High Temperature Heat Exchanger Project:
Quarterly Progress Report April 1, 2007 through June 30, 2007

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High Temperature Heat Exchanger Project

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Quarterly Progress Report
April 1, 2007 through June 30, 2007

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## Contents

1. UNLV Design and Testing Group (UNLV) ................................................................. 3
2. Metallic Materials Selection and Characterization (UNLV) ................................. 13
3. Materials, Design and Modeling for C/SiC Ceramic Heat Exchangers (University of California, Berkeley) ................................................................. 17
4. Corrosion Studies of Candidate Structural Materials in HIₓ Environment as Functions of Metallurgical Variables (GA) ................................................................. 22
5. Chemistry Support Studies (UNLV) ................................................................. 29
6. Development of an Efficient Ceramic High Temperature Heat Exchanger (Ceramatec, Inc.) ................................................................. 33
7. Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells through Improved Electrodes and Electrolytes (UNLV) ................................................................. 38
8. The Development of Self Catalytic Materials for Thermochemical Water Splitting Using the Sulfur-Iodine Process (MIT) ................................................................. 41
1.0 UNLV Design and Testing Group

1.1 HTHX Thermal Systems Design (PI: Yitung Chen, UNLV)

1.1.1 Research Highlights

- **Ceramatec Sulfuric Acid Decomposer.** Modeling with different reacting flow channel configurations (ribbed-surface channels, hexagonal channels, and diamond-shaped channels) was performed. The probability of failure for the one channel geometry with different reacting flow channel configurations was calculated to be zero in the three principal directions for all of the cases.

- **Bayonet Heat Exchanger.** The Matlab code for calculating the probability of failure using a two-dimensional axisymmetric model of the bayonet decomposer was developed. The probability of failure was calculated for the inner and outer SiC walls, and the intermediate quartz wall of the decomposer and found to be zero for all of the walls. The exact temperatures of the external wall measured from the experiment at SNL were applied to the thermal boundary conditions and used to calculate flow, heat transfer and chemical reactions. Geometry of one-fourth of the packed bed region with cylindrical and spherical pellets was created, and the periodic boundary conditions were applied. Calculations of fluid flow and heat transfer with cylindrical and spherical pellets in the packed bed region were performed.

- **Shell and Tube Heat Exchanger.** Numerical simulations of a 3-D straight tube configuration of the high temperature shell and tube heat exchanger and chemical decomposer have been performed to examine flow distributions on the tube side. The heat exchanger and decomposer have 24 internal tubes. The flow calculations have been studied for the different three cases.


1.1.2 Technical Progress Report

**Numerical Analyses with Chemical Reactions and Optimization Studies for the Ceramatec Sulfuric Acid Decomposer**

Study of the Ceramatec sulfuric acid decomposer with different reacting flow channel configurations (ribbed-surface channels, hexagonal channels, and diamond-shaped channels) using the Arrhenius constant obtained from Dan Ginosar at INL for 1 wt % Pt was performed. Since this activation energy (32,670.69 J/mol) is smaller than that used in the previous calculations (88,034 J/mol), it is easier to decompose the sulfuric trioxide and the decomposition percentage can reach almost 80% for the diamond-shaped reacting flow channels with the baseline operation conditions as shown in Table 1. The mass flow rate of reacting flow for all of the cases is $3.148 \times 10^{-6}$ kg/sec. The table also shows that pressure drop for the five alternative designs increases significantly when compared to the baseline design. However, even the case with the highest pressure drop (two hexagonal layers channel with 100% overlap) is still within the 10 kPa design limits of the decomposer pressure drop.
Table 1. Results of calculations for baseline and alternative designs.

<table>
<thead>
<tr>
<th>Design Description</th>
<th>Area of chemical reaction, m²</th>
<th>Volume of reacting flow, m³</th>
<th>Area/Volume, m²/m³</th>
<th>Percentage of SO₃ decomposition, %</th>
<th>Pressure drop, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straightforward channel baseline design (case 1)</td>
<td>8.864e-5</td>
<td>1.409e-8</td>
<td>6291</td>
<td>63.81</td>
<td>129</td>
</tr>
<tr>
<td>Ribbed lower surface channel - 0.1 mm (case 2)</td>
<td>9.320e-5</td>
<td>1.319e-8</td>
<td>7065</td>
<td>64.25</td>
<td>241</td>
</tr>
<tr>
<td>Ribbed lower surface channel - 0.2 mm (case 3)</td>
<td>9.756e-5</td>
<td>1.234e-8</td>
<td>7906</td>
<td>65.57</td>
<td>573</td>
</tr>
<tr>
<td>Two hexagonal layers channel with 50% overlap (case 4)</td>
<td>1.330e-4</td>
<td>1.903e-8</td>
<td>6989</td>
<td>76.31</td>
<td>802</td>
</tr>
<tr>
<td>Two hexagonal layers channel with 100% overlap (case 5)</td>
<td>1.359e-4</td>
<td>1.903e-8</td>
<td>7141</td>
<td>77.73</td>
<td>3816</td>
</tr>
<tr>
<td>Diamond-shaped layers channel (case 6)</td>
<td>1.480e-4</td>
<td>1.736e-8</td>
<td>8525</td>
<td>79.95</td>
<td>1570</td>
</tr>
</tbody>
</table>

Calculation of safety factor and probability of failure for a transient warming up regime with different operating pressures in He and SI parts of the baseline design Ceramatec HTHX has been completed. The transient regime started with no flow conditions at room temperature (20°C) and suddenly hot helium with temperature 950°C started to flow in the helium channel. For this regime the pressure in the He part is 1.5 MPa, the pressure in the SI parts is 0.1 MPa. The calculations have been completed for six different times: 0, 1, 10, 30, 60 and 120 seconds after the beginning of the helium flow. The results do not have significant difference as compared with results for the same regime but with equal operating pressures in the He and SI parts (1.5 MPa). The minimal safety factor appeared after 10 sec and was 3.837 (Figure 1). The probability of failure is close to zero for all of the cases. It can be concluded that a pressure difference of 1.4 MPa between He and SI parts of the decomposer does not significantly influence the decomposer safety.

Calculations of the probability of failure for the single-channel geometry with different reacting flow channel configurations (ribbed-surface channels, hexagonal channels, and diamond-shaped channels were performed. The probability of failure is equal to zero in the three principal directions for all of the cases.
Numerical Analysis of the Bayonet-type HTHX and Decomposer

The Matlab code for calculating the probability of failure using the two-dimensional axisymmetric model of the bayonet type decomposer was developed. The probability of failure was calculated for the inner and outer SiC walls, and the intermediate quartz wall of the decomposer. The results showed that the probability of failure is zero for all of the walls.

