High Temperature Heat Exchanger Project

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The UNLV Research Foundation
4505 Maryland Parkway
P. O. Box 452036
Las Vegas, NV 89154-2036

Anthony E. Hechanova, Ph.D.
Project Manager
(702) 895-1457
(702) 895-2354 (FAX)
hechanova@unlv.nevada.edu

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1.0 UNLV Design and Testing Group

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

1.1.1 HTHX Thermal Systems Design Highlights

- The variation of sulfur dioxide production (throughput) of the baseline design of the Ceramatec sulfuric acid decomposer with total mass flow rate of reacting flow has been calculated. According to the calculations, the sulfur dioxide production increases as the total mass flow rate of reacting flow increases regardless of the fact that decomposition percentage of sulfuric trioxide decreases. A parametric study of the baseline design of the Ceramatec sulfuric acid decomposer was performed.

- The thermal performance using various channel geometries for the decomposer was studied. The baseline design (straight channels) has 89.5% thermal efficiency while the thermal efficiency of the alternative designs can be enhanced up to 95.9% (for the diamond-shaped channel design).

- Stress analysis of a transient regime (shutdown process) of the baseline design Ceramatec HTHX was completed. The transient regime started from working condition, and then all of the inlets and outlets closed simultaneously. After that the temperature distribution in the ceramic part of the decomposer started to change and reached practically uniform distribution (maximal temperature nonuniformity in the ceramic part was less than 5 K) in two minutes. During this time the maximum principal stresses were lower than the allowable tensile strength for the ceramic material. The results indicate that the design is safe for the transient regime.

- Calculation of the safety factors and probabilities of failure for a transient regime of the baseline design Ceramatec HTHX was completed. The transient regime started from no flow conditions in room temperature (20 C) and suddenly the hot helium with temperature 950 C started to flow in the helium channel. The safety factors and probabilities of failure were calculated for six different times: 0, 1, 10, 30, 60, and 120 seconds after beginning of the helium flow. For all of the calculation times the safety factors were more than one. The minimum safety factor appeared after 10 sec and is equal to 3.8. The probability of failure is close to zero for all of the cases. The results show that the design is safe for the unsteady regime or the start up process.

- Matlab code for safety factor calculation using a two-dimensional axisymmetric model of bayonet type decomposer was created. Using the code, the safety factor was calculated for inner and outer SiC walls and intermediate quartz wall of the decomposer. The minimum safety factor obtained for all of the walls is 17 which indicates that the design is safe for the baseline geometry and operation conditions.

1.1.2 HTHX Thermal Systems Design Technical Summary

Numerical Analyses with Chemical Reactions and Optimization Studies for the Ceramatec Sulfuric Acid Decomposer
The Arrhenius constants (activation energy $E_a$ and pre-exponential factor $A_r$) obtained from experiments in the packed bed area (provided by Dan Ginosar, INL) were applied to the single channel model of the baseline Ceramatec heat exchanger and decomposer design with straight channels. The constants are: $E_a=32670.69$ J/mol and $A_r=0.16$ s$^{-1}$ for 1 wt % Pt. Because the obtained activation energy (32670.69 J/mol) is smaller than that used in previous calculations (88,034 J/mol) the sulfur trioxide is easier to decomposed and the decomposition percentage reached 83.6% for the $1.574 \times 10^{-6}$ kg/sec mass flow rate in the single channel (Figure 1). The percentage decomposition of SO$_3$ also depends on the channel length (Figure 2) and operation pressure (Figure 3). All of the parametric studies shown in Figures 1, 2, and 3 (mass flow rate, channel length and pressure) are varying with residence time. All of the results from the parametric studies fall under the same line (Figure 4). Therefore the high SO$_3$ conversion is just the result of the increased residence time.

**Figure 1:** Percentage decomposition of SO$_3$ versus different mass flow rates in the reacting flow

**Figure 2:** Percentage decomposition of SO$_3$ versus channel length

**Figure 3:** Percentage decomposition of SO$_3$ versus operation pressure

**Figure 4:** Percentage decomposition of SO$_3$ versus residence time
The porous media approach was incorporated into the Ceramatec sulfuric acid decomposer model to calculate chemical reactions in the channels with complex shapes (i.e., hexagonal- and diamond-shaped channels). In this approach, the domain with channels of complex shape is simplified as a porous media zone with the same surface to volume ratio and appropriate viscous resistance, inertial resistance and porosity ratio. Such simplification reduced computation time tremendously. The modeling is now in progress.

Effects of using various channel geometries on the thermal performance of the decomposer were studied. The baseline design (straight channels) has 89.5% thermal efficiency while the thermal efficiency of the alternative designs can be enhanced up to 95.9% for the diamond-shaped channel design.

The variation of sulfur dioxide production (throughput) of the baseline design of the Ceramatec sulfuric acid decomposer with total mass flow rate of reacting flow was calculated. According to the calculations, the sulfur dioxide production increases as the total mass flow rate of reacting flow increases regardless of the fact that decomposition percentage of sulfur trioxide decreases as total mass flow rate of reacting flow increases.

**Stress Analysis and Optimization of Ceramatec HTHX**

Calculation of safety factors and the probability of failure for a transient regime of the baseline Ceramatec HTHX design were completed. The transient regime started from no flow conditions in room temperature (20 C) and suddenly the hot helium with temperature 950 C started to flow in the helium channel. The calculations of the safety factors and probability of failure was completed for six different times: 0, 1, 10, 30, 60, and 120 seconds after onset of the helium flow (Figure 5). For all of the calculation times the safety factor is more than one. The lowest safety factor appeared after 10 sec and is equal to 3.8. The probability of failure is close to zero for all of the cases. The results indicate that the design is safe for the unsteady regime.

