2009 DOE Hydrogen Program Review

Sulfur-Iodine Thermochemical Cycle

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This presentation does not contain any proprietary or confidential information

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

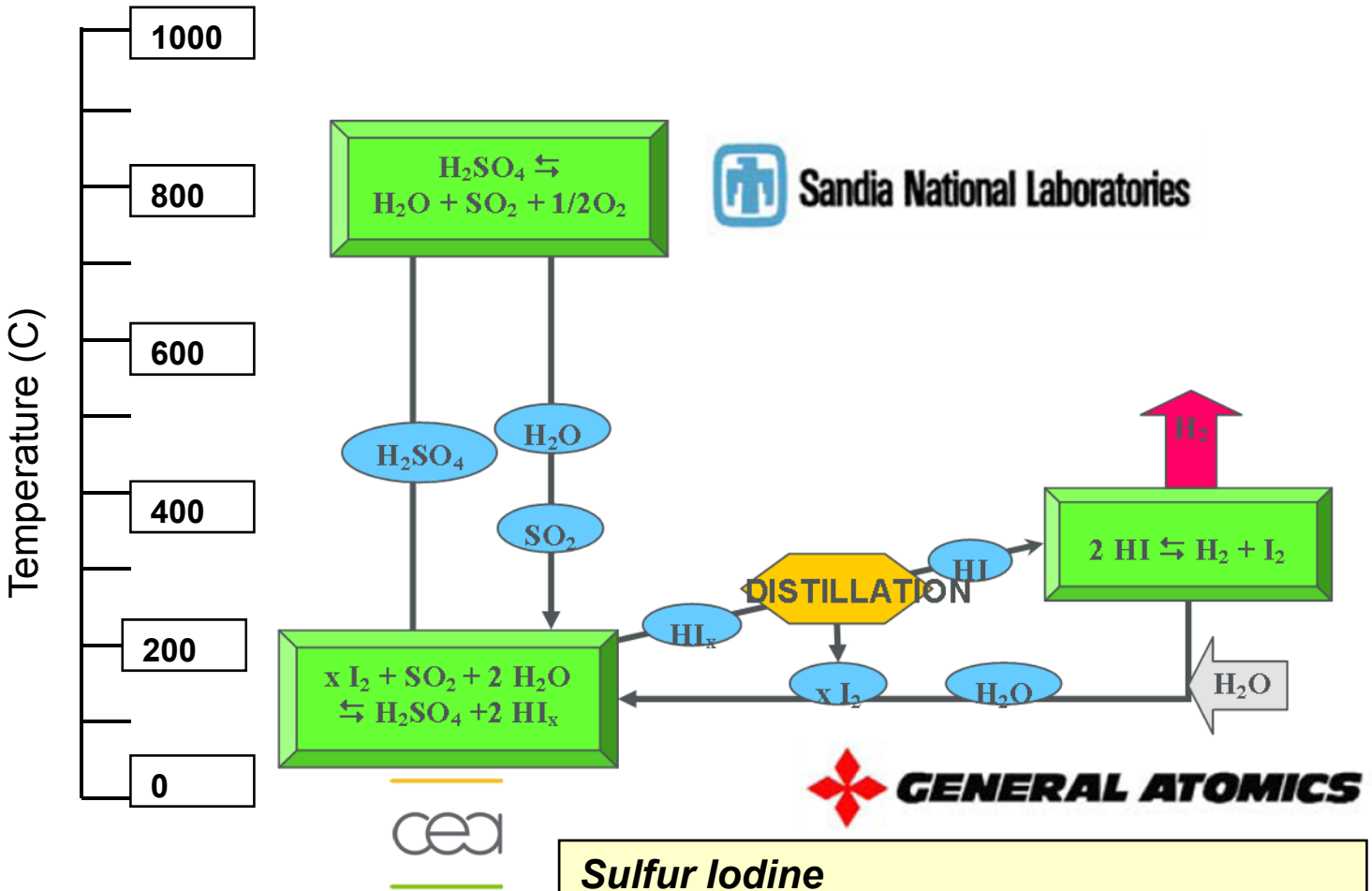
- **Evaluate the potential of the Sulfur-Iodine cycle for hydrogen production using nuclear energy**
  - DOE/NHI - CEA INERI Project (CEA, SNL, General Atomics)
  - Sulfur cycles – potential for high efficiency, relative development level
  - Approach - construct, operate an Integrated Lab Scale (ILS)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

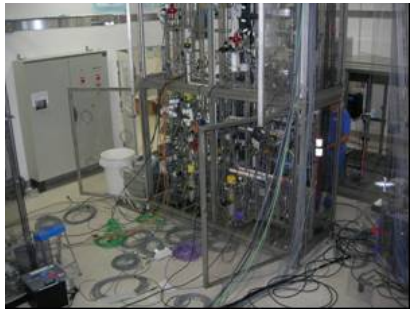
(1) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$

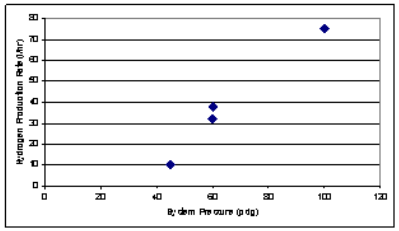
(2) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

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

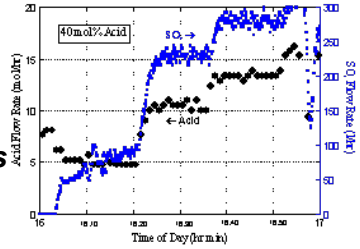
Sulfur-Iodine Integrated Lab Scale Experiment
ILS Approach

