# ADVANCED REACTOR, FUEL CYCLE, AND ENERGY PRODUCTS WORKSHOP FOR UNIVERSITIES

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# Thermochemical Cycles

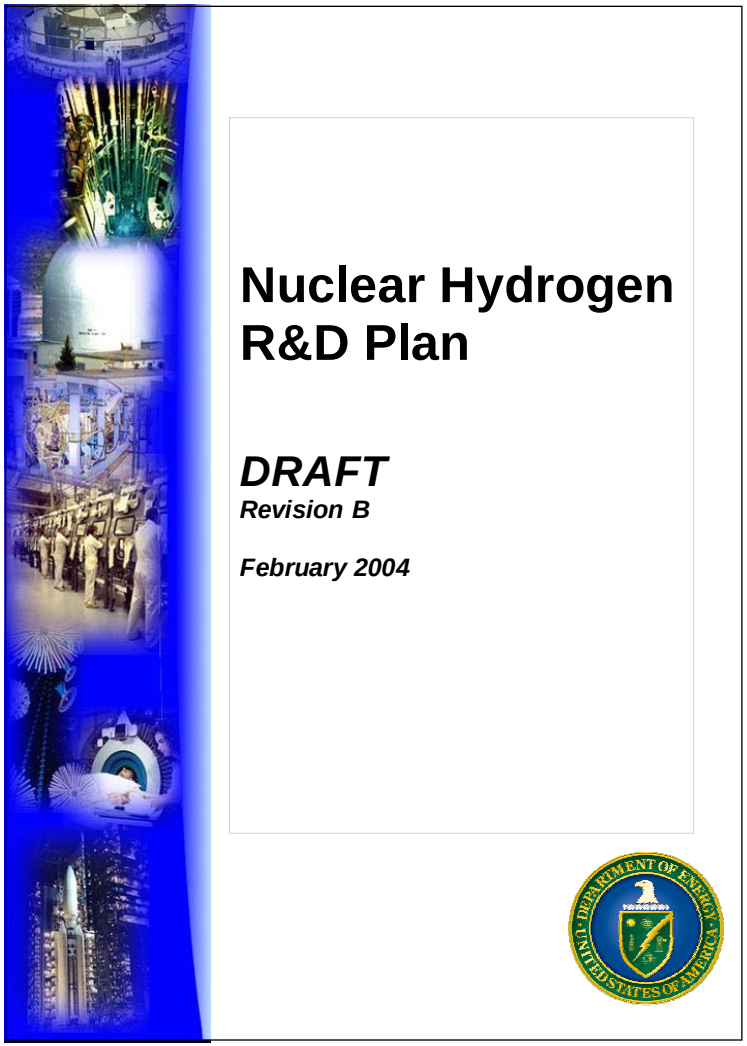
**Sandia National Laboratories**

***Workshop for Universities***
***Hilton Hotel, Gaithersburg, MD***
***March 4, 2004***

# NHI THERMOCHEMICAL CYCLE RESEARCH AREA INCLUDES

- **Develop thermochemical cycles for hydrogen production using high temperature nuclear reactor**
- **Thermochemical cycles (TC) for nuclear application**
  - Sulfur based cycles – Sulfur-Iodine (S-I), Hybrid Sulfur, Hybrid Sulfur- Bromine
  - Calcium-Bromine cycles – UT-3, variants of UT-3
  - Alternative cycles with potential for operation at lower temperatures or that have higher efficiency
- **Flowsheet Methodology**
  - Consistent flowsheet methodology for comparison of thermochemical cycles
- **High-temperature interface requirements for heat exchangers and materials**

# FY03 ACCOMPLISHMENTS - NHI R&D PLAN




- **Define Hydrogen production process R&D necesssary to demonstrate nuclear hydrogen production by 2017**
- **Primary research areas**
  - Thermochemical processes
  - High-temperature electrolysis
  - Systems interface and BOP
- **Two-tiered approach to reduce risk**
  - Baseline processes
  - Alternate processes
- **Three-phased scaling approach**
  - Laboratory-scale (<5 kW)
  - Pilot plant (500 kW - 1 MW)
  - Engineering-scale (20-50 MW)
- **Coordinated with other DOE Offices**

# FY03 ACCOMPLISHMENTS - TC CYCLES

- **Thermochemical cycles identified as promising approach for nuclear hydrogen production**

- **Thermochemical cycles**
  - **Series of chemical reactions to split water at lower temperatures than direct dissociation**
  - **Heat and water in, hydrogen and oxygen out**
  - **Favorable scaling (volume)**
  - **High efficiencies**
  - **Thermal energy process**
  - ***High temperature***
  - ***Corrosive components***
  - ***Limited R&D since 1980's***

$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2$ (850 C)

$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ (~120 C)