![Figure 5: Safety factor vs. time](image)
Stress analysis of a transient regime (shutdown process) of the baseline Ceramatec HTHX design was completed. The transient regime started from working condition and then suddenly all of the inlets and outlets closed simultaneously. After that the temperature distribution in the ceramic part of the decomposer started to change and reached practically uniform distribution (maximum temperature nonuniformity in the ceramic part was less than 5 K) in two minutes. During this time the maximum principal stresses were lower than the allowable tensile strength for the ceramic material. The result shows that the design is safe for the transient regime.

**Stress Analysis and Optimization of the Bayonet-type HTHX and Decomposer**

A Matlab code for safety factor calculation using a two-dimensional axisymmetric model of the bayonet-type decomposer was created. Using the code, the safety factor was calculated for the inner and outer SiC walls, and the intermediate quartz wall of the decomposer. The lowest safety factor obtained for all of the walls is 17, which indicates that the design is safe for the walls of the baseline geometry and operation conditions.

**Numerical Analysis of the Bayonet-type HTHX and Decomposer**

A parametric study of the decomposer for different operation pressures was completed. The conditions for the flow are: 600 °C inlet temperature, 53% SO₃ mass fraction, 47% H₂O mass fraction. Based on the parametric study, it was found that the percentage of SO₃ decomposition increases significantly as operation pressure increases for the constant mass flow rate (4.5⋅10⁻⁴ kg/sec). The main reason is because the resident time of the reaction flow increases as the operation pressure increases.

A literature survey for the flow calculations in packed bed zone with the different arrangement of pellets was completed. Also, a mesh independence study for the baseline bayonet design was completed.

A mesh system of the packed bed region of the bayonet type decomposer with cylindrical pellets of 5 mm length and diameter using uniform packing method was established (Figure 6). The fluid flow in the pebble bed region was calculated. The pressure drop for the case is 450 Pa (Figure 7).
Figure 6: Geometry and mesh of the packed bed zone (93,512 nodes 402,150 cells)

Figure 7: Pressure distribution in the packed bed zone, Pa
Numerical Analysis of Shell and Tube HTHX and Decomposer

A shell surrounding a tube is used to model the geometry of the shell and tube HTHX (Figure 8). Helium is being passed through the shell at 950°C inlet temperature and at 1 atm pressure with $3 \cdot 10^{-4}$ kg/s mass flow rate. The conditions for the mix flow are: $1.4 \cdot 10^{-4}$ kg/s mass flow rate, 700°C inlet temperature, 53% SO$_3$ mass fraction, 47% H$_2$O mass fraction at 1 atm pressure. Two-dimensional simulations were performed in order to verify the amount of heat transferred along the wall. Simulations were done for both counter (Figure 9) and parallel (Figure 10) flow arrangements. Decomposition of sulfur trioxide, temperature, pressure, and velocity distributions were obtained for both parallel (92%) and counter flow (93%) arrangements from the simulations.

A parametric study of different mass flow rates of helium passing through the shell of the shell and tube HTHX was accomplished. Based on the parametric study, it is found that the SO$_3$ decomposition increases as the mass flow rate of He through the shell increases (Figure 11). The reason for the increasing decomposition is the heat transfer through the tube wall increases as the mass flow rate of He through the shell increases. A parametric study of different diameters of the shell was also performed, where it is found that the decomposition of SO$_3$ increases as the diameter of the shell increases (Figure 12).
A literature survey of different configurations of the inlet and outlet manifolds for the shell and tube HTHX and decomposer with respect to flow distribution among the inside tubes was completed.
1.2 Scaled HTHX Tests (PI: Samir Moujaes, UNLV)

Computational fluid dynamic (CFD) simulations were performed for the test sections with Alloy 6061 as the structural material. CFD results were compared with experimental results. The high conductivity of the Alloy 6061 made an insignificant difference between single-sided and double-sided heating, while the contact resistances made the single-sided heating about 10% less than the double-side heating. The high conductivity of the material made the temperature across the channel walls more uniform.

Literature surveys were conducted on the Bayonet heat exchanger and other nuclear heat exchanger designs, the use of molten salts, and insulation design and testing.

A single-chamber test section with round-edge fins was designed, constructed, and tested with air as the working fluid. Hydraulic tests were performed under isothermal and heated conditions to measure the pressure drops across the fin area. Friction factors were calculated and compared with that of the square-edge fins (Figure 13). The volumetric flow rate was varied and corresponded to a range of Reynolds numbers between 1800 and 2600. The results show that the friction factors of round-edge fins are 40% less than that of the square-edge fins, as shown in Figure 14. The hydraulic diameter of the round-edge fins is only 1.5% larger than that of square-edge fins. The shape of the fins affected the pressure drop when the fluids enter and leave the fins. The different recirculation patterns generated are shown in Figure 15. The flow field for the square-edge fin was similar to flow contraction at a sharp-edged pipe inlet, where flow recirculation and pressure drop happens. With the round-edge fins, the flow recirculation and separation are much weaker.

Figure 13: SolidWorks drawing of square-edge and round-edge fins.
Figure 14: Friction factors for the fin area.

Figure 15: Streamlines of Re=2400 and isothermal.
2.0 UNLV Materials Selection and Characterization (PI: Ajit Roy, UNLV)

2.1 Highlights

- Extensive mechanical characterization of Alloy C-22 was performed.
- Tensile and metallurgical characterization of Alloys 617 and 718 was performed.

2.2 Technical Summary

The results of slow-strain-rate (SSR) testing on Alloy C-22 indicate that the ductility in terms of percent elongation and percent reduction in area was reduced at the elevated temperature (90°C) when tested in a similar aqueous environment (pH~1). In addition, the time to failure (TTF) and the true failure stress were reduced in the 90°C acidic solution. The engineering stress versus strain (s-e) diagrams, superimposed for different conditions, are illustrated in Figure 16.

