

High Temperature Heat Exchanger Project

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Department of Energy**

**Quarterly Progress Report
January 1, 2004 through March 31, 2004**

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UNLV Research Foundation
High Temperature Heat Exchanger (HTHX) Project
Quarterly Report

March 31, 2004

Summary

Program Management

- Mutually satisfactory language has been developed to permit signing of a subcontract between the General Atomics Corporation and the UNLV Research Foundation. The contract is signed.
- Early in Quarter 2, the General Atomics Task 1 work plan for the quarter was developed:
 - Task 1.1a Identify the range of HTHX applications for Gen IV hydrogen production
 - Perform review of the S-I process for hydrogen production using nuclear energy to identify the range of HTHX applications.
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 - Perform review of other hydrogen production concepts, such as high temperature steam electrolysis, to identify the range of HTHX applications.
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 - Perform a literature search of alternative heat transport fluids to identify operating conditions, material requirements, accumulated operating experience, and basic heat transport system requirements such as heating system requirements.
 - Task 1.1b Develop thermal systems concepts/designs and overall heat/mass balances for the range of Gen IV hydrogen production concepts
 - Develop initial schematic process flow diagrams for identified Gen IV hydrogen production processes and primary working fluids that show the flow paths of the primary working fluids between primary equipment items.
 - Task 1.1c Develop design specifications for HTHXs used for hydrogen production processes
 - Initiate development of design specification functions and requirements for each of the HTHXs identified to be required for hydrogen production using nuclear energy.
 - Task 1.1d Undertake thermal, thermal hydraulic, and structural analyses for selected advanced HTHX concepts for hydrogen production (and power conversion)
 - Support the thermal, thermal hydraulic, and structural analyses for selected advanced HTHX concepts performed by other team members. This is was planned as a level of effort activity

- Task 1.2 Support Demonstration Testing for Selected HX Systems
 - Collaborate with UNLV and the other team members on preparation of HTHX Technology Development Plan(s) (TDPs) and to provide support through review of Test Specifications and Test Plans required by the TDPs. This was planned as a level of effort activity.
- Task 1.3 Provide Progress Reporting
 - Provide monthly progress reports to UNLV on GA's work progress.

HTHX 2nd Quarter Highlights

- General heat exchanger requirements for nuclear-powered hydrogen production by the sulfur-iodine process were identified by documenting the range of process temperatures and heat flow requirements for several different production capacity scenarios.
- A study of the possible working fluids for the system used to transport nuclear heat from the reactor primary system to the hydrogen production system(s) was completed and documented. Sufficient work was accomplished on the review of the literature coupled with projected system performance requirements to recommend selection of the working fluid of the secondary heat transport system.
- The Nuclear Hydrogen Materials Planning Meeting took place at Oak Ridge National Laboratory on January 28, 2004. UNLV and General Atomics attended the meeting. Assignments for developing a draft materials plan were made at the meeting. The purpose of the meeting was to coordinate the development of the Hydrogen Materials Requirements Document. This included the assembling of materials requirements inputs, development of an outline/strawman, and discussion of materials testing priorities. At the meeting, several hydrogen production concepts and various materials were discussed with no attempt to down select. There was clearly continued interest in the Liquid Silicon Impregnated Carbon Composite materials. So the UNLV HTHX Design and Testing proceeded with the LSI carbon composite offset strip-fin heat exchanger as an initial concept for study.
- A weekly Nuclear Hydrogen Initiative Conference Call began in February with facilitation by DOE program managers; scheduled for Tuesdays, participants are technical leads from national laboratories, DOE and contract managers.
- The second meeting of the Material Advisory Group was held at UNLV on March 18, 2004 involving representatives from GA, SNL, ANL, INEEL, ORNL and UNLV to review the draft summary of the materials inputs received from the participants of the previous meeting held at ORNL in January 2004. The operating conditions for nuclear hydrogen generation using the proposed sulfur-iodine (S-I), calcium-bromine (Ca-Br) and high-temperature electrolysis (HTE) cycles were reviewed to prepare a draft materials requirements summary. It is anticipated that this summary report will outline the near-term hydrogen materials testing priorities and the overall testing program. All in the materials testing effort area are anxiously awaiting publication of the draft materials requirements document.
- UNLV hosted the Hydrogen Materials and Membranes Meeting on March 18 and 19. The purpose of these meetings was to finalize the discussion of the Hydrogen Materials Requirements Document mentioned above. A diverse group of experts met

to identify materials requirements and candidates. Documentation detailing the materials information will satisfy the initial needs from a Materials Selection Advisory Committee.

- UNLV Principal Investigator Anthony Hechanova represented the HTHX Project at the Advanced Reactor, Fuel Cycle, and Energy Products Workshop for Universities in Washington, DC, on March 4 and 5. The workshop provided an opportunity for discussion regarding university-appropriate research concepts that support technical needs in the Nuclear Hydrogen Initiative. Sidebar meetings were also held specifically to discuss the UNLV program logistics with Paul Pickard (SNL) and Amy Taylor (DOE); collaborations with Ron Ballinger (MIT), Mark Garland (USC), Bill Corwin (ORNL), and Mel Buckner (SRTC); and, overall program with Shane Johnson (DOE).
- UNLV Principal Investigator Anthony Hechanova visited the Savannah River Technology Center (SRTC) on March 31. The day was full with presentations, discussions, and tours of major departments interested in hydrogen production issues. Of particular interest to the NHI HTHX project is the interest on the part of SRTC to build a materials testing facility for high-temperature (1000 C) sulfur decomposition studies. A facility of this type is needed to address major technical issues with materials compatibility in the very aggressive environments of the sulfur-based concepts. This activity may be more appropriate for industrial or national lab facilities than for universities.
- During 2004-spring quarter, UCB experimental work continued to focus on helium permeation testing experiments of CVI-carbon-coated LSI test samples at room temperature under stresses generated by helium pressures of 7 to 10 MPa. The first version of the test apparatus was completed and initial tests with air and copper plate showed very good sealing.
- Intensive information exchange between Jan Schulte-Fischedick at the DLR and UCB continued on the UCB compact plate-type LSI C-C/SiC heat exchanger work. DLR reviewed the thermal design calculations for the off-set strip fin version of the ceramic heat exchanger, and concluded that the plate-type heat exchanger mass could be much lower than for the current tube-in-shell design they are developing for use in a high-temperature indirect-combustion air Brayton cycle they are developing under their EU-funded HITEX project.
- General Atomics Corporation is establishing testing capability to investigate corrosion effects on heat exchanger and vessel materials in the presence of hydrogen iodide, HI. Facility preparation, development of test apparatus and procurement of test samples is nearly complete.

HTHX Design Studies

- **HTHX applications parameter range**

A review was completed to identify the range of High Temperature Heat Exchanger (HTHX) applications required by the sulfur-iodine (S-I) process for hydrogen production using nuclear energy. The primary reference used in identifying the HTHXs required by the S-I process is [1]. Based on the information in this report, the HTHXs in the S-I hydrogen production process are in the sulfuric acid decomposition section and hydrogen iodide decomposition section.

The criterion used for identification of the HTHXs in the S-I process was for either one of the working fluids to have a temperature greater than 400°C. Eleven (11) such HTHXs were identified. A listing of these heat exchangers along with their heat loads are provided in Table 1 for two plant configurations:

- 1) a full scale plant using the thermal output of 2400 MWt and,
- 2) a plant using 50 MWt output proposed for hydrogen production demonstration as part of the Next Generation Nuclear Power (NGNP) project.

The full-scale plant would be able to generate 4200 mole of hydrogen per second. The NGNP hydrogen demonstration would produce 87.5 mole of hydrogen/second.

The E200 series heat exchangers listed in Table 1 are part of the sulfuric acid decomposition section. The E300 series heat exchangers are part of the hydrogen iodide decomposition section. All of the heat exchangers except the E206 Recuperator and the E202-1 Preheater/Cooler use heat from the nuclear power plant as the heat source. The inlet and outlet temperatures, pressures and molar flow rates for each of the eleven heat exchangers was identified.

The required heat supply to the hydrogen production process can be divided into three sectors according to the temperature required by the process. The highest temperature heat is required by the sulfuric acid decomposer, vaporizer and preheater (components E207, E205, and E204). This sector uses 47.02% of the heat supplied by the nuclear heat source. The next sector consists of the flash heaters used in the isobaric concentration of sulfuric acid (components E202-2, E202-3, and E202-4). This sector uses 14.78% of the heat supplied by the nuclear heat source. The final sector consists of the sulfuric acid preheater (component E215), and the reboiler (component E306) and condensate reheater (component E307) in the hydrogen iodide reactive still. The remaining heat supplied to this sector is 38.20% of the nuclear heat source. The flow of the heat between these three sectors is depicted in Figure 1.

The process analysis performed in the NERI report [1] assumed a temperature of 850°C supplied to the hydrogen production process. For the NGNP, the temperature supplied to the hydrogen production process could be as high as 975°C. The temperature of the working fluid that is returned to the reactor could be as low as 320°C and as high as 450°C. Table 2

presents possible intermediate temperatures for combinations of inlet and outlet temperatures to the hydrogen production process.

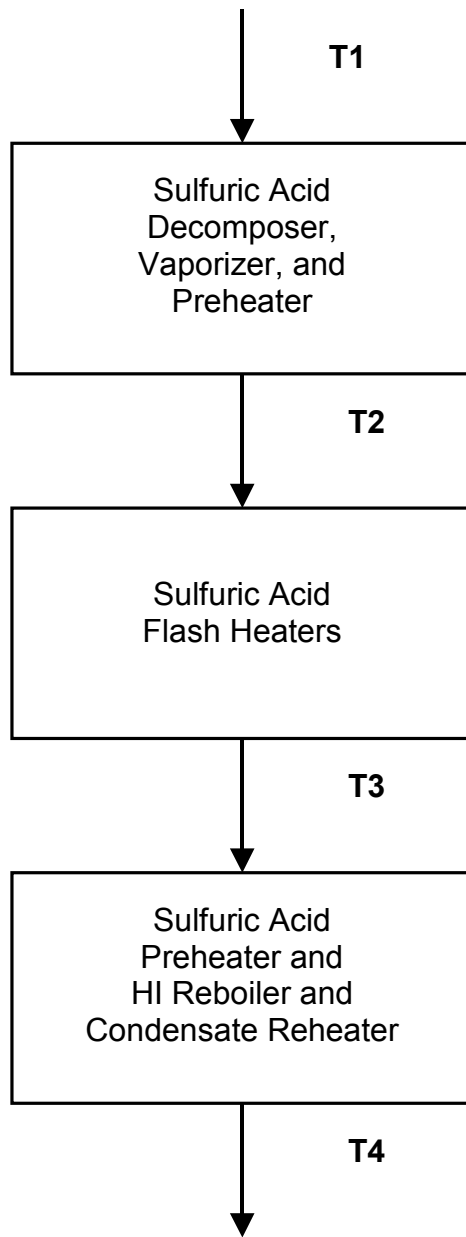
[1] Brown, L. C., G. E. Besenbruch, R. D. Lentsch, K. R. Schultz, J. F. Funk, P. S. Pickard, A. C. Marshall, and S. K. Showalter, "High Efficiency Generation of Hydrogen Fuels Using Nuclear Power," General Atomic report GA-A24285, Rev. 1, December 2003.