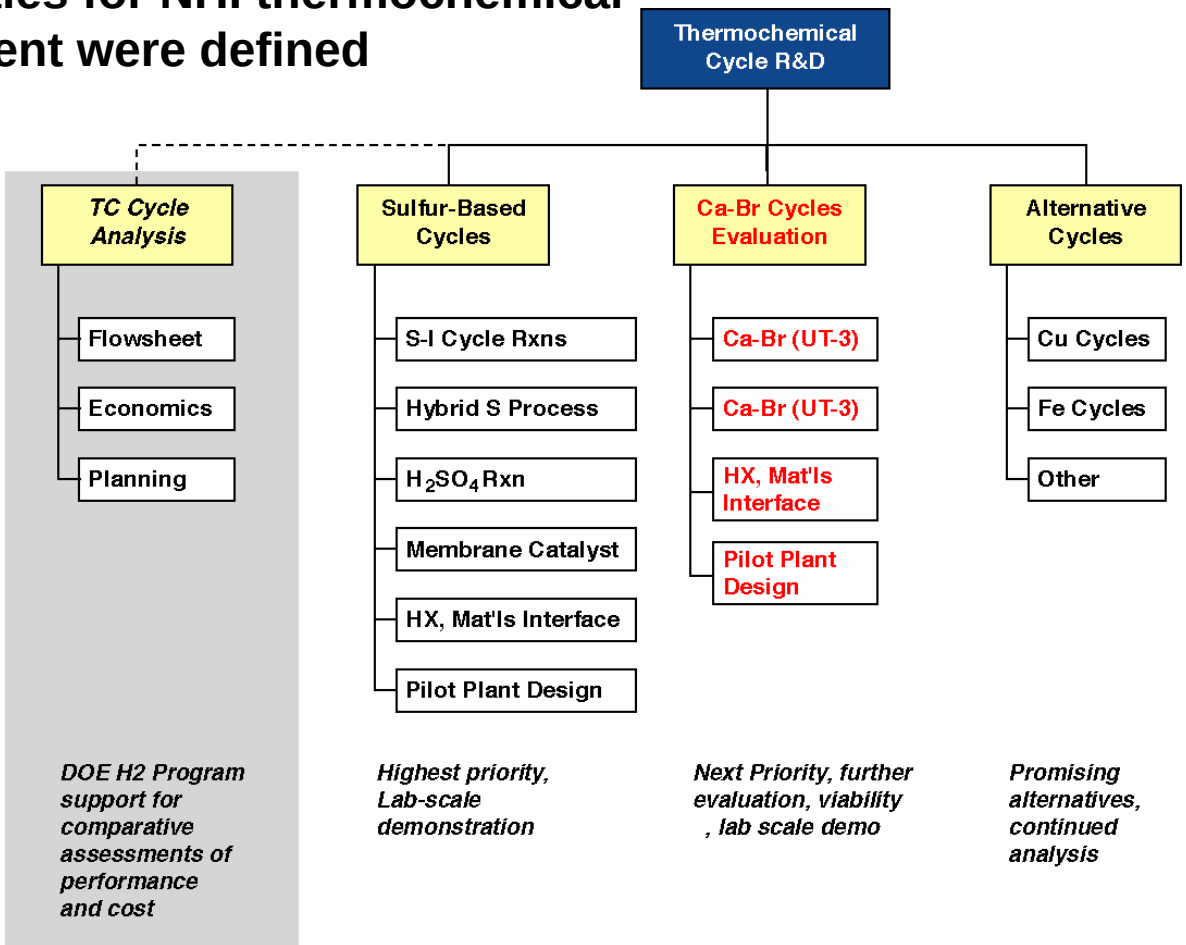
$2HI \rightarrow H_2 + I_2$ (~400 C)

$H_2O \rightarrow 1/2O_2 + H_2$ (Net)

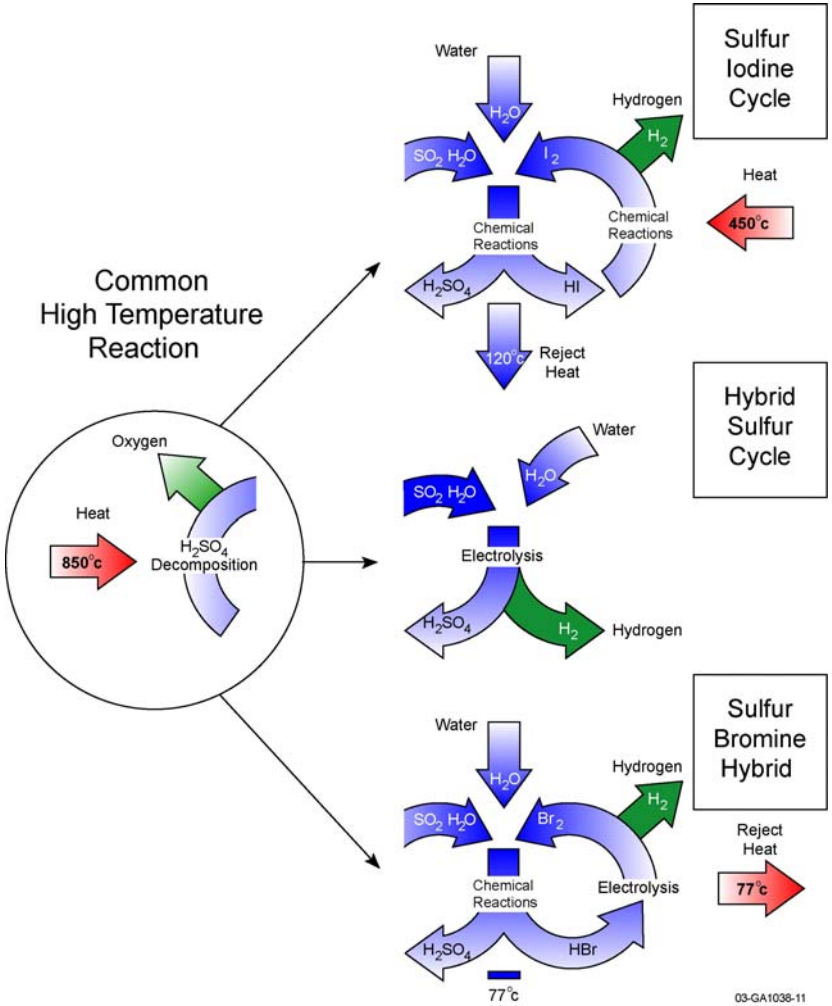
**Sulfur – Iodine Thermochemical Cycle**