![s-e Diagrams of Alloy C-22 (SSR Testing)](image)

*Figure 16: s-e Diagrams of Alloy C-22 (SSR Testing)*

The results of CPP testing in an identical acidic environment indicate that the magnitude of the corrosion potential (E_{cor}) and the critical pitting potential (E_{pit}) became more active (negative) with increasing temperature. A similar observation has been made in prior testing. A CPP diagram, obtained in the acidic solution at ambient temperature, is illustrated in Figure 17, showing a negative hysteresis loop.
The application of controlled anodic potentials (+100 mV and +300 mV wrt $E_{\text{pit}}$, Ag/AgCl) to the test specimens during SSR testing resulted in reduced TTF. The cracking susceptibility in terms of TTF was more pronounced at the more noble controlled potential (+300 mV, Ag/AgCl) with respect to $E_{\text{pit}}$.

For Alloy C-22, the occurrence of the dynamic strain aging (DSA) phenomenon was observed within a temperature regime of ambient to 600 °C. The lowest failure strain was seen at 600 °C, at which a maximum value of dislocation density ($\rho$) was observed. The variation of $\rho$ with temperature is illustrated in Figure 18.
The results of tensile testing under different strain rates indicate that the maximum height of serrations (at the onset) was observed at 600 C. The overall tensile data are currently being analyzed to determine the activation energy and the work hardening index. The s-e diagrams of Alloy C-22, superimposed as a function of temperature (400, 600 and 700 C) are shown in Figures 19 and 20 for strain rates of $10^{-3}$ and $10^{-4}$ sec$^{-1}$, respectively.

*Figure 19: s-e Diagram vs. Temperature for Alloy C-22*
The results of tensile testing involving Alloys 617 and 718 indicate that both alloys exhibited enhanced yield strength at temperatures above 600°C. For Alloy 617, the phenomenon of increased yield strength, also known as yield strength anomaly (YSA), was noted at 800°C and 900°C. For Alloy 718, the phenomenon of YSA was noted at temperatures of 700°C and 800°C. X-ray diffraction (XRD) technique was used to identify the brittle phases, if any, formed due to the transformation of austenitic phase at these temperatures. The results of XRD study are currently being analyzed.

The fractographic evaluation of the broken Alloy 617 specimens revealed intergranular brittle fractures at 100°C. However, the morphology of failure at room temperature and 600°C was ductile, showing dimples. At 700°C, however, tiny cracks were observed in the SEM micrographs along with predominantly dimpled microstructures. The SEM micrographs are illustrated in Figure 21.
(a) Room Temperature, 100 X

(b) 100 C, 100X
Figure 21: SEM Micrographs of Alloy 617

The SEM micrographs of Alloy 718 tested in tension revealed predominantly ductile failures at room temperature and 100 C. However, tiny cracks were also seen in these micrographs. At 600 C, the fracture morphology was ductile, showing dimpled microstructure (Figure 22).
(a) Room Temperature, 400X

(b) 100 C, 400X
Figure 22: SEM Micrographs of Alloy 718
3.0 Materials, Design and Modeling for C/SiC Ceramic Heat Exchangers, (PI: Per Peterson, UCB)

3.1 Highlights

- The Teflon molds have been milled by CNC at UC Berkeley and will be sent to the German Aerospace Center (DLR) for manufacturing of ceramic heat exchangers to be used to test methods to coat internal flow passages with corrosion resistant pyrolytic carbon.
- Progress on the global thermal and stress modeling methods for compact heat exchangers includes thermal transient results for the offset strip fin regions of the intermediate heat exchanger (IHX) when hot and cold pumps trip.
- Coding on a new layout for modeling the inlet and outlet manifolds of the IHX is underway. This new approach also uses the porous media approximation and more closely resembles the geometry used by Heatric.
- A tritium transport analysis for the in IHX and intermediate loop will be undertaken.

3.2 Technical Progress Summary

Teflon molds for heat exchanger manufacturing tests

Teflon molds for the fabrication of the ceramic high temperature heat exchanger have been successfully fabricated using computer numeric control (CNC) at UC Berkeley (Figure 23).

![Figure 23: Teflon molds for ceramic heat exchanger manufacturing at DLR](image)

These Teflon molds will be sent to the German aerospace center (DLR - Deutsche Zentrum für Luft- und Raumfahrt) where the ceramic Si/SiC heat exchanger article will be manufactured (geometry shown in Figure 24).
These ceramic test parts will then be returned to Berkeley which will coordinate the chemical vapor deposition (CVD) coating with pyrolytic carbon at Hypertherm (the vendor that has provided similar CVD coating services to UCB in the past). The closed flow path geometry will reveal process capability in coating the closed interior surfaces of the flow channels which ultimately must provide corrosion resistance with liquid fluoride salts. Upcoming work will focus on further process optimization to reduce residual porosity and to improve lamination methods. Corrosion coupon samples of Si/SiC will also be coated and then transferred to the University of Wisconsin for corrosion testing with liquid salts.

Continuing work in the area of ceramic heat exchangers will shift in focus toward design, analysis and experiments for liquid salt compatibility. Again, this will include work to apply CVD pyrolytic carbon coatings to SiC composite samples for liquid salt corrosion testing, and further analytical work on corrosion and safety issues for liquid salt intermediate loops. A detailed report on previous UC Berkeley work in this area was released.

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

Last quarter, UC Berkeley continued work to develop a global thermal and fluid mechanics model for compact ceramic and metal heat exchangers based on the porous media approximation. This approximation is valid when the flow structures in the heat exchanger are small compared to the overall heat exchanger size, and when these flow structures are repeated in such a way that they can be represented as repeating unit cells such as in offset strip fin heat exchangers and Heatric type heat exchangers. Further work will continue in this area in the following months.