The exact temperatures of the external wall measured from experiments at SNL have been applied to the thermal boundary conditions and used to calculate flow, heat transfer and chemical reactions in the decomposer. The calculated sulfur trioxide decomposition percentage is 19%. The decomposition percentage is smaller than that with the assumption of uniform temperature of the external wall. This is due to the average temperature in the packed bed region for the case of the applied measured temperature distribution being less than that for the case with an assumption of constant temperature external wall.

Geometry of one-fourth of the packed bed region with cylindrical and spherical pellets was created as shown in Figures 2-5, and the periodic boundary conditions have been applied. A mesh independence study was performed. From this study, 499,084 cells and 96,623 nodes were selected for cylindrical pellets (Figure 6), while 519,939 cells and 101,979 nodes were selected for spherical pellets (Figure 7). The mass flow rate is $0.43 \times 10^3$ kg/s. The fluid flow calculation with no solids inside (i.e. hollow sphere) was numerically tested and completed. The pressure drop was found to be 260 Pa for cylindrical and 280 Pa for spherical pellets (Figures 8 and 9, respectively).
Figure 2: Dimensions of the geometry with cylindrical pellets.

Figure 3: Dimensions of the geometry with spherical pellets.

Figure 4: Boundaries of the geometry with cylindrical pellets.

Figure 5: Boundaries of the geometry with spherical pellets.
Figure 6: Computational mesh of cylindrical pellets in Gambit (91,484 nodes and 469,561 cells).

Figure 7: Computational mesh of spherical pellets in Gambit (60,516 nodes and 295,115 cells).

Figure 8: Pressure distribution in the domain with cylindrical pellets, Pa.
Calculations of fluid flow and heat transfer with cylindrical and spherical pellets in the packed bed region have been performed. The temperature for the outer wall was 900°C and the inner wall was 700°C. Mass flow rate was 0.43x10^{-3} kg/sec. Calculated temperature distributions in the fluid and solid (silicon carbide pellets) parts are shown in Figures 10 and 11. According to the numerical results, temperature was uniformly distributed along the pellets for both cylindrical and spherical pellets cases. The reason being that the thermal conductivity of the silicon carbide is much higher than that of the fluid.
Numerical Analysis of Shell and Tube HTHX and Decomposer

Numerical simulations of 3-D straight tube configuration of the high temperature shell and tube heat exchanger, and the chemical decomposer were performed to examine flow distributions on the tube side. The heat exchanger and decomposer has 24 internal tubes with 0.016 m diameter and 1.5 m length. The mass flow rate of the mixture of sulfur trioxide and water vapor passing through the tubes is 0.044 kg/sec. The flow calculations have been studied for the following three cases:

- **Case 1 (Baseline design):** Calculations of fluid flow were performed on the straight tube configuration without a packed bed but with a catalyst (Figure 12). Results of the calculation showed that the flow maldistribution in the tubes is very serious. The fluid velocities in tubes near the axial line are more than twice those in the peripheral tubes as shown in Figure 13.

- **Case 2: (Baseline design with baffle in inlet manifold):** A baffle plate was designed and placed midway between the inlet tube and the core of the header as shown in Figures 14 and 15. With the baffle, the flow maldistribution inside the tubes was reduced significantly (the maximum velocity variance inside tubes is about 40%). Thus, this type of arrangement can be very useful in the high temperature shell and tube heat exchanger and decomposer with the catalytic bed being placed on the shell side.

- **Case 3: (Tube configuration with pebble bed in inside tubes):** Fluid flow calculations were performed for the tube configuration with packed bed in the whole length inside of tubes as shown in Figure 16. The baffle plate has been avoided. In this case, the flow distribution among the inside tubes was uniform. The packed bed zone has a very high flow resistance, and the flow is distributed in the header section such that the flow in the tubes is uniform. However, the pressure drop in this case is 30 kPa, which is much larger than that for the Cases 1 and 2 that have a pressure drop of about 0.3 kPa.

![Figure 12: Geometry of the baseline design.](image)
Figure 13: Y-velocity distributions at the midsection of the decomposer for baseline design, m/s.

Figure 14: Baffle plate

Figure 15: Location of baffle plate.
1.2 Scaled HTHX Tests (PI: Samir Moujaes, UNLV)

Thermal experiments were performed to calculate the Nusselt numbers. Single-chamber test sections were performed to determine the global thermal performance of the off-set strip fin heat exchanger apparatus using room air and the Alloy-Acrylic test sections with interchangeable round-edge fins and square-edge fins with electric heating pads. Experiments were performed by controlling the flow rate to make the Reynolds number vary between 1800 and 2500, which covers the range of the prototypical intermediate heat exchanger (IHX) design conditions. The two electric heating pads provide the same heating flux to simulate the sandwiched Helium channels in prototype IHX. The two electric heating pads were controlled separately to create two heated sides using the same heat flux at the top and bottom surfaces. Different heating fluxes were used to adjust the heating power.

The resulting Nusselt numbers from the round-edge fins and square-edge fins test sections are shown in Figure 17. The hydraulic diameter of the round-edge fins test section was 1.5% higher than that of the square-edge fins, and friction factors of the round-edge fins test section were about 40% less than those of square-edge fins. The heat transfer surface of the round-edge fins test section was 2.5% less than that of the square-edge fins. The Nu of the round-edge fins test section was 10% less than that of the square-edge fins. The experimental data showed that with the same heating power and flow rate, the outlet air temperature of round-edge fins was 1 to 2 °C lower than that of the square-edge fins. With almost identical heat loss between these two test sections, the square-edge fins test section had better heat transfer ability, but with a marked increase of the pump power. Suggested ways to increase the heating capacity of the IHX is to make the round-edge fins have shorter gaps, or increase the number of rows of fins in the flow direction.
A single-chamber test section made from Alloy 6061 using a dimensional ratio of 1:3 square-edge fins with two electric heating pads was built and tested. A counterflow double-chamber test section made from Alloy 6061 using a dimensional ratio of 1:2 round-edge fins was designed and tested. Room temperature air was used as a surrogate for Helium. Hot deionized (DI) water was used as the heating source without consideration of the Reynolds number range since there was no way to closely match the Reynolds number and heating capacity of the DI water and air simultaneously. The air flow rates were adjusted to have the Reynolds number varied between 1800 and 2500.

Nusselt numbers of the whole Alloy single-chamber test section of 1:3 ratio square-edge fins are compared with that of the whole Alloy test section double-chamber test section of 1:2 ratio round-edge fins in Figure 18. Similar to the 1:3 Alloy-Acrylic test sections with different fins, the Nusselt numbers of round-edge fins were 15% lower than that of the square-edge fins.
2.0 Metallic Materials Selection and Characterization (PI: Ajit Roy, UNLV)

Duplicate crack-growth-rate (CGR) testing involving compact tension (CT) specimens of Alloys-22 and 276 have recently been completed in air at ambient temperature to determine crack propagation under cyclic loading (da/dN) as a function of ΔK. Based on the fracture mechanics concept, a steady-state CGR can be determined from the plot of da/dN vs. ΔK. Figures 19 and 20 illustrate the variation of da/dN versus ΔK for Alloys-22 and 276, respectively.

