UT-BATTELLE

Materials for High-Temperature Thermochemical Processes

D. F. Wilson & W. R. Corwin, Oak Ridge National Laboratory

S. Sherman & J. Kolts, Idaho National Laboratory

P. Pickard, Sandia National Laboratory

DOE Hydrogen Program Annual Review

Crystal City, Virginia

May 23-26, 2005

PDP20

NHI Materials for TC Processes Task Focuses on Planning & Coordinating

Timeline

- Project start date FY04
- Project end date FY08
- Percent complete ~10%

Barriers

- Thermochemical (TC) process service environments
  - High temperature
  - Corrosive
  - Lack of sufficient testing capabilities for TC conditions

Budget

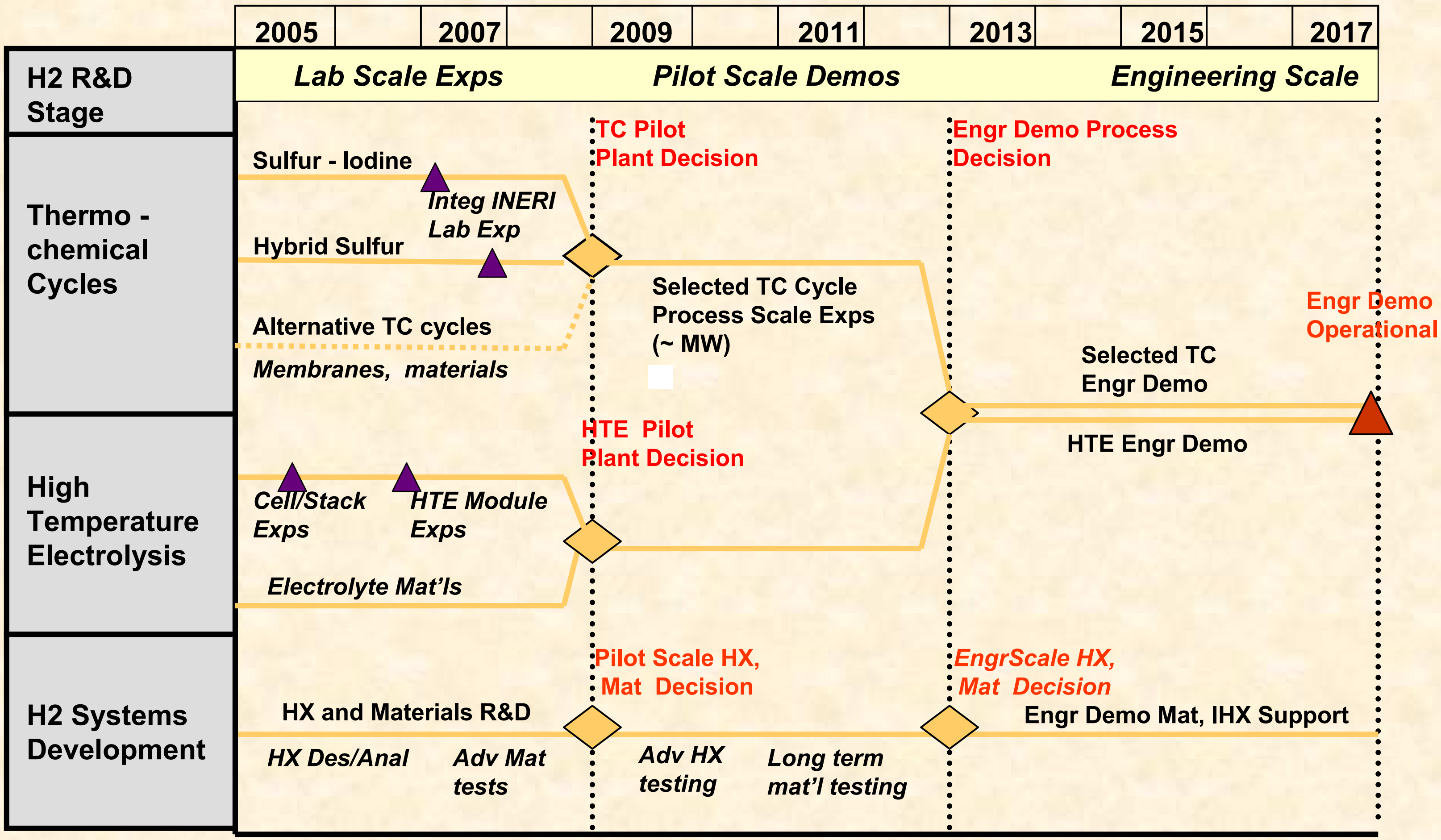
- Total project funding – 1M$
  - DOE share: 1M
  - Funding received in FY04: 0.05M
- FY05 Funding: 0.1M