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





H2 production vs HI section pressure

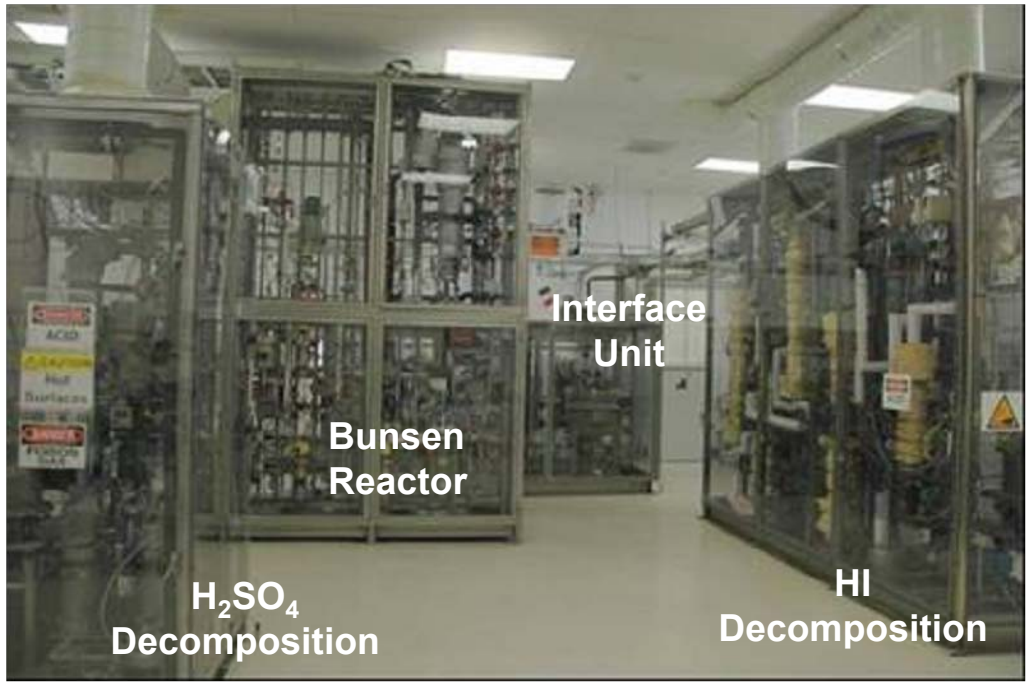


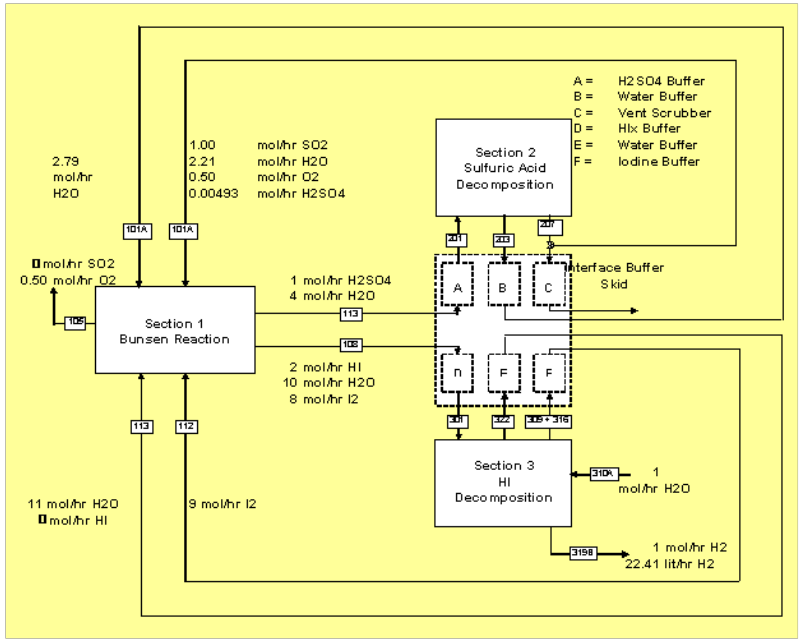
SO2 production vs H2SO4 flow rate

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

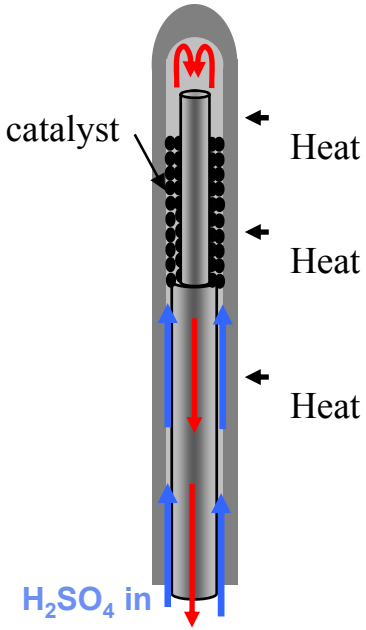
- ***HI decomposition (GA)***
  - Diagnostics, control, flow systems developed and tested, reliable
  - Multiple stand-alone operations, to examine pressure dependence of H_2 production and materials behavior
  - Hydrogen production experiment using CEA Bunsen section feed material ~75 liters/hr - 12/08