Figure 19: da/dN vs. ΔK for Alloy-22.

Figure 20: da/dN vs. ΔK for Alloy-276.
CGR under cyclic loading can be governed by an equation, known as Paris law, as given below.
\[
da/dN = A \left(\Delta K\right)^m
\]

Where,
- \(da/dN\) = CGR under cyclic loading
- \(\Delta K = (K_{\text{max}} - K_{\text{min}})\)
- \(K_{\text{max}}\) = Maximum stress intensity factor
- \(K_{\text{min}}\) = Minimum stress intensity factor
- \(a\) = Crack length
- \(N\) = Number of cycles
- \(A\) = Constant
- \(m\) = Slope of the linear portion of this plot
- \(R = (K_{\text{min}}/K_{\text{max}})\)

The magnitude of \(m\) can be determined from the plot of \(\log(da/dN)\) versus \(\log(\Delta K)\), as shown below. This equation represents a straight line with an intercept of \(\log(A)\) and a slope of \(m\).

\[
\log(da/dN) = \log(A) + m \log(\Delta K)
\]

The magnitudes of different relevant parameters, determined from recent CGR experimental work, are given in Table 2 showing their individual values from duplicate testing involving each alloy. An evaluation of these data indicates that the slope (\(m\)) of the linear portion (steady state crack growth) ranged between 4.0 and 4.5. Literature data on CGR of Alloys-22 and 276 do not exist yet. Thus, a comparative analysis cannot be made.

<table>
<thead>
<tr>
<th>Material</th>
<th>(K_{\text{max}}, \text{MPa}\sqrt{\text{m}})</th>
<th>(K_{\text{min}}, \text{MPa}\sqrt{\text{m}})</th>
<th>(a_i, \text{mm})</th>
<th>(a_f, \text{mm})</th>
<th>(\Delta a, \text{mm})</th>
<th>Slope, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.39</td>
<td>77.33</td>
<td>2.839</td>
<td>7.733</td>
<td>7.076</td>
<td>16.08</td>
</tr>
<tr>
<td>Alloy-276</td>
<td>26.32</td>
<td>65.98</td>
<td>2.632</td>
<td>6.598</td>
<td>7.098</td>
<td>15.095</td>
</tr>
<tr>
<td></td>
<td>26.26</td>
<td>65.84</td>
<td>2.626</td>
<td>6.584</td>
<td>7.076</td>
<td>15.081</td>
</tr>
</tbody>
</table>

\(a_i = \text{Initial Crack Length}\) \hspace{1cm} \(a_f = \text{Final Crack Length}\) \hspace{1cm} \(\Delta a = \text{Crack Extension}\)

The determination of critical stress intensity or fracture toughness (\(K_{\text{IC}}\)) has also been attempted using CT specimens of Alloy-276. The resultant data are given in Table 3. \(P_Q\) and \(K_Q\), shown in this table, represent the conditional load and stress intensity factor, respectively, as described in the ASTM designation E 399. The magnitude of \(P_Q\) was determined from the load versus displacement plot (Figure 21). It should be noted that the determination of \(K_{\text{IC}}\) was based on CT specimens having a thickness of 0.25 inch. \(K_Q\) was taken equivalent to \(K_{\text{IC}}\).

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Pre-crack Length, mm</th>
<th>(P_Q), kN</th>
<th>(K_Q), MPa\sqrt{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.82</td>
<td>11.90</td>
<td>128.08</td>
</tr>
<tr>
<td>2</td>
<td>2.60</td>
<td>12.98</td>
<td>116.15</td>
</tr>
</tbody>
</table>
\[ K_Q = K_C \]

![Image of displacement and load graph](image)

**Figure 21: Determination of the Magnitude of \( P_Q \).**

The results of SCC testing using DCB specimens of Alloys-22 and 276 are given in Tables 4 and 5, respectively. These data suggest that the final loads imparted by the wedges of different thicknesses were dropped significantly at the conclusion of the desired testing duration. Correspondingly, the final stress intensity factor \( (K_f) \) was also reduced appreciably.

**Table 4: Results of DCB Testing of Alloy-22.**

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>( P_i ) (lb)</th>
<th>( P_f ) (lb)</th>
<th>( \Delta P ) (lb)</th>
<th>( \Delta a ) (in)</th>
<th>( K_i ), ksi( \sqrt{\text{in}} )</th>
<th>( K_f ), ksi( \sqrt{\text{in}} )</th>
<th>( \Delta K ), ksi( \sqrt{\text{in}} )</th>
<th>( T ), hours</th>
<th>( \Delta a/T ), in/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>538</td>
<td>428</td>
<td>110</td>
<td>0.026</td>
<td>32.12</td>
<td>26.11</td>
<td>6.01</td>
<td>1440</td>
<td>1.81 \times 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>440</td>
<td>363</td>
<td>77</td>
<td>0.028</td>
<td>26.43</td>
<td>22.22</td>
<td>4.21</td>
<td>1440</td>
<td>1.94 \times 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>475</td>
<td>396</td>
<td>79</td>
<td>0.027</td>
<td>28.42</td>
<td>24.13</td>
<td>4.29</td>
<td>1440</td>
<td>1.87 \times 10^{-5}</td>
</tr>
<tr>
<td>4</td>
<td>540</td>
<td>402</td>
<td>138</td>
<td>0.029</td>
<td>32.52</td>
<td>24.68</td>
<td>7.84</td>
<td>1440</td>
<td>2.01 \times 10^{-5}</td>
</tr>
<tr>
<td>5</td>
<td>620</td>
<td>575</td>
<td>45</td>
<td>0.027</td>
<td>37.02</td>
<td>34.96</td>
<td>2.26</td>
<td>720</td>
<td>3.75 \times 10^{-5}</td>
</tr>
<tr>
<td>6</td>
<td>603</td>
<td>503</td>
<td>100</td>
<td>0.026</td>
<td>35.50</td>
<td>30.98</td>
<td>6.06</td>
<td>1440</td>
<td>1.86 \times 10^{-5}</td>
</tr>
</tbody>
</table>