Partners

NHI TC Program

- Industry (GA, Cerametec)
- Universities (UNLV, MIT, UCB)
- Labs (INL, ORNL, SNL)

NHI Materials for TC Processes Plans and Coordinates R&D through FY 2008



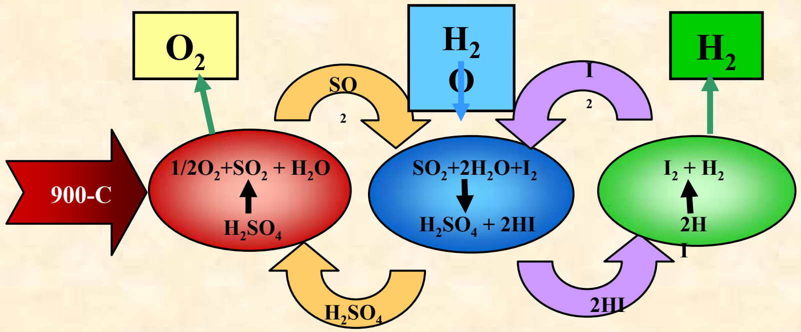
Objectives of Materials for High-Temperature Thermochemical Processes Are:

- Assess range of service conditions for NHI Thermochemical processes (Sulfur cycles, Ca-Br, others)
- Identify candidate materials of construction for cycle components (alloys, ceramics, refractories)
- Develop materials testing approach and priorities to support NHI TC cycle development (NHI Materials Development and Testing Plan)
- Coordinate materials planning for NHI and monitor "evolving" research and development activities

System Interface and High Temperature Heat Exchanger Programs at INL & UNLV are part of this activity (S. Sherman, INL, coordinates)

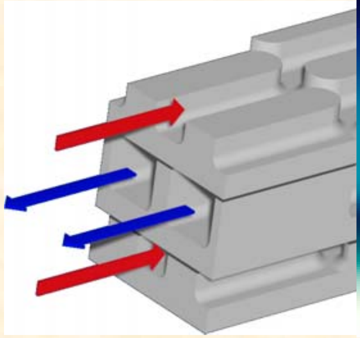
Thermochemical Cycle R&D Areas Include:

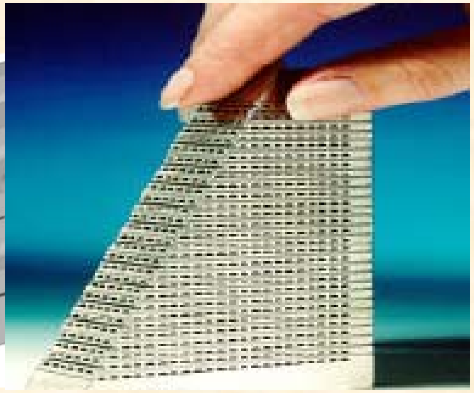
- Thermochemical Cycles *(Scaling, efficiency)*
  - *Sulfur cycles (S-I, Hybrid)*
  - *Alternate, Ca-Br*
- System Interface *(High temp materials and HX design*