Transient thermal modeling in two dimensions is complete for each of the three phases in the offset strip fin portion of the IHX (hot fluid, solid, and cold fluid). The analysis in this case uses
fluids in counter flow and permits cross flow in each phase. Preliminary work showing the transient temperature distribution in the solid is shown below for scenarios where fluid pumps shutdown. Should the molten salt (hot fluid) pump trip, the transient thermal response from a steady state operating temperature distribution occurs over roughly 4 seconds, as shown in Figure 25. If the high-pressure helium (cold fluid) pump trips, the transient thermal response from the same steady state operating temperature distribution occurs over roughly 5 seconds (Figure 26). In this case the slower hot molten salt can be seen affecting the temperature in the solid by advancing a well defined temperature front from left to right.

![Figure 25: Four-second thermal transient in solid layer of HX after hot fluid pump trip](image)

![Figure 26: Five-second thermal transient in solid layer of HX after cold fluid pump trip](image)

Inlet and outlet manifold geometry for the molten salt has recently changed from that shown in the engineering sketch shown in Figure 27 to that shown in Figure 28. The latter geometry more closely resembles the Heatric design. The code in the thermal model is being rewritten to reflect this change.

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Tritium transport model for the IHX and liquid salt intermediate loop

At hot leg temperatures, metals have high permeability to tritium; this implies that any tritium not recovered in the primary loop may readily diffuse to the secondary loop through a metallic intermediate heat exchanger (IHX). Furthermore, the high temperature in the metallic wall of the hot leg could present an important transport path for tritium into the insulation system surrounding the piping for the liquid salt. This pathway is not expected in the helium piping which, because it is designed for high pressure, has an insulated and much cooler outer wall which makes it relatively impermeable to tritium.

The identification of the hot leg as a possible pathway for tritium merits further evaluation. This evaluation will explore the concentration of tritium in the intermediate loop, the flux out of the intermediate loop and into the insulation system or at the process heat exchangers. The process heat exchangers will be made of silicon carbide, which has very low permeability to tritium, likely reducing tritium transport through the process HX at the cold end of the intermediate loop.
4.0 Corrosion Studies of Candidate Structural Materials in HIₓ Environment as Functions of Metallurgical Variables (PI: Bunsen Wong, General Atomics)

4.1 Highlights

- Long-term immersion testing of Ta parts in a H₃PO₄-HIₓ circulating bath is ongoing.
- Immersion testing of Ta-10W and Ta welds in boiling H₃PO₄ in both concentrated H₃PO₄ and H₃PO₄ with both HI and I₂ was performed to study corrosion behavior.
- B₃, Ti, and SiC were tested in HI + I₂ + H₂ (HI gaseous decomposition).
- The testing of a Ta coated swagelok valve for 1160 cycles (88 hours) was completed. The valve was constantly actuated during the test. The majority of the valve parts did not show any sign of corrosion, nor wear.

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

Testing of qualified materials in a non-static iodine separation environment with circulating acid is continuing this quarter. Long-term behavior of processed Ta parts is currently being tested. The test system has been modified earlier in the quarter so that it can circulate the acid continuously up to 3 weeks at a time.

Figure 29 shows a section of Ta-2.5W tube that has been immersion tested in a H₃PO₄-HIₓ circulating bath for 1036 hours. There is staining on the specimen at the conclusion of this long-term test but no pitting or other sign of corrosion has been observed. A more detailed characterization is ongoing. A section of Ta-10W tubing jointed with a Ta weld has also been tested in the same environment (Figure 30). After 830 hours, the weld does not show any degradation. The sample will be tested for up to 1000 hours. In addition, a Ta-10W tensile specimen is being tested in the iodine separation circulation system to understand the environment’s effect on mechanical properties.
Figure 29: A Ta-2.5W tube section that has been tested in the $H_3PO_4$ and $HI_x$ circulating bath.

Figure 30: A Ta-10W tube section with a Ta weld that has been tested in the $H_3PO_4$ and $HI_x$ circulating bath.
4.3 Immersion Testing of Materials in boiling $H_3PO_4$ ($H_3PO_4$ Concentration)

In this quarter, focus was placed on characterizing the corrosion behavior of Ta-10W in both concentrated $H_3PO_4$ and $H_3PO_4$ with both HI and I$_2$. Figure 31 shows a Ta-10W coupon that has been treated in boiling 95wt% $H_3PO_4$ acid for over 1000 hours. There is no sign of corrosion in the coupon but some phosphate remains on the surface. To understand the effect of the addition of HI and I$_2$ on Ta-10W, a Ta-10W tube section that has been jointed together with a Ta weld was tested in boiling iodine separation overflow ($H_3PO_4$-14.4HI-0.7I$_2$-16.1H$_2$O-wt%) at 190°C. There is no obvious sign of corrosion after 1072 hours, but a dark deposit can be observed around the edges of the tube (Figure 32). It is being analyzed. Testing of Ta-10W tensile specimens in both environments is currently ongoing.

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<th>0 h</th>
<th>496 h</th>
<th>1072 h</th>
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*Figure 31: Ta-10W coupon tested in 95wt% boiling $H_3PO_4$. No corrosion is observed.*

*Figure 32: A Ta-10W tube with jointed with a Ta weld that has been tested in the iodine separation overflow ($H_3PO_4$-14.4HI-0.7I$_2$-16.1H$_2$O-wt%) at 190°C.*
4.4 Testing of Materials in HI + I₂ + H₂ (HI gaseous decomposition)

B3 specimens were tested in the HI gaseous decomposition this quarter as it, along with B2, have been chosen as one of the materials of construction for the ILS. Figures 33 and 34 show the B3 coupons that have been tested in the HI gaseous decomposition and iodine condensation environment respectively. No corrosion can be observed at this stage, similar to the behavior of B2. Figures 35 and 36 show the B3 C-ring and U bend specimens tested in the HI decomposition setting. No crack has developed. Testing of pre-cracked C-22 and C-276 DCB specimens to study crack growth is ongoing.