*Environment: Room-Temperature Acidic Solution (pH~1)*
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>$P_i$, lb</th>
<th>$P_f$, lb</th>
<th>$\Delta P$, lb</th>
<th>$\Delta a$, in</th>
<th>$K_i$, ksi $\sqrt{\text{in}}$</th>
<th>$K_f$, ksi $\sqrt{\text{in}}$</th>
<th>$\Delta K$, ksi $\sqrt{\text{in}}$</th>
<th>$T$, hours</th>
<th>$\Delta a/T$, in/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>433</td>
<td>317</td>
<td>116</td>
<td>None</td>
<td>27.7</td>
<td>20.3</td>
<td>7.4</td>
<td>360</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>498</td>
<td>341</td>
<td>157</td>
<td>None</td>
<td>33.6</td>
<td>23.0</td>
<td>10.6</td>
<td>360</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>561</td>
<td>380</td>
<td>181</td>
<td>0.007</td>
<td>37.8</td>
<td>25.7</td>
<td>12.1</td>
<td>360</td>
<td>$1.94 \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>442</td>
<td>302</td>
<td>140</td>
<td>0.012</td>
<td>26.8</td>
<td>20.3</td>
<td>6.5</td>
<td>720</td>
<td>$1.67 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>519</td>
<td>350</td>
<td>169</td>
<td>0.019</td>
<td>35.0</td>
<td>23.9</td>
<td>11.1</td>
<td>720</td>
<td>$2.64 \times 10^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td>601</td>
<td>424</td>
<td>177</td>
<td>0.028</td>
<td>40.5</td>
<td>29.0</td>
<td>11.5</td>
<td>720</td>
<td>$3.89 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

*Environment: Room-Temperature Acidic Solution (pH~1)*

$P_i$ = Initial load  
$P_f$ = Final load  
$\Delta P$ = Change in load  
$\Delta a$ = Crack extension  
$K_i$ = Initial stress intensity factor  
$K_f$ = Final stress intensity factor  
$\Delta K$ = $K_i$ $-$ $K_f$  
$T$ = Time  
$\Delta a/T$ = Overall crack growth rate
3.0 Materials, Design and Modeling for C/SiC Ceramic Heat Exchangers, (PI: Per Peterson, UCB)

3.1 Objectives and Scopes

Within the UNLV Research Foundation High Temperature Heat Exchanger (HTHX) project the University of California, Berkeley (UCB) has the role of developing technologies for intermediate heat transport of high temperature process heat from the Next Generation Nuclear Plant (NGNP) reactor to the hydrogen production process. In this work, UCB has developed ceramic compact heat exchangers for use in the IHX, and has studied these materials for use in the hydrogen production heat exchangers. Because the studies of the ceramic IHX showed that they could not be qualified in time to meet the NGNP schedule, UCB has refocused its efforts to support design and assessment of the use of liquid salts for the NGNP intermediate loop. Work in this area has two primary task areas, (1) liquid salt intermediate loop dynamic analysis, with a particular focus on the transient thermal and stress response of Heatric-type IHX heat exchangers, and (2) liquid salt chemistry and corrosion control, with a particular emphasis on assessing corrosion control methods for the Si/SiC composites likely to be used for the process heat exchangers, and analysis of tritium transport phenomena in the loop.

3.2 Highlights

- The German Aerospace Center (DLR) has provided UCB test coupons made out of the Silicon/Silicon Carbide (SiSiC/C) for corrosion testing with Flinak liquid salt at the University of Wisconsin. Coating application testing will occur at Hypertherm for the purpose of evaluating the effectiveness of coating the internal flow passages with corrosion resistant pyrolytic carbon.
- Progress on the global thermal model and stress analysis for compact heat exchangers includes completion of the fluid dynamic modeling for the new Heatric-type geometry of the IHX.
- A consolidated thermal hydraulic model for the IHX is also near completion and has been named the Compact Heat Exchanger Explicit Thermal And Hydraulics code or CHEETAH.
- An analysis of tritium transport from a helium cooled reactor through the intermediate loop is continuing.

3.3 Technical Progress Summary

3.3.1 Materials Testing of Silicon Silicon Carbide Si/SiC

UC Berkeley has just received 13 Si/SiC test coupons from the German Aerospace Center (DLR - Deutsche Zentrum für Luft- und Raumfahrt) shown in Figure 22. These test coupons are based on the BioKer material, and exhibit varied surface porosity and roughness. UC Berkeley will coordinate the chemical vapor deposition (CVD) coating of these test coupons with silicon carbide followed by pyrolytic carbon at Hypertherm (the vendor that has provided similar CVD coating services for UCB in the past). Subsequently, the coupons will be subjected to high temperature corrosion testing in Flinak liquid salt at the University of Wisconsin.
Continuing work in the area of ceramic heat exchangers will shift in focus toward design, analysis and experiments for liquid salt compatibility. This will include further analytical work on corrosion and safety issues for liquid salt intermediate loops, and studies of approaches to CVD coat the internal surfaces of ceramic heat exchangers that can be used for sulfuric acid thermal decomposition. A detailed report on previous UC Berkeley work in this area was released.

![Figure 22: Si/SiC coupons for pyrolitic carbon CVD and corrosion tests.](image)

**3.3.2 Teflon molds for heat exchanger manufacturing test**

After manufacturing the Teflon molds for the fabrication of the ceramic high temperature heat exchanger (HTHX) at UC Berkeley, the molds were sent to DLR where the ceramic Si/SiC heat exchanger article will be manufactured. DLR recently returned the molds to UC Berkeley so that they could be rebuilt from thicker Teflon so to stiffen the base of the mold for improved dimensional accuracy. DLR will provide heat exchangers fabricated using these molds, which will be used to study CVD coating methods for internal surfaces.

**3.3.3 Compact heat exchanger thermal/mechanical design study**

UC Berkeley continued work to develop a global thermal and fluid mechanics model for compact ceramic and metallic heat exchangers based on the effective porous media (EPM) approximation. In particular, the work focused on the numerical modeling of the liquid salt inlet and outlet manifold. The IHX geometry is such that the liquid salt (LS) plate’s inlet and outlet
pipes are attached to the side of the heat exchanger assembly. This means that a sophisticated array of distribution channels is needed to evenly distribute the liquid salt over the IHX’s liquid salt plate. For this reason, the fluid dynamics model for the LS plate contains over 30 regions with different effective permeabilities. The computational model has been set up so that the flow resistance in each of the regions within the manifolds can be adjusted independently, relative to the other sections in the diffuser.

Recently a design change was made to the LS manifold to make it more closely resemble the type used by Heatric. Writing the code for this new geometry was a primary focus early in the quarter. The latter half of the quarter was spent consolidating the codes written for the inlet, outlet and offset strip fin regions of the IHX into one consolidated thermal hydraulics code. The hydraulic component of this consolidation is now complete and strong progress is being made on the heat transfer model. The consolidated thermal and hydraulics model will be called the Compact Heat Exchanger Explicit Thermal And Hydraulics (CHEETAH) code. This code will provide a global transient temperature distribution for the IHX. A steady state pressure distribution for the liquid salt plate of the IHX was solved by CHEETAH, and the results can be seen in Figure 23.