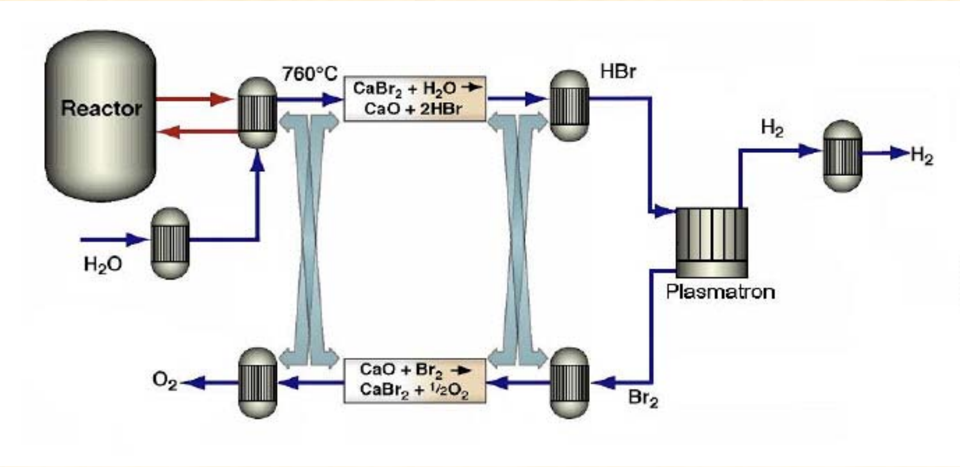


S-I Thermochemical Cycle

Interface Technologies (HX, Materials)







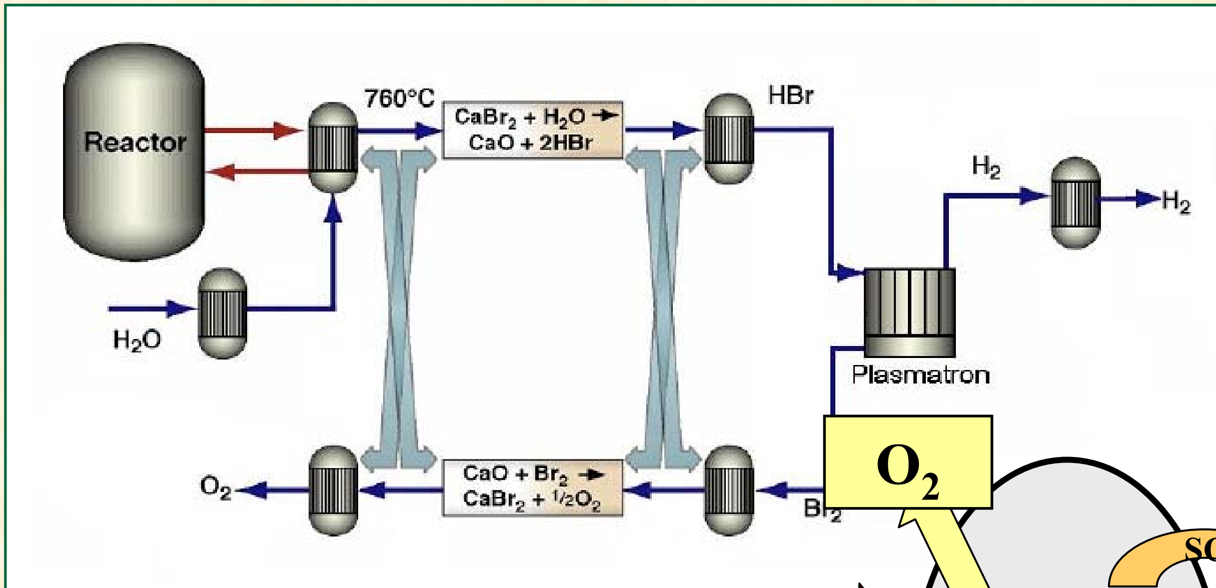
Calcium Bromine Cycle

Other TC Cycles with Potential for Lower Temperature or Higher Efficiency Include:

- Copper chlorine (GRI H-6)
  - <550°C; low peak temperature
  - Issue: higher efficiency electrolysis
- Iron chloride (Ispra Mark 9, GRI I-6)
  - 650°C; low peak temperature
  - Issue: suppress competing chemical reaction
- Iron chlorine (GRI B-1)
  - 925°C; more mature
  - Issue: suppress competing chemical reaction
- Copper sulfur (GRI H-5)
  - 827-900°C; potential for higher efficiency
  - Issue: economics of scaling hybrid processes; higher efficiency electrolysis
- Vanadium chlorine
  - 925°C; full flowsheet available
  - Issue: high peak temperature; conflicting data on one reaction