# FY03 ACCOMPLISHMENTS - TC R&D AREAS

**Research priorities for NHI thermochemical cycle development were defined**



# FY03 ACCOMPLISHMENTS - SULFUR "FAMILY"

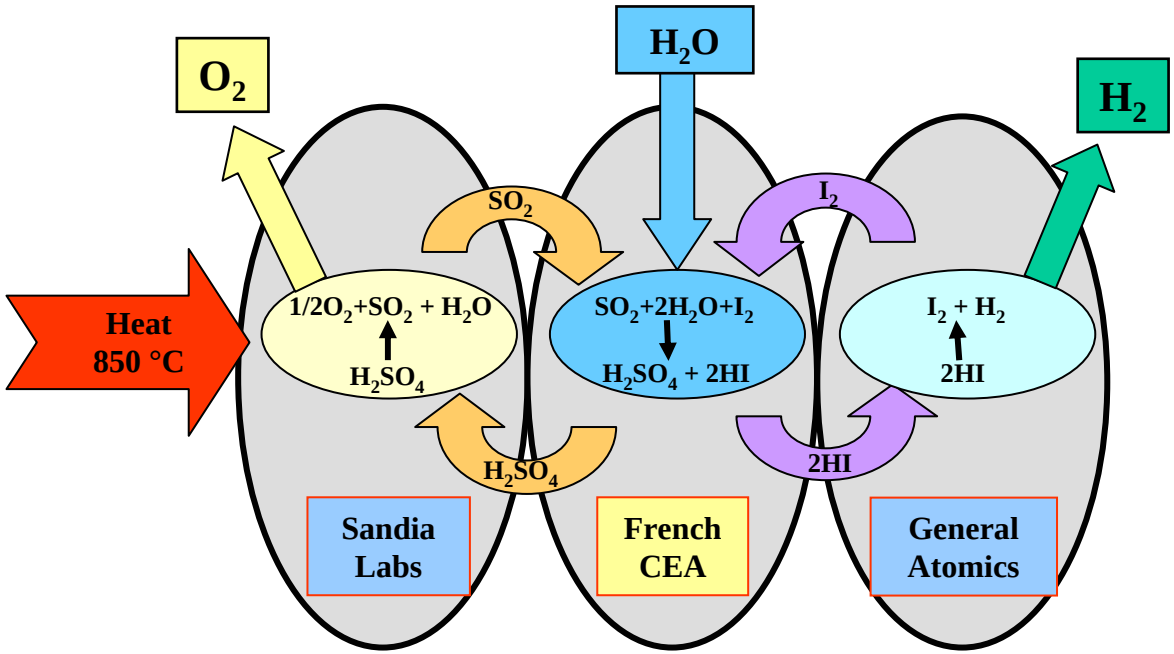



- **Sulfur "Family" of cycles selected as highest priority baseline processes**
  - Sulfur Iodine
  - Hybrid Sulfur
  - Sulfur Bromine
- **High overall efficiencies**
- **Most extensively demonstrated thermochemical processes**
- **Reduced risk based on number of process options**

# FY03 ACCOMPLISHMENTS - S – I PROCESS

♦ **Initiated Sulfur-Iodine thermochemical cycle development. (INERI – CEA, GA, SNL)**

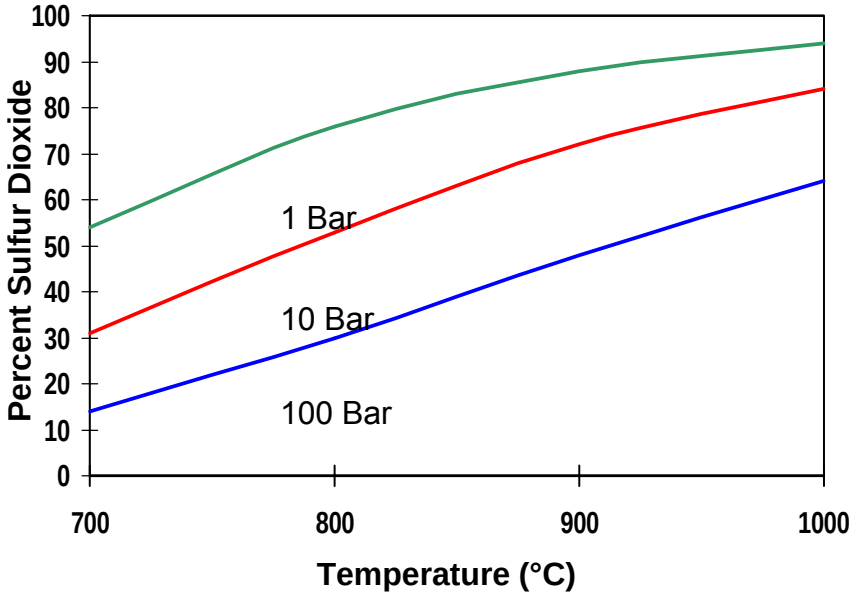
- Developed reference S-I system flowsheet
- Identified component reaction section design requirements
- Preliminary design of $H_2SO_4$ and HI decomposition sections
- Identified candidate high-temperature materials

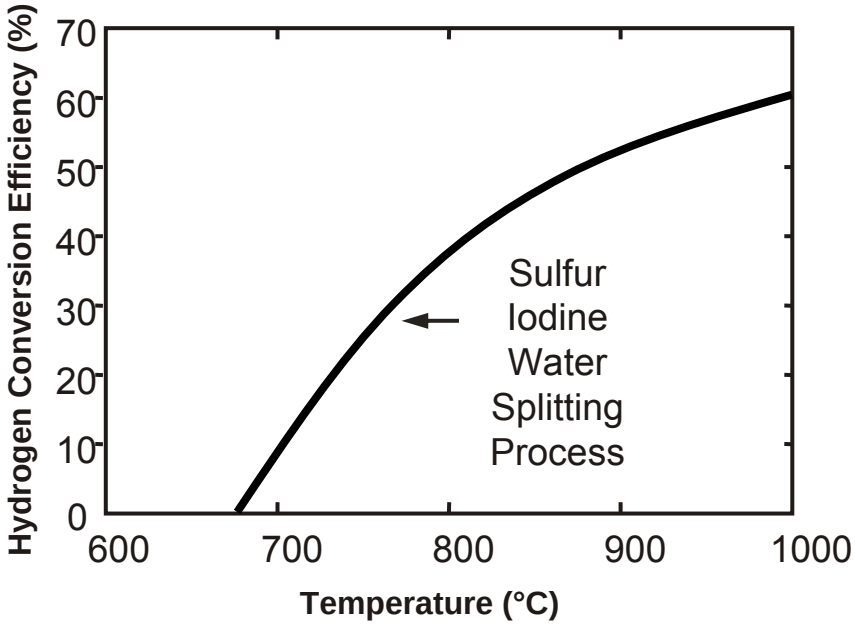


# FY03 ACCOMPLISHMENTS - S-I EFFICIENCY

**Temperature effect on cycle efficiency key issue for Sulfur cycles.**

$H_2SO_4 \Leftrightarrow SO_3 + H_2O \Leftrightarrow SO_2 + H_2O + 1/2\ O_2$




**Process step efficiency issues identified for FY04 evaluation.**

# WORK IN PROGRESS FOR FY04 (TASK AREAS)

## Develop thermochemical cycles for nuclear hydrogen production

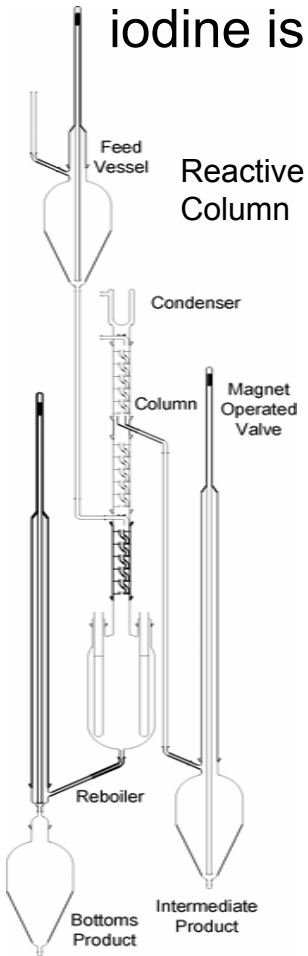
- **Flowsheet Methodology Assessment**
- **Thermochemical Process Evaluation**
- **Sulfur-Iodine Cycle**
  - Flowsheet analysis, laboratory-scale experiments
- **Hybrid Sulfur**
  - Conceptual design, electrolyzer technology assessment
- **Calcium – Bromine Cycle**
  - Flowsheet analysis, conceptual design
- **High Temperature Membrane Assessment**
- **High Temperature Heat Exchangers**
- **Materials for Thermochemical cycles**