![Figure 23: CHEETAH: Steady state pressure dist. for the IHX liquid salt plate manifold.](image)

The global temperature distributions calculated with CHEETAH will then be exported to the finite element analysis software ANSYS for mechanical stress analysis. The resulting mechanical stress analysis will close the design optimization loop by revealing the most highly stressed areas in the HX design. These areas will then be redesigned to be more robust. Subsequent analyses evaluating stress at the channel level will also provide insight into the possible creep effects at the channel level.
3.3.4 Tritium transport model for the IHX and liquid salt intermediate loop

The objective of this study is to evaluate the tritium permeation at the high temperatures (~1200K) in the helium cooled Very High Temperature Reactor (VHTR) and a liquid-salt intermediate loop, and to find the appropriate solutions to bring the concentrations below the regulatory requirements.

In a helium cooled VHTR, tritium is mostly produced by thermal neutron absorption on $^3$He. About 5 grams of tritium (50,000 Ci) is produced in the primary coolant during the first year after the startup of the reactor. The study shows that during the next few years approximately 0.5 grams of tritium (5,000 Ci) will enter the coolant. The regulatory limit (1 Bq/g of H$_2$) is reached if 0.2 mg of tritium permeates through the process heat exchanger (PHX) in one year.

A numerical model has been developed to study the tritium transport model. Due to the fast diffusion times of tritium, a lumped mass model has been employed. The inventories of tritium in the different parts of the reactor are calculated using finite difference equations in time. Some preliminary results for the helium cooled reactor with a helium intermediate heat transfer loop can be seen in Figure 24. The results for the same helium cooled reactor transferring heat to a liquid salt intermediate loop can also be seen in Figure 25. These results assume diffusion limited transport regime and represent the reactor startup period, which is when tritium poses the greatest challenge.

![Fig. 24: Tritium inventory for He/He case.](image1)

![Fig. 25: Tritium inventory for He/LS case.](image2)

These results show that tritium diffuses very promptly to the secondary loop through the metallic intermediate heat exchanger (IHX). Indeed, at 1200 K, the permeability of the metal is so high that the steady state between the primary and the secondary coolants is almost instantaneous (same curve) as can be seen in Figure 25. It is also worth noting that the permeability of silicon carbide to tritium in the PHX is about five orders of magnitude lower than the permeability in the metallic alloy proposed for the IHX.
Oxide films on the surface of the exchanger could reduce the permeation of tritium. Still, interaction between the liquid salt and the silicon carbide has yet to be studied in detail.

The permeation of the tritium through the hot leg piping between the IHX and PHX is also being evaluated. The high temperatures in the metallic wall of the hot leg could present an important transport path for tritium into the insulation system surrounding the piping. If this path turns out to be important, a significant fraction of the tritium could be separated from the heat transfer fluid in the insulation gap of the hot leg. This tritium could then be vented or captured and it would further reduce the concentration of tritium in the intermediate loop and in the hydrogen product.
4.0 Corrosion Studies of Candidate Structural Materials in HIₓ Environment as Functions of Metallurgical Variables (PI: Bunsen Wong, General Atomics)

4.1 Immersion Testing of Materials in HIₓ-H₃PO₄ (Iodine Separation)

The focus of this quarter was to study the effects of the chemical environment on the mechanical properties of Ta-10W. A tensile specimen machined from Ta-10W was immersed in the H₃PO₄ - HIₓ circulating bath for more than 1500 hours. Figure 26 shows the progression of the specimen during the test, and no evidence of corrosion was present. The specimen will be returned to UNLV for tensile testing.

![Figure 26: A Ta-10W tensile specimen that has been in the H₃PO₄ and HIₓ circulating bath.](image)
In support of the ILS, the corrosion property of tungsten carbide has been determined. A ball that can be used for sealing in a valve was submerged in a H₃PO₄ - HIₓ static bath. Figure 27 shows the ball after 216 hours of testing and only a slight stain can be observed on the surface and no weight loss could be recorded. Hence, WC can be used with this environment.

\[ \text{Figure 27: A tungsten carbide ball that was tested in the H}_3\text{PO}_4\text{ and HI}_x \]

4.2 Immersion Testing of Materials in Boiling H₃PO₄

In this quarter, testing of Ta-10W tensile specimens was completed in both boiling concentrated H₃PO₄ and boiling H₃PO₄ with both HI and I₂. Figures 28 and 29 show the progression of the specimens that have been tested in both environments respectively. In contrast to the iodine separation specimen, both specimens have a significant phosphate scale that remained on them after the test. After removal of this scale, a smooth clean surface was observed in both specimens, thus there was probably no significant corrosion on the specimen. The specimens will be returned to UNLV for tensile testing to determine the effect of the chemical environment on mechanical properties.

\[ \text{Figure 28: A Ta-10W tensile specimen that has been tested in boiling 95wt\% H}_3\text{PO}_4\text{ at 240 C.} \]
Figure 29: A Ta-10W tensile specimen that has been tested in boiling $H_3PO_4$-14.4HI-0.7I$_2$-16.1H$_2$O -wt% at 190°C.

A tungsten carbide specimen was also tested in boiling concentrated phosphoric acid. Figure 30 shows the sample after 480 hours of testing, and there is sign of corrosion. Purple deposit has also been observed in the post test liquid, which may have been a result of oxidation of the cobalt binding agent used to sinter the tungsten carbide. More detailed examination of the specimen is underway.

Figure 30: A tungsten carbide sample tested in boiling 95wt% $H_3PO_4$ acid.
4.3 **Testing of Materials in HI + I₂ + H₂ (HI gaseous decomposition)**

Testing of C-22 and C-276 double cantilever beam (DCB) specimens was completed in the HI decomposition environment. The specimens were pre-cracked at UNLV and loaded with a wedge. Figures 31 and 32 show the two specimens respectively. Optical inspection of the C-22 specimen did not show any visible crack before immersion. However, it seems that a crack developed after about 500 hours of testing. In addition, there is also evidence of pitting near the crack region. For the C-276 specimen, a crack can be observed in the as received specimen. There was no significant change in the size of the crack after the test. More detailed examination of the specimens will take place after they are pulled apart at UNLV.

![Figure 31: C22 DCB specimen that was tested in the HI decomposition.](image)

The testing of B3 specimens continued this quarter. Test results are similar to those of B2 and no crack has developed in the stress corrosion specimens (see Figures 33 - 36). Testing should be completed next quarter.
Figure 32: C276 DCB specimen that was tested in the HI decomposition.

Figure 33: B3 coupon tested in the HI gaseous decomposition environment.
Figure 34: B3 coupon tested in the iodine condenser of the HI gaseous decomposition system.

Figure 35: B3 c-ring specimen tested in the HI gaseous decomposition system.
Figure 36: B3 u-bend specimen tested in the HI gaseous decomposition system.
5.0 Chemistry Support Studies (PI: Allen Johnson, UNLV).