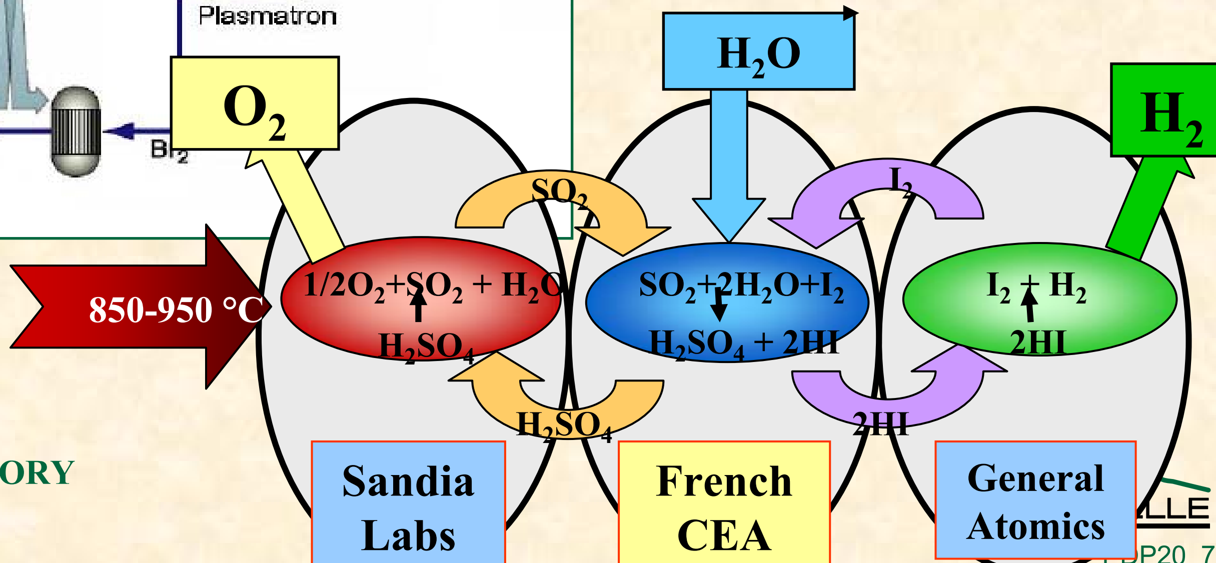
Approach to Planning & Coordinating Includes:

- Understand the chemistry and temperature of various process steps
- Identify possible materials for use in these steps
- Establish test program to evaluate the materials/process



Sulfur Iodine Cycle

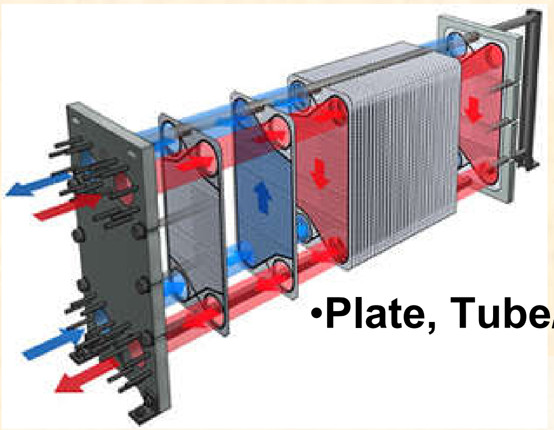
- *HI section (GA)*
- *H2SO4 Section (SNL)*
- *Bunsen (CEA)*
- *Materials (INL, ORNL, Univ, Ind)*