- ***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

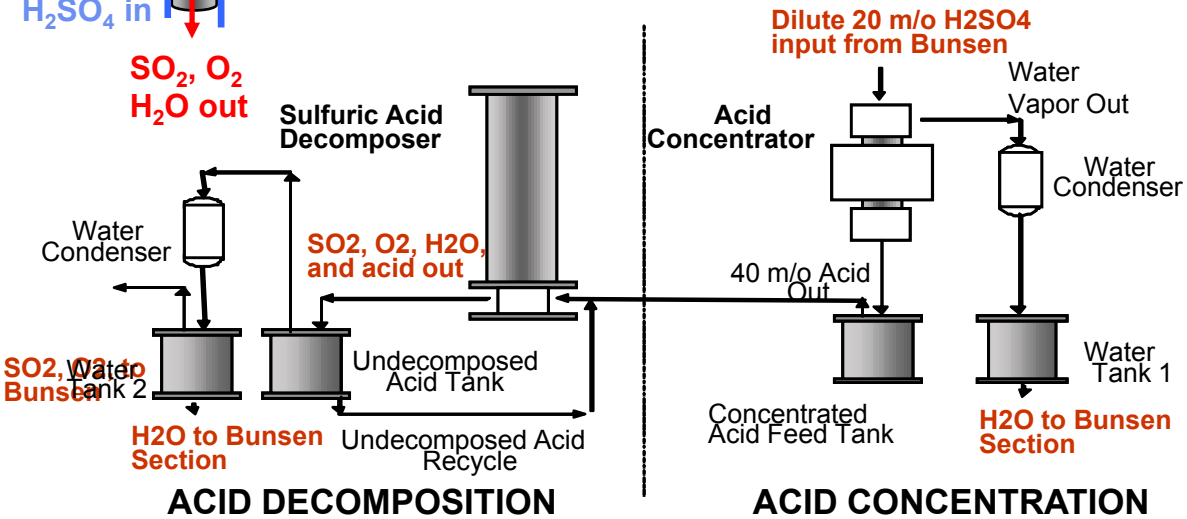
- ***H_2SO_4 decomposition experiments (SNL)***
  - Experiments completed up to 900 C, to explore temperature, pressure, and flow rate dependencies.
  - Operated in integrated mode with CEA section (SO_2 section)
  - Multiple operations with no corrosion issues identified.

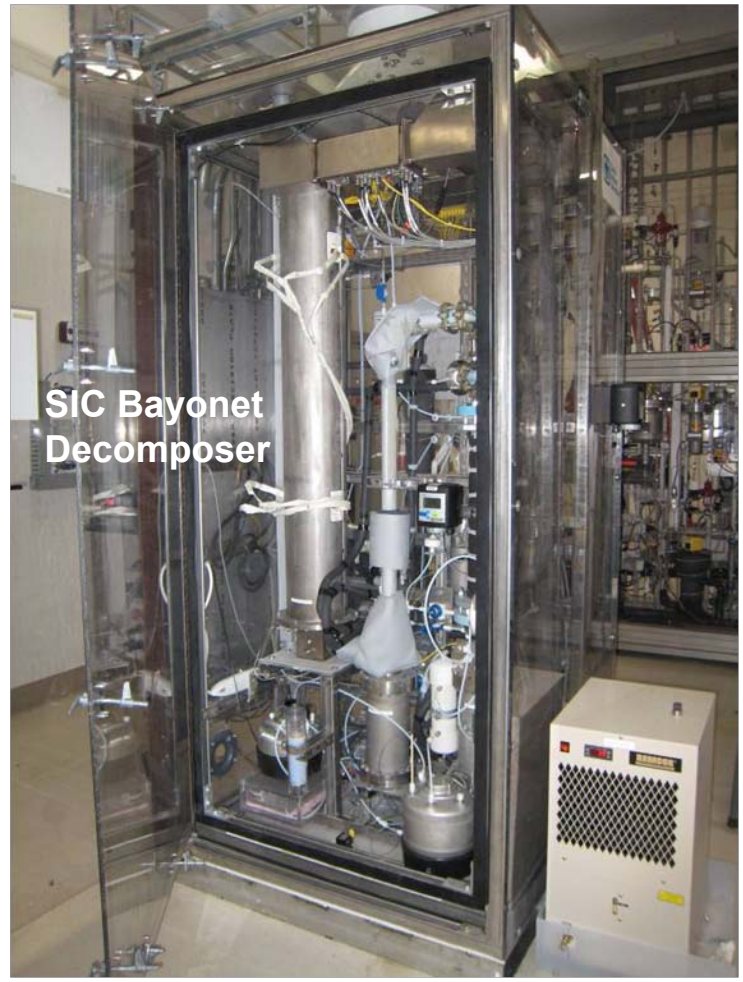
Sulfuric Acid Decomposition Section

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

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

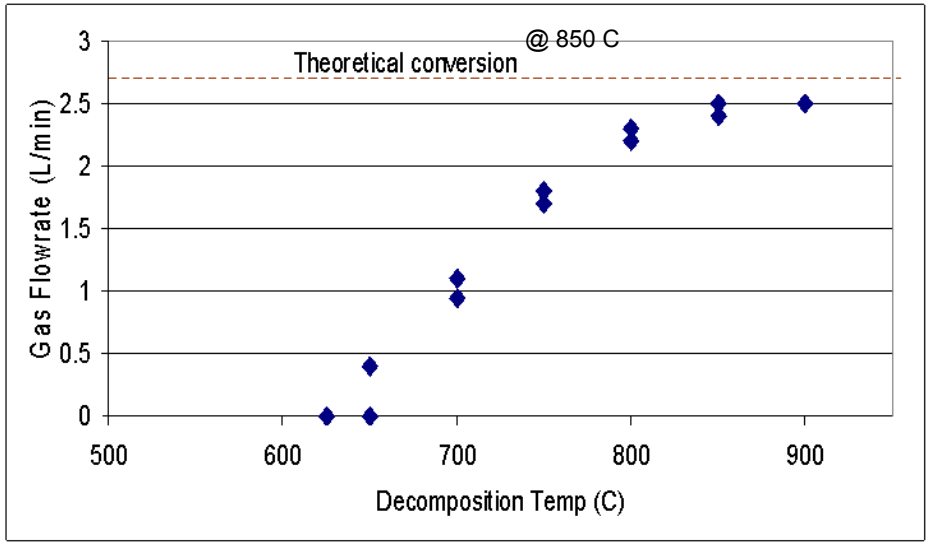
$$SO_3\ (g) \rightarrow SO_2\ (g) + 1/2O_2\ (g) \qquad \sim 800\ C$$