![Figure 33: B3 coupon tested in the HI gaseous decomposition environment.](image)

![Figure 34: B3 coupon tested in the iodine condenser of the HI gaseous decomposition system.](image)
Also, a Ti grade 2 coupon was retested as it was previously believed to have been disintegrated in the HI decomposition environment. The coupon was found to be intact after 366 hours even though corrosion has been observed. However, the coupon once again totally disintegrated upon further testing.

Testing of porous SiC, a candidate for a high temperature hydrogen membrane reactor has been completed. As expected, no corrosion has been observed (Figure 37). Design work to fabricate a hydrogen membrane separator based on porous SiC is ongoing.
4.5 Functionality Testing of Valve in Flowing HI$_x$

The testing of a Ta coated swagelok valve for 1160 cycles (88 hours) has been completed. The valve was constantly actuated during the test. The majority of the valve parts did not show any sign of corrosion, nor wear. Figure 38 shows the ball of the valve which looks intact and so does the housing of the valve (Figure 39). However, corrosion has been observed on the bolt that drives the ball. Closer examination shows the Ta coating on the surface has been cracked which led to corrosion underneath the Ta coating (Figure 40). The crack in the surface can be attributed to incorrect assembly of the valve at the bolt was not tight in the slot. New parts are being waited upon to continue valve testing.
Figure 40: Driving bolt from a Ta-coated ball valve. Corrosion under the Ta coating has been observed due to damage to the coating from incorrect installation.
5.0 Chemistry Support Studies (PI: Allen Johnson, UNLV)

5.1 Highlights

- A new analytical system for studying reaction mechanisms and catalytic activity the modifies an existing system was investigated.
- Six samples supplied by Ceramatec were tested using x-ray photoelectron spectroscopy (XPS) to evaluate acid gas infiltration.

5.2 Technical Summary

Ceramic samples (supplied by Ceramatec) were analyzed for stability in H$_2$SO$_4$ decomposer environment – only a few seemed to escape unscathed at a depth of 1.4 microns.

Future studies with ceramic and clad metal samples have been planned with Ceramatec and General Atomic, respectively. The General Atomic samples will be provided as they appear in testing of the bench scale prototype.

Future direction of the Chemistry component of the project was determined – investigations of the mechanisms and catalyst activity of sections of the SI thermochemical hydrogen production cycle; in particular, the H$_2$SO$_4$ decomposer chemistry; will begin.

The first quarter of 2007 involved primarily in two efforts. The first effort involved the continuation of investigations in 2006, and the second effort involved determination of the best effort allocation in 2007 going forward.

A proposal was made to study the reaction mechanisms and catalytic activity of materials in the H$_2$SO$_4$ decomposer utilizing a corrosion tolerant mass spectrometer built from current parts of the HI removal facility. UNLV hosts an EPA laboratory, giving task members access to analytical equipment removed from EPA service, which can serve as the basis for a new apparatus, such as the corrosion resistant mass spectrometer (MS). An MS system used for GC/LC/solids inlet studies was obtained, very similar to the requirements for the system shown in Figure 41.

It is expected that the old MS will have to be replaced, but the vacuum vessel and vacuum instrumentation can be reused in this application. This, added to the previous acquisition of corrosion tolerant pumping components and mass spectrometers, gives a head start on 2007 scope.

Issues involving the Ta clad metal section planned for the HIx section of the lab scale prototype were discussed with General Atomics. Initial results indicate that stability of the cladding may be an issue. As failed cladded samples become available, this task will study the failure interface to determine if unexpected contamination of the interface has led to premature failure, as has been seen in many similar failure scenarios.
Using XPS, 6 Ceramatec samples were analyzed: CoorsTek Alumina 4, CoorsTek Alumina 6, Ceradyne gas pressure sintered Si$_3$N$_4$ G12, Ceradyne hot pressure sintered Si$_3$N$_4$ H12, Ceramatec laminated SiC L8 and Morgan SiC M10. They all (except CoorsTek Alumina 4 used as a baseline sample) were exposed to acid and air at 900 C for 1000 hrs.

Samples were analyzed at 4 different depths: as received, after sputtering of 10 s with Ar, depth profile (about 1,400nm from the surface), after sputter depth profile.

It was found that the atom percentage of S ~1,400nm from the surface of Alumina 4, Alumina 6, Si$_3$N$_4$ G12, Si$_3$N$_4$ H12, SiC L8 and SiC M10 are 0; 0.164; 0.817; 0.537; 0.733 and 0.369 respectively. This indicates that acid gas infiltration of the ceramics occurred for all of the ceramics, but Alumina 7 and SiC M10 have the lowest infiltration. Characteristic sputter depth profiles for these ceramics are shown in Figure 42.

Except Alumina 4 (as a baseline sample) and Alumina 6, depth profile of all samples (in the range of about 1,400 nm) showed changes in composition (generally oxidation). The ratios between component elements are far from their expected composition (Figure 43).

From survey and depth profile data, Alumina 6 and SiC M10 seem most stable and thus promising for further study.
Figure 42: Depth Profile of Alumina 4 (Baseline sample).
The green line is the O line, and the red line is the Al line.

Figure 43: Depth profile of Alumina 6.
The red line is the Si line, and the pink line is the N line.