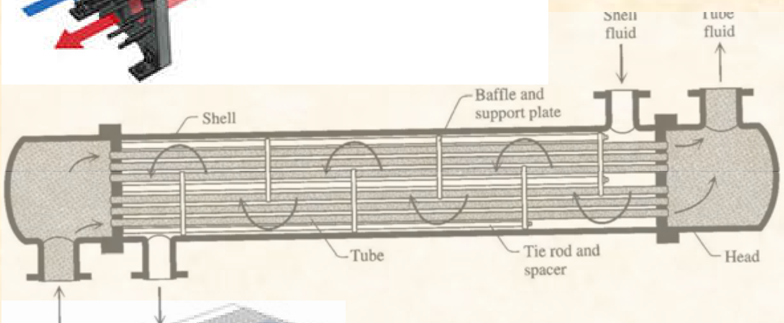
Materials for High-Temperature Thermochemical Processes - Technical Accomplishments Include:

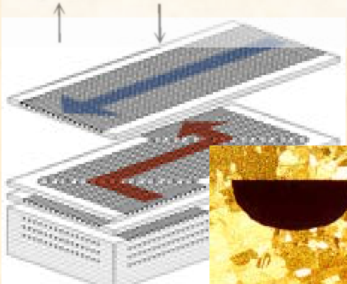
- Completed assessment of NHI TC cycle service conditions, candidate materials
- Issued report: Materials Requirements for Nuclear Hydrogen Generation Systems
  - Identifies chemistry and temperatures for key process steps
  - Identifies candidate materials for major component in NHI TC cycles
  - Identifies testing approach and prioritizes materials R&D needs

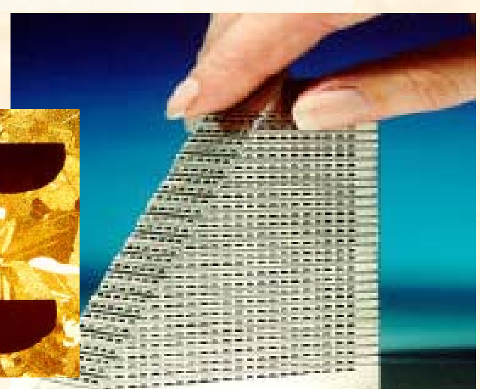
Heat Exchanger Materials and Design Are Key Issues for Thermochemical Cycles



- Plate, Tube/Shell

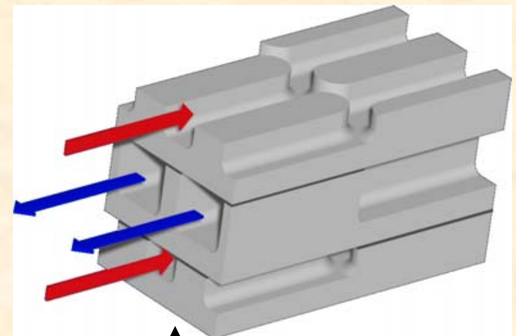






- Heatrix

- Advanced Ceramic Materials (SiC, C-SiC)



Offset-fin C-SIC Composite plate heat exchanger

$H_2O + SO_3 + SO_2 + O_2$

Decomposer ← Incoloy 800 HT, 610, SiC, Pt, or Au coatings, Catalysts: Pt, Cu, Fe_2O_3

Candidate Materials

$H_2O + H_2SO_4 + SO_3$

Vaporizer ← Incoloy 800H,AL610, high Si steel, SiC, Si3N4, Hastelloy G, C-276

H_2SO_4 + <<xH_2O

Concentrator ← Glass(steel), plastics, ceramics, Hastelloy B-2, C-276, AL610, high Si steel, noble metals

$H_2SO_4 + xH_2O$

❖ Coordinated by S. Sherman at INL

Technical Accomplishment-Isolate Chemical and Temperature Environments (H_2SO_4 & HI) Generation

S-I Bunsen Reaction (120 – 130 °C; 0.1 to 0.3 MPa)