# WORK IN PROGRESS FOR FY04 (TASKS)

- **Flowsheet Methodology Assessment (ANL)**
  - Establish consistent flowsheet analysis for evaluation of NHI thermochemical cycles (FY04 start)
- **Thermochemical Process Evaluation (ANL)**
  - Initial NHI flowsheet analysis implementation (FY04 start)
- **Sulfur-Iodine Cycle (SNL, General Atomics)**
  - Flowsheet analysis for alternative approaches to $H_2SO_4$ and HI decomposition sections
  - Laboratory experiments to demonstrate key technologies and components for HI and $H_2SO_2$ sections
  - Engineering materials testing program definition
  - Final design for lab-scale demonstration experiments

# WORK IN PROGRESS FOR FY04 - HI SECTION

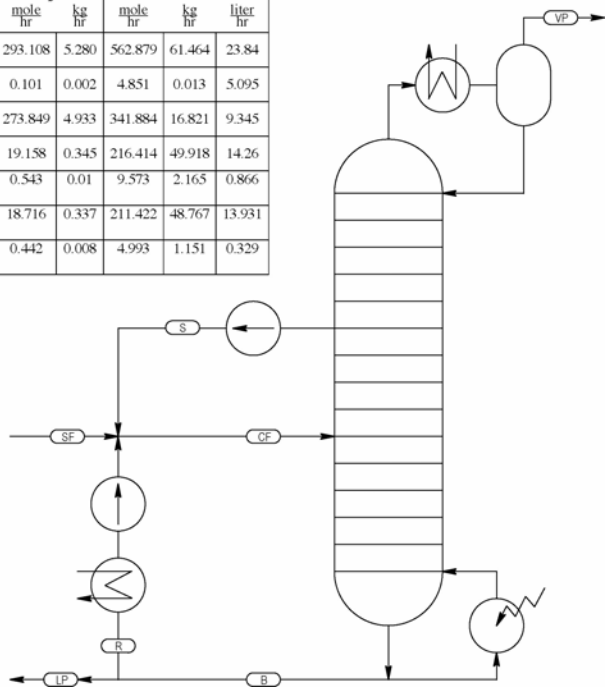
HI separation and decomposition challenging. 16% of hydrogen iodine is decomposed, remaining hydrogen iodine is recycled




Reactive distillation Column

| | T | P | HI | | $H_2$ | | $I_2$ | | $H_2O$ | | Total | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | °C | bar | mole/hr | kg/hr | mole/hr | kg/hr | mole/hr | kg/hr | mole/hr | kg/hr | mole/hr | kg/hr | liter/hr |
| Column Feed | 262 | 22 | 55.586 | 7.110 | 0 | 0 | 214.184 | 54.362 | 293.108 | 5.280 | 562.879 | 61.464 | 23.84 |
| Vapor Product | 25 | 22 | 0.018 | 0.002 | 4.461 | 0.009 | 0 | 0 | 0.101 | 0.002 | 4.851 | 0.013 | 5.095 |
| Sidedraw | 251 | 22 | 42.735 | 5.466 | 0 | 0 | 25.299 | 6.421 | 273.849 | 4.933 | 341.884 | 16.821 | 9.345 |
| Bottoms | 310 | 22 | 3.91 | 0.500 | 0 | 0 | 193.347 | 49.073 | 19.158 | 0.345 | 216.414 | 49.918 | 14.26 |
| System Feed | 25 | 22 | 9.03 | 1.155 | 0 | 0 | 0 | 0 | 0.543 | 0.01 | 9.573 | 2.165 | 0.866 |
| Recycle | 310 | 22 | 3.82 | 0.489 | 0 | 0 | 188.886 | 47.941 | 18.716 | 0.337 | 211.422 | 48.767 | 13.931 |
| Liquid Product | 310 | 22 | 0.09 | 0.011 | 0 | 0 | 4.461 | 1.132 | 0.442 | 0.008 | 4.993 | 1.151 | 0.329 |

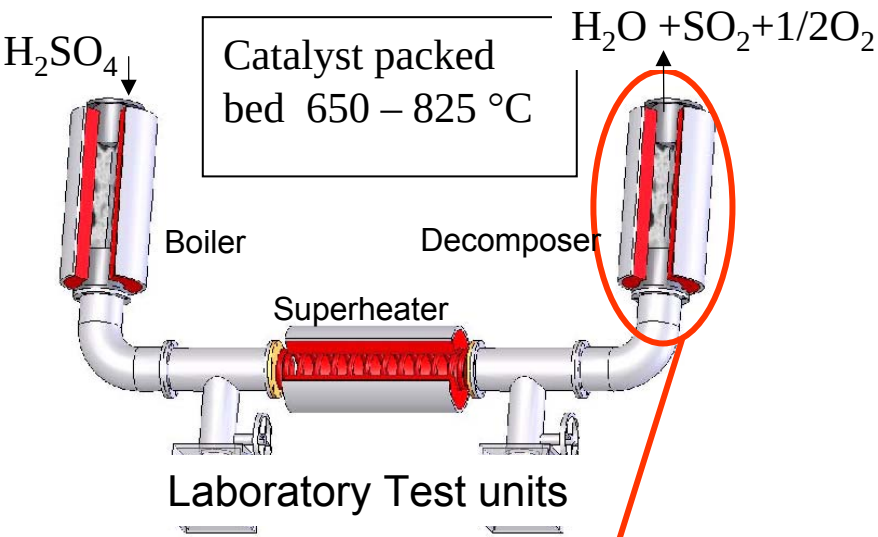
- Reactive distillation is being investigated for HI decomposition.
- Laboratory experiment (glassware) addresses viability
- Extractive distillation, electrodialysis, membranes being examined