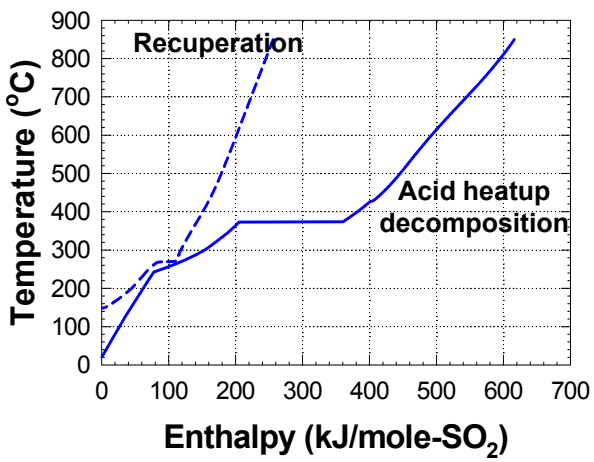
Sulfuric Acid Decomposition Section

Results

Additional parametric studies were performed

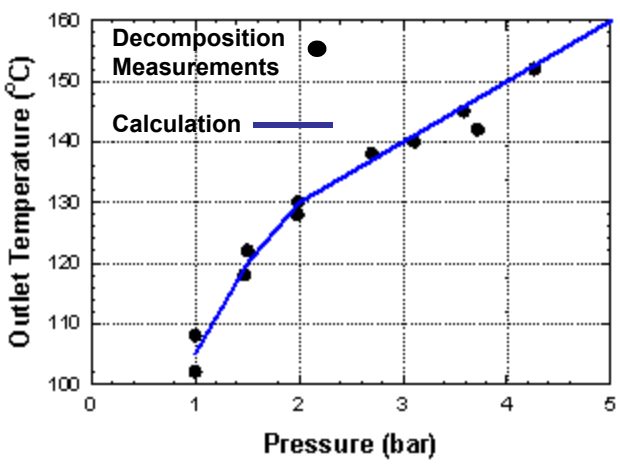
- Acid decomposer operation reproducible through ~30 cycles
- SO2 production controlled by inlet flow rate (up to 300 l/hr @ 850 C)
- Near theoretical conversion at design flow rates
- Significant SO2 conversion at 700 deg C (ext. bayonet temperature)
- SO_2 production rate limited by heat transfer to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