Stage	Environment (wt%)	Candidate material
Main Reaction	8 H_2O; 2 H_2SO_4; 80 I_2; 7 HI; 0.5 O_2; 1.7 SO_2	Ta, Zr, Si_3N_4, SiO_2, Al_2O_3, B2, 242, Hastelloy C-276, and Nb-1Zr coating
H_2SO_4 Boost Reactor	57 H_2O; 43 H_2SO_4; 0.1 SO_2; trace I_2	
HI Phase SO_2 Stripper HX	trace H_2SO_4; 87 I_2; 7 HI; 0.2 SO_2; 6 H_2O;	
Vessel for Bunsen Reaction HXs	Ranges listed above	Florocarbon-lined (Teflon, Kynar, etc.) low alloy steels

Technical Accomplishment-Isolate Chemical and Temperature Environments (H_2SO_4 Concentration)

S-I H_2SO_4 Concentrator

Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Primary side	<450	0.1-6.8	He/molten salt	Hastelloy B2 & N, SiC, C-C composites, C276, 800/800H, Hi-Si steel (Duriclor 51M), glass-lined steel, Au, Pt, & Nb coatings
Secondary side	<400	0.1	0-0.1 SO_2; 57-98 H_2SO_4; 2-42 H_2O; trace I_2	

Technical Accomplishment-Isolate Chemical and Temperature Environments (H_2SO_4 Vaporizer)

S-I H_2SO_4 Vaporizer

Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Primary side	580 to 380	0.1-6.8	He/molten salt	Hastelloy B2, G & N, SiC, C-C composites, Si_3N_4, C276, 800/800H, Hi-Si steel (Duriclor 51M), glass-lined steel, Au-, Pt-, & Nb-coatings
Secondary side	330 to 530	0.7	Liquid-Vapor 98-71 H_2SO_4; 0-22 SO_3; 2-7 H_2O;	

Technical Accomplishment-Isolate Chemical and Temperature Environments (H_2SO_4 Decomposer)

S-I H_2SO_4 Decomposer

Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Primary side	950 to 800	0.1-6.8	He/molten salt	Hastelloy B2, SiC, C-C composites, Si_3N_4, 242, 214, C276, 800HT, Nb-1Zr, Au-, Pt-, Cu-, & glass-coatings, Pt-, Cu-, & Fe_2O_3-catalysts
Secondary side	530 to 900	0.7	Inlet-Outlet 71-20 H_2SO_4; 22-13 SO_3; 7-16 H_2O; 0-40 SO_2; 0-10 O_2	

Technical Accomplishment-Isolate Chemical and Temperature Environments (HI Decomposition)

S-I HIx Reactive Distillation

Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Inlet feed stream	262	2.2	11 HI; 81 I_2; 8 H_2O	Ta, Ta-10W, Mo, Nb, Nb-1Zr, Zircaloy 702, SiC, vitreous carbon, C-C composites, Bulk metallic glasses
Outlet column bottom	310	2.2	1 HI; 98 I_2; 1 H_2O	
H_2 scrubber/ condenser	221 to 25	2.2	66 HI; 32 H_2O; 2 H_2	

Technical Accomplishment-Isolate Chemical and Temperature Environments (HI Decomposition)

S-I HIx Phosphoric Acid Reactor

Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Concentrated H_3PO_4	132 to 211	0.1	96 H_3PO_4; 4 H_2O	TBD based on relevant industrial experience
Custom column	120 to 241	0.3-0.9	74 H_3PO_4; 11 HI; 4 I_2; 10 H_2O	
Dilute H_3PO_4	250	0.95	87 H_3PO_4; 13 H_2O	
Iodine outlet	120	0.2-0.7	99.9 I_2; 0.1 H_2O	

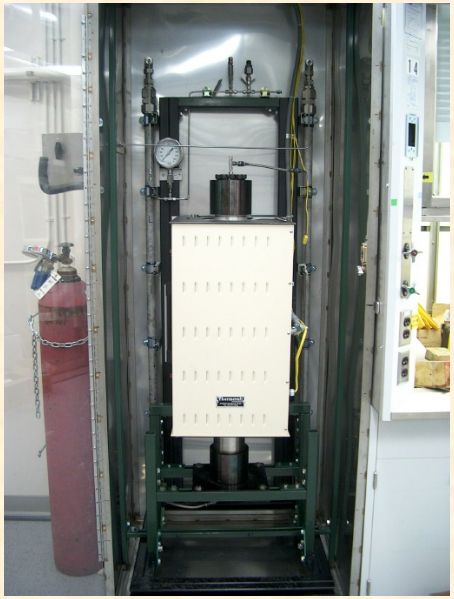
Materials Testing for NHI Thermochemical Cycles Has Been Initiated - HI Decomposition

