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**

1. \( \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \)
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. \( \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \)
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

**ILS Approach**

**Develop, test 3 reaction sections**
- HI decomposition - extractive distillation (Gen Atomics)
- H$_2$SO$_4$ – SiC bayonet decomposer and concentrator (SNL)
- Co-current Bunsen reactor (CEA)

**Integrate 3 sections at GA**
- Experiment facility at GA completed FY06
- H$_2$SO$_4$ 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

• **H₂SO₄ 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 SO₂ at 40 mole %, SO₂ 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 (H₂ generation) in absence of I₂ demonstrated
  – Liquid extraction experiments on I₂ -- 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 I₂, H₂0
  – I₂, SO₂ 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

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

### Equations
1. \( 
   \text{H}_2\text{SO}_4 \text{ (l)} \rightarrow \text{H}_2\text{O} \text{ (g)} + \text{SO}_3 \text{ (g)} \quad \sim 500 \text{ C} 
   
2. \( 
   \text{SO}_3 \text{ (g)} \rightarrow \text{SO}_2 \text{ (g)} + \frac{1}{2}\text{O}_2 \text{ (g)} \quad \sim 850 \text{ C} 
   
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### Diagram

- **Flowchart:**
  - **SO$_2$, O$_2$ to Bunsen section**
  - **Water to Bunsen section**
  - **Gas-liquid separation**
  - **Heat exchanger**
  - **Central Storage skid**
  - **Acid concentrator**
  - **SiC cathode integrated decomposer**
  - **Acid demister separator**
  - **Recycled acid**
  - **H$_2$SO$_4$ in**
  - **SO$_2$, O$_2$, H$_2$O out**

- **Pressurized ~2.2 bar**
- **Vacuum ~0.05 bar**

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- **Heat Exchanger**
- **Central Storage skid**
- **Acid Concentrator**
- **SiC Cathode Integrated Decomposer**
- **Acid Demister Separator**
- **Recycled Acid**
- **H$_2$SO$_4$ in**
- **SO$_2$, O$_2$, H$_2$O out**
- **Bayonet**
- **Concentrated Acid Tank**
- **Acid separator**

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**Additional Details:**
- **70 – 90°C**
- **110 – 130°C**
- **140 – 180°C**
- **150 – 200°C**
Sulfuric Acid Decomposition Section

**Results**

**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

**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

![Graph showing SO$_2$ Production as Function of Acid Flow Rate and Concentration (0.69 meter Bayonet, 850 °C)]
• Recuperation of product stream heat with incoming acid stream
• Product stream output ~ 200 °C, SO₃ recombines at cold end, recycled
• Liquid acid components – commercially available glass, Teflon lined
Manifold multiple bayonet units in a tube and shell HX arrangement.

**Sulfuric Acid Decomposition Section**

**Bayonett Decomposer Scale up Approach**

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
Catalyst stability for extended operation remains a key issue.

- Supports studied: SiO$_2$, γ-Al$_2$O$_3$, ZrO$_2$, α-Al$_2$O$_3$ 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.

SO$_2$ yields over Pt/TiO$_2$ (left) and Pt/αAl$_2$O$_3$ (right) at 800 and 850 °C.

- CuCr$_2$O$_4$, NiCr$_2$O$_4$, FeTiO$_3$ - leaching problems.
- Activity of FeTiO$_3$ and NiFe$_2$O$_4$ decreased at the highest temperature.
- Cu Fe$_3$O$_4$ spinel promising at high temperatures.

SO$_2$ yields with temperature

WHSV = 50 g acid/g cat./hr

SO$_2$ production rate, 850°C

WHSV = 2,000 g acid/g cat./hr, 850°C
Section 3 - HI Decomposition

Overview

Extractive distillation method selected for HI decomposition
- Separates I$_2$ and H$_2$O from HI,
- Decomposes HI into H$_2$ and I$_2$,
- Return I$_2$ and H$_2$O to Section 1

Key Issues
- Uncertainty in HI/I$_2$/H$_2$O VLE
- High recycle water volumes
- H$_3$PO$_4$ concentrations to extract HI$_x$
- Materials – corrosion, catalysts

Recent Experiments
- Determine operating regime for H$_3$PO$_4$
- Determine effect of H$_3$PO$_4$ concentration and flow ratio on HI-H$_2$O extraction efficiency
- Corrosion testing for HI, I$_2$, H$_2$O environment
Section 3- HI Decomposition

HI Decomposition Parameter Experiments

- Effect of H$_3$PO$_4$ concentration and flow ratio on the HI-H$_2$O extraction efficiency

- H$_3$PO$_4$ operating space for the extraction and distillation sections over lap

Boiling point curve of concentrated H$_3$PO$_4$ 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 ($\text{HI}_x; \text{HI}_x + \text{H}_3\text{PO}_4; \text{conc. H}_3\text{PO}_4$) and Hastelloys ($\text{HI} + \text{I}_2 + \text{H}_2$) for Section III use

- Testing of processed Ta alloy parts in Iodine Separation ($\text{HI}_x + \text{H}_3\text{PO}_4$) and conc. $\text{H}_3\text{PO}_4$ 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. $\text{H}_3\text{PO}_4$ lead to corrosion in some candidates

- Stress corrosion testing of C-22 and C-276 in HI Decomposition ($\text{HI} + \text{I}_2 + \text{H}_2$) showed no crack initiation; crack growth testing is on going
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** - increase 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 H₂ 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 H₃PO₄.
Primary reaction of SO₂, H₂O and I₂ to form HI and H₂SO₄
Delivers HIₓ (HI, H₂O, I₂) to section 3 (lower phase)
Delivers H₂SO₄ 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
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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
9/2008 | 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)
• **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
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.