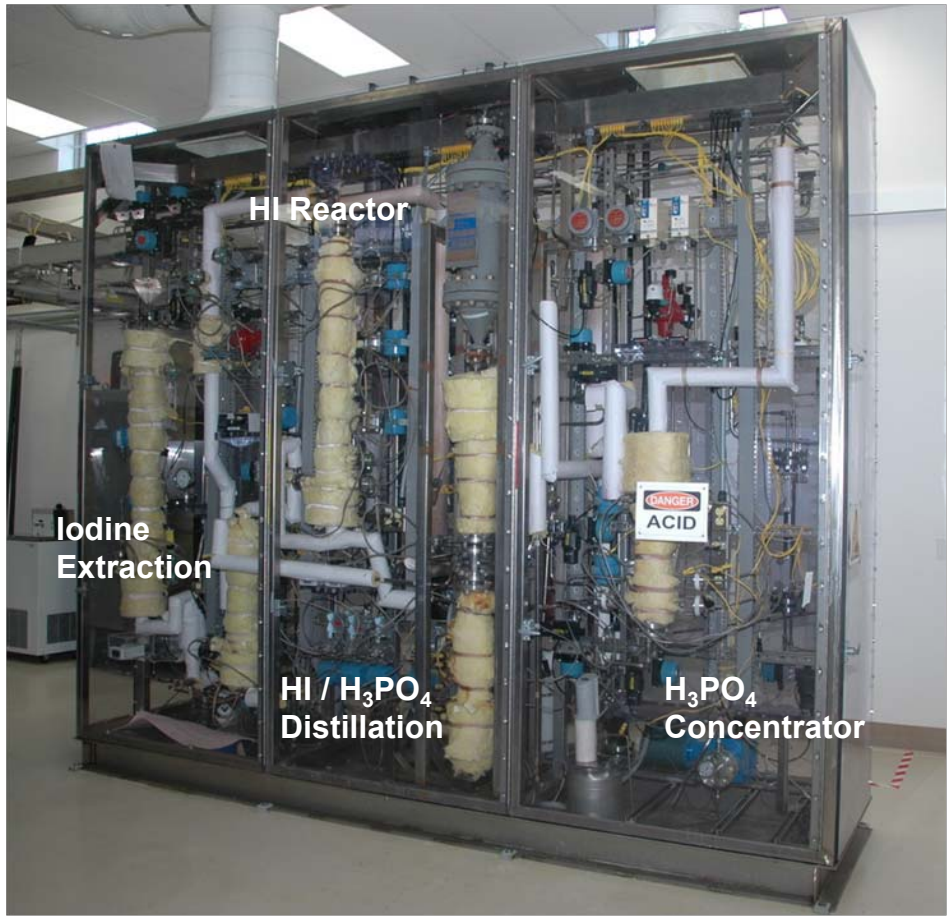
Bayonet decomposer pinch point analysis

- 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

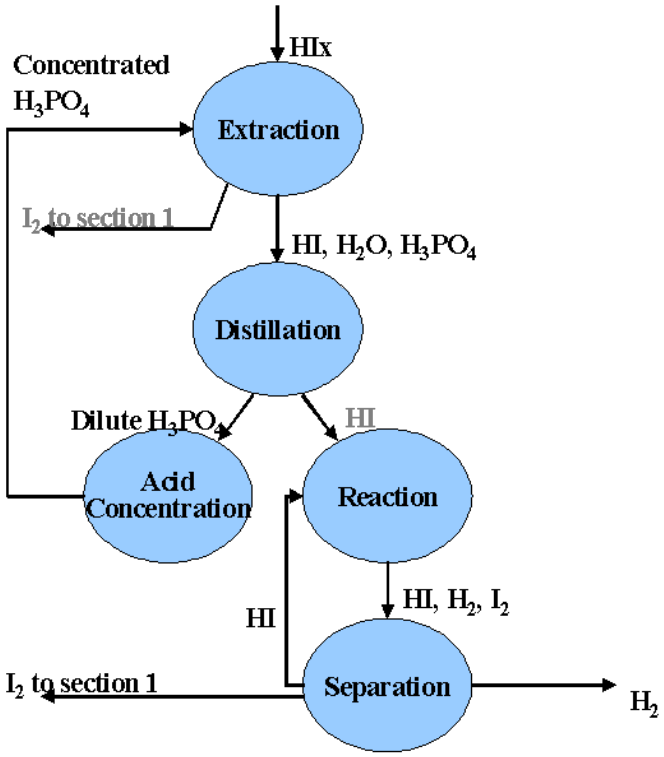


Section 3- HI Decomposition

Overview



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



Extractive distillation method

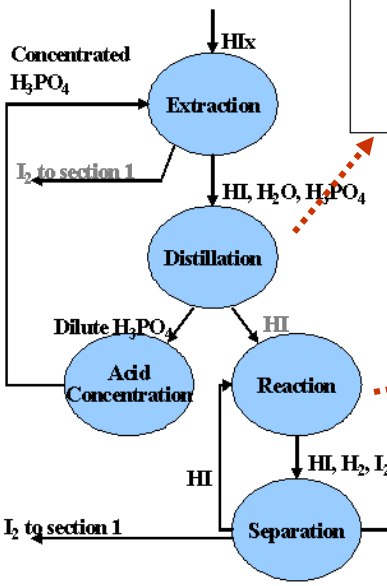
- H_3PO_4 – separates HI/H_2O from I_2
- HI distilled from H_3PO_4,
- HI decomposed at ~ 400 C to H_2 and I_2
- Undecomposed HI recycled to HI reactor
- I_2 returned to Bunsen reactor section

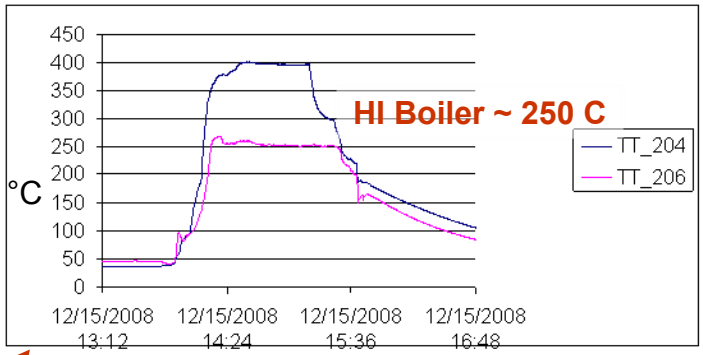
Key Issues

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

Section 3- HI Decomposition Section

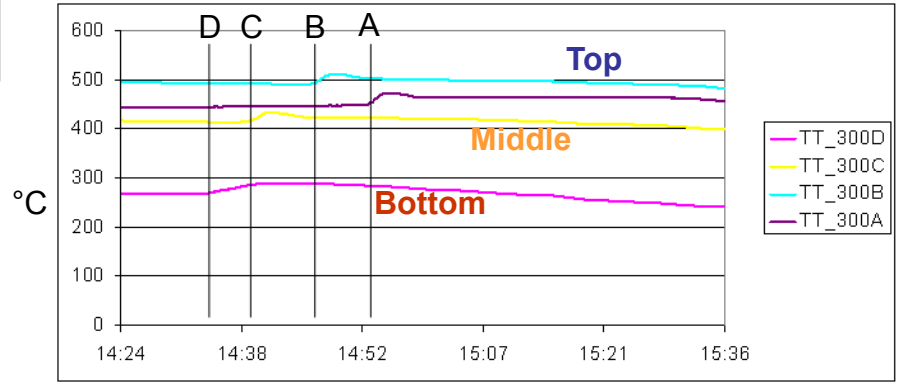
HI section H2 run with Bunsen section feed 12/08