Table 1
Heat Loads of High Temperature Heat Exchangers

	4200 mol H ₂ /s from 2400 MWt	87.5 mol H ₂ /s from 50 MWt
E207 Decomposer	749.528 MW	15.615 MW
E206 Recuperator	3 @ 147.027 MW ea.	9.189 MW
E205 Vaporizer	566.819 MW	11.809 MW
E204 Vaporizer Preheater	62.181 MW	1.295 MW
E202-4 Stage 4 Flash Heater	116.684 MW	2.431 MW
E202-3 Stage 3 Flash Heater	121.838 MW	2.538 MW
E202-2 Stage 2 Flash Heater	194.825 MW	4.059 MW
E215 Preheater	4 @ 21.897 MW ea.	1.825 MW
E202-1 Preheater/Cooler	4 @ 61.714 MW ea.	5.143 MW
E306 Reactive Still Reboiler	40 @ 24.885 MW ea.	20.738 MW
E307 Condensate Reheater	40 @ 0.924 MW ea.	0.770 MW

Table 2
Temperature of Working Fluid Supplying Heat From Reactor

T2 Temperature (°C)	T3 Temperature (°C)	Outlet Temperature (°C)
Inlet Temperature of 850°C		
600.8	522.5	320
614.9	541.0	350
638.4	571.9	400
661.9	602.8	450
Inlet Temperature of 975°C		
667.0	570.2	320
681.1	588.8	350
704.6	619.6	400
728.1	650.6	450



Reactor Heat Supply to Hydrogen Production Process

Figure 1.

- **HTHX design requirements and specifications**

The main criteria for selection of heat transfer fluid were identified to be:

- Heat exchange surface area of high-temperature intermediate heat exchanger;
- Coolant flow rate;
- Capacity for fluid pumping;
- Compatibility with structural materials.

The candidate fluids considered for the heat transfer fluid are as follows:

- Gases: (helium, carbon dioxide, nitrogen, hydrogen, nitrogen, air and argon);
- Liquid metals and their alloys (sodium, potassium, NaK, lithium, lead, bismuth, and lead-bismuth alloy);
- Molten salts (Li_2BeF_4 , $0.58\text{NaF}-0.42\text{ZrF}_4$, and $0.42\text{LiF}-0.29\text{NaF}-0.29\text{ZrF}_4$).

The main thermophysical characteristics determining heat transfer properties of the heat transfer fluid under operating conditions are: density, specific heat capacity, heat conductivity, viscosity. In addition, for fluids that are solid at normal atmospheric conditions, melting and boiling temperatures need to be taken into account.

Gas fluids

Table 3 provides a comparison of gaseous coolants based on thermophysical characteristics and relative circulation capacity needed to pump the gas (with equal heat exchange surface areas). The comparison shows that hydrogen has the best combination of thermophysical properties among all gases. However, hydrogen is not a good candidate for the heat transfer fluid because of its high explosion danger in case of a leak from the heat transfer system. Additionally, under high temperature and pressure conditions, hydrogen embrittlement can be caused requiring the use of special materials or surface treatments for containment of the hydrogen.

The next best gaseous heat transfer fluid is helium. Helium was chosen many years ago as the coolant for high temperature gas reactors because of these characteristics. There is now considerable experience available in design and operation of high-temperature reactors with helium coolant in addition to experience with equipment and systems typical for a heat transfer system using helium as the heat transfer fluid. One important experience baseline that exists with helium is on-line helium purification. The experience indicates purification of a small by-pass stream of the helium heat transport fluid, as typically done in the primary coolant systems of high temperature reactors, will be sufficient to maintain tritium in the heat transfer fluid to acceptable levels.

Table 3
Thermophysical parameters of gaseous coolants
and relative circulation capacities at 0.1 MPa and 673° K

Parameter	H ₂	He	N ₂	Air	CO ₂	Ar
Molecular mass	2	4	28	28.95	44	39.95
Density, kg/m ³	0.035	0.072	0.491	0.508	0.771	0.724
Specific heat capacity, C _p , 10 ³ , J/(kg·K)	14.58	5.193	1.09	1.07	1.06	0.603
Heat conductivity coefficient, λ·10 ³ , W/(m·K)	348	287	50.7	52.1	47.2	33.9
Dynamic viscosity, μ·10 ⁶ , Pa s	15.4	34.3	30.9	33	30.2	41.1
Prandtl number	0.644	0.648	0.659	0.68	0.71	0.628
Relative circulation capacity needed for pumping	1	5.1	34.41	34.06	38.12	128.7

Liquid metal fluids

Liquid metals (sodium, potassium, NaK, lithium, lead, bismuth, and lead-bismuth alloy) also have good combination of thermophysical properties. At present, there is considerable experience in applying sodium both in the primary and secondary circuits of fast reactors including experience with equipment and systems typical for a sodium coolant heat transfer circuit.

However, liquid metals such as sodium, potassium, sodium-potassium alloy are not capable of transferring high temperature heat because they have low boiling temperatures (below 900 °C).

Application of other liquid metals that have high boiling temperatures also have relatively high melting temperatures. The use of these fluids would require:

- Equipping the heat transfer circuit with a special heating system that would heat the circuit up before filling it with coolant. This system would need to be in a standby mode during the whole operating period to keep the temperature in the circuit above the freezing point in case of reactor shutdown;
- Developing a special technology and design of auxiliary equipment (purification system, drainage and washing system) for servicing, repair, and replacement of secondary circuit equipment and heat exchanger components.

Molten salts

Table 4 provides a comparison of the thermophysical properties of molten salts with high pressure helium. The most important difference is the volumetric heat capacity, ρc_p , of molten salts is over two orders of magnitude greater than that of high-pressure helium.

Table 4

Thermophysical properties of helium and three reference molten salts (approximate values at average intermediate loop temperature of 700°C), (ρ -density, c_p -specific heat, k -thermal conductivity, ν -viscosity).

Material	T_{melt} , °C	T_{boil} , °C	ρ , kg/m ³	C_p , kJ/kg°C	ρc_p , kJ/m ³ °C	k , W/m°C	$\nu \times 10^6$, m ² /s
Li ₂ BeF ₄ (Flibe)	459	1,430	1,940	2.34	4,540	1.0	2.9
0.58NaF- 0.42ZrF ₄	500	1,290	3,140	1.17	3,670	2.1	0.53
0.42LiF- 0.29NaF- 0.29ZrF ₄	460	?	2706	1.47	3,978	2.1	1.64
Helium (7.5 MPa)	—	—	3.8	5.2	20	0.29	11.0

The much higher volumetric thermal capacity (ρc_p) of molten salts, compared to high-pressure helium, has a large effect upon the relative heat transfer capability. In general, a molten salt system would use piping 1/5 the diameter, and pumping power 1/20 of those required for high-pressure helium. These large differences in pumping power and pipe size would tend to reduce the capital cost of the heat transfer system. However, because molten salts are solid at normal atmospheric conditions, the heat transfer system would require the same type of complex heating and auxiliary equipment identified above for the liquid metal heat transfer system. These requirements would tend to offset the lower capital cost associated with pumping power and pipe size.

Significant R&D would be required for use of a molten salt as the heat transfer fluid. Representative required R&D activities include the following:

- Validation of salt coolant chemical stability under maximal operating temperatures, up to ~950°C;
- Development of coolant operation technology (purification, control, maintaining stable chemical composition, etc.) and its implementation at the plant;
- Validation of corrosion/erosion resistance of materials used in the heat transfer circuit and heat exchange equipment under operating conditions
- Tests on thermophysical properties and heat exchanger effectiveness.

There are two other important considerations regarding the use of a molten salt that need to be taken into account. The first of these is the potential for ingress of the molten salt into the primary circuit. This could potentially happen if the pressure in the heat transfer circuit is ever higher than in the primary circuit. Such events would result in long-term outage of the plant while the secondary coolant is removed from the primary circuit. The second important consideration is at the interface with the hydrogen production facility. For the Sulfur-Iodine hydrogen production process, the heat transfer system interfaces with a heat exchanger for transfer of the heat into a sulfuric acid decomposition process. Should there ever be a leak of the fluoride salt into the process, HF would be formed which would have a catastrophic effect on the hydrogen production process.

A final consideration in selection of the heat transfer fluid relates to the proximity of the hydrogen production plant to the nuclear reactor plant. If the hydrogen plant were located distant from the nuclear plant, there would be a potential incentive for the use of a molten salt as the heat transfer fluid to minimize piping and pumping power costs. If, on the other hand, the hydrogen plant can be sited close to the nuclear plant, helium heat transfer fluid would have merit. Preliminary evaluations indicate there are no strong reasons for the hydrogen plant to be located distant from the nuclear plant. The key reasons for this are:

- The safety characteristics of the nuclear plant are such that it would have no impact on the hydrogen plant.
- The hydrogen inventories of the hydrogen plant(s) are sufficiently limited to impose no threat to the nuclear plant.
- Environmental effects of the hydrogen plant (e.g. fumes) are amiable to control by proven measures routinely used in chemical process plants (such as a berm between the nuclear and hydrogen plant).

In summary,

- Liquid metals are not viable candidates for the heat transport fluid because of either relatively low boiling temperatures (~900°C) or high melting temperatures.
- Molten salts are attractive because of their high volumetric heat capacity but because of their relatively high melting temperature would require significant auxiliary systems that offset the heat transfer capacity benefit.
- Molten salts would also require significant R&D efforts on chemical stability, operational technology, corrosion/erosion and thermophysical properties.
- There are significant risks interfacing a molten salt heat transfer system with the nuclear and hydrogen production plants
- There is considerable experience in using helium for heat transfer in high temperature reactors, including helium purification that can be used to satisfy tritium control requirements.
- Helium would be compatible for interfacing with both the nuclear and hydrogen plants without significant risk.
- The hydrogen production plant can be sited close to the nuclear plant to minimize the quantity of large diameter piping required for the use of helium as the heat transport fluid.

Based on the results of these largely qualitative evaluations, the conclusion has been reached the most optimal fluid to be used as heat transport system fluid is helium at a pressure of > 5Mpa.

- **Thermal systems modeling and preliminary designs**

The offset strip fin heat exchanger concept is shown in Figure 2. The computational domain that was used to solve for the flow uses periodic and symmetry boundary conditions as shown in Figure 3. The use of this type of domain was validated in the literature in similar research.

