Overview

Timeline

- Project start date: 9/03
- Project end date: 9/08
- Percent complete: 50%

Budget

- Total project funding
  - DOE/NE: $5,700k
- Funding received in FY05: $1,930k
- Funding for FY06: $1,870k

Barriers

- Barriers addressed
  Nuclear Hydrogen Initiative R&D Plan – Material performance and component design and testing for: intermediate heat exchanger and high-temperature thermochemical water splitting (H₂SO₄ decomposition and HI decomposition). Improved materials for High Temperature Electrolysis.

Partners

- UNLV, UC Berkeley, MIT, General Atomics, Ceramatec, Argonne National Lab
Objectives

To assist DOE-NE in the development of hydrogen production from nuclear energy through:

• Identification and testing of candidate materials for heat exchanger components.
• Design of critical components in the interface and sulfur iodine thermochemical process.
• Fabrication and testing of prototypical components.
• Innovative materials development.
Approach

• Task 1: Heat Exchanger Component Design
  – Optimization, transient hydrodynamic, and thermal studies of off-set strip fin HTHX
  – Numerical analyses with chemical reactions and optimization studies for Ceramatec sulfuric acid decomposer
  – Stress analysis and optimization of Ceramatec HTHX
  – Numerical analysis of metallic Heatric-type sulfuric acid decomposer
• Task 2: Identification and testing of candidate metallic materials for heat exchanger components
  – Evaluation of material strength and corrosion properties
  – Materials tested: Alloy C-22, C-276, Waspaloy, 617, and 800H up to 1000 C.
  – Nb-1Zr, Nb-7.5Ta, Zr705, Ta-2.5W, and Ta-10W up to 400 C (for HI decomposition).
• Task 3: Heat Exchanger Prototype Testing
  – Experiments with surrogate materials to validate hydrodynamic and overall heat transfer coefficients from CFD results
  – Prototype to model ratio is 1:3 for the off-set strip fin design
• Task 4: Analytical Studies of the Effects of Acid Exposure on Structure Materials
  – Elemental analysis and bonding structure to identify phenomena (e.g. oxide formation and thickness)
• Task 5: Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells
  – Use of dense film electrodes and electrolyte made by Atomic Layer Deposition
  – Elucidate the surface and bulk reaction mechanisms at the O₂ electrode
  – Determine the oxidation state of the nickel and the structure of the electrode/electrolyte interface during cell operation
Approach

• Task 6: Corrosion and Crack Growth Studies of Materials in HIx Environment
  – Screening of 22 candidate materials using immersion coupon exposure
  – Long term testing including crack initiation and growth studies and cladding options

• Task 7: Ceramic-Based High Temperature Heat Exchanger Development
  – Evaluation of mechanical and thermal properties of preferred ceramic materials
  – Validation through prototype fabrication and empirical testing.

• Task 8: Materials Design and Modeling for C/SiC Compact Ceramic Heat Exchangers
  – Demonstration of C/SiC composite heat exchanger fabrication using polymer infiltration and pyrolysis (PIP).
  – Perform C/SiC HX thermal and mechanical analysis
  – Perform comprehensive C/SiC heat exchanger safety analysis

• Task 9: Development of Self Catalytic Materials for Thermo-chemical Water Splitting Using the Sulfur-Iodine Process
  – Material chemistry identification, alloy procurement and metallurgical characterization
  – Determination of Catalyst Effectiveness
  – Determination of Mechanical Properties
  – Prototypic Shape Fabrication & Testing
Temperature (K) Contours in the Middle Region of an off-set strip fin heat exchanger

Helium side
\[ \Delta T = 377K \]

Liquid salt (LS) side
\[ \Delta T = 419K \]
Effects of Gap Length on HX Performance
Velocity Distribution for the Optimized Geometry for the Ceramatec Sulfuric Acid Decomposer

Optimized geometry

Y Velocity

Position (m)

Velocity distribution at the midsection of the channels
Computed Pressure Distributions (Pa) for the Ceramatec Coupon Test

With no measurement channels

With measurement channels
Accomplishments: Task 2: Identification and testing of candidate metallic materials for heat exchanger components

- Four structural materials, namely Alloy C-22, Alloy C-276, Alloy 800H and Waspaloy have been identified and characterized for heat exchanger applications.
- The results of tensile testing up to a temperature of 1000°C revealed a gradual reduction in tensile strength with increasing temperature, as expected.
- All four alloys exhibited significant ductility up to 600°C. However a significant drop in ductility was observed above this temperature.
- Failure strain for all four alloys were gradually reduced in a critical temperature range followed by its enhancement beyond this range. This phenomenon may be the result of dynamic strain ageing. For Waspaloy, a maximum dislocation density (\(\rho\)) was observed at 300°C.
- Ductile failures were observed up to a temperature of 600°C for all tested materials. However, intergranular failure was observed with Waspaloy at 800°C possibly due to the precipitation of Boron at the grain boundaries.
Engineering Stress vs Strain Diagrams at Different Temperatures