Screening → Development → Prototype

Screening	Development	Prototype
Immersion Coupons	Crack Initiation & Growth, Long Term Testing, Cladding	S-I Loop/Pilot Plant Testing

❖ ***Work being performed by GA***

- S-I corrosion test facilities constructed for corrosion tests on selected coupons and stress specimens
- Screening tests underway for HI section materials
- Longer term testing, advanced materials activities being defined



Immersion corrosion test system II

Materials Testing for HI_x Section Has Begun

- ❖ **Refractory metals and ceramics have shown the best corrosion performance to date**

new tested

Zr705

Nb-1Zr

Sintered SiC

❖ HI_x materials testing (UNLV and GA)

- ♦ 22 coupons from four classes of materials: refractory and reactive metals, superalloys and ceramics, have been screened.

Excellent	Good	Fair	Poor
Ta-40Nb, Nb-1Zr, Nb-10Hf, SiC(CVD), SiC(Ceramatec sintered), Mullite	Ta, Ta-10W, Nb, Nb-7.5Ta, SiC (sintered) Si-SiC (3 kinds)	Mo-47Re, Alumina	Mo, C-276, Haynes 188, graphite*, Zr702, Zr705

* structurally sound but absorbed HIx

- ♦ Long term corrosion performance testing has started
  - effect of HI_x on stress corrosion
  - cost reduction through cladding

Technical Accomplishment-Isolate Chemical and Temperature Environments (Ca-Br Cycle)

Reaction Beds During HBr Production (0.1 MPa)

Stage	Temperature (°C)	Environment (wt%)	Candidate materials
HX primary side	750	He/molten salt	Hastelloy N, 232, 214, 713 cast, RA330
HX secondary side		100 $CaBr_2$ & H_2O to 100 CaO & HBr	
Bed support			Ceramics/catalysts TBD
Reaction vessel	300 to 750	100 H_2O & 0 HBr to 0 H_2O & 100 HBr with trace O_2	If insulated, Ni-Clad low alloy steel, If not, 713LC, 214, Ni_3Al, MA956, MA754
Reaction vessel insulation	750		$CaTiO_3$, Al_2O_3

Technical Accomplishment-Isolate Chemical and Temperature Environments (Ca-Br Cycle)

Reaction Beds During Regeneration (0.1 MPa)

Stage	Temperature (°C)	Environment (wt%)	Candidate materials
HX primary side	<590	He/molten salt	Hastelloy N, 232, 214, 713 cast, RA330
HX secondary side		100 Br_2 & CaO to 100 $CaBr_2$ & O_2	
Bed support			Ceramics/catalysts TBD
Reaction vessel	200 to 590	100 Br_2 & 0 O_2 to 0 Br_2 & 100 O_2	If insulated, Ni-Clad low alloy steel, If not, 713LC, 214, Ni_3Al, MA956, MA754
Reaction vessel insulation	<590		$CaTiO_3$, Al_2O_3

Technical Accomplishment-Isolate Chemical and Temperature Environments (Ca-Br Cycle)

Reaction Beds to Plasmatron HX (0.1 MPa)

Stage	Temperature (°C)	Environment (wt%)	Candidate materials
Primary side	750 to 50	100 HBr & 0.1 H2O to 3 Br_2 & 97 HBr with trace H_2O	Ni, B2, 214, 232, Hastelloy N, stainless steel, Si_3N_4, Nb-1Zr
Secondary side	25	H_2O	

Plasmatron HX (0.1 MPa)

Stage	Temperature (°C)	Environment (wt%)	Candidate materials
Inlet	50	3 Br_2 & 97 HBr with trace H_2O	300 series stainless steel
Outlet	<<300	50 HBr, 25 Br_2, & 25 H_2	