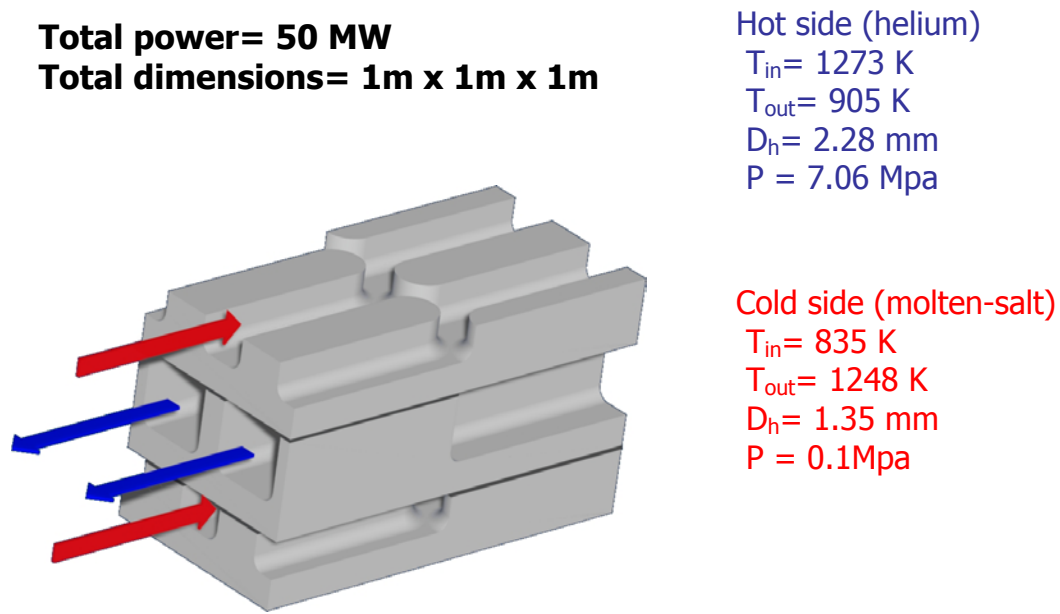


Figure 2. Offset strip fin heat exchanger concept and operating conditions.

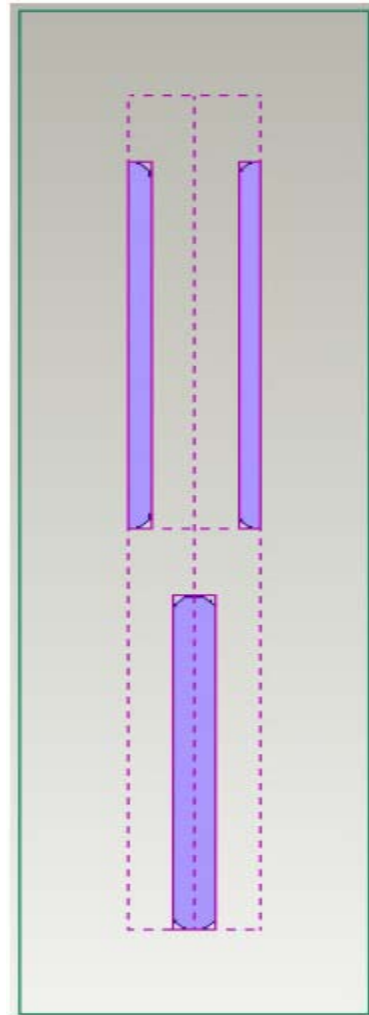
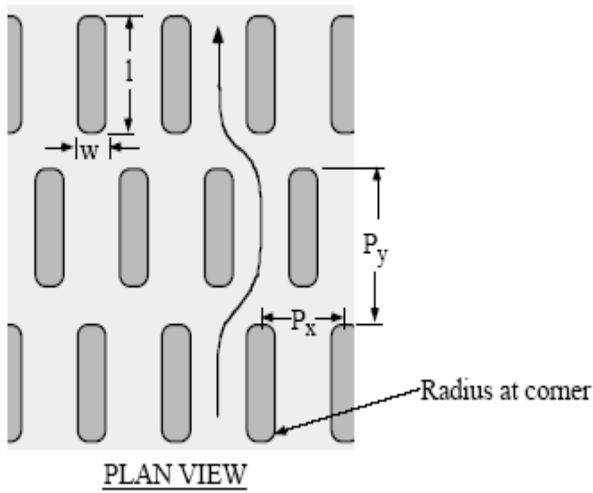


Figure 3. The figure on the right gives the computational domain that takes advantage of symmetry as seen in the plane view on the left.

The commercial software FLUENT was used to simulate 2-D fluid flow and heat transfer for the helium side of the heat exchanger. Similarly the boundary conditions used were periodic boundaries in the stream wise direction and a symmetric boundary was used in the span width. When initializing the periodic boundary condition a specified mass flow rate and a specified value of bulk stream temperature is input. The maximum velocity and the average velocity were obtained between the fins. The results were obtained for varied values of Reynolds numbers by specifying different values of mass flow rate. Vortices were observed at the trailing edge of the offset strip-fins (as seen in Figure 4) at all values of Reynolds numbers over 100 for the helium side which is an expected phenomenon.

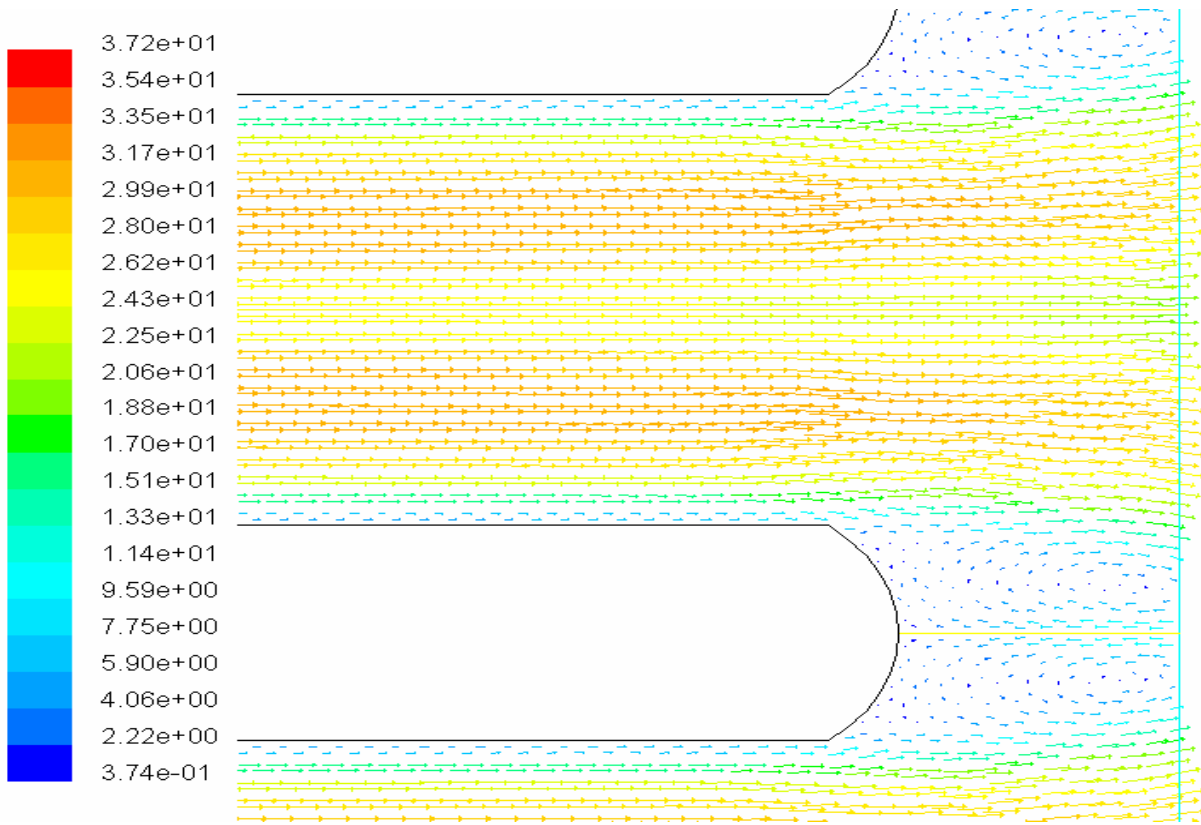


Figure 4. Helium-side velocity vectors on the trailing edge (units in m/s).

It was also observed that the occurrence of vortices at the trailing edge of the fins depend upon the aspect ratio. For the case with a fin thickness of 1mm and a length of 10 mm vortices are observed but were reduced when the fin thickness was reduced. Geometry optimization will require manufacturing issues since dimension are already very small. An attempt will be made to reduce deleterious effects in the stagnation regions. As the vortices regions are considered to be hot-spots during heat transfer because of the thermal stress on the material. Numerical simulation was performed at different offset distances in the streamwise direction. It was decided not to reduce the fin thickness any further keeping in mind the manufacturing difficulties.

As expected, the flow obtained between the fins was found to be non-fully developed which adds to heat transfer enhancement. The temperature profiles obtained (see Figure 5) were found to be relevant considering the constant wall temperature boundary condition as well as the convective heat transfer boundary conditions which were assumed.

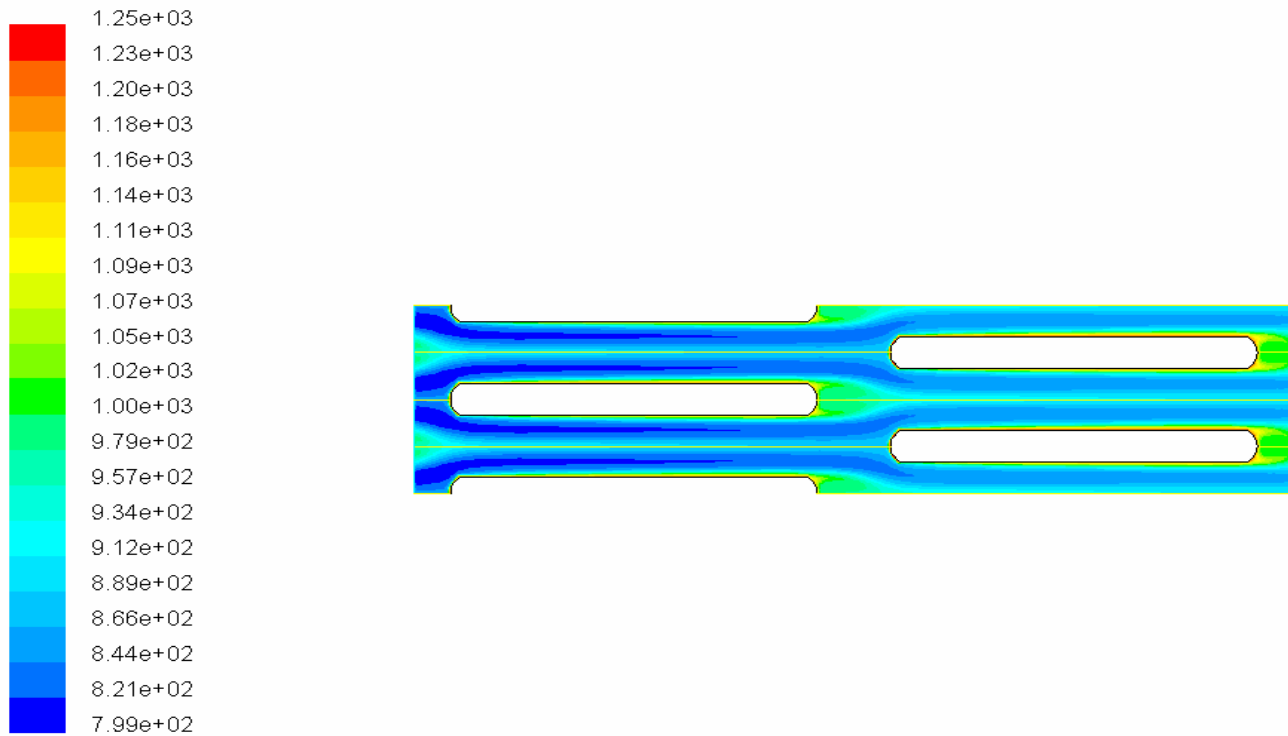


Figure 5. Helium-side temperature contours (units in degrees K).