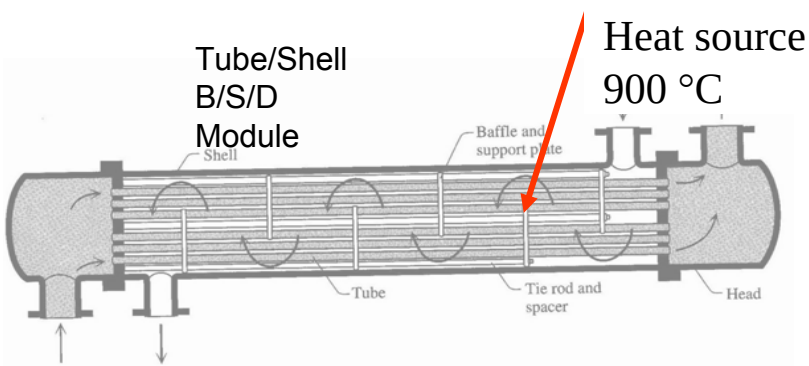


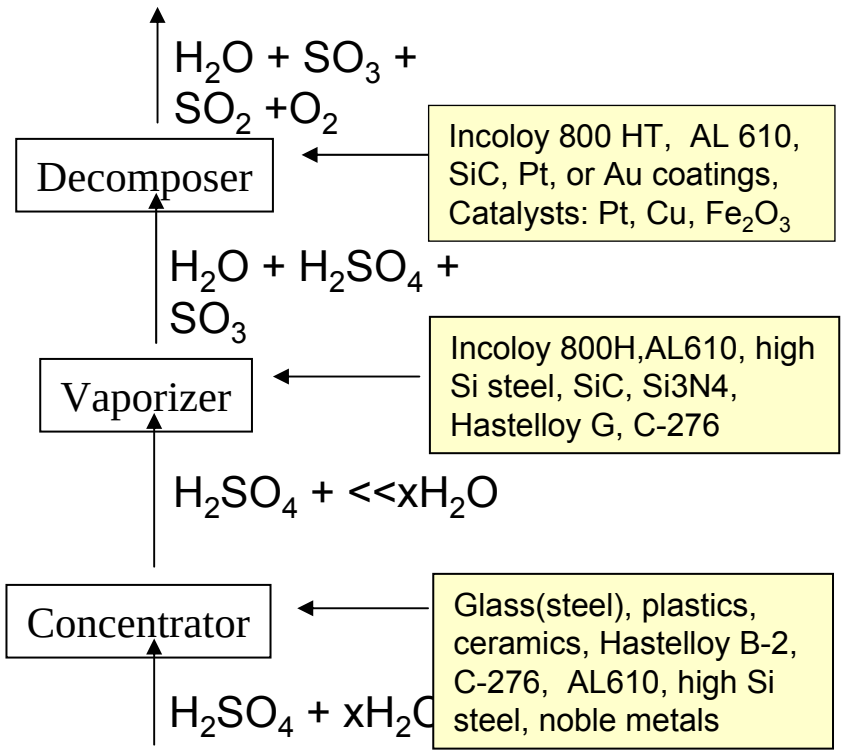

Reactive distillation flowsheet

# WORK IN PROGRESS FOR FY04 - $H_2SO_4$ SECTION

$H_2SO_4$ decomposition common to all Sulfur family cycles. Important materials issues for each phase.

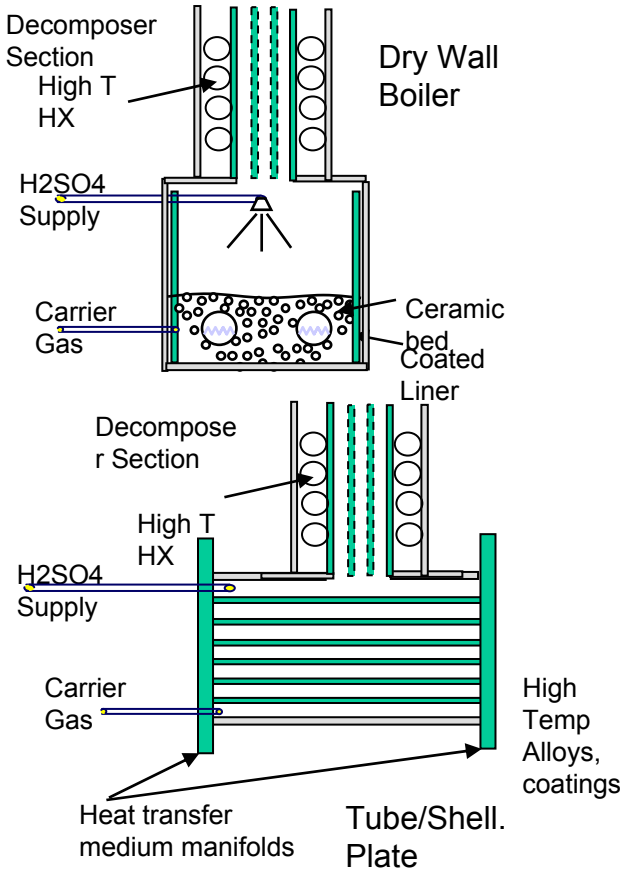


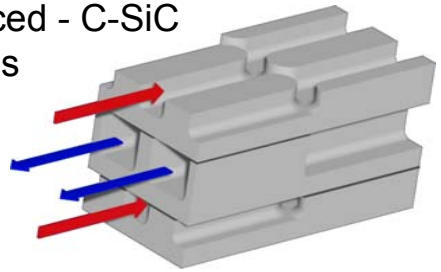
# WORK IN PROGRESS FOR FY04 – HX, MATERIALS

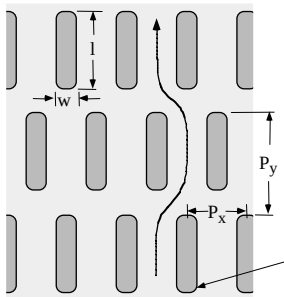
Innovative heat exchanger designs, materials will be evaluated