Alloy C-22

Alloy C-276 Stress vs Strain

1 ksi = 6.8948 MPa

RT
100
200
300
400
500
600
800
1000

Strain

Stress (ksi)
Engineering Stress vs Strain Diagrams at Different Temperatures

Waspaloy

Alloy 800H

1 ksi = 6.8948 MPa

1 ksi = 6.8948 MPa
Dislocation Density ($\rho$) vs Temperature

Temperature (ºC)

$\rho$ (No/m$^2$)

Waspaloy
Scanning Electron Micrographs

Waspaloy, 800°C, 100X

EDS Analysis of Waspaloy
Accomplishments:  Task 3: Heat Exchanger Prototype Testing

• Experimental testing lab is basically setup.
• 80% of the instrumentation has been ordered, installed, and tested.
• Hydrodynamic testing rig for a single-chamber test section with air as the working fluid has been setup and tested. Hydrodynamic tests began.
• Several problems associated with de-ionized water as working fluid in acrylic test section were solved: bubbles on the testing surface and sealing of the fins and walls.
Single-chamber Testing Setup with De-ionized Water
Single-chamber Testing Setup with Room Air

- Inline Centrifugal Fan
- Bypass Valve
- Flowmeter
- Test Section
- Optical Table

- Pressure Transducer
- Data Acquisition
- Flow Meter
- Bypass Valve
Accomplishments: Task 4: Analytical Studies of the Effects of Acid Exposure on Structure Materials

• SEM and XPS investigations performed on samples exposed to Hydrogen Iodide
• Oxide layers were characterized for Ta-2.5W, Nb-10Hf, and Nb-1Zr.
• Failure analysis was conducted for Nb-1Zr.
Ta-2.5W characterization

TaW – 1000 hours - Weld A side 1
Nb-10Hf Characterization

A 1-2\textmu m surface oxide, Nb$_2$O$_5$ by XPS was observed.
Nb1Zr Characterization

Nb-1Zr (unfailed) XPS showed an oxide layer that was of varying thickness from 200-1000 nm deep, composed of Nb₂O₅. However, even at very shallow distances (~10nm) significant reduced Nb was observed.
Accomplishments: Task 5: Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells

- X-ray absorption and emission spectroscopy of reference powder materials of NiO, LaSrMnO, and ZrYO were performed.
- Synchrotron experiments at the Advanced Photon Source (ANL) were conducted in February and March 2006, films will be sent to UNLV.
Electrochemical Characterization
Results for the 150 nm reference LCM electrode at 800°C

Potentiostatic measurements for the electrode current density

Electrochemical Impedance Spectroscopy for the electrode area specific resistance (ASR)
First results with *in situ* cell:
Absorption spectroscopy at the Mn K edge during current conditioning of LSM electrode at -0.6V at 800°C in air
First results:
XES and XAS reference spectra of electrodes and electrolyte

![Graph 1: Emission Energy vs. Intensity](image1)

![Graph 2: Absorption Energy vs. Intensity](image2)
Accomplishments: Task 6: Corrosion and Crack Growth Studies of Materials in HIx Environment

- Ta-2.5W, Ta-10W and Nb-10Hf were determined to be suitable for high temperature use in HIx.
- Stress corrosion studies showed the dependence of mechanical properties on environment.
- Material test system for three different environments within extractive distillation were completed.
- Ta-2.5W has the best performance in HIx + H₃PO₄.
Long term immersion results

<table>
<thead>
<tr>
<th></th>
<th>HI&lt;sub&gt;x&lt;/sub&gt;</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corrosion Rate</td>
<td>hours</td>
<td>mpy</td>
</tr>
<tr>
<td>Ta-2.5W - 1</td>
<td>2072</td>
<td>0.0035</td>
<td>0.00009</td>
</tr>
<tr>
<td>Ta-2.5W - 2</td>
<td>1040</td>
<td>0.0148</td>
<td>0.00038</td>
</tr>
<tr>
<td>Ta-10W</td>
<td>1078</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Nb-10Hf</td>
<td>1120</td>
<td>0.036</td>
<td>0.0009</td>
</tr>
<tr>
<td>Nb-7.5Ta</td>
<td>1128</td>
<td>0.266</td>
<td>0.0068</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>HI&lt;sub&gt;x&lt;/sub&gt; + H&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample</td>
<td>Corr. rate (mpy)</td>
</tr>
<tr>
<td></td>
<td>Nb-1Zr (1)</td>
<td>-0.92</td>
</tr>
<tr>
<td></td>
<td>Ta-2.5W</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>0.239</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Nb-7.5Ta</td>
<td>22.97</td>
</tr>
<tr>
<td></td>
<td>Nb-1Zr (2)</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>38.91</td>
</tr>
<tr>
<td></td>
<td>Nb-10Hf</td>
<td>40.49</td>
</tr>
<tr>
<td></td>
<td>Zr705</td>
<td>91.32</td>
</tr>
<tr>
<td></td>
<td>C-276</td>
<td>139.88</td>
</tr>
<tr>
<td></td>
<td>C-22</td>
<td>147.07</td>
</tr>
</tbody>
</table>
Accomplishments: Task 7: Ceramic-Based High Temperature Heat Exchanger Development