Using the convective heat transfer boundary condition the heat transfer coefficient of the external side as well as the external temperature was given as input. In the next step heat transfer from the molten salt channels also needs to be given as input because of the 2-D treatment. It was also observed that the occurrence of vortices at the trailing edge of the fins depend upon the aspect ratio. In our case with a fin thickness of 1mm and a length of 8 mm vortices are observed but were reduced when the fin thickness was reduced so an optimized design will need to consider manufacturability.

The heat transfer coefficient for the offset strip fin design has been recalculated using a new definition of hydraulic diameter that accounts for differences in the geometry from that used in the correlation of Manglik and Bergles. The physical properties of helium and molten salt are estimated at the average fluid temperatures on the helium side ($T=1089$ K, $p=7.06$ MPa) and molten salt side ($T=1041$ K, $p=0.1$ MPa).

The results of the calculations give:

Helium side:

$$Pr=0.65923$$

$$Re=2030.07$$

$$Nu=14.986$$

$$h=3042.75 \text{ kg}/(\text{s}^3 \cdot \text{K})$$

Molten salt side:

$$Pr=11.88353$$

$$Re=55.3$$

$$Nu=6.475$$

$$h=5426.87 \text{ kg}/(\text{s}^3 \cdot \text{K})$$

It has been decided that the concepts of 2-D studies of fluid flow and heat transfer on the helium side cannot be applied to the molten salt side due to a low ratio of the channel height to its width (1:1.75). Due to this low ratio, 3-D effects on the molten salt side can not be neglected. The other reason for moving to a 3-D simulation is interest in calculating local temperatures which requires a 3-D simulation between fluids instead of confining the temperature on the wall or specifying the heat flux. The FLUENT software should allow one to determine the temperature distribution on the wall and inside the solid material, and to find locations of hot spots and heat traps needed for the fin designing process. The temperature and local heat transfer coefficient values will then be used for thermal stress analyses.

Before creating a complete 3-D model for the offset strip fins, we will first create a simplified 3-D model that will consist of several channels of rectangular cross section inside the solid for helium and molten salt, and to observe the temperature distribution in the solid material and local heat transfer coefficient distribution on the surface of the wall. This geometrical simplification is needed for time saving on generating a 3-D mesh. The results of this simplified case will allow us to monitor whether the FLUENT software can accurately solve this class of problems, and to understand the boundary conditions treatment in FLUENT on the solid-fluid interface which is easier to do on a simple 3-D geometry.

- **Scaled HTHX design and testing**

It is proposed to obtain composite material coupons to test impermeability to gases such as helium, liquid metal infiltration, and leak testing under mechanical stress. Prof. Per Peterson of UC Berkeley has contacted a number of researchers and companies to investigate the manufacturing and cost of coupons. The proposed test program has not changed since last quarter. Briefly, the test program will consist of the following phases:

- **Leak Test.** UCB has an apparatus in which to test 2" D disks, 1-1.5 mm thick. One side will contain pressurized He. Tensile stresses up to 100 MPa will be applied to the point of potential cracking.
- **Characterization.** UNLV has facilities for post-testing examination such as SEM and TEM.
- **Loop Test.** Place coupons in flow loop potentially sited at UNLV. A pot test would not be very interesting since carbon is very robust to molten salt.
- **HTHX Component Tests.** Repeat tests with heat exchanger elements in place of coupons.

During 2004-spring quarter, UCB experimental work has focused on helium permeation testing experiments of CVI-carbon-coated LSI test samples at room temperature under stresses generated by helium pressures of 7 to 10 MPa. UCB finished the first version of the test apparatus. The initial tests with air and copper plate showed very good sealing. A vacuum pump was connected to the device and a small leakage rate was detected. The pressure-flow rate characteristic curve of the vacuum pump was achieved, which is needed to for later leakage rate measurement. Preparations are underway for the final version of the helium permeation test device and the permeation experiment will begin as soon as test coupons are received from German Aerospace Center (DLR).

Professor Peterson has been having an extensive information exchange with DLR on the preparation methods for the helium permeation samples for the melt-infiltrated composites. DLR currently can only manufacture materials with a thickness of no less than 3 mm. Calculations on the test plate diameter were reviewed using the 3 mm thickness limit. It seems that coupon discs with 50mm to 60 mm outside diameter and 3 mm thickness, both CVD or CVI carbon coated and uncoated, should be proper for the helium permeation test. Agreement has been reached with the DLR to fabricate and provide helium permeation test coupons. DLR will provide at least 20 specimens with 50 mm in diameter and 3 mm in thickness of both the splint as well as the chopped fiber based C/C-SiC in middle May. Total cost will be EUR 4500. Melt infiltrated (MI) SiC splint-based material with cordierite coating is a potential material for the hydrogen processing fluid heat exchangers.

Postdoctoral researcher Fenglei Niu has joined this project at UCB in March. He has extensive experiences in thermal hydraulics experiment work. He will be responsible for the experiment work, heat exchanger experimental design, and other related work. His joining will enhance UCB's research team for this project.

UCB has contacted three US composite vendors, recommended by Jerry Youngblood and Russ Jones at PNL, to do the carbon CVD/CVI coatings. Two vendors, COI Composites and Starfire Composites appear to have the correct set of capabilities to perform the types of fabrication processes we need. Discussions are proceeding regarding the costs and types of coupons needed. Starfire has capabilities in melt infiltration (MI), but their primary activity is in polymer infiltration and pyrolysis (PIP) processing (using a polymer precursor that yields SiC when fired in an inert-gas furnace). Starfire has already fabricated plate-type heat exchangers very similar to those required using the PIP process. Figure 6 shows carbon fiber reinforced SiC matrix heat exchanger with sub-millimeter flow channels by Starfire. They used carbon felt preform material, cut the flow channels using a saw blade, bonded the plates together and then used multiple PIP processing steps to create a leak-tight part. Basing on Starfire's work, PIP method seems to be another very promising route to construct high temperature carbon composite heat exchangers for nuclear hydrogen production besides MI route. PIP method will be included in the feasibility research while keeping parallel activity with DLR for the MI route.

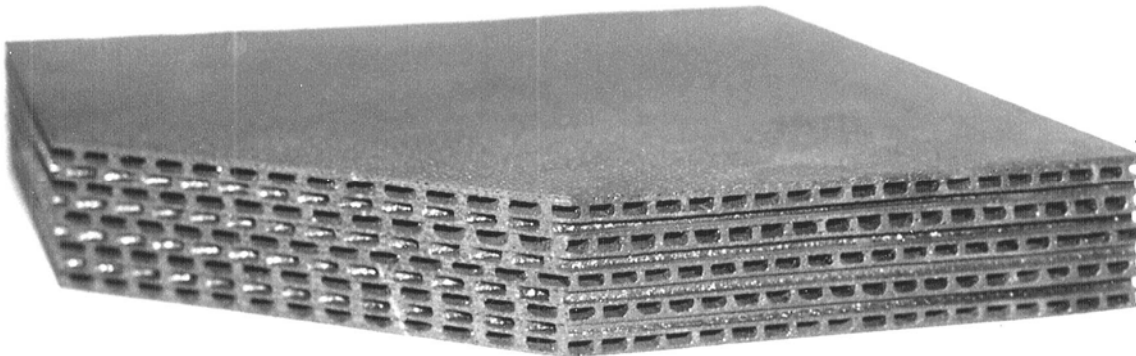


Figure 6. Compact C/SiC Cross-Flow Heat Exchanger with 0.025" Channel Walls (Credit Starfire Inc.)

UCB's goal in this contract year is to identify combinations of fibers, die-embossing methods, and graphitization and MI or PIP processing parameters that result in compact heat exchangers that have low leakage with high-pressure helium.

Intensive information exchange has taken place during this quarter with Jan Schulte-Fischedick at the DLR, regarding UCB's compact plate-type LSI C-C/SiC heat exchanger work. DLR reviewed the thermal design calculations for the off-set strip fin version of UCB's ceramic heat exchanger, and rapidly concluded that the plate-type heat exchanger mass could be much lower than for the current tube-in-shell design they are developing for use in a high-temperature indirect-combustion air Brayton cycle they are developing under their EU-funded HITEX project. The rising interest in the plate configuration of LSI HXs for a much broader range of high-temperature applications outside of nuclear hydrogen may in turn help more rapid development of this technology. In particular, it is hoped that DLR will divert some of their manpower resources from their tube-type HX program into work on the plate-type version, which will enable more rapid progress for the HTHX Project as well. UCB's calculation result of flue gas to helium HX for the EFCC process closely matched the

result from DLR's independent calculation, which verified the off-set strip fin plate HXs preliminary design methods.

Literature review about fabrication approaches for generating leak-tight LSI structures, review of environmental barrier coating approaches for protecting LSI C/C-SiC substrates from S-I process fluids, and review of molten fluoride salt solubility with carbon and SiC materials, are being continued.

- **Materials Characterization and Testing**

UNLV hosted the Hydrogen Materials and Membranes Meeting on March 18 and 19. The purpose of these meetings was to finalize the discussion of the Hydrogen Materials Requirements Document mentioned above. A diverse group of experts met to identify materials requirements and candidates. Documentation detailing the materials information will satisfy the initial needs from a Materials Selection Advisory Committee.

The second meeting of the Material Advisory Group was held at UNLV on March 18, 2004 involving representatives from GA, SNL, ANL, INEEL, ORNL and UNLV to review the draft summary of the materials inputs received from the participants of the previous meeting held at ORNL in January 2004. The operating conditions for nuclear hydrogen generation using the proposed sulfur-iodine (S-I), calcium-bromine (Ca-Br) and high-temperature electrolysis (HTE) cycles were reviewed to prepare a draft materials requirements summary. It is anticipated that this summary report will outline the near-term hydrogen materials testing priorities and the overall testing program. All in the materials testing effort area are anxiously awaiting publication of the draft materials requirements document.