Technical Accomplishment-Isolate Chemical and Temperature Environments (Ca-Br Cycle)

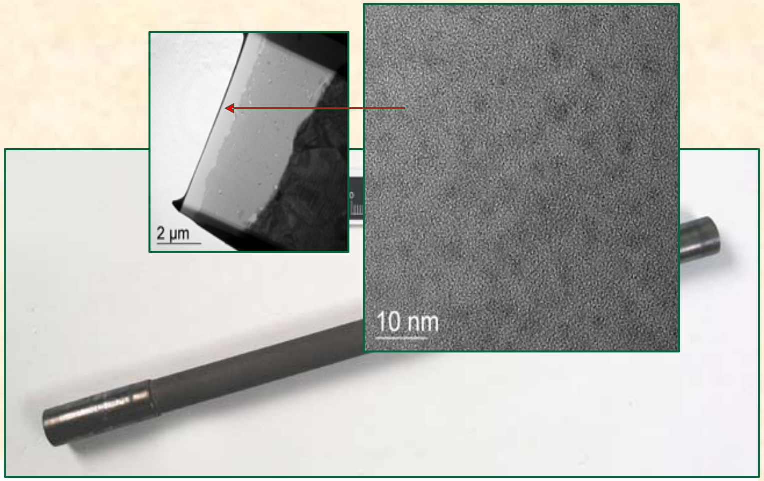
Other Components

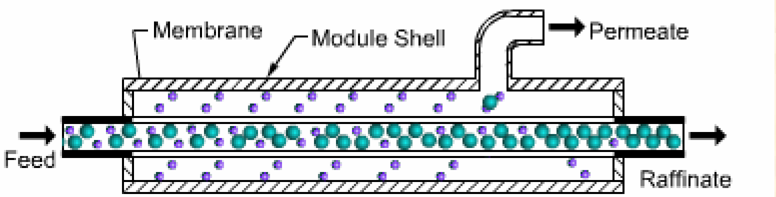
Stage	Temperature (°C)	Pressure (MPa)	Environment (wt%)	Candidate materials
Multistage compressors	100 to 335	0.005 to 3.5	30 H_2, 4 Br_2, & 2 H_2O	TBD based on industrial experience
Steam superheater Primary side	750 to 850	6.8-0.1	He/molten salt	617, 625, 230, B2, 214, 242, Hastelloy N
Steam superheater Secondary side	750	0.1	H_2O	

Summary of High Priority R&D

- **Prioritized high due to technical viability issues associated with high temperature/corrosive environments**
  - **Sulfur Cycles (S-I, Hybrid S)**
    - **H_2SO_4 concentrator, vaporizer**
    - **HI reactive distillation column**
    - **Inorganic membranes**
      - **Potential for increased product formation**
      - **Potential for reduced operating temperature**
  - **CaBr**
    - **Reactive bed HX**
    - **Ca-Br/HBr HX**
    - **Reaction bed vessel**

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





Future Work

- FY05 – Revise and update materials selection document

- FY06 - Develop a prioritized, integrated materials evaluation program
  - So as to establish engineering feasibility

Publications and Presentations

- Materials Requirements for Nuclear Hydrogen Generation Systems, ORNL TM, 2004
- W. R. Corwin, *NHI Materials Selection and R&D Plan*, NHI Materials Planning Meeting, UNLV, Las Vegas, Nevada, May 17, 2004
- W. R. Corwin, *NHI Materials Selection and R&D Plan & NHI Membrane Studies Update*, NHI Semiannual Program Review, DOE HQ, Germantown, Maryland, September 21-22, 2004
- W. R. Corwin, *High Priority Materials R&D for NHI*, NHI Materials Program Review Meeting, ORNL, February 10, 2005

Hydrogen Safety

What is the most significant hydrogen hazard associated with this project?

- Hydrogen explosiveness/flammability (4 to 75 vol.%) during performance evaluation

What are you doing to deal with this hazard?

- Work will be performed under the safety envelopes of the various testing organizations
- Use both administrative and physical controls
  - Work review/authorization
  - Volume/pressure controls
  - Sensors