5.1 Highlights

- Characterization of structural materials continued for thermochemical hydrogen cycle facilities (in particular the S-I cycle).
- Studies were conducted of process liquids from thermochemical hydrogen cycles.

5.2 Materials Characterization

Ta coated steel ferrules used in the General Atomics (GA) skid were obtained. They had failed at the point where they swaged into the TaW allow tube of the facility. XPS and SEM investigations were started – the XPS investigations were completed, but the SEM investigations are continuing.

XPS found a high level of carbon on the tantalum – this was not unexpected, since carbon can be deposited from environmental sources. With a few nm of material removed (Figures 37 and 38) by Ar ion sputtering, one normally sees a decrease of carbon signal, and this is seen with the TaW tube sample. The ferrule, on the other hand, showed increased carbon with carbon levels high up to a micron into the surface (Figures 39 – 41). This is probably due to either porosity in the coating, leading to significant penetration of carbon into the Ta coating, or incorporation of carbon (perhaps as carbide) into the layer during deposition. In either case, this observation is not suggestive of the expected Ta layer.

![Figure 37: TaW tube as received. Note high C levels.](image-url)
Figure 38: TaW tube. Note substantial decrease in C levels after 7nm of sputtering.

Figure 39: Ta coated ferrule as received. Note very high C levels.

Figure 40: Ta coated ferrule after 7nm sputter. Note increase in C levels (possibly due to O decrease).
SEM investigations in progress will help resolve questions about possible Ta coating morphology; a non-failed part has been requested to see if the compositional and morphological differences can be observed.

5.3 Process Monitoring

As part of the 2007 scope of the Chemical Support function of the UNLV project, workers at GA and Sandia have been engaged in discussions with UNLV about process fluid analysis of the Integrated Lab Scale (ILS) facility. This effort has been particularly successful in finding synergies between existing facilities and efforts and the analytical requirements of the ILS. In particular, ex-situ analysis has started using UNLV assets, and instrumentation for location at GA for in-situ studies at the ILS have been found in current inventory.

Investigations of process fluids have been started using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to look at the iodine and sulfur levels. Initial results indicate the migration of sulfur all through the cycle.

These samples will be looked at, at least initially, using a variety of techniques. In particular, X-Ray Fluorescence (XRF) and X-ray Photoelectron Spectroscopy (XPS) will be the primary methods. These techniques, if found to be appropriate, can be used on samples dried onto aluminum foil supports, and shipped at low cost and high stability in that form. Further, it becomes trivial to create a “library” of samples for later analysis. XRF and XPS are very general
methods for determination of elemental composition (and in the case of XPS oxidation state) and so, not only process parameters can be monitored - but corrosion residues can be traced as well.

In-situ probes of the process liquids are being investigated. IR and Raman spectroscopic methods are being pursued.

Previous work by Gelbard (Sandia) and others has shown that IR is an appropriate way to look at sulfur oxides in these systems. The diamond window Attenuated Total Reflection (ATR) IR technique is the decided upon technique to attempt. These systems have recently been found to be very useful for process analytics, and the diamond should be rather resistant to these liquid streams. Some development will have to be done to mount the diamond into the ILS; two vendors have been contacted who are interested in pursuing this.

Raman would get equivalent data to IR studies using laser radiation – in this case quartz or sapphire windows could be used. The Raman microscope at UNLV will be used for this feasibility study.

Lastly, the Corrosion Resistant Mass Spectrometer task will be used in the plan to model the behavior of the high temperature gas phase sections of the ILS. The facility will be used to develop and qualify candidate catalysts for the process. The facility has been designed to be carried on a rolling bench/rack – it will be possible to interface the CRMS to the ILS, if this is determined to be appropriate.

The IR, Raman, and Mass Spectrometer efforts will start with the new funding, although the planning phase is occurring now.
6.0 Development of an Efficient Ceramic High Temperature Heat Exchanger (PI: Merrill Wilson, Ceramatec, Inc.)

6.1 Program Highlights

- Experiments to determine the temperature dependence for oxidation of candidate heat exchanger materials was conducted. Additional sulfuric acid vapor exposure experiments to improve the statistical quality of the corrosion data continued.
- A revised design of the heat exchanger that utilizes the enhanced micro-channel features as analyzed by UNLV is nearly complete. Based on the associated stress calculations, a reliability analysis can also be completed.
- The initial full-size wafer components have been completed, using the Rev 2.0 design of the decomposer. These are awaiting shipping to the appropriate recipient(s).
- Ceramic to ceramic joining samples have demonstrated shear strengths greater than 100 MPa (original design target). Processing methods are being refined in order to implement the joints into stack assemblies.

6.2 Research Accomplishments

6.2.1 Materials Corrosion

A 1,000 hour-long exposure experiment of additional samples of Ceramatec’s laminated silicon carbide and Ceradyne’s gas-pressure sintered Si₃N₄ was performed in order to determine the temperature dependence for oxidation. The samples were exposed in an environment containing 60 mole% H₂SO₄, 30 mole% H₂O, 9.5 mole% O₂, and 0.5 mole% N₂ at 875 °C and ambient pressure. The strength of the specimens was measured after 1,000 h of exposure, results are shown in Table 6. The results indicate that the strength of Ceradyne gas-pressure sintered Si₃N₄ decreases as the exposure temperature increases. On the other hand, the strength of Ceramatec’s silicon carbide is not highly temperature dependent. Weight change measurements will be made and these will be converted to approximate oxidation rates following analysis of surface chemistry and microscopic analysis of the cross section of specimens. Possible explanations for the decrease in the strength values for the silicon nitride material are lower growth rates of silicon-oxynitride corrosion products relative to silica ones and less crack blunting effects, higher viscosity of silicon-oxynitride corrosion products relative to silica ones and less crack blunting effects, internal oxidation of grain boundary phases present in higher amounts than the silicon carbide material, and sintering aid or impurity affects on the corrosion product not present in the silicon carbide.

An additional 1,000 hour-long exposure of additional samples of Ceramatec’s laminated silicon carbide (SiC) and Ceradyne’s gas-pressure sintered silicon nitride (Si₃N₄) in 30 mole% H₂SO₄, 60 mole% H₂O, 9.5 mole% O₂, and 0.5 mole% N₂ at 900 °C was performed in order to improve the statistical significance of the corrosion testing data. The values of the four-point, flexural strength of both materials for each experiment are shown in Table 7. There was no statistical difference in the strength of the laminated silicon carbide (SiC) made at Ceramatec, Inc. measured in each experiment. The value of the strength of the silicon nitride (Si₃N₄) appeared to be slightly greater in the second experiment.
Table 6: Strength vs. Temperature after exposure to 60 mole% H₂SO₄, 30 mole% H₂O, 9.5 mole% O₂, and 0.5 mole% N₂.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Avg. Strength (MPa)</th>
<th>95 % CI (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramatec SiC</td>
<td>Unexposed</td>
<td>403</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>875, 1 000h</td>
<td>595</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>900, 600 h</td>
<td>481</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>950, 600 h</td>
<td>564</td>
<td>76</td>
</tr>
<tr>
<td>Ceradyne Si₃N₄</td>
<td>Unexposed</td>
<td>708</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>875, 1 000 h</td>
<td>871</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>900, 600 h</td>
<td>719</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>950, 600 h</td>
<td>625</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 7: Four-point, flexural strength experimental results.