The Nuclear Hydrogen Materials Planning Meeting took place at Oak Ridge National Laboratory on January 28, 2004. UNLV and General Atomics attended the meeting. Assignments for developing a draft materials plan were made at the meeting. The purpose of the meeting was to coordinate the development of the Hydrogen Materials Requirements Document. This included the assembling of materials requirements inputs, development of an outline/strawman, and discussion of materials testing priorities. At the meeting, several hydrogen production concepts and various materials were discussed with no attempt to down select. There was clearly continued interest in the Liquid Silicon Impregnated Carbon Composite materials. So the UNLV HTHX Design and Testing proceeded with the LSI carbon composite offset strip-fin heat exchanger as an initial concept for study.

- **General Activities**

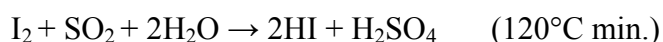
UNLV developed a general description of processes and environments for the three most prominent Nuclear Hydrogen Initiative hydrogen production processes under consideration. These processes are the sulfur-iodine cycle, the calcium-bromine cycle, and the high temperature electrolysis process. The UNLV assessment is documented in their quarterly report and is reproduced here.

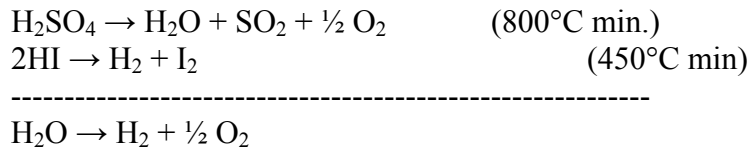
UNLV Assessment

Selection of structural metallic materials and alloys for high-temperature heat exchangers (HTHX) to generate hydrogen using nuclear power source poses a major challenge to scientific and engineering communities. These materials must possess excellent resistance to numerous environment-induced degradation and superior high-temperature metallurgical properties. Three different water splitting cycles namely, sulfur-iodine(S-I), calcium-bromine (Ca-Br) and high-temperature electrolysis (HTE) have recently been proposed to generate hydrogen. A brief description of each cycle is given below.

S-I Cycle

The S-I process is a thermo-chemical water splitting cycle, consisting of three chemical reactions, which sum to the dissociation of water. These reactions are as follows:





Theoretically, only water and heat need to be added to the cycle. Heat energy enters a thermo-chemical cycle through one or more endothermic high-temperature chemical reactions. Heat is rejected via exothermic low temperature reactions. All of the reactants, other than water, are regenerated and recycled.

A great deal of the necessary input energy is used in the separation steps. In addition, the process steps occur in various phase states that include mostly liquids, gases, and even a two-phase liquid process. Complex modeling is necessary to determine the predicted cycle efficiency. A thermal efficiency of hydrogen production of greater than 50% can be achieved in this cycle. Since the constituents of the cycle are highly reactive, they must be safely contained while maintaining the challenging reaction conditions. Accordingly, choice of materials and component fabrication techniques for the chemical process, especially the heat exchangers, will provide interesting challenges.

Figure 7 shows a concept for driving the S-I process using process heat from a modular helium reactor (MHR). The intermediate heat exchanger (IHX) would consist of helium-to-helium heat-exchanger modules housed within a vessel, along with the primary coolant circulator. The chemical reactions shown in this figure would each be driven in multiple, parallel trains of process equipment. Alternatively, the intermediate heat transfer fluid could be a high-temperature, low-pressure molten-salt, depending upon tradeoffs between pumping power, heat-exchanger mechanical design, and materials performance.

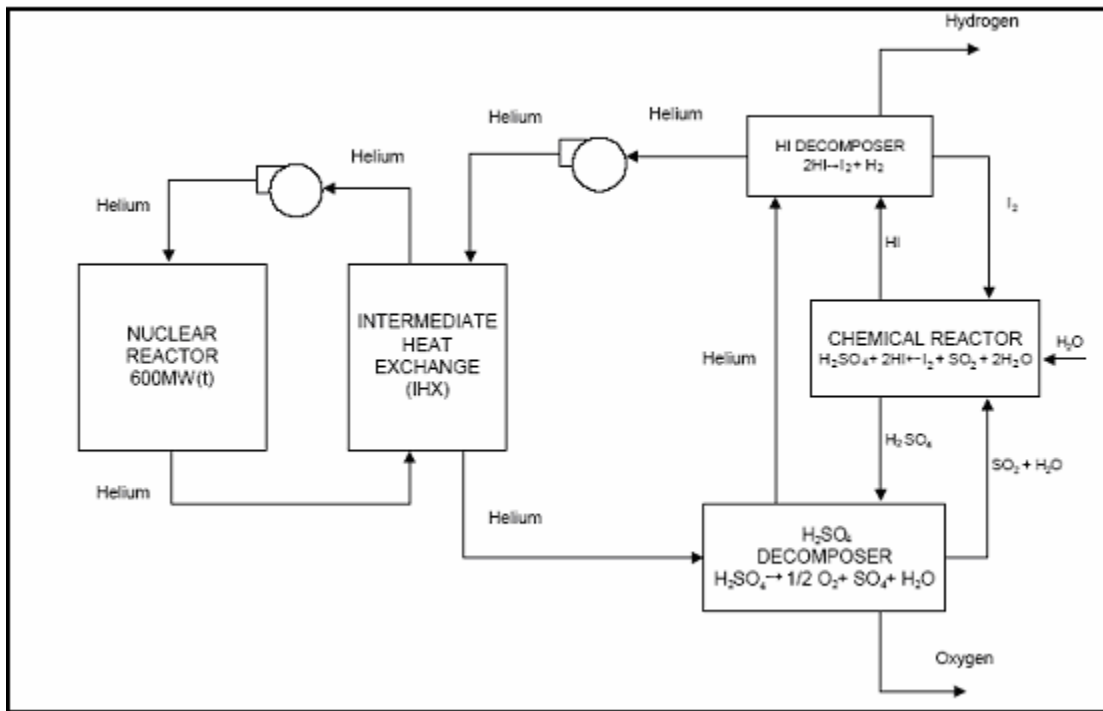


Figure 7. Concept of Modular Helium Reactor with a Sulfur-Iodine Hydrogen Production Plant

Ca-Br Cycle

The different steps and related chemical reactions involved to generate hydrogen using the original Ca-Br cycle are shown below.

- Water splitting with HBr formation (1000 K)
 $\text{CaBr}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HBr}$
 This reaction slows at highest temperature.
- Oxygen formation (823 K)
 $\text{CaO} + \text{Br}_2 \rightarrow \text{CaBr}_2 + 0.5\text{O}_2$
- Bromine regeneration (493 K)
 $\text{Fe}_3\text{O}_4 + 8\text{HBr} \rightarrow 3\text{FeBr}_2 + \text{Br}_2$
- Hydrogen formation from FeBr₂ (923 K)
 $3\text{FeBr}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HBr} + \text{H}_2$

This stage is high-temperature, and produces a dilute, wet H₂ product.

The chemical reactions in the modified Ca-Br cycle are given below.

- Water splitting with HBr formation (1000 K)
 $\text{CaBr}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HBr}; \quad \Delta G_T = + 2.185 \text{ eV/molecule}$
- Oxygen formation (823 K)
 $\text{CaO} + \text{Br}_2 \rightarrow \text{CaBr}_2 + 0.5\text{O}_2, \quad \Delta G_T = -0.806 \text{ eV/molecule}$
- Hydrogen production and Bromine regeneration (338 K)
 Non-thermal plasma will be used; this is low temperature stage with easy separation
 $2\text{HBr} + \text{plasma} \leftrightarrow \text{H}_2 + \text{Br}_2, \quad \Delta G_T = + 1.186 \text{ eV/molecule (50\% conversion)}$

HTE

High-temperature electrolysis uses the technology of solid-oxide fuel cells to split steam into hydrogen and oxygen. The cells operate at 700-850°C and have the electrical potential reversed from that of fuel cell mode. A schematic diagram of an HTE plant is shown in Figure 8 and a cross-section of an individual cell is shown in Figure 9.

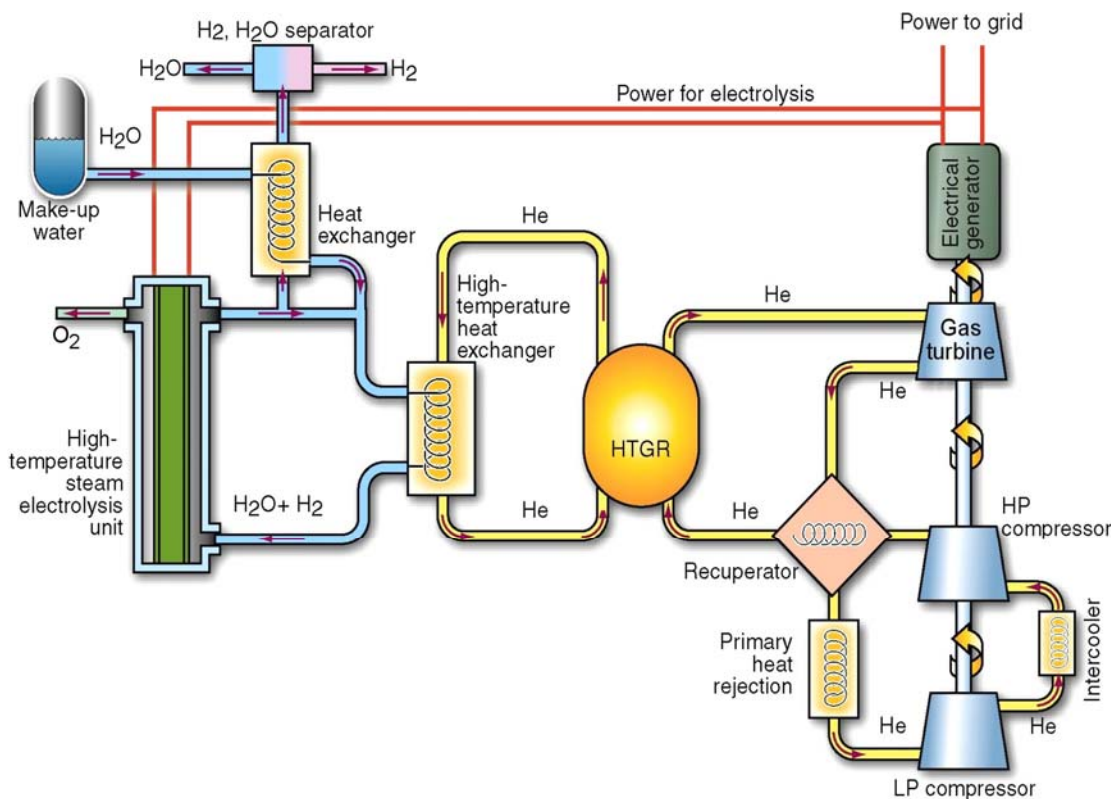


Figure 8. High-Temperature Electrolysis Plant

The materials challenges in the development of high-temperature electrolysis are divided into two categories: those within the cells themselves and those in the surrounding plant.