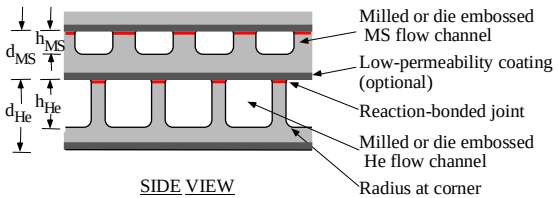

•Printed Circuit-Heatrix

•Advanced - C-SiC materials






Offset-fin C-SIC Composite plate heat exchanger

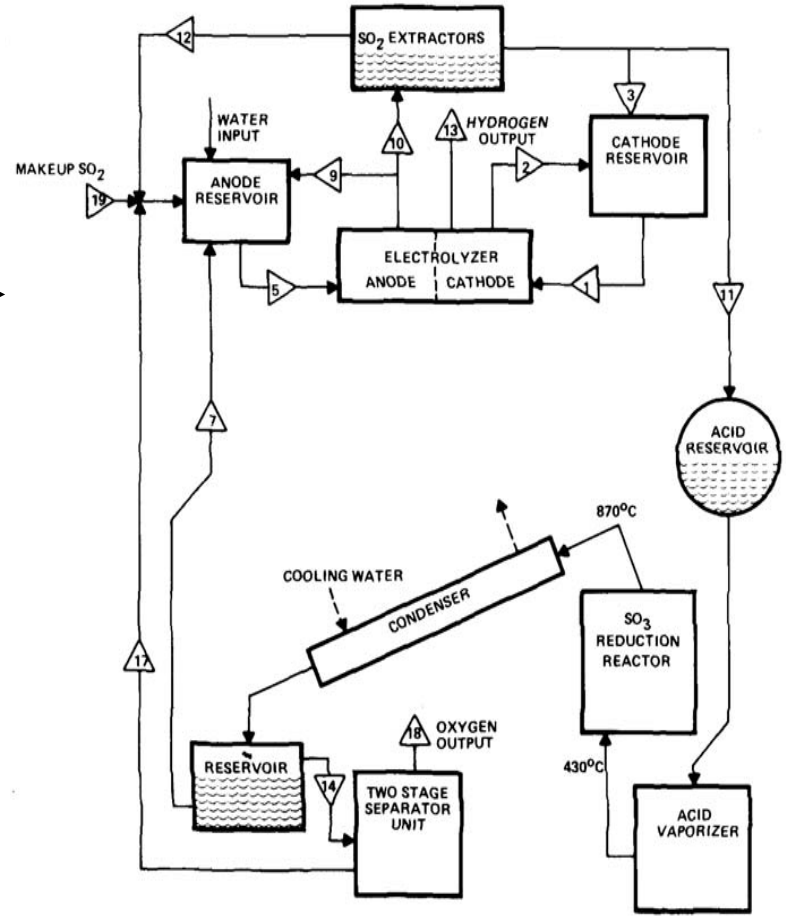


# WORK IN PROGRESS FOR FY04 – MATERIALS

| Process Regime | Conditions | Candidate Materials | Compatibility | Comments |
|---|---|---|---|---|
| **$H_2SO_4$ Concentration** | 300 – 450K, 50%<br>300 – 420K, 50-75%<br>450-700K 75-95%<br>($H_2SO_4$, iodine species, impurities) | Glass lined steel, plastics, ceramics<br>Hastelloy B-2, C-276<br>Incoloy 800H, AL610, high Si steel, Au or Pt plating | Hastelloy B-2 < 0.1 mm/yr for concentrations up to 60%<br>High Si steel corrosion ~0.1 mm/yr for concentrated acid, higher for low concentrations | Concentration requires different materials<br>Options identified for most<br>Coatings, platings<br>B-2 @ low conc<br>High Si steel fab issues |
| **$H_2SO_4$ Vaporization**<br>**H2O+SO3** | 600 – 800K,<br>Contaminants,iodine | Structural: Incoloy 800H<br>AL610, high Si steel,<br>SiC, Si3N4<br>Hastelloy G, C-276 | 800H, 800 HT<br>High Si steel (SiO2)<br>~ no corrosion in 1000hr test @75 to 95% acid (JPN)<br>C-276 ~1mm/yr @ 476 hrs | Coated materials (Pt) cost issue<br>Ceramics promising<br>Dry wall boiler design<br>Data needed with iodine contamination |
| **$H_2SO_4$ Decomposition** | 800 – 1200K,<br>$H_2O$, $H_2SO_4$, $SO_3$, $SO_2$, $O_2$<br>Contaminants,iodine | Structural: Incoloy 800 HT, Inconel 800 H (with Aluminide coatings), AL 610<br>ceramics, Pt, or Au coatings<br>Catalysts: Pt, Cu, $Fe_2O_3$ | Incoloy, Inconel Bare – 2 to 4 mg/cm2, 1000 hr-1173K<br>Aluminide coatings – approx 1 mg/cm2 in 1000 hr @ 1173<br>Intergranular corrosion observed for 800 H<br>Noble metal coatings | Incoloy 800HT-address intergranular corrosion<br>C-SiC composites should be examined<br>Pt coating may serve function of catalyst and reduce corrosion |

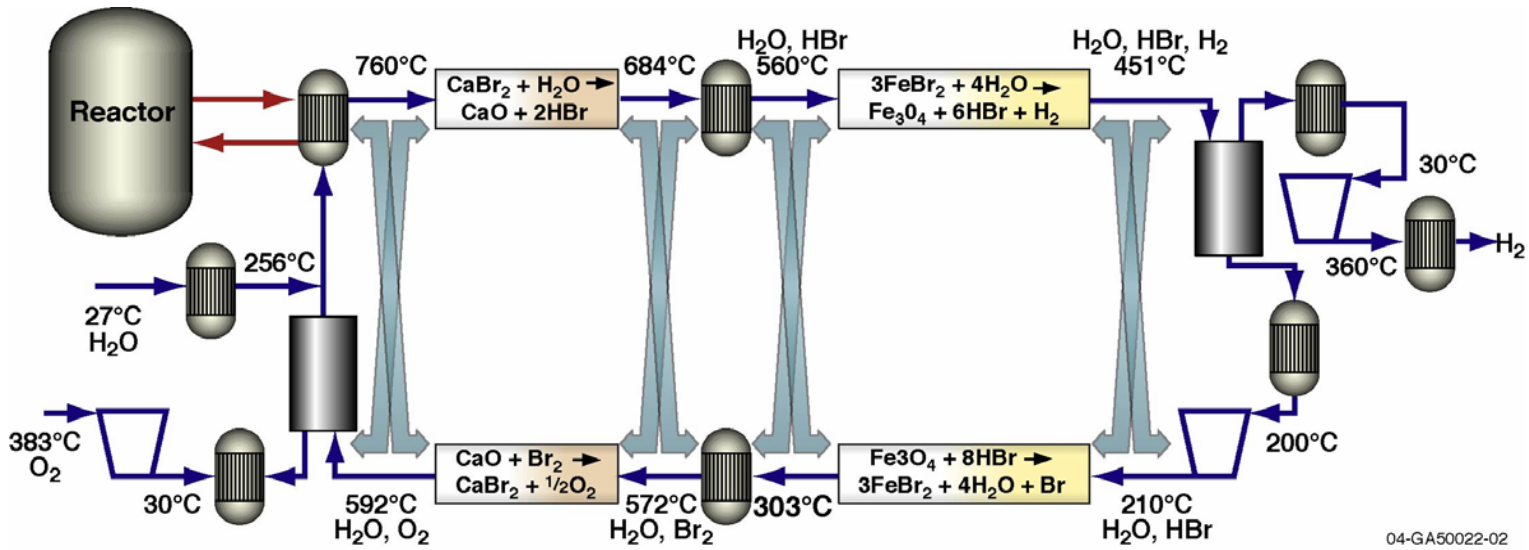
# WORK IN PROGRESS FOR FY04 - HYBRID SULFUR