- Preferred candidate materials tested 1000 hours in steam/$H_2SO_4$/air environments at 900$^\circ$C.
- Mechanical Strength: Silicon Carbide & Silicon Nitride – all increased strength; Alumina – decreased strength.
- Weight Gain: Very slight weight gains < 0.1%/1000 hrs. Silicon Carbide & Silicon Nitride form stable “healing” $SiO_2$ layer. Alumina has corrosion products that are to be determined.
- Compact shell and plate heat exchanger was designed with high performance micro-channels for low volume and low cost.
- Flow/heat transfer coupons designed and fabrication began. Experiments started.
- Thermo-mechanical evaluations are underway.
Compact Shell and Plate Design

- High Performance Micro-Channels
- Low Volume, Low Cost
Flow and heat transfer coupons

- Sub-section of Micro-Channel Plate Design.
- Flow Dynamics & Heat Transfer Characteristics
- Design & Modeling Validation
Heat Exchanger Validation

• Coupon Structures
  – Models
    • Conjugate Flow-Heat Transfer
    • Pressure Drop
    • Flow Distribution
  – Experimental
    • Dynamic Sensing
    • Multi-tap Transducer (18)
    • Sensor Averaging

Components

Experimental

CFD Model
Thermo-Mechanical Design

Thermal Loads

Mechanical Stresses

Design Safety Factor = 2.75
Accomplishments: Task 8: Materials Design and Modeling for C/SiC Compact Ceramic Heat Exchangers

- Completed detailed design for ceramic compact helium-to-liquid-salt HX for thermal/mechanical analysis.
- Demonstrated fabrication of mm-scale fins with thru and blind (preferred) reusable teflon molds.
- Studying use of reactive metal control for flinak coolant to mitigate effects of process fluid ingress.
Detailed design for ceramic compact helium-to-liquid-salt HX for thermal/mechanical analysis
Fabrication of mm-scale fins with thru and blind (preferred) reusable teflon molds

Upcoming work will demonstrate plate lamination to create complete compact ceramic HX
Reactive metal control for flinak coolant to mitigate effects of process fluid ingress

Finite solubility of Na metal in flinak measured, shows potential for this method to be applied for intermediate heat transport for S-I process

Quartz tube with flinak sample crucible for equilibrium measurement

• Initial Alloys Produced and Characterized
  – Alloy 800 + Pt
  – Alloy 617 + Pt

• Catalytic Behavior Confirmed

• Catalyst Effectiveness System Construction Finished
  – System In operation
  – Initial Data Developed

• Final Alloy Composition Identified
  – Alloy 800 + 1% Pt
  – Alloy 617 + 1% Pt

• Compact Heat Exchanger Design Finalized
  – Heatric PCHE Design.
Alloy 800 + 5 wt% Pt - After Test
Student Photo-Working with Catalytic Effectiveness System
Results-Alloy 800 + 5% Pt
Future Work

- **Task 1:** Heat Exchanger Component Design – Continue numerical analyses for candidate designs, including chemical reactions, and perform optimization studies. Validate numerical results with experimental data.

- **Task 2:** Identification and testing of candidate metallic materials for heat exchanger components – Evaluate the performance of Alloy 617 and Ta alloys. Perform fracture toughness and crack growth studies of candidate materials. Develop understanding of deformation mechanisms at elevated temperatures.

- **Task 3:** Heat Exchanger Prototype Testing – Complete thermal and hydraulic testing single-chamber loops. Perform flow visualization. Design and machine double-chamber test sections (counterflow, gas and liquid).

- **Task 4:** Analytical Studies of the Effects of Acid Exposure on Structure Materials – Continue specimen analyses for materials exposed to HI by General Atomics. Analyze specimens exposed to sulfuric acid by Ceramatec.

- **Task 5:** Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells – Next experimental campaign at the Advanced Light Source in May 2006. Conduct surface sensitive x-ray analysis at UNLV. Compare reference LCM electrochemical performance with non-tailored and epitaxially oriented La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) model electrodes.
Future Work

• Task 6: Corrosion and Crack Growth Studies of Materials in HIx Environment – Complete materials screening for iodine separation, phosphoric acid concentration and HI gaseous decomposition and initiate long term testing. Conduct tests to study the stress corrosion behavior of materials in these environments.


Responses to Previous Year Reviewers’ Comments

• Questions were fielded and answered by DOE-NE program manager David Henderson.