6.1 Highlights

- Pt-containing alloys were received from the vendor.
- Buttons were cast and the microstructures were studied. When compared to the earlier heats of material, which contained unexpectedly high carbon content, the new alloys are much cleaner and represent what would be achievable in commercial practice.

6.2 Material Chemistry Identification, Alloy Procurement and Metallurgical Characterization

New Alloys

As a part of the refocusing of the program, the new alloy characterization task will focus on a detailed characterization of the Pt-added alloys. The new work plan is focused on the following alloy compositions:

- Alloy 800H + 1 wt% Pt
- Alloy 800H + 2 wt% Pt
- Alloy 800H + 5 wt% Pt
- Alloy 617 + 1 wt% Pt
- Alloy 617 + 2 wt% Pt

The above alloys were in amounts necessary to perform detailed catalytic characterization and a limited amount of mechanical properties determination. The new materials were received in January 2007. Detailed information on the as-received heats from the vendor (Special Metals Corporation-Process Laboratory) is listed in Table 1. A photograph of a typical ingot of the as-received heats is shown in Figure 44.

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<td>617 + 1 wt% Pt</td>
<td>D1-10921</td>
<td>0.044</td>
<td>0.0012</td>
</tr>
<tr>
<td></td>
<td>D1-10929</td>
<td>0.033</td>
<td>0.0010</td>
</tr>
<tr>
<td>617 + 2 wt% Pt</td>
<td>D1-10922</td>
<td>0.044</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td>D1-10923</td>
<td>0.041</td>
<td>0.0013</td>
</tr>
<tr>
<td>800H + 1 wt% Pt</td>
<td>D1-10924</td>
<td>0.061</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>D1-10925</td>
<td>0.066</td>
<td>0.0013</td>
</tr>
<tr>
<td>800H + 2 wt% Pt</td>
<td>D1-10926</td>
<td>0.066</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td>D1-10927</td>
<td>0.041</td>
<td>0.0014</td>
</tr>
<tr>
<td>800H + 5 wt% Pt</td>
<td>D1-10928</td>
<td>0.071</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
Microstructure of 800H+Pt and 617+Pt Alloys

Five heats each of Alloy 800 H + Pt chemistry, and Alloy 617 + Pt chemistry were received from Special Metals Inc. Processing Laboratory of New Hartford, NY. Platinum additions were made to the base alloys in nominal amounts of 1 wt%, 2 wt%, and 5 wt% (Alloy 800H only). The cast buttons were approximately 5.4 cm diameter and 2.5 cm thickness, weighing between 1.4~1.8 lbs.

Each sectioned alloy was mounted with cold setting epoxy resin in a 3.18 cm D cylindrical mold. Room temperature curing epoxy resin (Epo-Kwick) was mixed with hardener in proportions of 5:1 and was poured into molds over the samples and hardened in a period of 1 hour. After mounting, each sample was ground with SiC paper of 240, 400, and 800 grit successively, and then polished with 6 μm and 1μm diamond pastes. Final surface preparation was obtained with 0.05μm Al2O3 paste polishing.

Based on the previous work (Rigual, D.A., MIT MS Thesis, 2003), Alloy 800H + Pt chemistry materials were etched with a weak version of glyceregia (12 parts glycerol, 3 parts HCl, 1 part HNO3). For Alloy 617 + Pt chemistry materials, a stronger version of glyceregia (3 parts glycerol, 3 parts HCl, and 1 part HNO3) was used. Each material was etched in 1 minute intervals interrupted with ultrasonic cleansing in an ethanol bath in order to periodically monitor microstructure development via optical magnification at 100 X. The etch times and etchants used on each of the materials investigated herein are included in the Tables 2 and 3, along with reference figure numbers of micrographs.

<table>
<thead>
<tr>
<th>%Pt</th>
<th>Etchant Chemistry</th>
<th>Etch Time (sec)</th>
<th>Reference Figures (Optical)</th>
<th>Reference Figures (SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12 glycerol, 3 HCl, 1 HNO3</td>
<td>300</td>
<td>45, 46</td>
<td>55, 56</td>
</tr>
<tr>
<td>2</td>
<td>12 glycerol, 3 HCl, 1 HNO3</td>
<td>420</td>
<td>47, 48</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>12 glycerol, 3 HCl, 1 HNO3</td>
<td>300</td>
<td>49, 50</td>
<td>58, 59</td>
</tr>
</tbody>
</table>

Table 2: As cast Alloy 800H + Pt
Table 3: As cast Alloy 617 + Pt

<table>
<thead>
<tr>
<th>%Pt</th>
<th>Etchant Chemistry</th>
<th>Etch Time (sec)</th>
<th>Reference Figures (Optical)</th>
<th>Reference Figures (SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 glycerol, 3 HCl, 1 HNO₃</td>
<td>90</td>
<td>51, 52</td>
<td>60, 61</td>
</tr>
<tr>
<td>2</td>
<td>3 glycerol, 3 HCl, 1 HNO₃</td>
<td>45</td>
<td>53, 54</td>
<td>62, 63</td>
</tr>
</tbody>
</table>

The microstructures in the as cast form were developed via optical microscopy and are shown in Figures 45-54 below. Figures 55-63 show Scanning Electron Microscope (SEM) micrographs for the new materials. When compared to the earlier heats of material, which contained unexpectedly high carbon content, the new alloys are much cleaner and represent what would be achievable in commercial practice. The samples for SEM analysis were intentionally over-etched to facilitate SEM analysis so the exaggerated etching of some of the micrographs is an artifact of this process.