- **Hybrid Sulfur Cycle Assessment -- $2H_2O + SO_2 \longrightarrow H_2 + H_2SO_4$**
  - **Least complex thermochemical cycle**
  - **Thermochemical and electrolysis step – hybrid scaling**
  - **1970s (Westinghouse) demonstration 200 hours at ambient pressure.**
  - **Potential for improvement in cell efficiency.**
  - **Issues – H2SO4 decomposition, electrolzer design, materials**
  - **FY04 – system conceptual design , electrolyzer technology assessment**



# WORK IN PROGRESS FOR FY04 – Ca-Br CYCLE

Calcium - Bromine cycle assessment (UT-3 -Japan, modified UT-3).

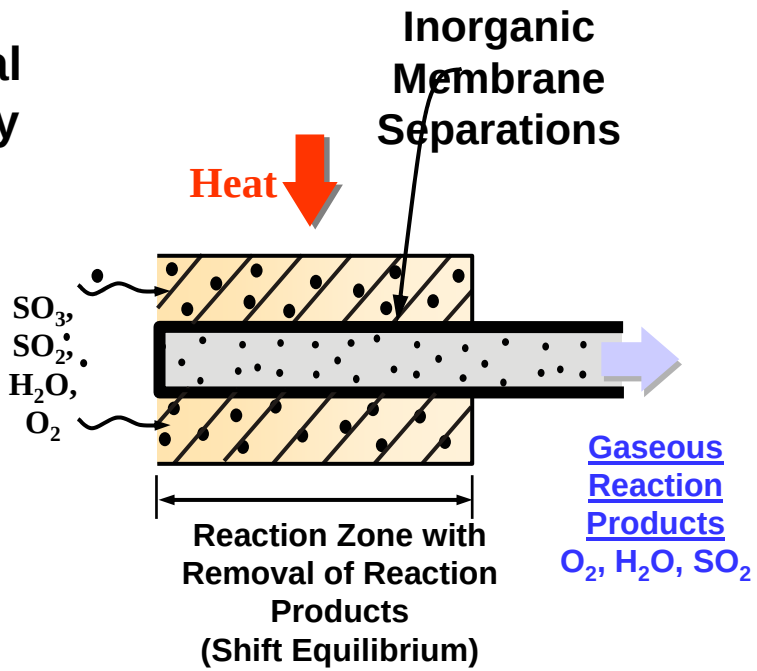



- **Lower temperature process (750ºC)**
- **Solid – gas reactions**
- **Flowsheet analysis and conceptual design for most promising cycle**
- **Solid reaction bed stability for cyclic reactions issue**
- **Alternative H2 generation reactions – electrolytic and cold plasma**

# WORK IN PROGRESS FOR FY04 - MEMBRANES

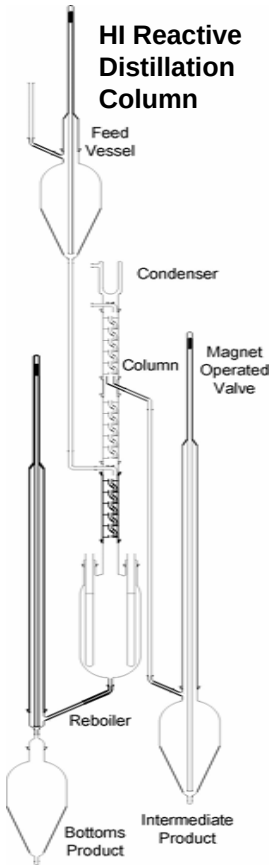
## Membrane assessment for high temperature thermochemical cycles (ORNL)

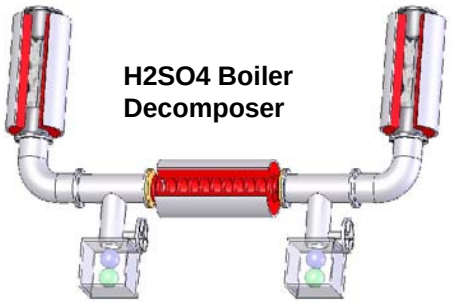
- **Efficiency or viability of thermochemical cycles may be significantly improved by membrane separations**
  - Removal of reaction products to reduce temperature requirements
  - Separations to reduce recycle volumes
- **Significant advances in membrane technology since 1980**
- **Temperature range and corrosive environment present new issues -- no data for sulfur systems**
- **Prelimianry evaluation indicates viability.**

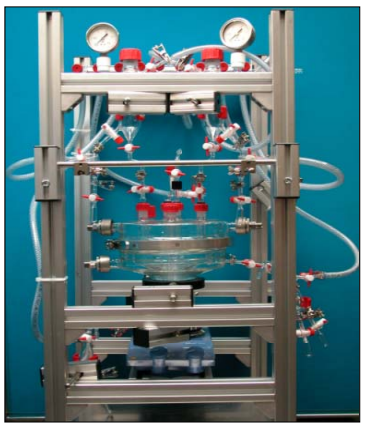


# PLANS FOR FY05–07 - LAB SCALE S-I EXPERIMENT

- **The focus of thermochemical research for the next 3 years will be on lab scale demonstration of candidate processes.**
  - **Prototypic conditions, engineering materials**
  - **Component reaction experiments FY2005**
  - **Integrated lab scale demonstration operation in FY2007 (100 l/hr)**
  - ***Pilot plant decision by FY2012***



Primary Reactor (CEA)

