (CEA)

*Counter-current Bunsen reactor*

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

- $SO_2$, $H_2O$ 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)




- Early test results indicated better control of $I_2$ flow rates required
  - $H_2SO_4$ phase dilute, excess water at startup
  - HI phase dilute, insufficient $I_2$ flow
- Cross phase contamination, phase separation insufficient
- Improved $I_2$ pumping and metering required
- CEA has modified $I_2$ feed system and DP cells for liquid level control

# Bunsen Section Status (CEA)

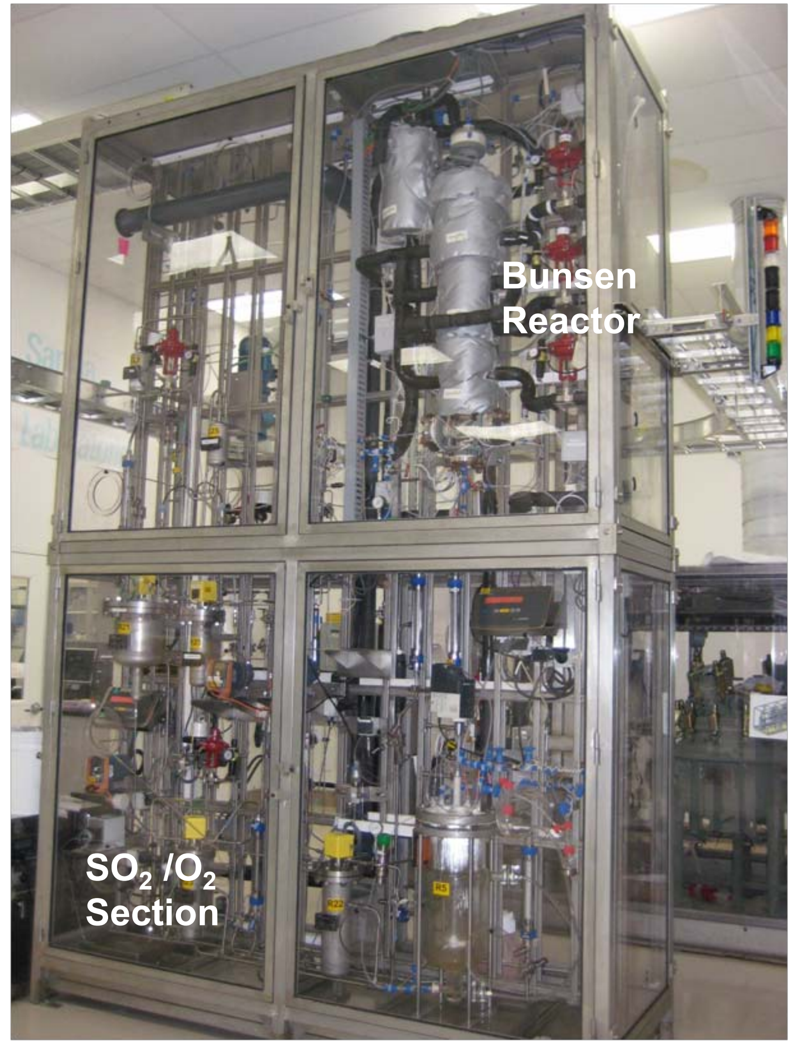
*12/08 Run Results*

## Section 1 has had partial success

- Upper Phase- $H_2SO_4$
  - 12.2 wt%
    - Reactor starts filled with $H_2O$, concentration increased from 1 to 12.2 wt%
    - Need longer runs to reach equilibrium
- Lower Phase- HI
  - 57.8 wt%
    - **Lower phase on target**

Upper phase sample

Lower phase sample



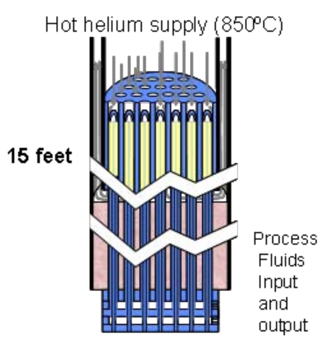

*CEA Bunsen Section assembled at GA experiment site.*

# Materials issues encountered with ILS

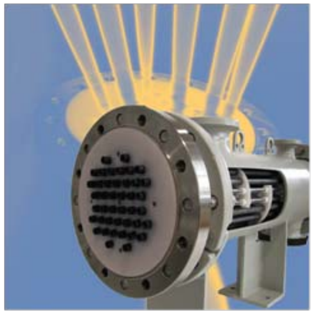
- Ta alloy vessel failures encountered (embrittlement, Ta materials defects)
  - Ta vessel and piping use was due to small scale of ILS experiments.
  - Larger scales allow more materials selection options (glass lined, Ta lined steels)

- **HI section** - Glass lined steel at lower temperatures, ceramic lined coated steel at high temperatures
- **Bunsen** - Glass lined steel worked well, teflon fittings not suitable
- **H2SO4** – SiC bayonet, glass lined steel worked well