Figure 45: Grain and precipitate structure of cast Alloy 800 H + 1 wt% Pt, 100 X.
(weak glyceregia - 300 sec)
Figure 46: Grain and precipitate structure of cast Alloy 800 H + 1 wt% Pt, 200 X. (weak glyceraria - 300 sec)

Figure 47: Grain and precipitate structure of cast Alloy 800 H + 2 wt% Pt, 100 X. (weak glyceraria - 420 sec)
Figure 48: Grain and precipitate structure of cast Alloy 800 H + 2 wt% Pt, 200 X.
(weak glyceregia - 420 sec)

Figure 49: Grain and precipitate structure of cast Alloy 800 H + 5 wt% Pt, 100 X.
(weak glyceregia - 300 sec)
Figure 50: Grain and precipitate structure of cast Alloy 800 H + 5 wt% Pt, 200 X. (weak glyceregia - 300 sec)

Figure 51: Grain, dendrite and precipitate features of cast Alloy 617 + 1 wt% Pt, 200 X. (strong glyceregia - 90 sec; overly etched to reveal dendrite structure inside the grains)
Figure 52: Grain, dendrite and precipitate features of cast Alloy 617 + 1 wt% Pt, 500 X. (strong glyceregia - 90 sec; overly etched to reveal dendrite structure inside the grains)

Figure 53: Grain and precipitate structure of cast Alloy 617 + 2 wt% Pt, 200 X. (strong glyceregia - 45 sec)
Figure 54: Grain and precipitate structure of cast Alloy 617 + 2 wt% Pt, 500 X. (strong glyceregia - 45 sec)

Figure 55: Grain structure of cast Alloy 800 H + 1 wt% Pt, 200 X, weak glyceregia - 300 sec.
Figure 56: Grain boundaries of cast Alloy 800 H + 1 wt% Pt, 3500 X, weak glyceregia - 300 sec.

Figure 57: Grain structure of cast Alloy 800 H + 2 wt% Pt, 150 X, weak glyceregia - 420 sec.
Figure 58: Grain structure of cast Alloy 800 H + 5 wt% Pt, 200 X, weak glyceregia - 300 sec

Figure 59: Grain boundaries of cast Alloy 800 H + 5 wt% Pt, 5000 X, weak glyceregia - 300 sec
Figure 60: Grain, dendrite and precipitate features of cast Alloy 617 + 1 wt% Pt, 350 X, strong glyceregia - 90 sec (Overly etched to reveal dendrite structure inside the grains)

Figure 61: Dendrites and grain boundaries of cast Alloy 617 + 1 wt% Pt, 3500 X, strong glyceregia - 90 sec (Overly etched to reveal dendrite structure inside the grains)
Future work will focus on the characterization of both the catalytic effectiveness of these new alloys as well as the characterization of the electrochemical behavior of these alloys. The new alloys, unlike the original set of alloys melted for this project, exhibit a much cleaner
microstructure that is uninfluenced by the excessive carbide precipitation that occurred in the older alloys. This was due to a higher amount of carbon (2-3X the normal specification) in the original heats. The new heats can be expected to perform much better. Samples for electrochemical testing and catalytic effectiveness tests have been made and 617 + 1 wt% Pt samples are shown in Figures 64-65 below.

*Figure 64: 617 + 1 wt% Pt, 1.58 cm diameter disc cut by abrasive waterjet for electrochemical testing.*

*Figure 65: 617 + 1 wt% Pt, 254 μm thickness disc cut by Wire EDM for catalytic effectiveness testing.*
7.0 Development of an Efficient Ceramic High Temperature Heat Exchanger (PI: Merrill Wilson, Ceramatec, Inc.)

7.1 Highlights

- The next round of high temperature gas exposure experiments has extended beyond the mid-point of 500 hours of exposure. Additional ceramic samples have been delivered to INL (Tom Lillo) for high-pressure liquid/vapor exposure at near boiling conditions of the proposed SI process.
- The fabrication of full-sized wafers has begun. These should be completed by mid-May.
- Most of the hardware required for boiling corrosion testing of heat exchanger materials has arrived. The test equipment and procedure is undergoing its hazard review.

7.2 Technical Summary

Materials Corrosion

Corrosion testing on joining samples under high temperature air (900 C - baseline conditions) and under high temperature sulfuric acid/water/oxygen conditions began in December 2006 and was completed in January 2007.

An exposure experiment of additional samples of Ceramatec’s laminated silicon carbide and Ceradyne’s gas-pressure sintered Si$_3$N$_4$ was initiated in order to improve the statistical significance of the corrosion data. The samples are being exposed in an environment containing 60 mole% H$_2$SO$_4$, 30 mole% H$_2$O, 2 mole% O$_2$, and 8 mole% N$_2$ at 900 C and ambient pressure. Weight change of surface microstructure and surface chemistry will be analyzed after 1000 h of exposure.

In addition, samples of Ceramatec’s laminated silicon carbide and Ceradyne’s gas-pressure sintered Si$_3$N$_4$ were sent to Tom Lillo at Idaho National Laboratory for corrosion testing in pressurized environments. Dr. Lillo will expose the specimens in sulfuric acid at about 400 C and 14 bar (200 psi) for 300 h. In conjunction with Ceramatec’s experiments using boiling sulfuric acid at ambient pressure these experiments will indicate whether corrosion is enhanced by pressure.

Thermal Conductivity

Several samples have been fabricated using process variations to Ceramatec’s silicon carbide. These samples and others (when completed) will be sent out for thermal conductivity testing. The objective is to find a reliable silicon carbide formulation with a lower thermal conductivity.

Porous Catalyst Support

A process for creating porous ceramic structures from a polymer tape material is currently being adapted. Objectives for 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 be able to tailor build structures with a given porosity. Third a microchannel device will be built with increased surface area for catalysis using the porous material within dense ceramic.