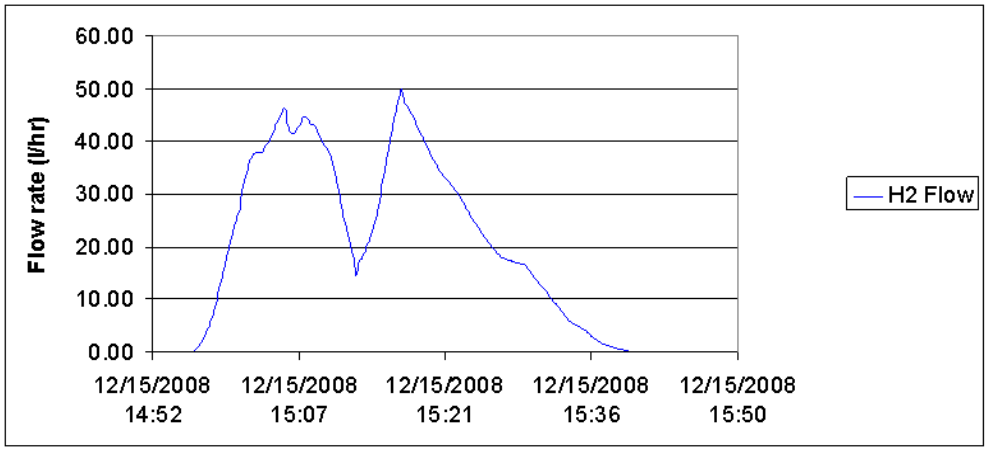




HI distillation column temperature profile at 5 bar, integrated run

HI adsorption/reaction temperature front moving through HI reactor



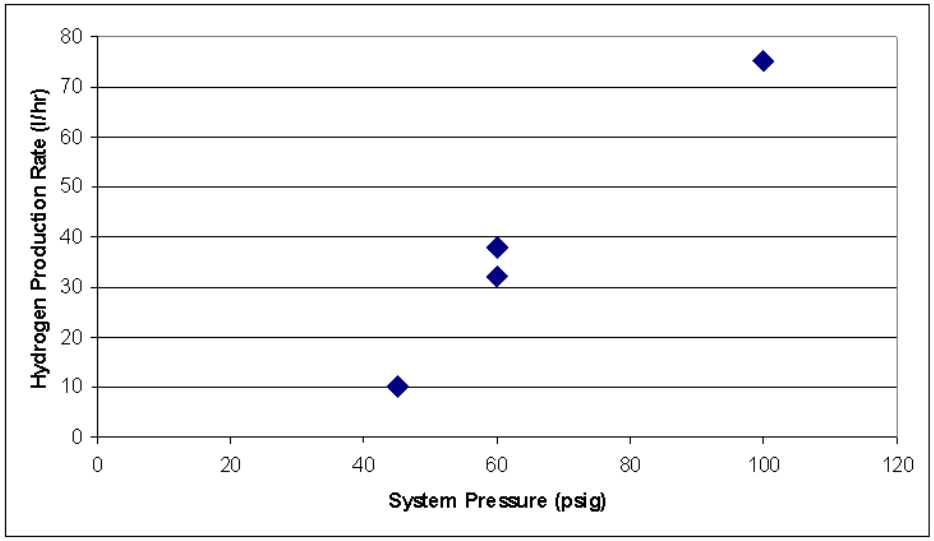


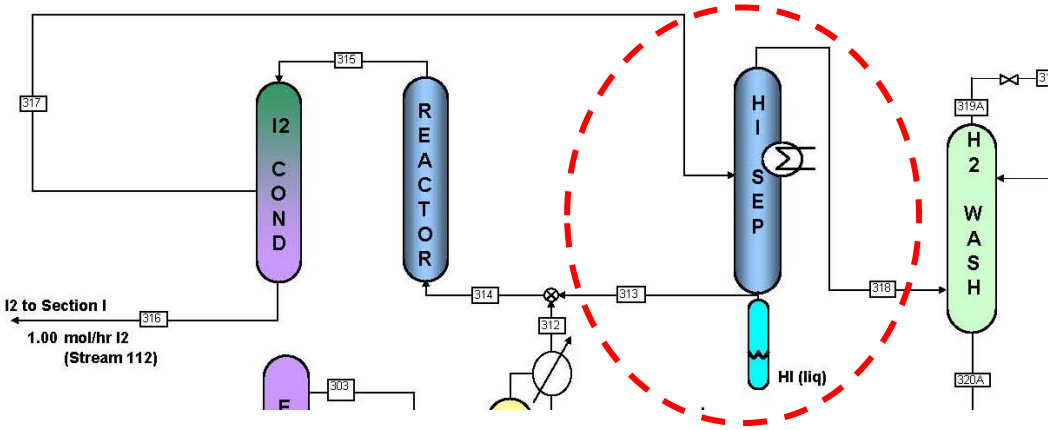
H_2 integrated production run ~50 l/hr with partial recycle

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





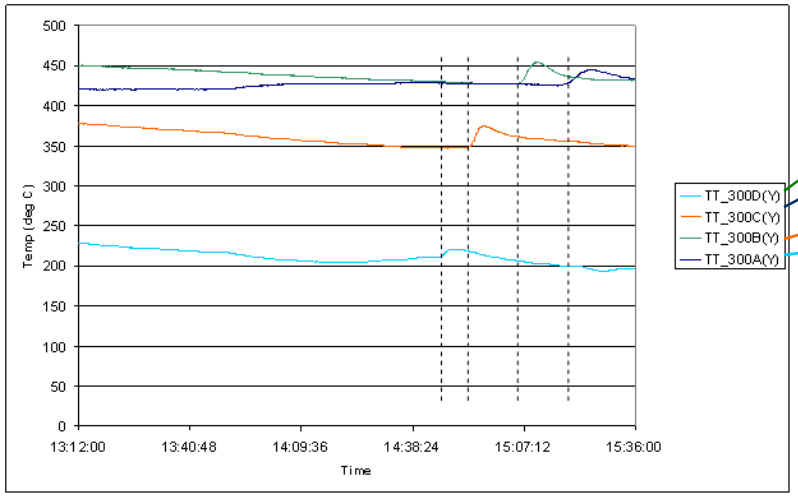
Predicted vs Experimental H2 production

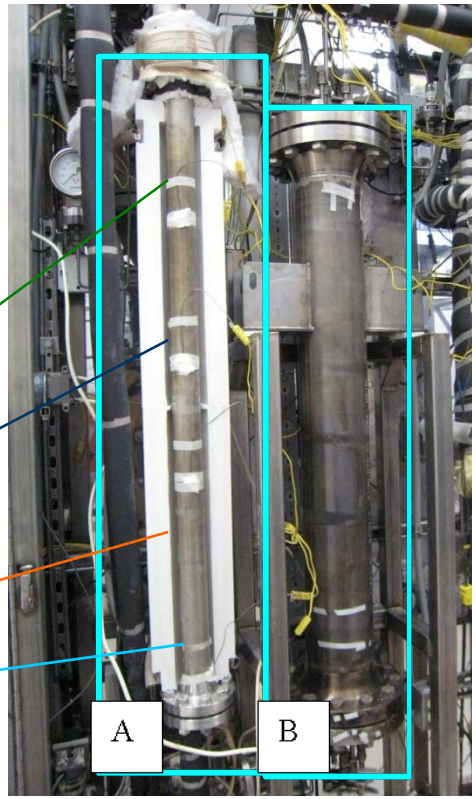
HI feed in HIx	17 mol/hr
HI distilled to reactor	8.5 mol/hr
Predicted H_2 produced with no recycle	0.85 mol/hr (19 l/hr)
H_2 actually produced	2.7 mol/hr (60 l/hr)