# PLANS FOR FY05–07 – LAB SCALE S-I EXPERIMENT

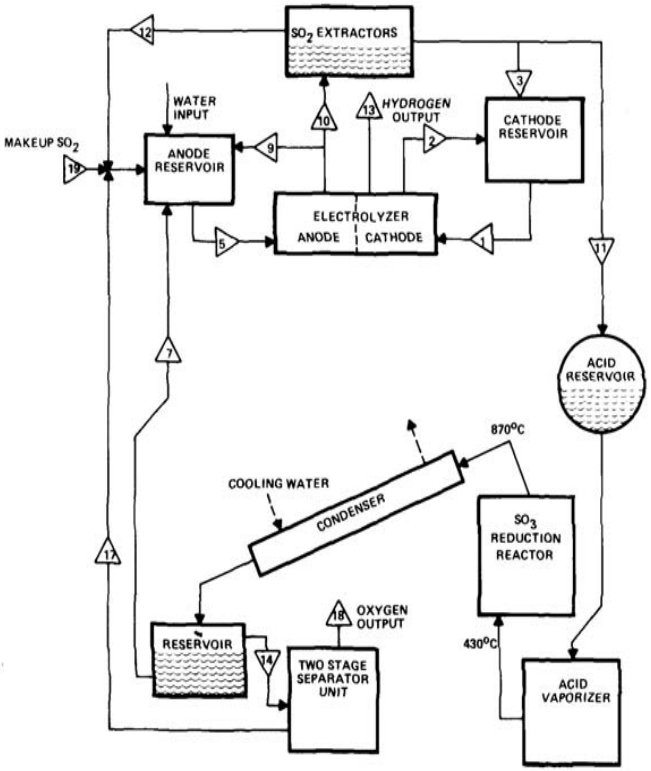
**S-I integrated laboratory scale demonstration (100 l/hr)**

- Construction and testing of HI and $H_2SO_4$ components (SNL, GA, FY05)
- Materials testing for high temperature $H_2SO_4$ service and HI compatibility (UNLV, FY05-07)
- Membranes development for $H_2SO_4$ reaction products separation at temperature and HI recycle reduction (ORNL, FY05-07)
- Development of components and control system for integrated lab scale experiments (CEA, SNL, GA) FY06
- Conduct integrated S-I cycle demonstration experiments (CEA,SNL, GA - FY07)

# PLANS FOR FY05 – 07 - HYBRID SULFUR

## Hybrid Sulfur lab scale demonstration

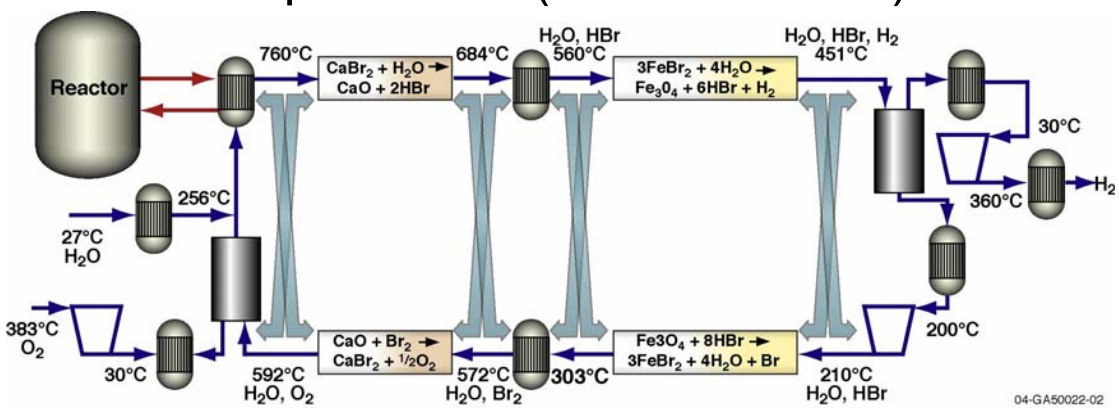
- Hybrid sulfur conceptual design, cost assessment (FY05)
- Electrolyzer cell design, construction (FY05)
- Electrolyzer materials development, testing (FY05-07)
- Lab scale $H_2O$ + $SO_2$ electrolyzer experiments (FY06)
- Construct integrated hybrid sulfur demonstration (FY07)



# PLANS FOR FY05 – 07 - Ca-Br CYCLE

**Calcium – Bromine lab scale demonstration experiments**

- Calcium -Bromine
  - Investigation of alternative H2 generation processes for Ca-Br – electrolysis, plasma (ANL, FY05-07)
  - Conceptual Ca-Br system design and preliminary cost evaluation (ANL – FY05)
  - Lab-scale experiments component reaction experiments (ANL- FY06)
  - Integrated demonstration experiments (ANL- FY07-08)



# PLANS FOR FY05 - 07

## Alternative thermochemical process flowsheet evaluation

| | Peak Temp (°C) | Number of Reactions | Reported Flowsheet Efficiency % * | Cycle Status | Advantages | Key Issues |
|---|---|---|---|---|---|---|
| **Promising Alternatives** | | | | | | |
| Copper-chlorine hybrid | 550 | 4 | 46 (Est.) | Rxn demo | Low peak temperature | Higher efficiency electrolysis |
| Iron-chlorine | 650 | 3 | 47-49 (Est.) | Rxn Demo | Low peak temperature | Need to suppress competing chemical reactions[8] |
| Copper – sulfur hybrid | 827 | 5 | 68-73 (Est.) | Rxn demo | Potential for high efficiency | Economics of scaling hybrid processes<br>Higher efficiency electrolysis |
| Vanadium-chlorine | 925 | 5 | 40.5-42.5 | Rxn demo | Potential for improvement ($O_2$ membrane) | Very-high-temperature Oxygen membrane<br>Conflicting data on one reaction |

# BUDGET (FY04)

## FY04 NHI Thermochemical Cycle Budget

| Thermochemical Cycle Tasks | Organizations | FY2004 Budget |
|---|---|---|
| | | |
| Thermochemical Methodology | ANL | 150 |
| Process Evaluation | ANL | 100 |
| Sulfur Iodine Cycle* | SNL/GA | 730 |
| Hybrid S Cycle | TBD | 150 |
| Ca-Br Cycle | ANL | 250 |
| Membrane Assessment | ORNL | 75 |
| Heat Exchanger | UNLV | 450 |
| Materials | UNLV | 525 |
| | | |
| Total | | 2430 |

* INERI (750K$)