To date a formulation of the porous tape has been cast and will be fired such that porosity, surface area and permeability can be measured. Other tape formulations will be batched shortly.

**Heat Exchanger Fabrication**

The process of producing 60 test coupons by the end of June is in progress. These coupons are to be used in flow testing, bonding and other areas of the project. The fabrication methods are similar to previous months, while paying attention to opportunities to improve efficiency and yield of larger quantities of parts. Improvements in technique have already improved yield from the final over cut step.

Other areas of work include the adaptation of techniques from coupon fabrication to creating larger wafers. Six wafers are planned to be ready for testing by the middle of May.

**Heat Exchanger Joining**

During the month of January, joining samples underwent corrosion testing. These samples were tested under high temperature air (900 C baseline conditions) and under high temperature sulfuric acid/water/oxygen conditions. These samples were exposed for 500 hours. The shear strength of the joints, before and after testing, is shown in Table 4. Although the strength of the polymer-derived joints were lower than previously fabricated (50 MPa), the strength values of all the joints were not affected by exposure to either sulfuric acid or air at 900 C for 500 h. Additional testing and analysis will be performed.

<table>
<thead>
<tr>
<th>Type</th>
<th>Unexposed</th>
<th>H2SO4/H2O/Air</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength (MPa)</td>
<td>95% CL (MPa)</td>
<td>Strength (MPa)</td>
</tr>
<tr>
<td>Polymer Derived</td>
<td>13</td>
<td>3.6</td>
<td>9</td>
</tr>
<tr>
<td>Tape Bonded</td>
<td>97</td>
<td>6.8</td>
<td>101</td>
</tr>
</tbody>
</table>

*Table 4: Shear strength of joins before and after testing.*
8.0 Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells through Improved Electrodes and Electrolytes (PI: Clemens Heske, UNLV)

8.1 Research Accomplishments

In the past quarter, a set of LaSrMnO$_3$ (LSM) and LaSrCoO$_3$ (LSC) samples were received from ANL. These samples were deposited by Pulsed Laser Deposition (PLD) on yttria-stabilized zirconia (YSZ) in the Fall of 2006, and some of them were electrochemically current-conditioned at ANL. Furthermore, LSM and LSC thin films were investigated that were recently applied on YSZ by brush-deposition of a paste. During a recent experimental run at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (March 2007), all received samples were investigated using X-ray emission (XES) spectroscopy. The data is currently being supplemented by surface sensitive X-ray photoemission (XPS) experiments in the lab at UNLV.

Figure 66 shows survey XES spectra of all samples. The spectra show Sr M$_{4,5}$ emission at 131 eV and O K emission (in third order) at 525/3=175 eV, stemming from the solid oxide film (note that the O K emission is excited with higher harmonics/orders of the beam line, giving sufficient energy to create O 1s core holes). Moreover, a very weak Zr M$_{4,5}$ emission at 152 eV can be observed, which is attributed to emission from the YSZ substrate. Surprisingly, additional lines between 154 eV and 164 eV are found in the spectra of all LSC samples, which can be identified as S L$_{2,3}$ emission from a (predominantly) sulfate environment (see below). This finding is corroborated by XPS measurements, which also show a S 2p signal (at the surface). The binding energy of this line clearly indicates a sulfate environment. Note that no S emission lines can be found for all three LSC samples (independent of deposition technique) and on none of the LSM samples, suggesting that the sulfate formation is associated with the starting material for the LSC films.
One of the LSC spectra (brushed powder) also shows significant XES intensity at about 183 eV. This peak is tentatively assigned to Cl L$_{2,3}$ emission, and efforts have been made to correlate this assignment with the XPS measurements. While a weak Na peak can be clearly observed (indicating the possible presence of NaCl on the surface), the identification of Cl is difficult due to overlap of its pertinent core level lines with emission from La and Sr. The origin of NaCl on this particular surface is currently being investigated.

By tuning the excitation energy for the XES experiment, the different emission lines can be turned “on” or “off” by using energies above or below the respective absorption edge. Exemplarily, this is shown for the epitaxially grown LSC sample in Figure 67. Since some of the exciting photons are elastically reflected, the excitation energy can be derived from the so called “elastically scattered peak” (in Figure 67, these sharp and very intense features have been truncated at the top). The excitation-energy-dependent spectra help to understand the nature of the S L$_{2,3}$ lines observed in Figure 66. When using an excitation energy of 202 eV (black spectrum in Figure 67), the S L$_{2,3}$ emission of a sulfate is clearly observed, consisting of S 3s $\rightarrow$
S 2p and valence band → S 2p transitions. This sulfate L\textsubscript{2,3} spectrum is turned “off” when using an excitation energy of 172 eV, which is slightly below the L\textsubscript{2,3} absorption edge of sulfate. However, a S L\textsubscript{2,3} spectrum can still be observed, albeit with a different spectral signature, indicating a different chemical environment of the probed sulfur atoms. Comparison with other sulfur-containing compounds suggests that this emission stems from S atoms in a sulfide environment. The latter can be excited by a lower photon energy compared to the sulfate environment. Detailed XPS measurements are currently being conducted to detect the possible presence of a sulfide species at the surface, and, if possible, to identify the particular sulfide compound.

![XES spectrum](image)

*Figure 67: X-ray emission spectra of an epitaxially grown LSC film, excited with different photon energies.*

As mentioned above, comprehensive XPS experiments are currently being conducted to complement the discussed (and further) XES results. Furthermore, in the next quarter, scanning probe microscopy experiments will be conducted to elucidate the morphology of the probed samples. Finally, shipment of two sample series is expected soon – one series focusing on the surface modifications introduced by electrochemical current conditioning, and a second series focusing on the preparation of suitable SOEC electrodes with Atomic Layer Deposition (ALD).