<table>
<thead>
<tr>
<th>Material</th>
<th>Avg Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>95% Conf. Level (MPa)</th>
<th>Weibull Modulus</th>
<th>Char. Strength (MPa)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC (original)</td>
<td>518</td>
<td>87</td>
<td>49</td>
<td>6.7</td>
<td>554</td>
<td>12</td>
</tr>
<tr>
<td>SiC (repeat)</td>
<td>579</td>
<td>92</td>
<td>33</td>
<td>7.4</td>
<td>618</td>
<td>30</td>
</tr>
<tr>
<td>Si₃N₄ (original)</td>
<td>828</td>
<td>78</td>
<td>43</td>
<td>11.9</td>
<td>864</td>
<td>13</td>
</tr>
<tr>
<td>Si₃N₄ (repeat)</td>
<td>892</td>
<td>56</td>
<td>20</td>
<td>18.9</td>
<td>917</td>
<td>30</td>
</tr>
</tbody>
</table>

Two samples of each of Ceramatec’s laminated silicon carbide and Ceradyne’s gas-pressure sintered Si₃N₄ were tested in a high pressure corrosion apparatus at The Idaho National Laboratory. The corrosion rate of Ceramatec’s laminated silicon carbide is approximately 125 µm/year; Ceradyne’s gas-pressure sintered Si₃N₄, 62 µm/year. Additional evaluation of the specimens will be performed when the samples are returned to Ceramatec. Evaluation of the temperature dependence of corrosion of Ceramatec’s laminated silicon carbide and Ceradyne’s gas-pressure sintered Si₃N₄ will be reported in the FY07 interim report. Shakedown of apparatus for conducting corrosion experiments in boiling sulfuric acid and at the interface between liquid and vaporous sulfuric acid at the boiling point will be conducted prior to completing the FY07 interim report.

6.2.3 Heat Exchanger Reliability

The critical geometric dimensions have been determined for the reliability models based on the Revision 2.5 design. These inputs and operating conditions will be used for reliability models and compared to previous estimates.
6.2.4 Porous Catalyst Support

A process is being adapted for creating porous ceramic structures from a polymer tape material. Objectives of the first phase are to determine the processing parameters necessary to produce a sintered body with porosity within a given range. The second phase of this activity will be to determine what parameters control porosity and to tailor build structures with a given porosity. Three formulations of porous tapes have been cast and fired. These will be characterized in terms of porosity, surface area, and where possible permeability and strength will be measured.

6.2.5 Heat Exchanger Revision 2.5 Design

The layout for the Revision 2.5 has been completed, including the details of the slotted layers. The primary channels were constructed from offset layers of diamond shape polygons. These offset patterns require the internal fluid to porpoise up and down, forcing entrance-like conditions at each turn. These channel patterns also help distribute the flow evenly from side to side, minimizing non-uniformity.

The internal structure of this Rev. 2.5 design was based on design concepts from Ceramatec, Inc. and analyzed by Valery Ponyavin of UNLV. These analyses showed that the heat transfer effectiveness could be improved from 86% to about 95% in a sulfuric acid decomposer application. Likewise, the estimated decomposition of $SO_3$ to $SO_2$ and $O_2$ was increased from 60% to about 80%. Both factors can be attributed to the intensification of heat and mass transfer in micro-channels, especially those constructed from layers requiring flow turning.

These benefits come at the cost of an increased pressure drop and increased stresses within the ceramic body. The analyses of UNLV also predicted that the pressure drop and stress levels remained within the design window for the sulfuric acid decomposer.

The several layers are shown in Figures 42 – 46. The S1 layers, primary internal flow layers, are cut such that when one of the S1 layers is rotated 180°, the assembled two layer structure forms the offset pattern described. This bi-layer assembly is capped on one side with the HT (Heat Transfer) layer, which acts as the primary heat transfer surface. The other side is capped with the S2 layer, which helps provide for the internal manifolding within the wafer. This wafer has a plane of symmetry at the mid-plane, giving two heat exchange surfaces per wafer.

Components have yet to be made of this design because the assembly tooling has not been completed.
Figure 42: Revision 2.5 Assembly of Laser Cut Layers (HT-S1-S1-S2-S1-S1-HT).

Figure 43: Revision 2.5 S1 Layer Pattern

Figure 44: Revision 2.5 S2 Layer Pattern

Figure 45: Revision 2.5 Overcut Pattern

Figure 46: Revision 2.5 X-Section View
6.2.6 Heat Exchanger Fabrication

This quarter the fabrication of 60 flow coupons and 8 channeled wafers was completed. The flow coupons had an overall yield of 40%, partly due to an error in one of the sintering cycles. 88% of the channeled wafers produced were within required specifications. Future work will continue, focusing on producing wafers with more complex channel patterns, as well as improving methods of building stacked coupons.

In addition to channeled parts, some experimentation with porous SiC formulations for catalysis was completed. By varying the starting material and the volume fraction of pore former, it was demonstrated that it is possible to make SiC with different levels of porosity. Further work will attempt to make parts with a pre-determined porosity.

6.2.7 Heat Exchanger Joining

Additional experiments to develop a process for making leak tight joints between heat exchanger plates using pre-ceramic polymer precursors were initiated. During the month of May, several compositional and processing variables were investigated. It was found by using SEM analysis that the addition of pre-pyrolyzed AHPCS resulted in relatively dispersed large grain SiC in the joints. These large grains may result in a degradation of strength and/or joint uniformity. Hence, several variations in the formulations (SiC powder and liquid AHPS) and process variables (milling and mixing times and viscosity) were investigated. Using these variations, it was found that very uniform, small grain materials could be fabricated, and preliminary tests indicate that the bond strength is increased.

Very good results in sheer strengths have been achieved with 61 vol% solids, with a maximum of 144 MPa in test bars broken in double lap sheer testing. SEM analysis of these fractured joints revealed cracking within the sintered paste during the sintering process in part due to off-gassing and oxidation of the paste, but also attributable to other as-yet unidentifiable causes. These causes are presently being investigated and solutions to oxidation are being evaluated.