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





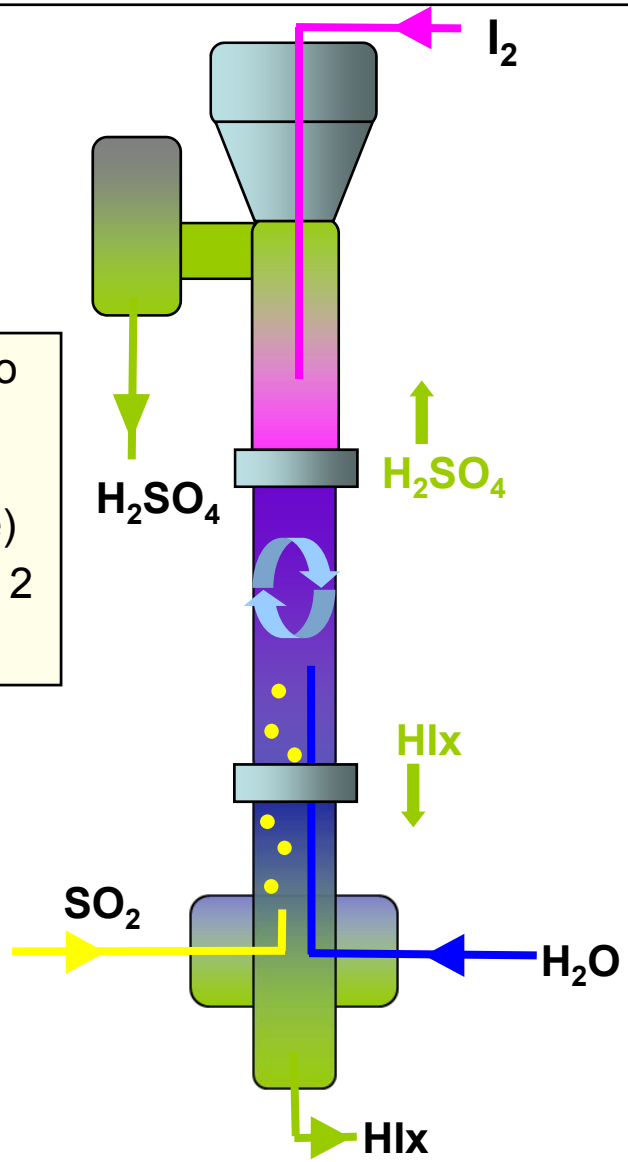
Reactor diameter	External temp 450°C	Internal temp 450°C
B 6”	2:16	5:49
A 2”	0:16	0:25

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)



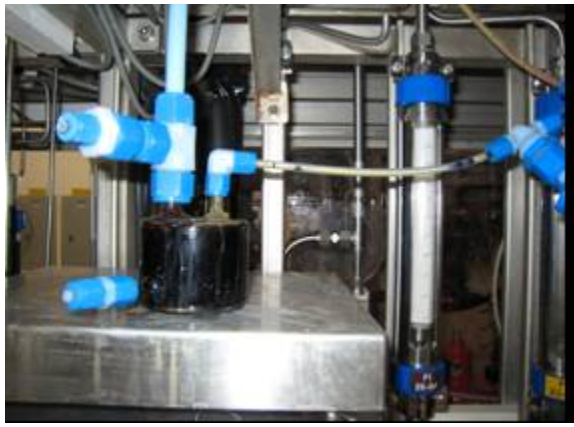
- Early test results indicated better control of I_2 flow rates required
  - H_2SO_4 phase dilute, excess water at startup
  - HI phase dilute, insufficient I_2 flow
- Cross phase contamination, phase separation insufficient
- Improved I_2 pumping and metering required
- CEA has modified I_2 feed system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

Bunsen Section Status (CEA)