The concept of HTE builds on the technology of Solid-Oxide Fuel Cells (SOFCs), using the same materials, but producing hydrogen and oxygen rather than electricity. DOE-FE and commercial interests have had very significant programs for the last two decades to develop SOFCs, particularly for use with coal gasification. The service conditions for such coal-based SOFCs are very severe, with temperatures above 1000° C and fuel gas containing the full range of products characteristic of the partial oxidation of coal, including CO₂, CO, H₂, SO₂, and various nitrogen oxides. In comparison, the service conditions of a solid oxide electrolytic cell is more benign, operating at lower temperatures (750° to 900° C) with the inlet and outlet gases consisting of only steam and hydrogen in differing proportions. The anode of the electrolytic cell contains the only instance of more severe conditions than an SOFC, since pure O₂ may be present if no diluent is used.

The reactions during high-temperature electrolysis are given below.

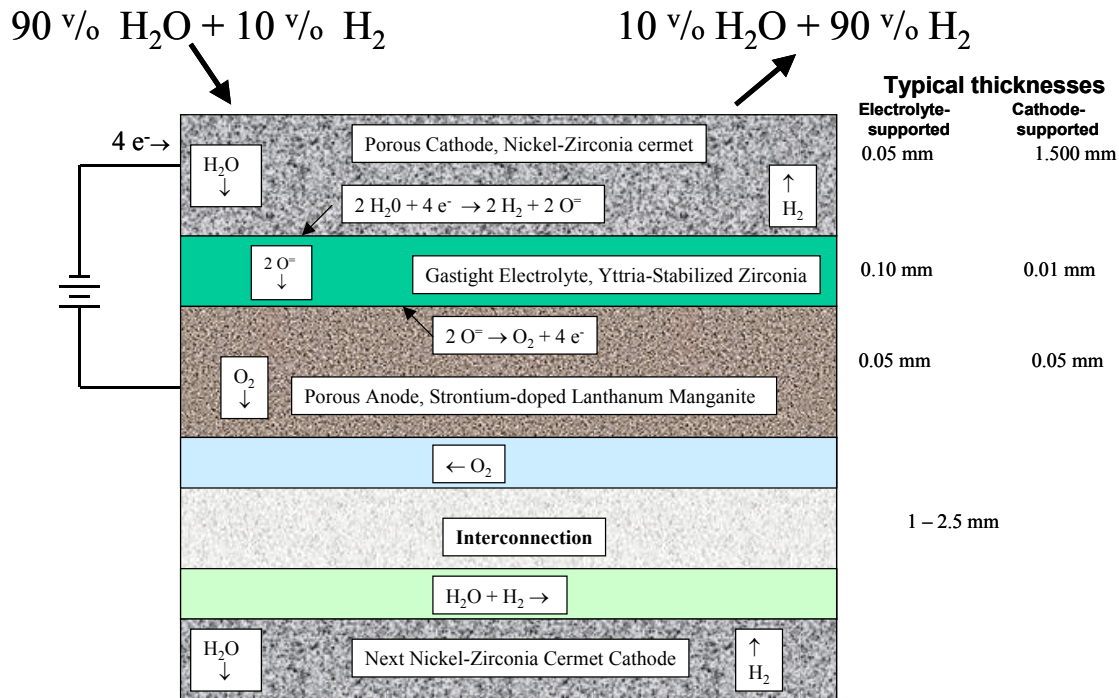
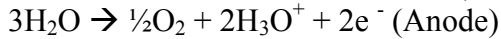
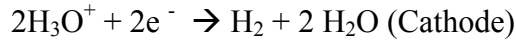


Figure 9. Components of Solid Oxide Cell used for High Temperature Electrolysis

Outside of the electrolytic cells proper, there are several materials challenges in the separation and handling of the hydrogen and oxygen.

Separation of the hydrogen steam exiting from the HTE cells can be done either through condensation of the steam or through the use of a membrane. Condensation requires cooling mixture and reheating of the condensed water, lowering the overall efficiency of the process. The use of an inorganic, hydrogen permeable membrane would allow nearly isothermal and constant pressure operation of the electrolytic plant. The durability of such a membrane in the reducing environment of the 800°C steam-hydrogen mixture will have to be investigated.

The other significant materials challenge lies in cooling the exiting oxygen stream. As mentioned above, if no diluent (e.g. nitrogen or air) is used, the piping and heat exchangers needed will be exposed to extremely oxidizing conditions. The primary sides of the oxygen cooler may have to be lined with a ceramic, at least in the high temperature region.

- **Candidate materials**

Based on the review of existing literature and numerous presentations at Oakridge National Laboratory (ORNL) on January 28, 2004 on prospective HTHX materials, six metallic materials have been identified for evaluation of their metallurgical and corrosion properties under relevant operating conditions. Their chemical composition and ambient temperature tensile properties are given in the Tables 5 and 6, respectively. A matrix of materials suitable under operating conditions for different cycles is shown in Table 7. It is worth-mentioning that testing of three nickel-base alloys namely Alloys C-22, C-276 and Waspaloy is well in progress at UNLV. Recently-generated tensile data at ambient temperature and 600°C in the presence of nitrogen are shown in Table 8. Comparisons of stress-strain diagrams at both temperatures are shown in Figures 10-12 for Alloy C-22, Alloy C-276 and Waspaloy, respectively.

Table 5
Chemical Composition of HTHX Materials (wt%)

Materials	Elements																
	Ni	Cr	Mo	C	Fe	Co	W	Si	Mn	V	P	S	Bo	Zr	Al	Ti	Cu
Alloy* C-276	Bal	14.5 to 16.5	15.0 to 17.0	0.01 (max)	4.0 to 7.0	2.5 (max)	3.0 to 4.5	0.08 (max)	1.0 (max)	0.35 (max)	0.02 (max)	0.01 (max)	-	-	-	-	-
Alloy* C-22	Bal	20.0 to 22.5	12.5 to 14.5	0.01 (max)	2.0 to 6.0	2.5 (max)	2.5 to 3.5	0.08 (max)	0.5 (max)	-	-	-	-	-	-	-	-
Waspaloy*	Bal	18.0 to 21.0	3.5 to 5.0	0.02 to 0.10	2.0 (max)	12.0 to 15.0	-	0.75 (max)	1.0 (max)	-	0.03 (max)	0.03 (max)	0.003 to 0.01	0.02 to 1.60	1.20 to 1.60	2.75 to 3.25	0.5 (max)
AL 610	14.0 to 15.5	17 to 18.5	0.20 (max)	0.018 (max)	Bal	-	-	3.70 to 4.30	2.00 (max)	-	0.020 (max)	0.020 (max)	-	-	-	-	0.50
Incoloy 800 H	30.0 to 35.0	19.0 to 23.0	-	0.05 to 0.10	Bal	2.00 (max)	-	1.00 (max)	1.50 (max)	-	-	0.015 (max)	-	-	0.15 to 0.60	0.15 to 0.60	0.75 (max)
Incoloy 800 HT	30.0 to 35.0	19.0 to 23.	-	0.06 to 0.10	39.5 (min)	-	-	1.0 (max)	0.2 to 0.6	-	-	0.015 (max)	-	-	0.15 to 1.6	0.3 To 0.6	

*Testing of Alloys C-276, C-22 and Waspaloy is ongoing at UNLV

Table 6
Standard Tensile Properties at Ambient Temperature

Material/ Heat treatment	YS	UTS	% El	% RA	Hardness
Alloy C- 276/ Solution Annealed	50.0	114.0	64 %	81 %	87 HRB
Alloy C- 22/ Solution Annealed	53.0	113.0	62 %	83 %	86 HRB
Waspaloy/ Solution Annealed	110.0	185.0	40 %	43 %	36 RC
AL 610/ -	46.8	103	58 %	--	86 HRB
Incoloy 800 H/ Solution Annealed	25	65	30 %	--	126 HRB
Incoloy 800 HT/ Annealed	35	80	45 %	--	126 HRB

Table 7
Matrix of Materials for Different Cycles

Cycle	Process Regime	Concentration / Contaminants	Operating Conditions		Suggested Materials
			Temperature	Pressure	
S-I	H ₂ SO ₄ Concentration	15%-95% acid H ₂ SO ₄ , iodine species, impurities	400 – 700K	8 Atm (approx.)	Alloy C-276* Incoloy 800H** AL610**
S-I	H ₂ SO ₄ Vaporization H ₂ O+SO ₃	90% - 95% acid Contaminants, iodine	600 – 800K	8 Atm (approx.)	Alloy C-276* Incoloy 800H** AL610**
S-I	H ₂ SO ₄ Decomposition	SO ₂ concentration strong function of temperature Contaminants, iodine	600 – 1200K	8 Atm (approx.)	Incoloy 800HT** Incoloy 800 H** (with Aluminide coatings) AL 610**
Ca-Br	Hydrobromic Acid	--	1023 K	--	Alloy C-22*
HTE	Molten salt	--	1173 K	0.1-0.25 MPa	Nickel Alloys (Proper alloy yet to be identified)
HTE	90 v/o H ₂ O, 10 v/o H ₂ 10 v/o H ₂ O, 90 v/o H ₂	--	1073 K-1173 K	2.5 MPa	Ni- ZrO ₂

* Materials currently included in the UNLV test matrix

** Materials yet to be included

Table 8
Tensile Properties at Ambient Temperature and 600°C

Material	Yield Strength (ksi)				Ultimate Tensile Strength (ksi)				% Elongation				% Reduction in area			
	Ambient temperature		600°C		Ambient temperature		600°C		Ambient temperature		600°C		Ambient temperature		600°C	
Alloy C-22	52.1		35.2		114.4		85.6		67.96		79.99		78.96		61.83	
	52.2	52.46 (Average)	34.0	34.6 (Average)	113.5	113.73 (Average)	84.1	84.85 (Average)	66.90	66.26 (Average)	80.00	79.99 (Average)	83.12	81.64 (Average)	66.89	64.36 (Average)
	53.1				113.3				63.93				82.84			
Alloy C-276	52.3		37.7		118.4		92.0		68.06		80.02		80.00		52.83	
	55.7	53.16 (Average)	36.6	37.15 (Average)	116.00	116.96 (Average)	90.4	91.2 (Average)	65.99	66.49 (Average)	79.99	80.00 (Average)	72.14	78.02 (Average)	61.71	57.57 (Average)
	51.5				116.5				65.44				81.93			
Waspaloy	97.6		87.9		170.2		144.6		39.04		42.02		43.03		32.95	
	105.5	100.23 (Average)	80.2	84.05 (Average)	167.7	167.9 (Average)	142.2	143.4 (Average)	38.70	40.55 (Average)	44.29	43.15 (Average)	43.40	42.96 (Average)	37.41	35.18 (Average)
	97.6				165.8				43.93				42.46			