As the vol% solids were reduced to 50 vol%, a dramatic decrease in sheer strength was also seen, yielding a maximum sheer strength value of 49.5 MPa. SEM analysis of these joints revealed surfaces with dramatically decreased solids; however, the cracking due to sintering was generally the same in this composition as with higher vol% solid compositions, suggesting that the cracking is not necessarily a function of lower solids content. With these results, further testing is now being focused on pastes with compositions greater than 50 vol% solids, but still less than 66 vol%, as discussed previously.
7.0 Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells through Improved Electrodes and Electrolytes (PI: Clemens Heske, UNLV)

7.1 Introduction

In close collaboration with Ceramatec and ANL, UNLV has teamed up to investigate the chemical structure and morphology of surfaces that are relevant to solid oxide electrolysis cells (SOEC) as well as solid oxide fuel cells (SOFC). Composition, structure, and chemical properties of samples provided by Ceramatec and ANL are analyzed at UNLV with a set of spectroscopic and microscopic surface and interface techniques. The experimental methods include x-ray and UV photoelectron spectroscopy, x-ray emission and absorption spectroscopy, and atomic force microscopy.

The work focuses on a comparison of the above-mentioned properties before and after testing at Ceramatec or ANL. This testing includes electrochemical conditioning, high-temperature stress testing, and long-term operation.

The results of the UNLV experiments are shared with the partners at Ceramatec and ANL, in order to give immediate feedback for the chemical surface processes occurring during testing and to assist in the development of more long-term stable devices.

7.2 Research Accomplishments at UNLV

In the past quarter, the collaboration between UNLV and Ceramatec was initiated. In a meeting between Ceramatec (represented by S. Elangovan and J. Hartvigsen) and UNLV (represented by T. Hofmann, L. Weinhardt, M. Bär, and C. Heske) at UNLV, fields of particular interest for an improvement of SOEC and SOFC systems were discussed. This discussion led to a detailed plan for experiments, and a list of necessary samples. The first set of samples is currently being prepared and will be shipped under inert conditions (packed under nitrogen). This careful packing helps to preserve the surface condition obtained at Ceramatec (i.e., prior to shipping) and is necessary for the surface sensitive experiments at UNLV.

First photoemission experiments were conducted on oxygen-evolution electrode samples from Ceramatec that we received through ANL. The samples were part of a long term stability test to study the influence of varying conditioning currents on the SOEC electrode which were performed at ANL. Two of the four samples were current-conditioned in a tube furnace at 830 °C for more than a month. For comparison, the other two were not conditioned. The conditioned samples and the unconditioned samples each consisted of a working electrode and a reference electrode, deposited on a Scandia-stabilized zirconia substrate. Both working electrodes had a diameter of approximately 8 mm, while the reference electrodes were only approximately 3 mm in diameter. The electrode nominally consists of a ~50 μm thick layer of LaSrCoO on top of a ~50 μm thick mixed layer of PrSrMnO and yttria-stabilized zirconia (YSZ) with a 50%/50% mixing ratio. All samples were investigated using surface sensitive X-ray photoelectron spectroscopy (XPS) in our lab at UNLV.

Figure 47 shows an example XPS survey spectrum of the working electrode of the conditioned
sample. To minimize sample charging and to cover the bare substrate around the electrode, a Ta mask was used. On the conditioned sample La, Co, Sr, and O were found, as expected from the electrode layout as described above. The spectra also exhibit small Pr and Zr signals through the LaSrCoO layer, which are an indication for diffusion or an incompletely (inhomogeneous) closed film. The surface also contains Pt and Bi, presumably from the mesh used for current conditioning at ANL. As a first test of this hypothesis, the mesh used for testing by Ceramatec was also investigated, but no Bi was found at the surface. In a next step, the composition of the mesh used by ANL (once obtained) will also be measured.

![Figure 47: XPS survey spectrum of the working electrode of the conditioned sample.](image)

All samples show a strong C signal stemming from adsorbates on the surface. With an improved sample packaging procedure, as discussed in the meeting with Ceramatec, this contamination will be reduced in future. The Ta, Zn, and part of the O and C signals found at the surface can be attributed to the utilized Ta mask. In the future, such signals can be avoided if larger samples are available for these studies.

In contrast to the tested sample, the as-prepared sample only shows lines of Pr, Mn, Co, Zr, O, and C, see Figure 48. No La or Co signal was found, which leads to the conclusion that the
LaSrCoO top layer was not deposited on these samples. A large Pr signal, a small Zr signal, and no Y signal were found. This is interesting because it indicates that the surface composition of the layer clearly differs from the expected 50:50 mix of PrSrMnO and YSZ (8 mol% Yttria). The surface is free of Pt and Bi, consistent with the hypothesis that these elements originate from the mesh used for the current conditioning at ANL.

Figure 48: X-ray Photoelectron spectra of the working electrode of the as prepared sample.

In the next quarter, plans are to investigate the sample series which has been discussed with Ceramatec. The first set of experiments will be complemented by atomic force microscopy (AFM) measurements to investigate the morphology of the sample surfaces.
8.0 The Development of Self Catalytic Materials for Thermochemical Water Splitting Using the Sulfur-Iodine Process (PI: Ronald Ballinger, MIT)

8.1 Technical Highlights

- A quartz chamber designed to hold the new alloy specimens was updated and thin disc-type specimens were polished and sectioned, being ready to go into the quartz chamber.
- Sample fabrication for the electrochemical and the catalytic effectiveness tests were completed.
- Upgrade in the electrochemical test cell was performed in order to achieve proper oxygen removal from the cell and to reduce noise in the test data. For the electrochemical characterization, a test cell using a 1 liter flat bottom flask has been constructed to allow the following items to be inserted into the solution chamber: the working electrode (test material), two counter electrodes, a Luggin capillary with salt-bridge connection to the reference electrode, inlet and outlet for an inert gas, and a thermometer. New alloys with Pt addition are currently being tested in the upgraded system.
- 800H + Pt alloys were tested in comparison with 800H without Pt and data analysis and further system tuning was performed.
- The working electrode assembly employs disc electrodes of 1.5875 cm diameter. The Pt added as cast materials were sectioned into such disc dimension and were mechanically polished up to 600 grit SiC paper. Two graphite rods are used for the counter electrodes, and Saturated Calomel Electrode (Hg/Hg₂Cl₂/Sat. KCl, +0.242 V vs. SHE) for the reference electrode. A test solution of 0.1 M Na₂SO₄ is prepared from ACS Grade reagent and de-ionized water. The solution deaeration to reduce the oxygen level is achieved by bubbling prepurified Ar-H₂ mixture. Overall test arrangement and procedures were set according to the ASTM Standards.
- An electrochemical interface, Solatron Model 1287 Potentiostat, is used to control the rate of the reactions occurring at the electrode surface. Also, Solatron 1260 Frequency Response Analyzer is employed to obtain additional corrosion cell parameters. Data acquisition system, incorporating a GPIB board with software packages of CorrWare/CorrView and ZPlot/ZView, is used for hardware control and data analysis.