12/08 Run Results

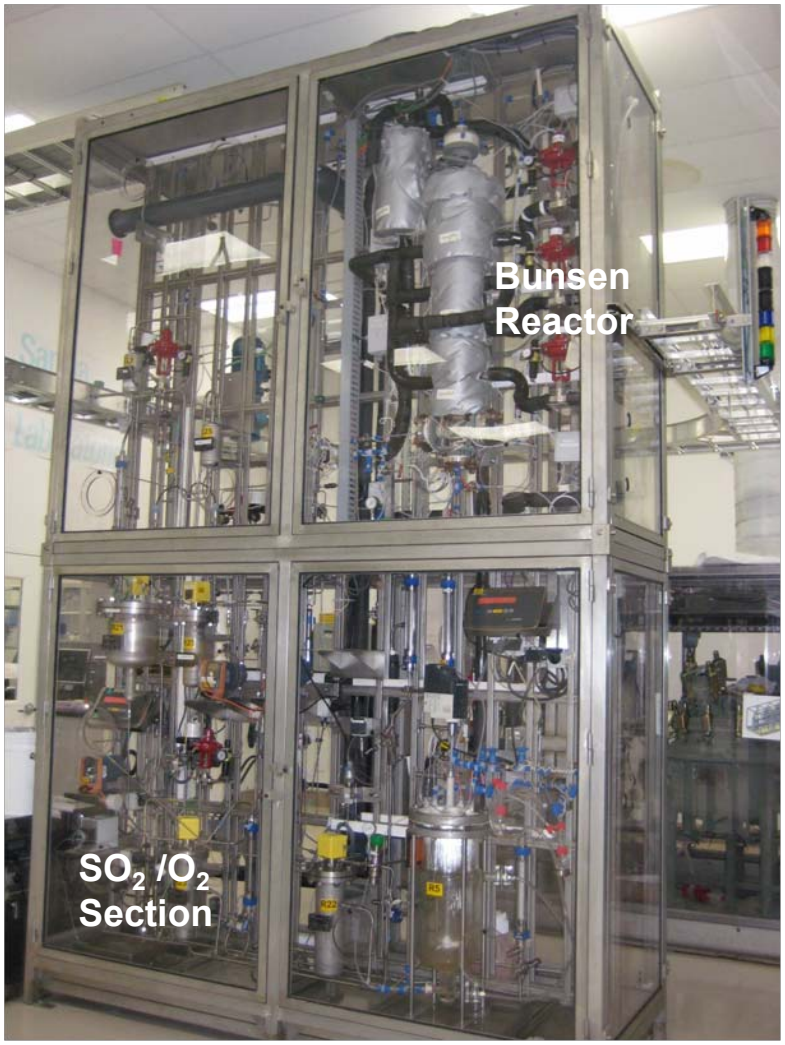
Section 1 has had partial success

- 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



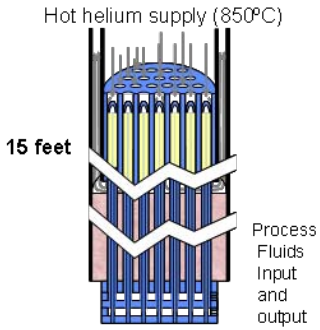
CEA Bunsen Section assembled at GA experiment site.

Materials issues encountered with ILS

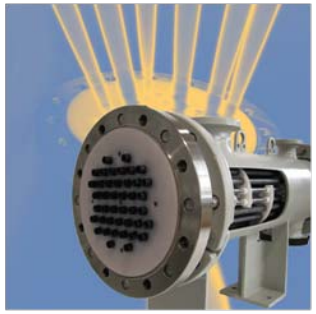
- Ta alloy vessel failures encountered (embrittlement, Ta materials defects)
  - Ta vessel and piping use was due to small scale of ILS experiments.
  - Larger scales allow more materials selection options (glass lined, Ta lined steels)

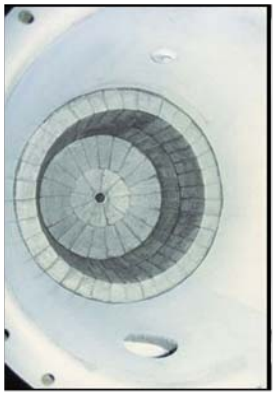
• **HI section** - Glass lined steel at lower temperatures, ceramic lined coated steel at high temperatures
• **Bunsen** - Glass lined steel worked well, teflon fittings not suitable
• **H2SO4** – SiC bayonet, glass lined steel worked well

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

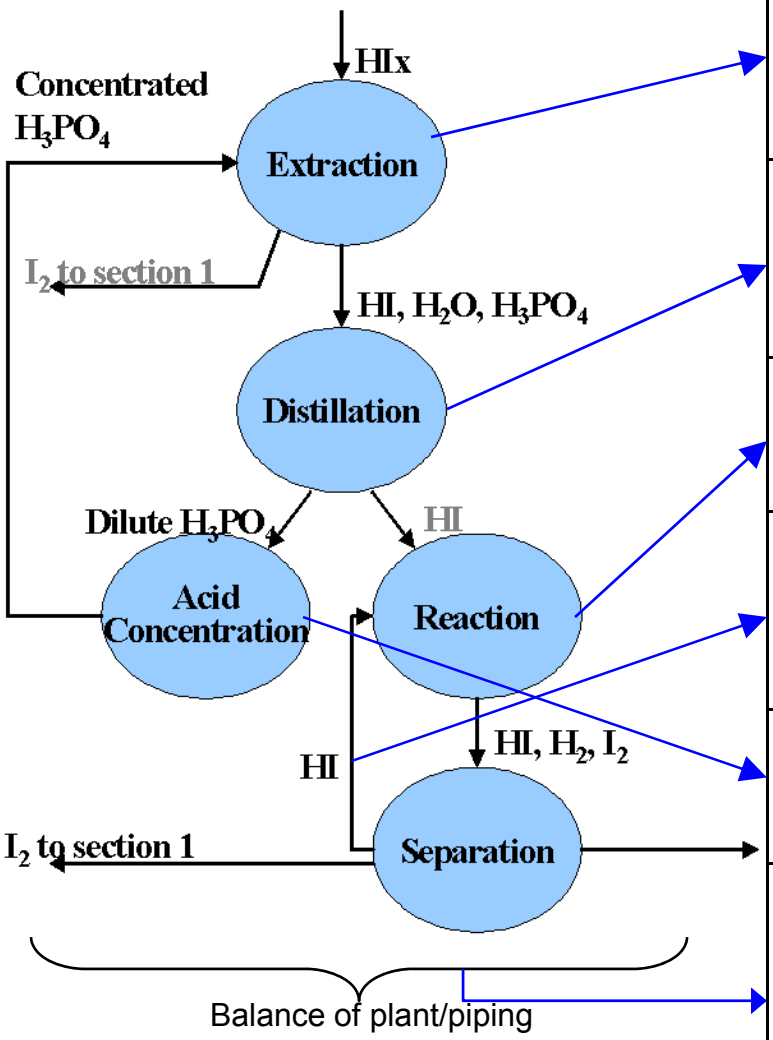

b. - FlowSiC shell and tube heat exchanger


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®) Ta alloys, Ta coated steel Nb alloys, Nb coated steel Ceramics	Ta-10%W pipe
Lined steel[a] Brick lined, coated steel Ta alloys, Ta coated steel Ceramics	Ta-10%W pipe
Hastelloy B2, B3, C276 Brick lined, coated steel Ceramics	Hastelloy C276 pipe
Lined steel Ta alloys, Ta coated steel Nb alloys, Nb coated steel Ceramics	Ta-10%W pipe
Hastelloy B2, B3, C276 Ta alloys, Ta coated steel Ceramics	Ta-10%W pipe
Lined steel Ta alloys, Ta coated steel Nb alloys, Nb coated steel Glass lined, ceramic lined	Ta-10%W tube 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 (H_2SO_4) phase acids of correct composition. GA completed multiple H_2 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 H_2SO_4 catalysts will also be conducted.*