Alloy C-22 Mechanical Properties

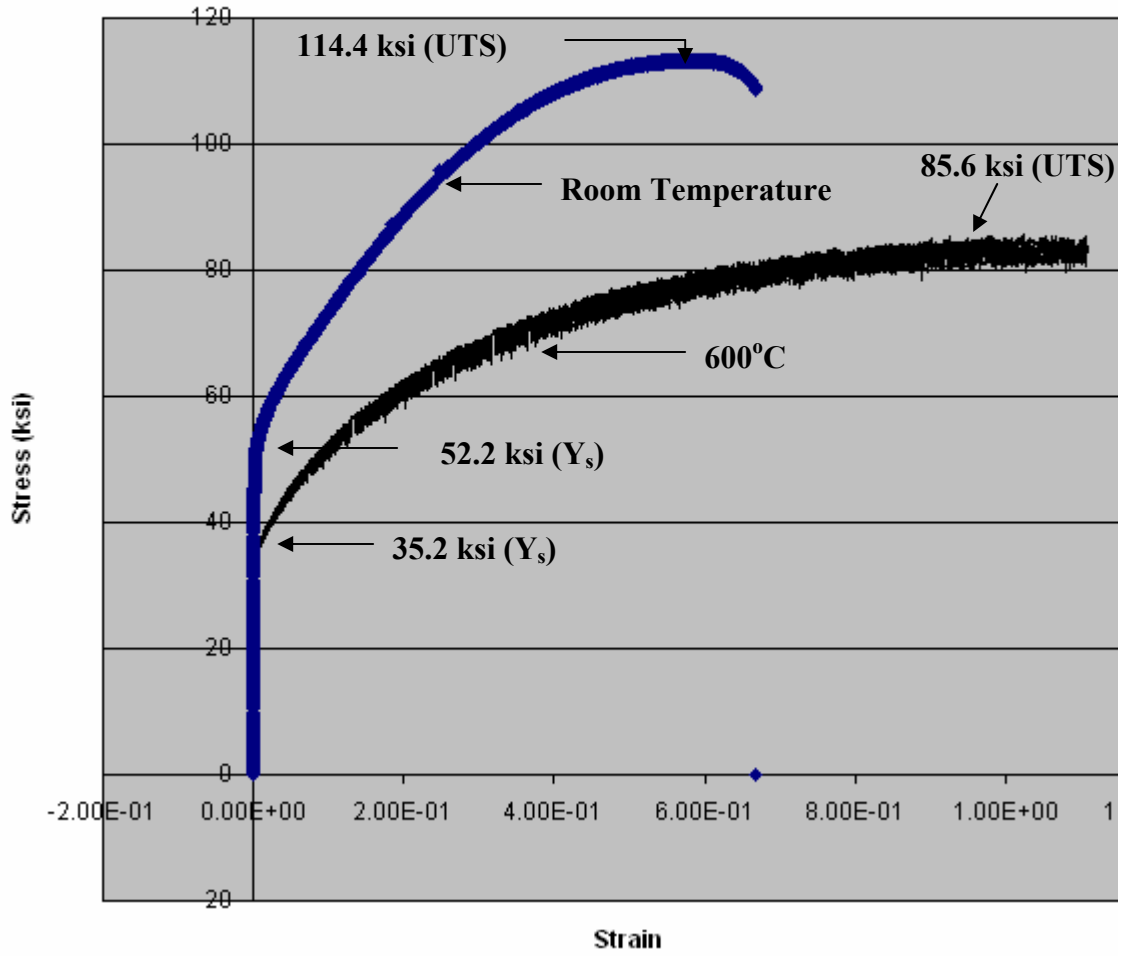


Figure 10. Stress-Strain Diagrams versus Temperature for Alloy-22

Alloy C-276 Mechanical Properties

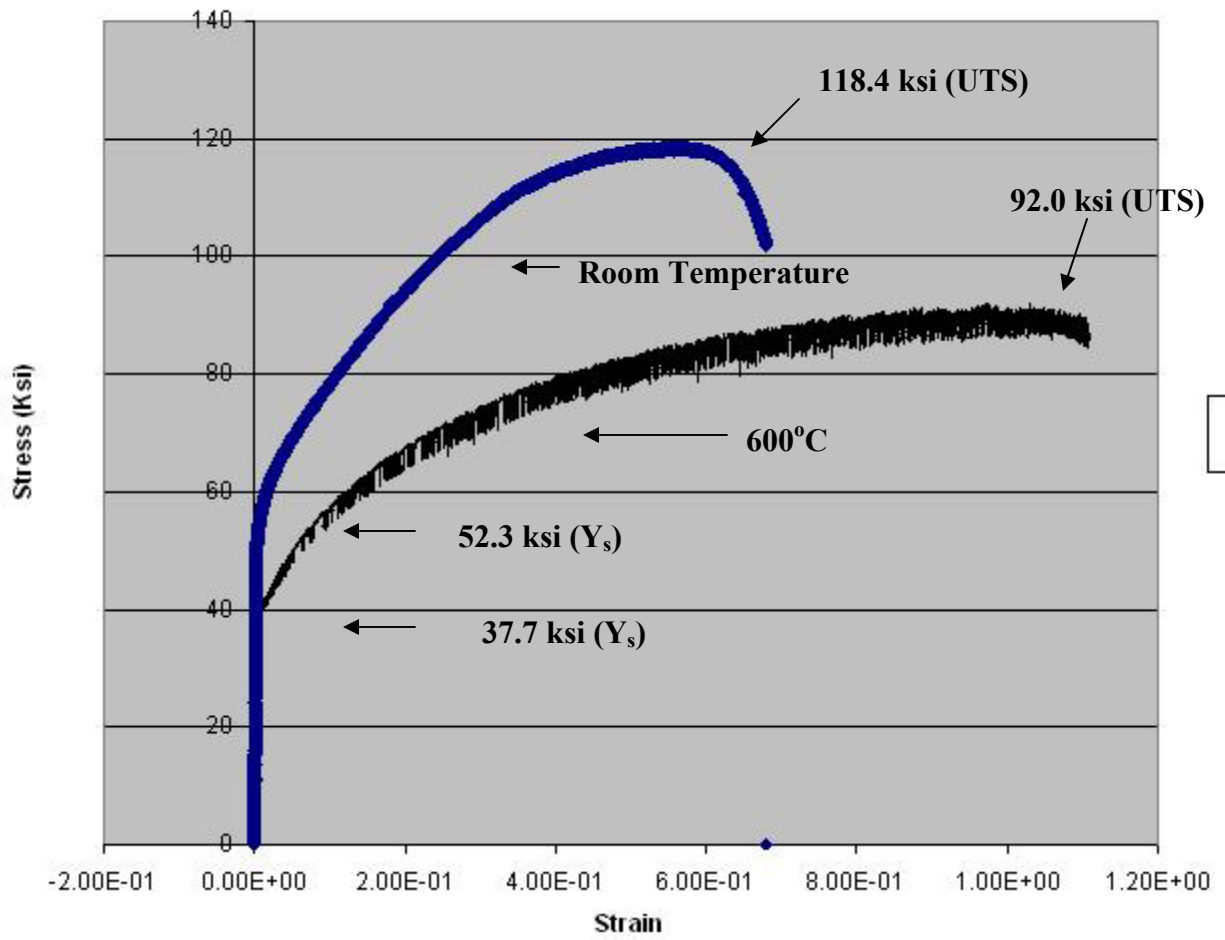


Figure 11. Stress-Strain Diagrams versus Temperature for Alloy C-276

Waspaloy Mechanical Properties

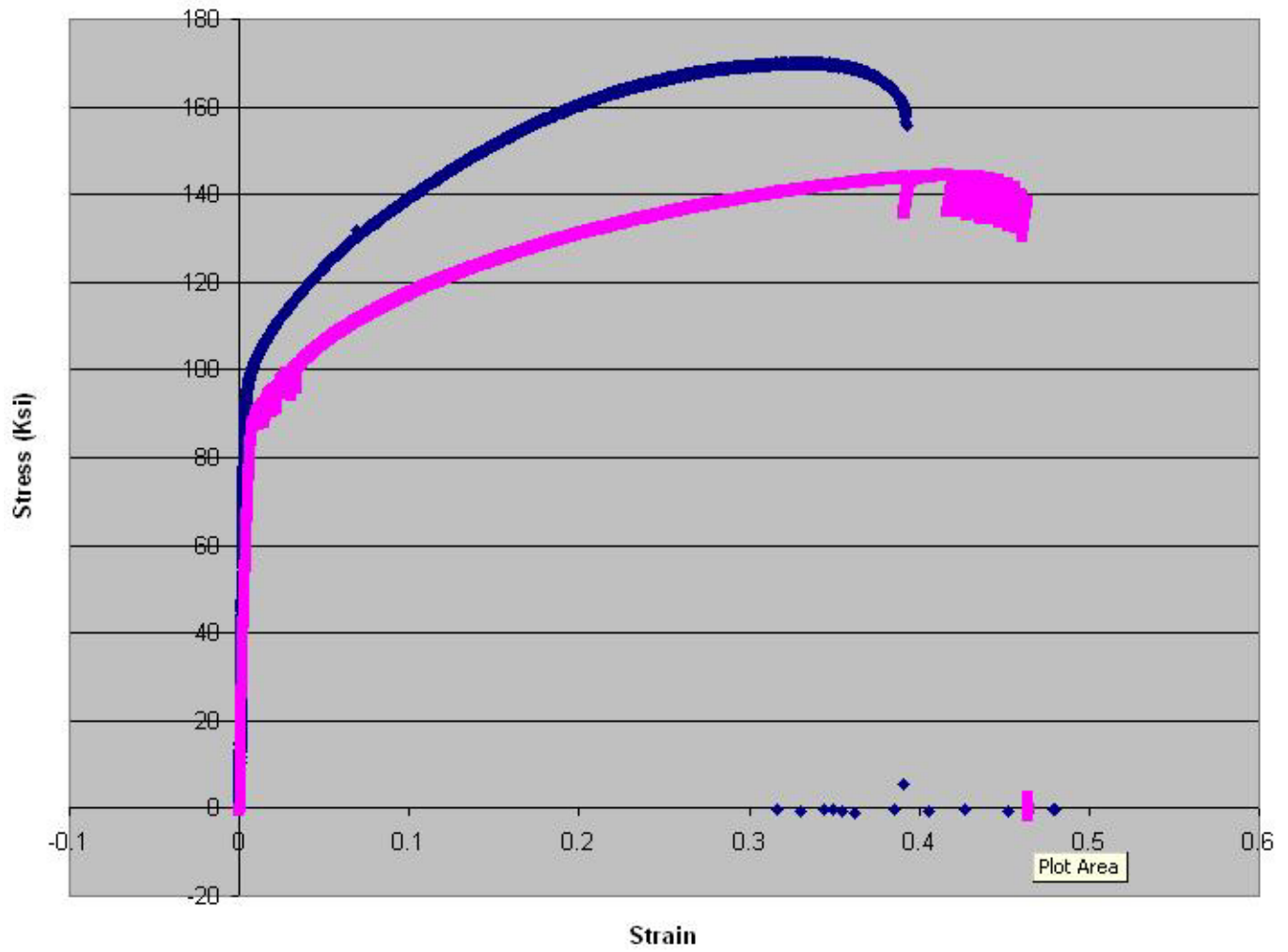


Figure 12. Stress-strain versus temperature for Waspaloy

Test and Analysis Implementation

General Atomics Corporation is establishing testing capability to investigate corrosion effects on heat exchanger and vessel materials in the presence of hydrogen iodide, HI. Facility preparation, development of test apparatus and procurement of test samples is nearly complete. The General Atomics Corporation report is summarized below.

