Determination of Pure Neutron Radiolysis Yields for use in
Chemical Modeling of Supercritical Water

by

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A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy
(Nuclear Engineering and Engineering Physics)

at the

UNIVERSITY OF WISCONSIN – MADISON

2007
Abstract

This work has determined pure neutron radical yields at elevated temperature and pressure up to supercritical conditions using a reactor core radiation. The data will be necessary to provide realistic conditions for material corrosion experiments for the supercritical water reactor (SCWR) through water chemistry modeling. The work has been performed at the University of Wisconsin Nuclear Reactor using an apparatus designed to transport supercritical water near the reactor core. Low LET yield data used in the experiment was provided by a similar project at the Notre Dame Radiation Lab.

Radicals formed by radiolysis were measured through chemical scavenging reactions. The aqueous electron was measured by two methods, a reaction with N₂O to produce molecular nitrogen and a reaction with SF₆ to produce fluoride ions. The hydrogen radical was measured through a reaction with ethanol-D₆ (CD₃CD₂OD) to form HD. Molecular hydrogen was measured directly. Gaseous products were measured with a mass spectrometer and ions were measured with an ion selective electrode. Radiation energy deposition was calibrated for neutron and gamma radiation separately with a neutron activation analysis and a radiolysis experiment. Pure neutron yields were calculated by subtracting gamma contribution using the calibrated gamma energy deposition and yield results from work at the Notre Dame Radiation Laboratory.

Pure neutron yields have been experimentally determined for aqueous electrons from 25° to 400° C at 248 bar and for the hydrogen radical from 25° C to 350° C at 248 bar. Isothermal data has been acquired for the aqueous electron at 380° C and 400° C as a function of density. Molecular hydrogen yields were measured as a function of
temperature and pressure, although there was evidence that chemical reactions with the walls of the water tubing were creating molecular hydrogen in addition to that formed through radiolysis. Critical hydrogen concentration behavior was investigated but a final result was not determined because a measurable oxygen yield was not seen at the outlet of the radiolysis loop.
Acknowledgements

First, I would like to extend my sincerest gratitude to my advisor, Paul Wilson for his support of this work. His mentorship has helped to development my research, professional, and writing skills and has kept my research on a well defined course. I would also like to thank Dave Bartels, who has been like a second advisor to me. His contributions to the design and methodology of this experiment have been the backbone of the work presented here.

I would like to thank everyone involved directly in this project. Luke Olson performed a large part of the initial thermo hydraulic design and testing of the apparatus. Mark Anderson and Paul Brooks have contributed greatly to the experimental design and equipment support. Robert Agasie, Michelle Blanchard, Steve Matusiewic, and the rest of the reactor staff have supported the work through reactor operation, resource sharing, and in handling radioactive materials. Dan Ludwig, Joe Prazak and Tim Setter have helped with data acquisition for the experiment. Also, the people associated with Argonne National Laboratory and Notre Dame: Steve Mezyk helped in the initial start-up of the project, Irek and Dorota Janik, have taken most of the low-LET data, and Simon Pimblott helped perform the MC/IRT analysis of the neutron room temperature G-value through computer simulation.

My thanks to all of the Engineering Physics staff including Professors Mike Corradini, Todd Allen, and Jake Blanchard, who have always been around for academic guidance over the past 5 years. Also, Pat Arnold, Rose Birzer, Dianne Francis, Joan Welc-Lepain and Mark Swandby have been essential in my scholastic and financial
guidance in graduate school. From the chemistry department, I would like to thank Professor Fleming Crim for joining my thesis committee.

This project was supported by the University of Wisconsin Nuclear Reactor (UWNR), the Notre Dame Radiation Laboratory, US-DOE NERI grant 02-060, and DOE Contract 00037404. The Notre Dame Radiation Laboratory is supported by the Office of Basic Energy Sciences at the United States Department of Energy. I want to thank the National Academy for Nuclear Training for the fellowship awarded to me during my Master’s work and Sandia National Laboratory for a fellowship following during my Ph.D. research time.

Finally, I would like to extend my deepest gratitude to my family and friends. To my wife, Nichole, I would like to offer my appreciation of the love and support she has given me through my graduate career. She has been there to encourage me and keep me going through the times when my research was not going as planned. Also, my gratitude goes to my parents Mark and Jeanette Edwards, who have given me never-ending support in my choice of career path and financial support throughout college. I would like to thank my grandparents, Don and Elizabeth Wright for supporting the cost of text books throughout college. In addition to this, my friends from UW-Madison including my brother Corey Edwards have kept my work fun and advised me with their own research experience. I would like to thank my high school physics teacher, Mr. Chapin, for preparing me for college science and always keeping up with current technology so that he can bring college level teaching and equipment into the classroom.
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1 Introduction

Water radiolysis complicates the design of nuclear reactors by creating reactive radicals that change the corrosion potential of water. The choice of correct materials for new reactor concepts depends on how extensively water is affected by radiolysis at specific conditions of temperature and pressure. The goal of the work presented in this document was to measure radiolysis yields at high pressure (24.8 bar) and temperature (up to 400°C) suitable for the modeling of water used in supercritical water reactors.

1.1 Nuclear Reactors

Nuclear power accounts for approximately 20% of current U.S. electricity production. Light water reactors (LWRs) have had an excellent safety record in the U.S. and have been constantly improving operations and efficiency. In the last few years, many reactors have applied for power up-rates and 20 year license extensions, keeping nuclear electricity production at 20% without building a new plant. