YEARLY and FINAL PROGRESS REPORT

Project Title: Thermal Cooling Limits of Sabotaged Spent Fuel Pools

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Recipient: The Pennsylvania State University
Applied Research Laboratory
North Atherton Street
State College, PA 168084-0030

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Subcontractors: N/A

Other Partners: N/A

Contact(s): Dr. Thomas G. Hughes, PI Dr. Thomas F. Lin, Co-PI
814-865-3418 814-863-4249
tgh@psu.edu oid@psu.edu

Submitted to: DOE Project Manager: Nancy Elizondo, elizonna@id.doe.gov
Procurement Services Division: psdrept@id.doe.gov

Project Objective: To develop the understanding and predictive measures of the post “loss of water inventory” hazardous conditions as a result of the natural and/or terrorist acts to the spent fuel pool of a nuclear plant. This includes the thermal cooling limits to the spent fuel assembly (before the onset of the zircaloy ignition and combustion), and the ignition, combustion, and the subsequent propagation of zircaloy fire from one fuel assembly to others.

Background: A National Academy of Sciences expert panel issued a public plea in 2005 to increase the security measures to safeguard the spent fuel pools of the nation’s nuclear plants. The panel strongly recommended increased research to assess the Maximum-Credible Scenarios (MCS) and to improve the current understanding of the hazardous conditions, as well as the thermal runaway condition of zircaloy ignition and combustion that would follow the loss of spent fuel pool water. This research is critical to improving the security of the nation’s nuclear plants as well as the spent fuel infrastructure of the next generation (Generation IV) nuclear units because they all share the common characteristic of having to cope with extended years of spent fuel pool cooling.

Status:

The status of the program for performance period from 1-May-2008 throughout 30-Apr-2009 covers extensive literature survey; thermo-chemical analyses of the zircaloy reaction at high temperature; the experimental design and buildup for the zircaloy ignition and combustion tests; as well as the first experimental execution of zircaloy-4 reaction with superheated steam as the oxidizer, as summarized next. Other tasks as proposed are planned for the third (final) year.

1.1. Thermochemical Processes of Zircaloy Reactions

After numerous studies conducted by the National Academies of Sciences and the Nuclear Regulatory Commission, spent fuel pools of existing and future nuclear power plants have been identified as a potential terrorist target.^[1, 2] A thorough literature survey was performed on all relevant articles on the combustion of Zircaloy-4 as well as the modeling of the ignition and combustion of Zircaloy-4. The survey helped to gain a solid background on the research completed on zirconium combustion and provided insight into the experiments conducted to date. The articles are arranged chronologically in each respective section below.

1.1.1. The Combustion and Heat Transfer Characteristics of Zircaloy-4 in a LOCA

Heat transfer experiments are important to consider in a severe accident situation. In most experiments regarding a LOCA (loss of coolant accident), only steam entrainment has been considered. In order to obtain accurate results pertaining to thermal runaway condition of the spent fuel pool, a complete experiment must be carried out taking air ingress into account. These experiments are particularly crucial in order to provide a foundation for future work regarding the propagation of zirconium fire from one rod (with higher decay power) to another (with lower decay power).^[3]

In 1979, Benjamin et. al.^[4] performed an analysis of the spent fuel heat-up following a LOCA using computer codes that were available at the time. Several variables were considered in these calculations including decay time, fuel element design, storage rack design, packing density, room ventilation, drainage level, etc. Figure 1.1 shows several configurations for bundles of zircaloy cladding in spent fuel pools.

The article demonstrated that the probability of a breach in containment or rupture of the cladding was extremely dependent upon the configuration of cladding assemblies and the ventilation available in the building. With perfect ventilation, the cladding temperature as a function of height is illustrated in Figure 1.2.

Self-sustaining oxidization occurs around a temperature of 1173 K. Although this is an approximate temperature, there is a possibility of a mass rupture if enough of the spent fuel rods reach this temperature. This would cause a local temperature increase, possibly leading to local clad melting. However, if ventilation is inadequate, the temperature profile changes and the cladding reached the “runaway” temperature of 1173 K quite easily.

In 2000, Powers^[5] proposed a study that examined the effects of air ingress on the zircaloy cladding. He proposed that the air would react exothermically with the molten or near molten zircaloy if the containment was breached and air was allowed to rush into the hot zone. In turn, this air could mix with the radioactive fuel, also causing a very exothermic reaction.

Figure 1.1 Configuration of Spent Fuel Assemblies.

He noticed that the heat of reaction for zirconium and air was almost double that of zirconium and steam. The reactions and their heats of reactions are shown as follows:

He also noticed that there was no accurate way to predict how the air would interact with the molten mixture. To date, there is no data available due to the complexity and hazards of such an experiment. He speculated that one of two results would be seen from an experiment:

- High temperatures would cause the cladding to melt and flow away from the encased uranium pellets, leaving them exposed to the air.
- High temperatures would cause the cladding to melt and dissolve the pellets, creating a mixture of cladding and fuel pellets, so-called “zircry” eutectic.

Figure 1.2 Typical Variation of Clad Temperature With Normalized Distance, Measured from Lowest End of Fuel Rod.

The extent of the damage depends greatly on the degradation state of the core. In the first case, the fuel pellets would have been exposed to the air, causing rapid and severe oxidation. This would have created hordes of radioactive particles that would have reacted further with the system and surrounding containment. In the second case, it is hard to predict what would have happened. He postulated that the mixture would react well enough with the air that it would melt through the containment facility, releasing deadly radioactive particles into the environment.

In 2004, Nagase and Fuketa^[6] performed experiments on small samples of Zircaloy-4 cladding to determine the behavior of high burn-up conditions in LOCA's. These small samples consisted of 0.5 meter (m) long test rods that had been pre-hydrated in 1220 K - 1500 K steam flow, then

quenched in water. This was done to observe if the cooling water would create a thermal shock to the system, fracturing the zircaloy.

As illustrated in Figure 1.3, the zircaloy cladding burst under pressure due to the rods being constrained at both ends.

By altering the initial concentration of hydrogen, there was a change in the time at which the cladding ruptured and the strain by which it ruptured. This only applied to the claddings that fractured under pressurization stress, not thermal shock. The claddings that fractured under thermal shock depended on the amount of oxidation present on the surface of the zircaloy. By increasing the initial hydrogen concentration, the amount of time the cladding took to burst decreased. In several places, precipitates of hydrides were found near the bursting zone. It was speculated that these could be causes for embrittlement of the cladding, which could lead to failure.

Figure 1.3 Bursting Phenomena of Zircaloy Tubing.

In this article, it was observed that the claddings could burst under pressure if they were constrained; this is something that has not yet been studied. Unexpectedly, they could burst when quenched with water if the initial hydrogen concentration was high enough. This raises the

question of how exactly the water and the zircaloy react with each other under normal conditions, and whether or not this will impact the cladding if a LOCA were to occur.

In 1999, Haste and Trambauer^[7], both members of a European Commission formed to study the QUENCH experiments of zircaloy, published a summary of findings from prior experiments and conducted new experiments. Four new tests were considered, titled QUENCH-01 through QUENCH-04. In these tests, a bundle of zircaloy cladding underwent a simulated LOCA, allowing the water to drain. What was special about these tests is that water was used to flood the empty fuel pool, cooling the cladding. Initially, the test bundle of zircaloy cladding had varying conditions, as shown in Table 1.1.

Table 1.1 Conditions for QUENCH Experiments.

Experiment	Pre-Oxidized?	Heat Rate (K/s)	Flooding Temperature (K)	Excess Hydrogen Produced (grams)
QUENCH-01	Yes	0.5	1870	26-30
QUENCH-02	No	0.9	1870 – 1970	190
QUENCH-03	No	0.6 – 1.3	2070	142
QUENCH-04	No	0.5 – 1.5	2100	12

These conditions drastically affected the outcome of the quenching experiments. The results of each experiment are as follows:

- QUENCH-01: Quenched steadily during flooding, with no signs of temperature excursions or hydrogen production. The bundle, however, was severely oxidized in the top portion, with large cracks present in the embrittled cladding.
- QUENCH-02: Showed strong temperature excursions and strong hydrogen production. Severe embrittlement occurred in the cladding, with parts melting in the top of the bundle.
- QUENCH-03: Same type of results as QUENCH-02, but with more damage to the top of the bundle.
- QUENCH-04: The bundle cooled rapidly several times, thus producing little hydrogen while cooling. This happened due to the bundle cooling quickly after the flooding.

In 2007, Duriez et. al.^[8], a part of the Severe Accident Research network of the European Commission discussed the effects of the zirconium cladding degradation in situations that involved air ingress. These experiments expanded upon previous ones that only included steam as the oxidizing environment.

It was seen in the experiments that the air ingress had little effect until a certain temperature was reached. At 1073 K, the addition of air had no effect to the overall oxidation rate of the system. Oxide layers of ZrO_2 were formed only with high concentrations of air, up to about 90%. However, at temperature of around 1573 K – 1673 K the oxidization rate increased dramatically with even less of a concentration of air in the mixture. The presence of nitrogen in the air was

also shown to produce an interesting phenomenon. At a concentration of 50% nitrogen to 50% steam mixture, the highest oxidation rates were observed with respect to the amount of product released and oxide formed. This demonstrated that air had a significant impact on the oxidization rates of Zircaloy-4.

1.1.2. Modeling of the Heat-up of Zircaloy-4 Cladding and Burn-up Conditions

To further investigate the LOCA phenomenon, a heat transfer model must be considered. During a LOCA, a complex heating and cooling cycle can be observed, which can be simulated by modeling of the system under different conditions.

In 2000, 19 partners involved in the COLOSS project aimed at improving the understanding of a LOCA. Adroguer^[9] published the findings from a number of experiments including the effects of hydrogen production, oxidization of cladding, and effects of molten zircaloy on the cladding geometry. From these experiments, software codes were established and implemented in programs to predict the effects of a LOCA. However, after these codes were run, several inadequacies were found to exist.

It was found that the early hydrogen rate was almost of equal importance to total hydrogen production in the system, with respect to explosion hazards and containment issues. The code implemented was weak in this regard, due to the program's difficulty in handling the oxidization of mixtures. With regards to the oxidization of the cladding, large uncertainties were present in the calculations. In all severe accident codes this topic is a large weakness. These weaknesses led to underestimation of hydrogen production in early stages and also during quenching.

In 2002, Ikeda et al.^[10] created a code, the IMPACT/SAMPSON code, to analyze a severe accident in a nuclear reactor or spent fuel pool. Even though other codes have been created and work for this specific purpose, the IMPACT/SAMPSON code involves a hydrogen reaction from the zircaloy – water reaction, something not found in many other codes. This term was investigated to be important in evaluating the integrity of the cladding during a LOCA. The coding was analyzed against a newer quench test, QUENCH-06, which took place at Forschungszentrum Karlsruhe (FZK).

After running both the simulation and the QUENCH-06 experiment, the two were compared for similarities. From the analysis, it was found that the simulation agreed relatively well with the QUENCH-06 test, with regards to the temperature distribution in the zircaloy bundle and the degradation caused by the zircaloy – water reaction. When the total hydrogen content was measured, both the simulation and test were within 20% of each other, a reasonably good agreement with previous correlations. The failure times matched almost exactly when compared between the prediction from the simulation and the actual experiment.

In 2007, the IAEA (International Atomic Energy Agency)^[11] completed a study on the dynamic modeling of fuel behavior in a LOCA. The investigation was carried out in conjunction with experimental and computational analysis. Multiple codes were used, each serving a separate purpose. The codes are as follows:

- System thermal-hydraulics codes
- Steady state fuel behavior codes
- Transient fuel behavior codes
- Steady state reactor neutronics codes
- Reactor dynamics codes

Several different parameters were taken into consideration in the modeling analysis, specifically the power peaking factors, fuel rod burn-up, and single failure criterion. With the power peaking factors, it was determined that the peaking factor should be determined conservatively to represent the power distribution of the fuel pool. Because the quenching of the cladding depends on the vertical position, a power distribution skewed more towards the top is more realistic. Sensitivity studies were used to determine each of the parameters because they are independent from one another. In future codes, the IAEA plans to couple all of the parameters together to create a relationship within the system.

1.2. Three Mile Island Discussion

Over the course of last three decades there have been two well-known meltdowns of nuclear power plants. The first of which was on March 28, 1979 in Pennsylvania at the Three Mile Island reactor. The second was the meltdown of the Chernobyl nuclear reactor on April 26, 1986. The Chernobyl accident is the worst nuclear reactor accident in history, but does not directly relate and will not be discussed. The Three Mile Island accident can be compared to the spent fuel pool situation. The partial core meltdown of Three Mile Island was contained by the reactor pressure vessel and the containment building, thus, little radiation was released to the environment. A similar fuel assembly meltdown in a spent fuel pool would have been disastrous,^[12] because of the lack of containment barriers.

At 4:00 AM on March 28, 1979, the main feedwater pumps stopped working due to an unknown electrical or mechanical failure. The failure caused the steam turbines and nuclear reactor to automatically shut down. This caused the safety system to stop removing the decay heat from the reactor, which in turn led to an over-pressurization of the system, an expected consequence of the automatic shutdown. A pilot-operated pressurizer relief valve (PORV) opened to release the pressure, and was set to close after the pressure reached a safe level. However, the valve did not close. Due to a lack of specific instrumentation, this information was not available to the operators, and cooling water started to leak out of the safety valve. This caused the core of the reactor to overheat. A simplified diagram of Three Mile Island is shown in Figure 1.4.^[12]

Because there was limited instrumentation to show the water levels in the core, the operators did not know that the core was leaking. Typically, the water level was judged by the pressure in the pressurizer. The operators believed the core was properly cooled with sufficient water due to the malfunctioning PORV. Slowly, the temperature of the nuclear fuel and zirconium cladding began to rise. The increased heat released from the cladding raised the temperature of the water,

causing it to boil. The temperature in the core was so high that the zirconium cladding began to melt. A chemical reaction took place between the steam and zirconium:

After the investigation of Three Mile Island, it was shown that about half of the fuel rods had melted during the accident.^[12] Something to be considered is if the zirconium will react with water at a realistic temperature range. This will be analyzed by the minimization of the Gibb's free energy change for this reaction.

Figure 1.4 Configuration of Three Mile Island Reactor.^[12]

1.3. Gibb's Free Energy

There are two main alloys of zirconium currently used in the spent fuel pools today, Zircaloy-2 and Zircaloy-4. The compositions of both are shown in Table 1.2.

Table 1.2. Zirconium Alloy Compositions (% Weight).^[13]

Alloy Name	Zirconium	Tin	Chromium	Iron	Nickel	Hafnium
Zircaloy-2	98.25	1.45	0.1	0.135	0.055	0.01
Zircaloy-4	98.23	1.45	0.1	0.21	0	0.01

Since Zircaloy-4 is comprised of 98.23% zirconium, it can be assumed in the Gibb's free energy equations that the other components of the alloy are negligible. The following chemical equation can be used to model the tendency of Zircaloy-4 to react with water under normal condition at 298 K:

Gibb's free energy can be used to explain how easily a reaction will progress. The more negative the Gibb's free energy, the more likely that the reaction will occur. To find the Gibb's free energy of the system, the following equation must be solved for at standard temperature (298 K):

$$\Delta G^\circ = \Delta H_f^\circ - T \cdot \Delta S^\circ \quad (1)$$

Table 1.3 lists the values of ΔH_f° (heat of formation) and ΔS° (entropy) for each species in the products and reactants at 298 K. The Gibb's free energy for the zirconium-water reaction is $-565.422 \frac{\text{kJ}}{\text{mol}}$. Being a negative number, it is apparent that zirconium oxidizes with water under normal conditions. However, the Gibb's free energy does not represent the rate of the reaction. The determination of the rate delves into a much more complicated discussion not pursued here.

Table 1.3 ΔH_f° and ΔS° Values for Several Compounds (298 K, 1 atm).^[14]

Compound	$\Delta H_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	$\Delta S^\circ \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$
Zr (s)	0	38.87
H ₂ O (l)	-285.830	69.950
H ₂ O (g)	-238.921	188.834
ZrO ₂ (s)	-1,097.463	50.359
H ₂ (g)	0	130.680

Referring back to section 1.2 on Three Mile Island, it was said that over half of the fuel claddings were found melted after the incident. To analyze the Gibb's free energy at an elevated temperature, the previous equation cannot be used. Instead, the following equation must be used, including the assumption that the heat of formation stays constant independent of temperature.

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\} \quad (2)$$

The Gibb's free energy at a temperature of 2150 K is much more negative, $-1,801.688 \frac{\text{kJ}}{\text{mol}}$. This shows that as the temperature of the zirconium increases, the more likely it will react with the surrounding liquid or steam. It can be assumed by the increased temperature that the rate will also increase, most likely by a large factor. The full calculations of Gibb's free energy for zirconium-water at 298 K, and zirconium-steam at both 298 K and 2150 K, are shown in Appendix A.

2.1. Thermochemical Analysis and Experimental Design

In order to determine the chemical species and temperature of the reaction products released by the combustion of Zircaloy-4 in various atmospheres, a chemical equilibrium software program was used. This program, dubbed SOLGASMIX, was acquired by Applied Research Laboratory in 1975 and updated in-house periodically throughout the years. Unlike a popular chemical kinetics program, CHEMKIN, this program solves for the equilibrium state of the chemical reaction. The program assumes that enough time has gone by that all of the species existing in the products have reached a steady state.¹

In order to run the program, chemical properties from every species possible in the particular chemical reaction must be found. These properties can be found within the JANNAF tables. The program has a large portion of these tables included with the packaging; however, JANNAF publishes new tables periodically, so the data contained in the program might not be up to date. A data set was created for each species, including $\Delta H_1 - \Delta H(T)$ (sensible heat), ΔG (Gibb's free energy), and ΔH_f (heat of formation), at varying temperatures. An excerpt from one of the data sets is shown below in Table 2.1.

Ideally, the data for each species would be listed at every temperature possible. However, it is only required that the data be listed up to the adiabatic flame temperature of the reaction, or slightly beyond. SOLGASMIX takes the values from the data sets and creates curve fit equations for each data listing for all temperatures. If the temperatures in the data input do not go as high as the adiabatic flame temperature of the reaction, there is a possibility that the data will be skewed due to the inability of the curve fits to give accurate results when extrapolating.

As the water level recedes during a LOCA (in core or in spent fuel pool), the sheer amount of heat given off by the cladding may result in a superheated steam situation, when the steam reaches a temperature higher than 373 K. Temperatures of 373 K and 800 K were used in the program to determine adiabatic flame temperatures.

The SOLGASMIX software was run under various conditions for the Zircaloy-4 mixture. These conditions were 100% steam, 100% humidity, 75% humidity, 50% humidity, 25% humidity, and 100% dry air. If the steam flow rate is high enough, air will be unable to enter the pool, resulting

¹ A complete technical report on the SOLGASMIX computer program can be found via Applied Research Laboratory, Technical Report No. TR 88-008, "Development of a Database of Thermochemical Parameters for Use With the SOLGASMIX Computer Program".

in a 100% steam condition. However, if the steam flow is low, air may be drawn in as a counter-current flow. Also, as the water level recedes, the amount of steam will decrease, allowing an inward flow of air. The varying conditions simulate what happens with respect to the water level of the pool, ending with a completely dry pool (assuming the Zircaloy-4 is not melted at this point). The humidity levels were calculated using a relative humidity relation of “X” kg of moisture to “Y” kg of air, shown in Figure 2.1.

Table 2.1 Data Set from JANNAF Tables.

Fe(OH) ₂			
Temperature (K)	$\Delta H - \Delta H(T)$	ΔG	ΔH_f
298.15	0	-306.666	-330.536
300	0.133	-306.518	
350	3.861	-302.471	
400	7.819	-298.365	
450	11.945	-294.223	
500	16.198	-290.056	
600	24.989	-281.665	
700	34.08	-273.207	
800	43.419	-264.681	
900	52.973	-256.067	
1000	62.714	-247.331

Figure 2.1 Graph of Humidity Ratio vs. Relative Humidity at 25°C for SOLGASMIX Program.

2.2. Zircaloy Burning Test Setup

In order to heat the Zircaloy-4 to its melting point of approximately 2150 K, a high-temperature heating element must be used. Very few heating elements, however, are able to be used up to and above this temperature. Also, the heating element must be sustainable throughout the entire experiment without being burned or rendered useless from the combustion process. Skin heating the Zircaloy-4 was chosen as the most favorable method because the resistivity of Zircaloy-4 is on par with other materials used as high-temperature heating elements.^[15] A chart was compiled from several different sources to show the differences in resistivity for several feasible heater rod materials, shown in Appendix B.

The total cladding sample length is 5-inches. To keep the combustion controlled and limited to a set section of the cladding, a 1-inch section in the middle of the cladding has its diameter machined down. This section was intended to produce a heat flux value comparable to that of actual spent fuel rods, approximately 50,000 W/m². A simple calculation was performed to determine this heat flux value, shown in Appendix C. The outer diameter of the thinned section was determined by the following equation:

$$V = \sqrt{\frac{2QL^2\rho R_o}{R_o^3 - R_i^3}} \quad (3)$$

With the given values of V the heat flux, length of the section, resistivity, and inner radius of the cladding, iterations were required to solve for a suitable outer diameter. A diameter of 0.340 inches was found to fit the given conditions. Given this diameter, a total of 1.244 volts (V) and 85 amperes (A) is required to achieve the heat flux condition. A complete table of the iteration process is shown in Appendix D. It should be noted that, depending on how high the peak cladding temperature reaches at the designed heat flux, it is possible we may have to resort to temperature control instead of heat flux control to achieve the sample ignition.

Figure 2.2 CAD Drawing of Zircaloy-4 (Cross-Section).

2.2.1. Integrated Thermocouple System

To determine the cladding temperature in the thinned and un-thinned zones, thermocouples were placed at three different locations inside of the cladding. Because the Zircaloy-4 is skin heated, and thus conductive, the thermocouples must be electrically insulated from the cladding. However, the thermocouples must not be thermally insulated from so an accurate temperature reading can be obtained. This was achieved by the placement of thin aluminum oxide (Al_2O_3) ceramic tubes inside of the cladding. CAD drawings of these tubes are shown in Appendix E. A dimensioned cross-section of the Zircaloy-4 cladding with the ceramics inserted is shown in Figure 2.2.

The regions where the thermocouples would be placed were designed to be as thin as possible despite the low thermal conductivity of aluminum oxide, $18 \text{ W/m}^2\text{K}$. Inside of these grooves, small Inconel rings are placed to allow the acquisition of an average circumferential temperature and the attachment of the thermocouples. There is a concern as to how much error the ceramics would produce in the temperature between the inside and outside of the cladding. To address this, a quick calculation can be done to determine the loss from such an insulator using the following equation:

$$q'' = -k(T_s - T_\infty) / r \ln(r_2/r_1) \quad (4)^{[16]}$$

To illustrate further the insides of the Zircaloy-4 cladding, a solid model was created and a section view is shown in Figure 2.3. The outer sheath is the Zircaloy-4 cladding, the white bulk is the aluminum oxide ceramics, and the darker slivers are the Inconel rings to which the thermocouples are attached.

Figure 2.3 Solid Model of Zircaloy-4 (Cross-Section).

2.2.2. Ignition/Combustion Chamber

The test chamber is comprised of a stainless steel tube with several ports for electrical connections, thermocouple access, inlets and outlets of oxidizer and exhaust, a vacuum line and

argon purge line, and glass windows for visual data recording. In Figure 2.4, the chamber is shown with no connections, attachments, etc.

The chamber was designed and constructed to allow both a vacuum and pressure build-up. There are copper gaskets located between each flange on the chamber. All of the fittings are either welded to the chamber, incorporate an o-ring seal, or are sealed with Teflon fittings. This prevents any leakage of exhaust into the atmosphere or atmospheric gasses into the chamber, which would oxidize the Zircloy-4 at increased temperatures. Each feature of the test chamber is described below.

Figure 2.4 Solid Model of Test Chamber.

- A. Glass Windows – The glass windows are located on both sides of the chamber, allowing video or photographs to be taken with enough light coming through the other window. They are sealed with an o-ring to prevent any leakage.
- B. Electrical Connection Ports – 0.5 inch copper rods protrude through ports located at these points. Teflon surrounds the copper connections to electrically insulate the chamber from the test specimen.
- C. Oxidizer Inlet – The oxidizer nozzle enters through the bottom of the test chamber, creating a cross-flow condition for the burning of the Zircaloy-4. The propane burner and steam generator are both located upstream of the nozzle.
- D. Exhaust Outlet – The exhaust can either exit through this port and then be collected via sampling chambers or exit through an exhaust hood located above the outlet.

E. Argon / Vacuum Purge – Vacuum and argon lines are connected to this port in order to purge the chamber, to removing any excess air before running a test. This is important to control the atmosphere inside of the chamber and reduce the possibility of oxidization to the Zircaloy-4.

F. Thermocouple Port – The Zircaloy-4 thermocouples protrude through a Teflon seal.

A cross sectional view of the test chamber can be found in Appendix F, as well as a dimensioned CAD drawing. The thermocouple data, along with the amperage data, will be recorded via a computer data acquisition system employing the LabView software. It will provide real-time temperature data and amperage data. A supplemental thermocouple located on the outside of test chamber will monitor the temperature of the chamber.

2.2.3. Propane Burner

A propane burner was used to increase the temperature of the steam above 373 K without having to pressurize it. The burner contained seven coils in series, totaling a length of 132.6 feet. Coils #1 through #4 were 0.25 inch stainless steel tubes, while coils #5 through #7 were 0.375 inch stainless steel tubes. The heat exchanger was heated using a propane burner rated at 122,000 BTU/hr.^[17] The gasses travel over the heat exchanger coils and out the top of the system, pulled by a high temperature blower connected via stainless steel piping. A model of the propane burner is shown in Figure 2.5.

Figure 2.5 Model of Propane Burner.^[17]

2.2.4. Auxiliary Equipment

The steam generator can produce 18 lb/hour of steam at various temperatures and pressures. The steam line is connected in part to the oxidizer inlet line, with a valve acting as a regulator to control the amount of steam flowing into the test chamber. This can be changed depending on what type of atmosphere is needed in a specific test. The steam generator is shown in Figure 2.6.

Figure 2.6 Photograph of Steam Generator.

The sampling chamber is located downstream of the exhaust outlet of the test chamber. There are four sampling tubes available to take samples with. All four chambers can have a vacuum pulled and the exhaust diverted into them via a solenoid. A picture of the sampling chamber is shown below in Figure 2.7.

To begin the experiment, a vacuum is pulled on the test chamber. An inert gas, such as argon, is purged into the chamber. This process is repeated several times to ensure any residual atmospheric gas are removed. When this is complete and a vacuum is held, the power supply to the zircaloy sample can be turned on. The propane burner and steam generator can be turned on at this time.

When the zircaloy sample has reached a temperature favorable for ignition, the oxidizer line is pressurized to a specific pressure, which correlates to a predetermined mass flow rate. The calculations for the mass flow rate are shown in Appendix G. These calculations assume a choked nozzle to achieve a constant mass flow rate. The chamber's pressure will increase as the oxidizer enters. Once the chamber is around one atmosphere, the exhaust is opened to negate any pressure buildup inside of the chamber. If the reaction does not happen too fast, the sampling chambers will have a vacuum drawn and then opened, allowing exhaust gasses from the reaction to enter the chambers. This process can be repeated as necessary for future experiments, as long as the ceramic insulators maintain their integrity inside of the sample.

Figure 2.7 Photograph of Sampling Chambers.

3.1. SOLGASMIX Software Testing

There are several options as to what can be solved for when running the software package. The main output of the program is a breakdown of which species exist in the products. Shown below in Figure 3.1 is a sample of the raw data from a run of 0% humidity (dry air), at a fuel temperature of 2100 K and oxidizer temperature of 800 K, and an A/F^2 ratio of 0.1. This excerpt shows the equilibrium data for elemental zirconium. Reiterating the input data, the program lists the element, chemical symbol, and reference state. As an output of the chemical reaction, the species, moles, moles of element, percent of element, and totals for the data, are listed.

² It must be noted that a typical A/F ratio was not used when using the SOLGASMIX program. In every case except the 100% steam condition, the A/F ratio referred to a molar ratio of elemental nitrogen to elemental zirconium (*e.g.* moles N : Zr). With the case of 100% steam, the A/F ratio was the molar ratio between elemental oxygen and elemental zirconium (*e.g.* moles O : Zr).

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SPECIES	MOLES	MOLES ZR	PERCENT ZR
ZR1(CR,L	0.88836E+02	0.88836E+02	88.84
N1ZR1(CR	0.10000E+02	0.10000E+02	10.00
O2ZR1(CR	0.11636E+01	0.11636E+01	1.16

TOTALS	0.10000E+03	100.00	

Figure 3.1 SOLGASMIX Distribution Report for Zirconium:
Humidity = 0%, $T_{\text{fuel}} = 2100 \text{ K}$, $T_{\text{oxidizer}} = 800 \text{ K}$, $A/F = 0.1$.

- Species (phase) - The name of the species 'element X' is contained in, with the phase of that species in parenthesis (CR for solid, L for liquid, and G for gas)
- Moles – The total moles of each species
- Moles 'element X' – The total moles of 'element X' in each respective species
- Percent 'element X' – The ratio of 'element X' in each species to total amount of 'element X'

An interesting discrepancy occurs when a particular elemental distribution lists a species that is not present in any other element's distribution. This occurs on numerous occasions with multiple species. For example, listing elemental oxygen and iron in the case of 0% humidity, 2100 K fuel temperature and 800 K oxidizer temperature, and an A/F ratio of 30, the result is shown in Figures 3.2 and 3.3.

Under the distribution report for iron, 82.31% of the iron is in the form of FeO (g). In the distribution report for oxygen, however, no FeO (g) is listed. This is due to the low concentrations of iron in the original Zircaloy-4 mixture (0.21% by weight), the high A/F ratio, and the eventual round off error associated with any small number calculations. To help with the small number calculations, all of the molar amounts elements in Zircaloy-4 were calculated on the basis of 100 grams (g). The root of this issue is the large A/F ratio and small initial percentage of iron. Therefore, it can be concluded that the percentage of oxygen in the form of FeO (g) is negligible compared to other species.

DISTRIBUTION REPORT: ELEMENT # 3			
CHEMICAL SYMBOL: O			
REFERENCE STATE: O2(REF)-XT			
SPECIES	MOLES	MOLES O	PERCENT O
O2(REF)-	0.23122E+03	0.46245E+03	66.24
O2ZR1(CR	0.10000E+03	0.20000E+03	28.65
N1O1(G)-	0.28453E+02	0.28453E+02	4.08
O1(G)-XT	0.52276E+01	0.52276E+01	0.75
SN1O1(G)	0.93023E+00	0.93023E+00	0.13
SN1O2(G)	0.20427E+00	0.40854E+00	0.06
CR1O2(G)	0.15671E+00	0.31343E+00	0.04

TOTALS		0.69778E+03	99.94

Figure 3.2 SOLGASMIX Distribution Report for Oxygen:
Humidity = 0%, $T_{\text{fuel}} = 2100$ K, $T_{\text{oxidizer}} = 800$ K, A/F = 30.

DISTRIBUTION REPORT: ELEMENT # 5			
CHEMICAL SYMBOL: FE			
REFERENCE STATE: FE1(CR,L)-XT			
SPECIES	MOLES	MOLES FE	PERCENT FE
FE1O1(G)	0.28742E+00	0.28742E+00	82.31
FE1(G)-X	0.61753E-01	0.61753E-01	17.68

TOTALS		0.34917E+00	99.99

Figure 3.3 SOLGASMIX Distribution Report for Iron:
Humidity = 0%, $T_{\text{fuel}} = 2100$ K, $T_{\text{oxidizer}} = 800$ K, A/F = 30.

3.2. Adiabatic Flame Temperature Results and Molar Composition Breakdown

There are two main values of interest, the adiabatic flame temperature and molar composition of the product mixture. When running the program, the menu will display an option to iterate for the adiabatic flame temperature. This will display the temperature in the output, as well as the iterations. However, there is no direct way to calculate the mole fractions of the mixture. A value in the input file can be toggled to print the molecular weights of each species. This can be useful, especially since the program already solved for the mass fraction of every species in the mixture. A small data sample is shown in Appendix H. With these two lists of values, mole fractions can be evaluated by the simple relation where Y_i is the mass fraction of species 'i' and MW_i is the molecular weight of species 'i':

$$\chi_i = \frac{Y_i / MW_i}{\sum_{j=1,n} Y_j / MW_j} \quad (5)^{[18]}$$

Adiabatic flame temperature calculations were performed for two oxidizer temperatures, 373 K and 800 K. It is expected that there is enough latent heat in the pool to superheat the steam. In the case that the steam is unable to be superheated, the 373 K case was run. In order to represent a case where the steam is superheated, a case was run with the oxidizer at 800 K. In both cases, the Zircaloy-4 temperature was 2100 K, just shy of its melting temperature of 2150 K. The results of the adiabatic flame temperature calculations show that the reaction is greatly independent of oxidizer temperature at low A/F ratios. At higher A/F ratios, however, the temperature decreases more rapidly in the 373 K case than the 800 K case, reaching a lower steady-state temperature. It can be seen from Figures 3.4 and 3.5 that the only noticeable difference in the results are found in the pure steam situation. Analyzing this data can give a reasonable picture as to what is happening with the reaction at a given A/F ratio. There are also a few 'spikes' in the curves for each case that can be explained quite easily.

1. A/F Ratio ~ 0.5 'spike'

At this ratio, it is consistently seen in the data that ZrO_2 (s) is present in the products in appreciable concentrations until an A/F ratio of 0.5 is reached. The production of ZrN (s) slows down dramatically and the production of ZrO (g) stabilizes. These factors cause a small temperature steadiness that last for only a few increments of the A/F ratio.

2. A/F Ratio ~ 1 'spike'

Zirconium has a high affinity for nitrogen, as shown in the raw data for the chemical equilibrium calculations. This affinity causes the zirconium to bond with the nitrogen to form ZrN . Since the A/F ratio used throughout the calculations has been defined as the ratio of N to Zr, an A/F ratio of one would coincide with a "stoichiometric" combustion process between Zr and N. Note that it is not stoichiometric in the sense that the overall reaction taking place is stoichiometric, just that the reaction between Zr and N at this ratio is stoichiometric. The following equation greatly simplifies the reaction and shows the relationship between Zr and N:

3. A/F Ratio ~ 7.52 'spike'

As with the previous case, it can be shown that at an A/F ratio of 7.52, the Zr and O are reaching another "stoichiometric" condition. Although zirconium can bond with oxygen to form ZrO, ZrO₂ stoichiometry is reached at this A/F ratio. The reaction between Zr and O₂ is as follows:

The adiabatic flame temperature in a reaction is always reached slightly rich of stoichiometric conditions, thus explaining the shift of the peak to the right of each respective A/F ratio 'spike'.

For the pure steam case, the jump in temperature at an A/F ratio of two can be explained in the same way, but with a slightly different reaction:

The mole fractions of the products were calculated for the cases of 50% humidity and 100% pure steam (fuel at 2100 K, oxidizer at 800 K). The following figures show the mole fractions for several A/F ratios, neglecting concentrations below 0.01%. As seen in Figure 3.6 and Figure 3.7, most of the constituents are present in very small concentrations.

4. Experimental Procedure and Results

Attempts to experimentally observe the zirconium ignition and burning tests were made in the current year, Apr-2009, based on the design and experimental buildup described in sections 2.2 and 2.2 above. The zircaloy-4 tubing samples were donated by Westinghouse Research Center.^[22]

Due to difficulties associated with the propane burner that supposedly will superheat the steam to the desired minimum temperature of 800 K, the steam could only achieve to a lower temperature of approximately 617 K (650 F). Thus there was really little expectation to observe the zirconium ignition or burning. Nevertheless, before we could redesign a molybdenum disilicide (MoSi₂) based super-heater to achieve sufficient oxidizer temperature (discussed next), the tests represented an optimum opportunity to check out the system.

With the EMI power supply (40V/125 Amp) a zircaloy-4 tube temperature of 1145 K (1600 F) was obtained. Insulation was then put around the Zircaloy-4 tube within the test chamber to reduce the amount of heat lost and finally it was decided that the center thin-wall zircaloy section needed to be increased from 1- to 2-inch long. All these were pursued to maximize the zircaloy temperature at the center section of the sample. With the new zircaloy-4 sample in place, it was heated again

Figure 3.4. Graph of Adiabatic Flame Temperature with Various Concentrations of Water Vapor at 373 K, Fuel at 2100 K.

Figure 3.5. Graph of Adiabatic Flame Temperature with Various Concentrations of Water Vapor at 800 K, Fuel at 2100 K.

Figure 3.6. Graph of the Mole Fractions of Species in 50% Humidity Product.

Figure 3.7. Graph of the Mole Fractions of Species in Pure H₂O(g) Product.

and a temperature of only 1200 K (1700 F) was observed.

It was then decided that a welder (with AC current up to 240 Amp) would be used as the new power supply, again for the purpose of boosting the sample temperature. It could only be used for two minutes for every 10 minutes. With this welder, a desirable zircaloy-4 sample temperature of 1478 K was achieved. Due to the malfunction of the propane burner, heater tapes were incorporated to the steam line, and with this setup, a pressure of about 342.7 KPa was achieved at the upstream of the oxidant injector nozzle at a temperature of about 617 K (still lower than desirable). The injector opening is 0.762-mm (or 0.03-inch) diameter, and under the choked flow condition, would deliver approximately 1.34 pounds of steam per hour. A schematic block diagram for the experimental setup is illustrated in Figure 4.1 below.

Figure 4.1 Schematic of the experimental setup

A data acquisition system was also developed to achieve not only data logging over time but also real-time visual monitoring of the experiment in progress. All the four zircaloy-4 sample's thermocouple readings, oxidizer pressure and temperature are included on the screen display. A checklist describing the experimental procedure was generated to ensure proper operation of the system and can be viewed in Appendix I at the end of this document.

Experimental Results

The first run of the system was conducted on April 8th, 2009. The conditions of this run were as follows: steam pressure upstream of the choked injector at 342.7 KPa (35 psig), steam

temperature at 617 K (650 F), the hottest zircaloy-4 sample temperature at 1478 K (2200 F). The steam flow rate was calculated to be approximately 1.69×10^{-4} Kg/s (or 1.34 lbm/hr) as it was issued into the pulled vacuum chamber, directing at the hottest location of the zircaloy sample. This run resulted in a quench of the zircaloy-4 sample due to the insufficient steam temperature. Video as well as all pressures and temperatures data were recorded and saved in the data acquisition system. Photographs were taken of the quenched Zircaloy-4 sample. A photograph of the glowing zircaloy-4 sample before the oxidizer injection and the post-quenched, cracked zircaloy-4 sample are shown in Figures 4.2 and 4.3, respectively.

Figure 4.2 Photograph of glowing zircaloy-4 sample

Figure 4.3 Photograph of quenched and subsequently cracked zircaloy-4 sample

5. Summary

Despite the non-ignition (or quenching) condition observed due to the malfunction of the propane burner that resulted in our utilization of heater tapes to superheat the steam to a significantly lower temperature than desirable, all experimental setup and objectives have been achieved. A further literature survey of the recent European works on degraded core phenomenon^[23] has confirmed that the zircaloy oxidation is highly exothermic and commonly leads to a runaway “oxidation temperature excursion” above 1473 K (2191 F) in steam and at as low as 1173 K (1651 F) in air. Thus the logical next course of development is to not only demonstrate a zircaloy-air ignition and sustained burning (since air ignition required lower oxidizer temperature) using a MD-33 (molybdenum disilide) heater to superheat the air to about 1650 F, but also to demonstrate the propagation of the zirconium from one ignited “hot” rod to an adjacent “cooler” rod. The specialty heater has already been designed, built, and tested, as seen in Figures 5.1 through 5.3. The air/steam super-heater is first electrically insulated by ceramic pieces of boron nitride (BN). The sub-assembly is then encased by a 3/8-inch stainless steel tubing with pre-instrumented thermocouples to monitor the heater temperature. The heater tube is then encased by a larger (1/2-inch) tube to provide the annular air (or steam) flow passage. The whole heater assembly utilizes Swagelok fittings without any weld, and conveniently facilitates ports for air-in and air-out. It is a key enabling experimental component that could achieve the near-term air ignition and next-phase steam ignition. An AutoCad design drawing of the air/steam super heater is illustrated in Appendix J.

A reliable analytical tool has been developed to predict the zircaloy reaction with various oxidizing conditions, closely simulating the spent fuel pool hazards anticipated. An unique future experimental design and buildup would also include the investigation of the “propagation” of the zirconium fire, namely from one hot (and ignited) zircaloy sample to a neighboring zircaloy sample which could be originally colder and un-ignited. A schematic of this type of zirconium fire propagation experiment is illustrated in Figure 5.4. It would closely represent a thermal runaway hazard of a spent fuel pool.

Figure 5.1 Concentric packaging concept with annular air/steam flow passage

Figure 5.2 Cross-sectional view of the air/steam heater

Figure 5.3 Photograph of an assembled air/steam super-heater

Figure 5.4 Schematic of test setuo for the zirconium fire propagation with a colder sample positioned next to the hot sample

6. References

- [1] "Safety and Security of Commercial Spent Nuclear Fuel Storage: Public Report," Committee on the Safety of Commercial Spent Nuclear Fuel Storage, National Research Council, Board on Radioactive Waste Management, National Academy of Sciences, 2005.
- [2] Alvarez, Robert. "What about the spent fuel?" Bulletin of the Atomic Scientists. Jan.-Feb. 2002. <<http://www.nirs.org/radwaste/atreactorstorage/alvarezarticle2002.pdf>>.
- [3] Hughes, T. G., and T. F. Lin. Reactor Engineering: "Thermal Cooling Limits of Sabotaged Spent Fuel Pools" Project Narrative for the DOE NEER Project DE-FG07-07ID14769 by Applied Research Laboratory, The Pennsylvania State University.
- [4] A. S. Benjamin, D. J. McCloskey, D. A. Powers, and S. A. Dupree, "Spent Fuel Heatup Following Loss of Water During Storage", NUREG/CR-0649, May 1979.
- [5] D. A. Powers, "Technical Issues Associated with Air Ingression During Core Degradation", SAND2000-1935C, September 2000.
- [6] F. Nagase and T. Fuketa, "Behavior of Pre-hydrided Zircaloy-4 Cladding under Simulated LOCA Conditions", Journal of Nuclear Science and Technology, Vol. 42, No. 2, p. 209-218, February 2005.
- [7] T. J. Haste and K. Tramaier, "Degraded Core Quench: Summary of Progress 1996-1999", NEA/CSNI/R(99)23, February 2000.
- [8] C. Duriez, M. Steinbruck, D. Ohai, T. Meleg, J. Birchley, and T. Haste, "Separate-Effect Tests on Zirconium Cladding Degradation in Air Ingress Situations", SARNET FI6O-CT-2004-509065, June 2007.
- [9] B. Adroguer, "Core Loss During a Severe Accident (COLOSS)", FIKS-CT-1999-00002, February 2000.
- [10] T. Ikeda, K. Katsuragi, and N. Shirakawa, "Analysis of International Standard Problem No. 45, QUENCH06 Test at FZK by Detailed Severe Accidents Analysis Code, IMPACT/SAMPSON", Journal of Nuclear Science and Technology, Vol. 40, No. 4, p. 246-255, April 2003.
- [11] International Atomic Energy Agency (IAEA), "Computational Analysis of the Behaviour of Nuclear Fuel Under Steady State, Transient and Accident Conditions", IAEA-TECDOC-1578, December 2007.
- [12] "Fact Sheet on the Three Mile Island Accident." 20 Feb. 2007. United States Nuclear Regulatory Commission. <<http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/3mile-isle.html>>.
- [13] Petrie, L. M., P. B. Fox, and K. Lucius. Standard Composition Library. United States Department of Energy. Nuclear Regulatory Commission. 1998. <<http://iriexp.iri.tudelft.nl/~leege/SCALE44/stdcmp.pdf>>
- [14] Chase, Malcolm W. NIST JANAF Thermochemical Tables. New York: American Institute of Physics, 1998.
- [15] Feith, Allen D., "Thermal Conductivity and Electrical Resistivity of Zircaloy-4", General Electric Company, October 1966..
- [16] Incropera, Frank P., David P. DeWitt, and Theodore L. Bergman. Fundamentals of Heat and Mass Transfer. New York: John Wiley & Sons, Incorporated, 2006.

- [17] Moore, J. T., and R. B. Smith. "Alternative Energy Sources for Low-Cost Torpedo Exercisability." Thesis.
- [18] Turns, Stephen R. An Introduction to Combustion: Concepts and Applications with Software. New York: McGraw-Hill Science, Engineering & Mathematics, 1999.
- [19] El-Wakil, M. M. "Nuclear Energy Conversion", American Nuclear Society Manuscript, p. 173, 1982.
- [20] Sutton, George P., and Oscar Biblarz. Rocket Propulsion Elements. New York: Wiley-Interscience, 2000.
- [21] El-Wakil, M. M. "Nuclear Heat Transport", American Nuclear Society Manuscript, p. 357, 1978.
- [22] Comstock, R. J., private communication, 2006.
- [23] "In-Vessel Core Degradation Code Validation Matrix," Update 1996-1999, Report by OECD/NEA Group of Expert, October, 2000.

Appendix A

Gibb's Free Energy Calculations

To calculate the Gibb's free energy for the zirconium and water chemical reaction, reaction (d), the Gibb's free energy equation is used. Data is taken from Table 1.3 and substituted into equation (1).

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (1)$$

The change in the heat of formation (ΔH°) and entropy (ΔS°) are calculated as follows:

$$\Delta H^\circ = \Delta H_f^\circ \text{ products} - \Delta H_f^\circ \text{ reactants} \quad (6)$$

$$\Delta H_f^\circ = \left(2 \cdot \Delta H_f^\circ \text{H}_{2(g)} + 1 \cdot \Delta H_f^\circ \text{ZrO}_{2(s)} \right) - \left(2 \cdot \Delta H_f^\circ \text{H}_2\text{O}_{(l)} + 1 \cdot \Delta H_f^\circ \text{Zr}_{(s)} \right)$$

$$\Delta H^\circ = -525.803 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = \Delta S^\circ \text{ products} - \Delta S^\circ \text{ reactants} \quad (7)$$

$$\Delta S^\circ = \left(2 \cdot \Delta S^\circ \text{H}_{2(g)} + 1 \cdot \Delta S^\circ \text{ZrO}_{2(s)} \right) - \left(2 \cdot \Delta S^\circ \text{H}_2\text{O}_{(l)} + 1 \cdot \Delta S^\circ \text{Zr}_{(s)} \right)$$

$$\Delta S^\circ = 132.949 \frac{J}{mol \cdot K}$$

Calculating the Gibb's free energy at 298 K (assuming a constant temperature):

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

$$\Delta G^\circ_{H_2O(l)} = -565.422 \frac{kJ}{mol}$$

Repeating the same process as before, the Gibb's free energy for the zirconium reaction with steam, reaction (a), can be solved for:

$$\Delta H^\circ = -619.621 \frac{kJ}{mol}$$

$$\Delta S^\circ = 549.799 \frac{J}{mol \cdot K}$$

Calculating the Gibb's free energy at 298 K (assuming a constant temperature):

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

$$\Delta G^\circ_{H_2O(g)} = -783.461 \frac{kJ}{mol}$$

The following equation can be used to solve for the Gibb's free energy at any temperature, assuming the heat of formation is constant over a range of temperatures. The Gibb's free energy is found at a temperature of 2150 K, the melting point of zirconium.

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\} \quad (2)$$

$$\Delta G^\circ(2150 K)_{H_2O(g)} = -1,801.688 \frac{kJ}{mol}$$

Appendix B

Resistivity of Various Heater Rod Materials

Figure B.1 Resistivity of Various Heater Rod Materials.

Appendix C

Heat Flux Value Calculation

A spent fuel assembly typically generates on the order of tens of kilowatts of heat upon discharge from the reactor. According to El-Wakil^[19], the highest spent fuel pool heat flux is no more than 10% of the highest decay power following a reactor shutdown. This stems from the heat generation of radionuclides dropping drastically after the array is removed from the reactor.

A conservative estimate of the decay power of a spent fuel pool assembly would be 0.6% (6% x 10%) of the full power of an array (19 x 19 fuel rods). The average operational thermal output of each fuel rod is 5.7 kW/ft, making the full thermal power of a 12 foot long fuel rod 68.4 kW. Taking 0.6% of 68.4 kW as mentioned before, the decay power for each rod of the assembly would be 0.41 kW.^[19]

This power represents an average heat flux of about 3,750 W/m² per rod. At a peak power location, it could be as high as 5,625 W/m². The value of 50,000 W/m² comes from a factor of 10 used to represent the hazard limit of a LOCA.^[19]

Appendix D

Zircaloy Diameter Iteration Given 50,000 W/m² Heat Flux

Current (Amperes)	Outer Radius (meters)	Outer Diameter (inches)	Voltage Drop Across 1" Section (Volts)
60	0.004165	0.328	0.554
65	0.004192	0.330	0.515
70	0.004220	0.332	0.481
75	0.004250	0.335	0.452
80	0.004282	0.337	0.427
85	0.004314	0.340	0.405
90	0.004348	0.342	0.386
95	0.004383	0.345	0.368
100	0.004419	0.348	0.353
105	0.004456	0.351	0.339
110	0.004494	0.354	0.326
115	0.004533	0.357	0.315
120	0.004573	0.360	0.304

Table D.1 Iteration of Zircaloy Diameters and Current Based on a Given Heat Flux (50,000 W/m²).

Appendix D (Continued)

Heat Flux Values for Thinned and Un-thinned Zircaloy Sections

Current (Amperes)	Heat Flux for Thinned Section (W/m ²)
60	51372
65	51172
70	51015
75	50888
80	50784
85	50699
90	50628
95	50567
100	50515
105	50471
110	50433
115	50399
120	50369

Table D.2 Heat Flux Value for Thinned Zircaloy Section.

Current (Amperes)	Heat Flux for Regular Section (W/m ²)
60	12592
65	14779
70	17140
75	19676
80	22386
85	25272
90	28333
95	31568
100	34979
105	38564
110	42324
115	46259
120	50369

Table D.3 Heat Flux Value for Un-Thinned Zircaloy Section.

Appendix E

CAD Drawings of Ceramic Insulators

Figure E.1 CAD Drawing of Zircaloy Alumina Ceramic Insulator, Non-Slotted.

Figure E.2 CAD Drawing of Zircaloy Alumina Ceramic Insulator, Slotted.

Appendix F

Test Chamber Solid Model and CAD Drawing

Figure F.1 Cross-Section of Test Chamber Solid Model Showing Zircaloy Sample with Electrical Connections, Fittings, and Nozzle.

Figure F.2 Dimensioned CAD Drawing of Test Chamber (Units are in Inches).

Appendix G

Choked Flow Calculations, Upstream Pressure and Pressure Ratio

The following equation can be used to find the downstream, or throat pressure (p), needed to maintain choked flow through the nozzle:

$$p = p_o \left(\frac{2}{k+1} \right)^{\frac{k}{k-1}} \quad (8)^{[20]}$$

If the upstream pressure (p_o) is fixed at 202,650 Pa (2 atm) or higher, a maximum value of p for choked flow can be calculated with the following values (at 800 K) for both steam and air:

$$p_o = 202,650 \text{ Pa}$$

$$k_{\text{air}} = 1.354$$

$$k_{\text{steam}} = 1.269$$

$$p_{\text{air}} = 108,651.7 \text{ Pa}$$

$$p_{\text{steam}} = 111,739.8 \text{ Pa}$$

Thus, p_{air} and p_{steam} must be less than 108,651.7 Pa and 111,739.8 Pa, respectively.

For choked flow, the critical pressure ratio p/p_o generally ranges between 0.53 and 0.57. The flow is considered to be choked if the ratio is less than or equal to said critical pressure ratio. The p/p_o values for both air and steam are as follows:

$$\frac{p_{\text{air}}}{p_o} = 0.5362$$

$$\frac{p_{\text{steam}}}{p_o} = 0.5514$$

Mass Flow Rate Through Nozzle

The following equation can be used to find the mass flow rate through the nozzle, assuming a 0.02" nozzle diameter:

$$\dot{m} = \frac{A p_o}{R T_o} \sqrt{2 g_c J c_p T_o \left[\left(\frac{p}{p_o} \right)^{\frac{2}{k}} - \left(\frac{p}{p_o} \right)^{\frac{k+1}{k}} \right]} \quad (9)^{[21]}$$

The values below were used to calculate the mass flow rate for air:

$$\frac{kPa \cdot m^3}{\sqrt{kJ/kg}} = \sqrt{1000} \text{ kg/s}$$

Note: 'g' and 'J' are equal to 1 in SI units, and $\sqrt{kJ/kg}$.

$$A = \pi r^2 = \pi \cdot (0.000254 \text{ m})^2 = 2.0268 \times 10^{-7} \text{ m}^2$$

$$p_o = 202,650 \text{ Pa}$$

$$k_{air} = 1.354$$

$$R_{air} = 287.05 \text{ J/(kg} \cdot \text{K)}$$

$$T_o = 800 \text{ K}$$

$$\frac{p}{p_o} = 0.5362$$

$$c_p = 1.0987 \text{ kJ/(kg} \cdot \text{K)}$$

$$\dot{m} = 5.803 \times 10^{-5} \text{ kg/s} = 0.4606 \text{ lbm/hr}$$

The values below were used to calculate the mass flow rate for superheated steam:

$$A = \pi r^2 = \pi \cdot (0.000254 \text{ m})^2 = 2.0268 \times 10^{-7} \text{ m}^2$$

$$p_o = 202,650 \text{ Pa}$$

$$k_{steam} = 1.269$$

$$R_{steam} = 461.5 \text{ J/(kg} \cdot \text{K)}$$

$$T_o = 800 \text{ K}$$

$$\frac{p}{p_o} = 0.5514$$

$$c_p = 2.421 \text{ kJ/(kg} \cdot \text{K)}$$

$$\dot{m} = 4.716 \times 10^{-5} \text{ kg/s} = 0.3743 \text{ lbm/hr}$$

Appendix H

Sample Data Listing from SOLGASMIX Program (Formatted Into Excel)

Table H.1 Sample Data Listing of Pure Air (0% Humidity) of SOLGASMIX Results
for Nitrogen, Oxygen, and Zirconium.

2100K, 800K			0% humidity																					
			% nitrogen				% oxygen								% zirconium									
F/A Ratio	Tad (800K)	Tad (373K)		N2(g)	ZrN(s)	ZrO(g)	ZrO2(s)	ZrO2(g)	SnO(g)	SnO2(g)	O(g)	NO(g)	O2(g)	Fe3O4(s)	CrO2(g)	HfO2(g)	Zr(s)	ZrN(s)	ZrO2(s)	ZrO(g)	Zr(g)	ZrO2(g)		
0.1	2699.22	2682.03	17.19		0	100		0	100		0	0	0	0	0	0	0	88.84	10	1.16	0	0	0	
0.2	3339.06	3306.25	32.81		0	100		0	99.97		0	0	0	0	0	0	0	77.67	20	2.33	0	0	0	
0.3	3757.03	3757.03		0	3.54	96.46		25	72.28		2.27	0.3	0	0	0	0	0.11	66.65	28.94	2.52	1.75	0	0.08	
0.4	3762.5	3762.5		0	10.82	89.17		76.33	15.44		6.95	1.03	0	0.12	0	0	0	55.91	35.67	0.72	7.11	0.27	0.32	
0.5	3792.97	3774.22	18.75		15.47	84.51		91.05	0		7.27	1.43	0	0.15	0	0	0.08	46.24	42.26	0	10.59	0.49	0.42	
0.6	3851.56	3837.5	14.06		22.83	77.15		92.53	0		5.53	1.67	0	0.17	0	0	0	39.54	46.29	0	12.92	0.87	0.39	
0.7	3883.59	3872.66	10.93		28.76	71.21		93.17	0		4.67	1.89	0	0.18	0	0	0	33.32	49.85	0	15.18	1.28	0.38	
0.8	3901.56	3893.75	7.81		33.14	66.82		93.41	0		4.2	2.12	0	0.19	0	0	0	27.09	53.46	0	17.39	1.68	0.39	
0.9	3914.84	3907.03	7.81		37.13	62.83		93.51	0		3.86	2.36	0	0.2	0	0	0	21.36	56.55	0	19.59	2.1	0.4	
1	3921.88	3915.63	6.25		39.87	60.08		93.4	0		3.66	2.66	0	0.2	0	0	0	15.28	60.08	0	21.74	2.48	0.43	
1.1	3927.34	3921.09	6.25		42.5	57.45		93.22	0		3.5	3.01	0	0.2	0	0	0	9.62	63.2	0	23.86	2.86	0.45	
1.2	3931.25	3923.44	7.81		45.01	54.93		92.97	0		3.36	3.39	0	0.2	0	0	0	4.4	65.92	0	25.96	3.25	0.47	
1.3	3916.41	3880.47	35.94		47.61	52.33		92.47	0		3.54	3.72	0	0.21	0	0	0	0.21	68.03	0	27.97	3.24	0.54	
1.4	3857.81	3809.38	48.43		52.06	47.89		91.49	0		4.75	3.48	0	0.21	0	0	0	0	67.05	0	29.81	2.33	0.77	
1.5	3789.84	3732.03	57.81		56.03	43.93		89.85	0		6.61	3.25	0	0.22	0	0	0	0	65.9	0	31.37	1.56	1.15	
1.6	3720.31	3698.44	21.87		59.53	40.44		87.43	0		9.22	3.05	0	0.22	0	0	0	0	64.7	0	32.56	1.01	1.72	
1.7	3692.97	3688.28	4.69		62.65	37.32		83.51	3.38		9.95	2.87	0	0.21	0	0	0	0	63.44	0.67	33.04	0.87	1.97	
1.8	3684.38	3679.69	4.69		65.37	34.6		79.02	8.47		9.52	2.71	0	0.21	0	0	0	0	62.27	1.77	33.1	0.85	1.99	
1.9	3677.34	3672.66	4.68		67.94	32.03		76.03	11.88		9.24	2.56	0	0.2	0	0	0	0	60.86	2.63	33.62	0.85	2.04	
2	3670.31	3665.63	4.68		70.2	29.77		72.95	15.39		8.94	2.44	0	0.2	0	0	0	0	59.53	3.58	33.96	0.84	2.08	
3	3617.97	3608.59	9.38		84.57	15.4		53.67	37.58		6.91	1.62	0	0.16	0	0	0	0	46.19	13.12	37.47	0.81	2.41	
4	3584.38	3571.88	12.5		91.75	8.22		43.85	48.96		5.78	1.22	0	0.14	0	0	0	0	33.89	22.79	40.81	0.81	2.69	
5	3560.16	3546.09	14.07		96.03	3.94		37.74	56.06		5.05	0.97	0	0.12	0	0	0	0	19.7	32.61	43.92	0.82	2.94	
6	3542.19	3526.56	15.63		98.9	1.08		33.73	60.74		4.56	0.81	0	0.11	0	0	0	0	6.46	42.4	47.1	0.85	3.18	
7	3697.66	3613.28	84.38		99.91	0		24.29	62.88		10.97	0.7	0	0.89	0.25	0	0	0	0	0	51.22	39.57	0.28	8.93
8	3790.63	3753.13	37.5		99.71	0.25		13.41	62.89		17.64	0.61	0	0.16	1.05	0	0	0	0	0	58.54	24.97	0	16.42
9	3792.97	3758.59	34.38		99.48	0.48		6.94	63.89		17.72	0.54	0	8.25	2.06	0.59	0	0	0	0	66.9	18.55	0	14.53
10	3753.13	3701.56	51.57		99.23	0.74		3.11	65.36		14.35	0.49	0	12	3.17	1.49	0	0	0	0	76.05	7.25	0	16.7
15	3232.03	3057.03	175		98.21	1.79		0	56.76		0.53	0.32	0	12.34	7.67	22.29	0	0	0	0	99.07	0	0	0.92
20	2935.94	2723.44	212.5		98.24	1.76		0	42.93		0	0.24	0	6.56	7.57	42.56	0	0	0	0	99.91	0	0	0
25	2630.47	2369.53	260.94		98.66	1.33		0	34.38		0	0.19	0	2.26	5.73	57.33	0	0	0	0	100	0	0	0
30	2389.06	2106.25	282.81		99.05	0.95		0	28.65		0	0.13	0.06	0.75	4.07	66.24	0	0	0	0	100	0	0	0
35	2202.34	1897.66	304.68		99.33	0.67		0	24.55		0	0.04	0.19	0.26	2.89	71.96	0	0	0	0	100	0	0	0
40	2053.13	1734.38	318.75		99.52	0.48		0	21.49		0	0	0.23	0.1	2.07	76.01	0.05	0	0	0	100	0	0	0
45	1928.91	1603.91	325		99.65	0.35		0	19.1		0	0	0.22	0	1.5	79.06	0.04	0	0	0	100	0	0	0
50	1828.13	1495.31	332.82		99.74	0.26		0	17.19		0	0	0.19	0	1.12	81.41	0	0	0	0	100	0	0	0

Appendix I

Checklist of System Procedure

Start up

- 1) Connect plugs to wall (steam generator (sg), steam generator power strip, heater tape, vacuum, and arc welder), connect plugs to steam generator power strip (pressure transducer, metering valve, and steam generator pump), connect BNC, CS3, and CS10 cables, connect thermocouples ☐
- 2) Setup video camera ☐
- 3) Turn on computer ☐
- 4) Open general data acquisition program (save data) ☐
- 5) Verify temperature/pressure (sg switch on) data is reading properly ☐
- 6) Open de-ionized water line ☐
- 7) Turn on steam generator pump (sg switch on) ☐
- 8) Turn on steam generator ☐
- 9) Set steam generator to 300F (40 minutes to pressurize) ☐
- 10) Connect arc welder to test chamber electrical ports ☐
- 11) Open air line for welded bellows sealed valves ☐
- 12) Open welded bellows sealed valve to bleed-off line ☐
- 13) Set voltage (~0.1V) to operate metering valve (sg switch on) ☐
- 14) Observe temperature/pressure (~650F, ~30-35psi) of oxidizer discharged to ambient (modifications as necessary) ☐
- 15) Purge chamber with argon and pull vacuum ☐
- 16) Close valve at vacuum connection on test chamber ☐
- 17) Connect vacuum to sampling chambers ☐
- 18) Turn on arc welder ☐
- 19) Heat zircaloy sample to above 2000F ☐
- 20) Turn off arc welder ☐
- 21) Pull vacuum in sampling chambers ☐
- 22) Simultaneously close welded bellows sealed valve to bleed-off line and open welded bellows sealed valve to test chamber – oxidizer injection ☐
- 23) Open solenoid to collect gas in sampling chambers ☐

Shut down

- 1) Close solenoid to collect gas in sampling chambers ☐
- 2) Close welded bellows sealed valve to test chamber ☐
- 3) Set voltage to 0V for metering valve ☐
- 4) Close deionized water line ☐
- 5) Turn off steam generator ☐

- 6) Disconnect arc welder from test chamber electrical ports ☐
- 7) Turn off vacuum ☐
- 8) Close air line for welded bellows sealed valves ☐
- 9) Verify that all data was saved ☐
- 10) Blow down steam generator ☐
- 11) Disconnect plugs to wall (steam generator (sg), steam generator power strip, heater tape, vacuum, and arc welder), disconnect BNC, CS3, and CS10 cables, disconnect thermocouples ☐

Plans for Next Year:

The scope of work in the next year will emphasize on air ignition experiments as described in the Summary section. Although some prior work has already been done to study the combustion of zirconium, these experiments are crucial in order to provide a foundation for future work regarding the propagation of zirconium fire from one rod (with higher decay power) to another (with lower decay power). This 'forest fire' effect could have devastating consequences if the propagation lasted for a long enough period of time.

To that future "zirconium fire propagation" effect, experiments will be conducted using a modified version of the current test chamber. This test chamber will be fitted with two zircaloy samples instead of one, as shown in Figure 5.4. Separate electrical connections will exist for each sample to allow for the differences in heat flux and temperature between claddings.

Patents: Plan to file patent for the molybdenum disilicide air/steam super-heater concept upon further verification of its performance.

Milestone Status Table: The milestone chart below reflects the status of the accomplishment compared against the proposed. Some specific tasks, although not explicitly stated in the original proposal, are also listed since they are in the critical path for the completion of the project as planned.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Literature review, model development, VLNR test preparation	9/30/09		Completed
2	Thermochemical analysis, zircaloy burning test preparation	4/30/08	9/30/08	Completed
3	Year-1 report	7/31/08	8/20/08	Submitted 8/15/08
4	Single sample zircaloy ignition and burning tests	1/31/09		Completed
5	Continuing thermochemical analysis and data analysis	2/28/09		Completed
6	Experimental design of zircaloy fire propagation	9/30/09		Completed
7	Design and tests of air/steam super-heater to facilitate ignition	9/30/09		Completed
8	Year-2 report	7/31/09	9/8/09	Submitted 9/8/09
9	Conducting tests for zircaloy fire propagation	3/31/10		In progress
10	Conducting tests for VLNR coolings	3/31/10		In progress
11	Data analysis for 9 and 10 above, and model development	4/30/10		In progress
12	Year-3 final report	7/31/10	9/10/10	Submitted 9/10/10

Budget Data (as of date):

			Approved Spending Plan			Actual Spent to Date (8/31/09)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	5/1/07	4/30/08	\$100,000	0	\$100,000	\$79,765	0	\$79,765
Year 2	5/1/08	4/30/09	\$100,000	0	\$100,000	\$116,813	0	\$116,813
Year 3	5/1/09	7/31/10	\$100,000	0	\$100,000	\$103,422	0	\$103,422
Year 4								
Year 5								
Totals			\$300,000		\$300,000	\$300,000		\$300,000

Spending Plan for the Next Year: N/A