The final design for the immersion corrosion set-up is complete. A schematic cross section of the test system is shown in Figure 14. The coupon sits inside a closed glass capsule filled with 180cc of the test medium (HIx). A 5-micron ID capillary tube connects the capsule interior and its exterior via. The role of the capillary is twofold: first, it allows pressure equalization between the capsule and the pressure vessel and secondly, the capillary's length and small ID acts as a diffusion barrier that minimizes the amount of corrosive vapor flowing out of the capsule.

The capsule is placed inside a closed ended mullite tube on top of a bed of activated charcoal. The mullite tube acts as spillage containment in the event the capsule breaks during experiment. The activated charcoal acts to absorb the HI and I₂ if there is a spill. The top of the mullite tube is filled with charcoal to absorb any test medium vapor that leaks outside the container either through the capillary or the tapered joint.

The specimen capsule- mullite tube combination sits on top of another bed of charcoal inside a 304 stainless steel pressure vessel. The vessel is pressurized with helium via the inlet. The entire pressure vessel sits inside the clam-shell tube furnace that heats the test set-up to the required temperature. At the end of each run, the furnace and pressure vessel will be brought down to room temperature. Once the cool down cycle is complete, the outlet valve will be opened to relieve the pressure within the pressure vessel. The specimen will then be retrieved from the capsule for cleaning and characterization. The test medium will be disposed as hazardous waste.

A commercial pressure vessel has been ordered. The 3-inch OD x 2-inch ID pressure vessel (1/2-inch wall), Model TOC15-40 high-pressure reactor, manufactured by High Pressure Equipment Company, is made from 304 Stainless Steel. The vessel is sealed with metallic gaskets for high temperature operation. The maximum room-temperature working pressure of the vessel is 5000 psig (345 bar) and it is rated at 4000 psi (276 bar) at 427C. The pressure vessel and the glass capsule have been ordered and their delivery is expected in mid-April. The mullite tube is already in house.

3. Other Equipment

The 3-zone tube furnace was tested and it is fully functional. A temperature offset was observed between the control thermocouple and the temperature in the middle of the furnace. Also, there is a significant axial gradient between the middle and ends at the

center of the furnace. These results are non unexpected. The controller thermal couple is close to the heating element, the best position for stable temperature control and over an inch from the centerline of the furnace. With the pressure vessel installed the gradients should be much less, but this will have to be verified once all the components have been installed.

A piping schematic of the apparatus is shown in 16. In order to reach 120 bar at the test temperature, the vessel will have to be pressurized with helium to approximately 52.6 bar at room temperature. The exact pressure required will depend upon the temperature distribution within the pressure vessel at operating temperature. At the beginning of each experiment, a helium bottle will be wheeled into the room and hooked up to the piping manifold to first flush and then bring the vessel to the required pressure at room temperature. The valves will then be closed and the helium bottle will be removed from the room. The pressure within the vessel will increase to the target value of 120 bar as the temperature is raised to 350°C. To minimize any corrosive vapor reaching the valves and pressure gauge, charcoal filter are place along the connections at the exits of pressure vessel.

4. Corrosion Specimens

The procurement of corrosion samples is almost complete. Table 9 shows a list of the material coupons that are in house.

5. OTHERS

- A 31 page Hazardous Work Authorization (HWA) has been completed. It is available upon request.
- A new materials survey report including HI decomposition using phosphoric acid and sulfuric acid decomposition is in progress and will be available upon request.
- Project personnel visited UNLV and toured the facilities of Prof. Ajit Roy. A plan for collaboration underway.

	<i>Materials</i>	<i>In House</i>	<i>Quantity</i>
1	Ta	√	3
2	Ta-10%W	√	3
3	Ta-40%Nb	√	3
4	Nb	√	3
5	Nb-1%Zr	√	3
6	Nb-7.5%Ta	√	3
7	Nb-10%Hf	√	3
8	Zircalloy 702	√	3
9	Zircalloy 705	√	3
10	Mo		
11	graphite		
12	SiC (sintered)	√	3 or more

Table 9. Immersion corrosion test materials coupons.



Figure 13. (a) Enclosure for the experimental set up (b) Blow vent at the top of the enclosure and (c) fume hood next to the enclosure for mixing HIX.

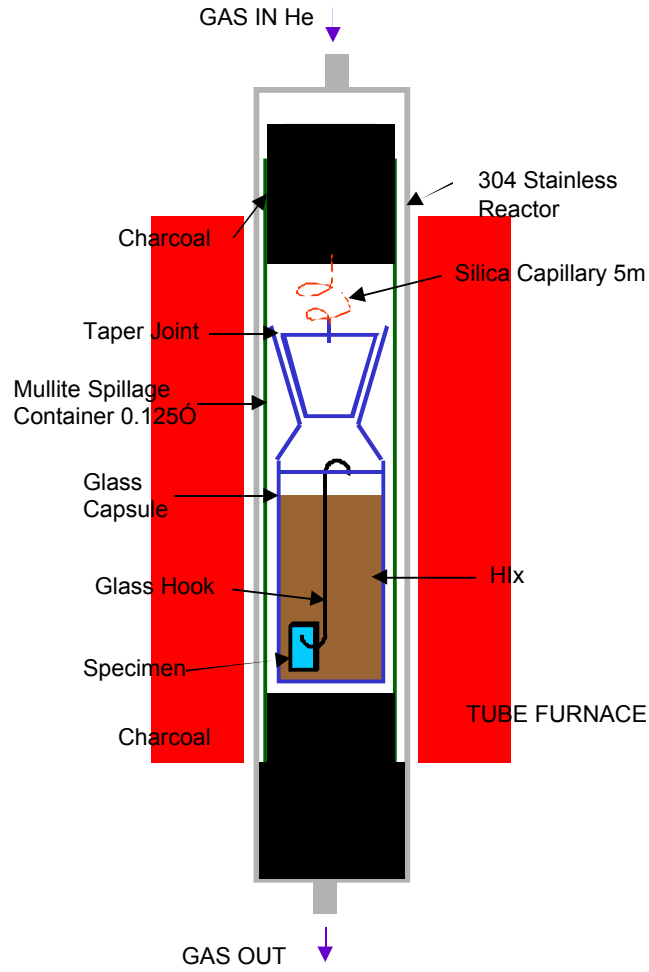


Figure 14. High temperature immersion corrosion test set up.

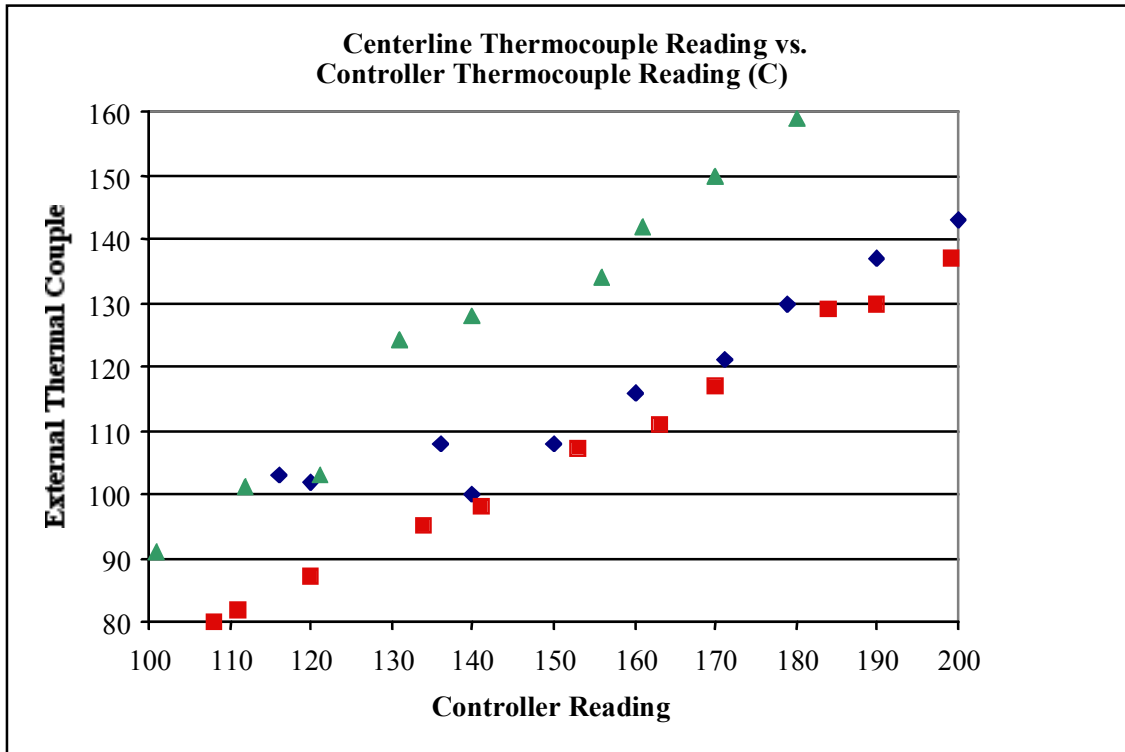


Figure 15. Three zone tube furnace temperature measurement.

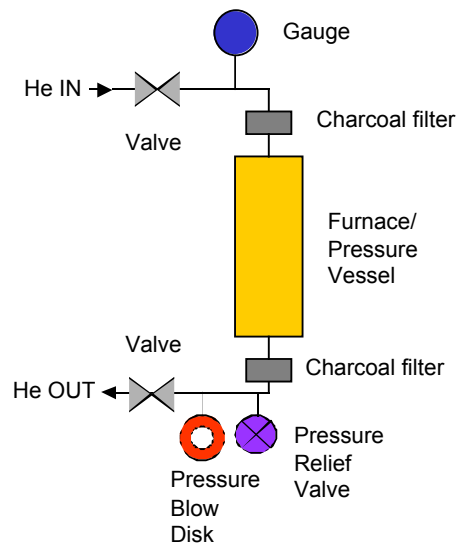


Figure 16. Piping Schematic