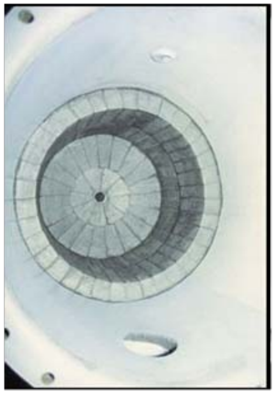
| Material Selection | ILS Test Environment |
|---|---|
| Ta-10%W pipe | Potential failure |
| Ta coated stainless | Minimal failure |
| Hastelloy C276 pipe | No failure |




a. -Multi-bayonet tube large scale heat exchanger



b. - FlowSiC shell and tube heat exchanger

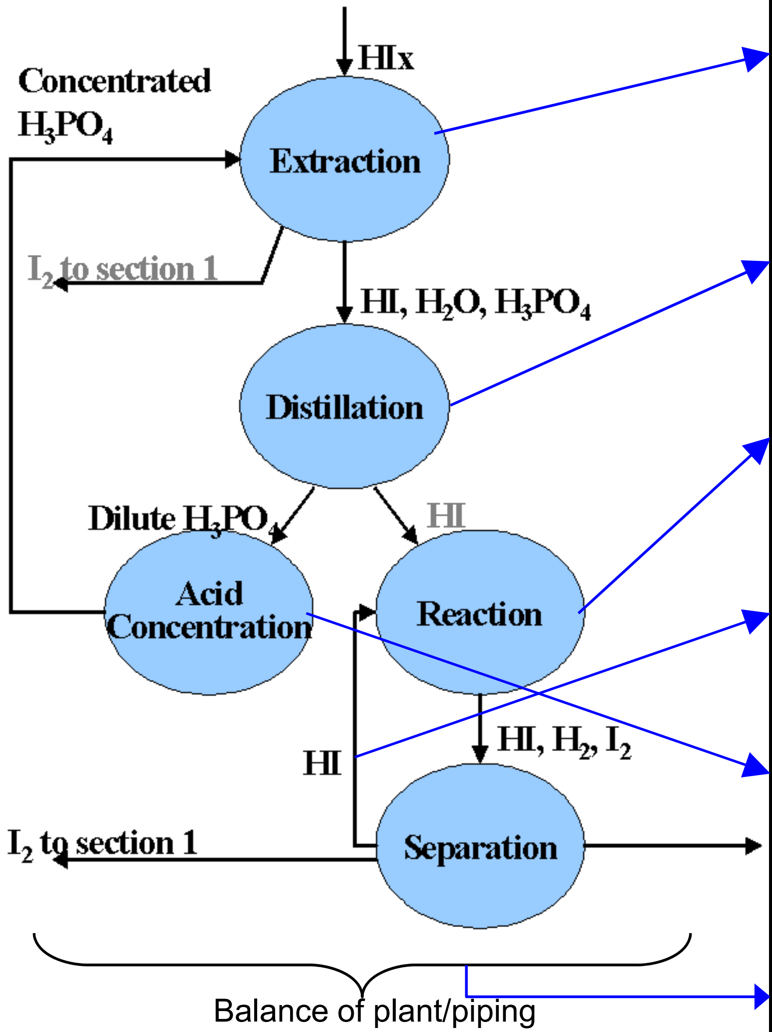


Ceramic (brick) lined vessel

**Cross section of failed Ta-10W 2" dia vessel**

# Section 3- HI Decomposition Section

## Scale-up options at larger scales




| Scale Up Material Candidates | ILS Material Selection |
|---|---|
| Lined steel (glass, Teflon®)<br>Ta alloys, Ta coated steel<br>Nb alloys, Nb coated steel<br>Ceramics | Ta-10%W pipe |
| Lined steel[a]<br>Brick lined, coated steel<br>Ta alloys, Ta coated steel<br>Ceramics | Ta-10%W pipe |
| Hastelloy B2, B3, C276<br>Brick lined, coated steel<br>Ceramics | Hastelloy C276 pipe |
| Lined steel<br>Ta alloys, Ta coated steel<br>Nb alloys, Nb coated steel<br>Ceramics | Ta-10%W pipe |
| Hastelloy B2, B3, C276<br>Ta alloys, Ta coated steel<br>Ceramics | Ta-10%W pipe |
| Lined steel<br>Ta alloys, Ta coated steel<br>Nb alloys, Nb coated steel<br>Glass lined, ceramic lined | Ta-10%W tube<br>Ta coated stainless |

# Sulfur Iodine ILS Project Summary

- **The DOE – CEA project on the ILS was completed in April 2009. Analysis and documentation of results underway**
  - Status
    - Equipment is being cleaned and put in safe shutdown condition.
    - Will be decommissioned in FY10
  - Results summary
    - Several partially integrated runs conducted to produce $H_2$ at up to 75 l/hr
    - Bunsen operations produced correct lower phase compositions, but with limited reliability
    - HI section operations show extractive distillation works – but is complex
    - Future directions would focus on reactive distillation
    - $SO_2$ production in bayonet near routine, no materials issues
  - Lessons learned
    - Larger scales would allow wider component and materials options
    - Reactive distillation experiments indicate a promising path forward
    - Materials studies identified critical areas

# Sulfur-Iodine ILS Experiment
## *Project Summary*

**Relevance**: *This project supports the DOE assessment of the Sulfur Iodine thermochemical cycle for large scale production of hydrogen using Generation IV reactors. The DOE technology decision for the NGNP hydrogen production technology will occur later this year.*

**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 operated numerous times in stand alone or partially integrated modes. 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 several Bunsen reactor tests, producing and separating the heavy (HI) and light (H2SO4) phase acids of correct composition. GA completed multiple 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 current project is now complete. Remaining work in FY09 is examining reactive distillation as a more efficient and lower cost option for the HI section. Continued research on improved H2SO4 catalysts will also be conducted.*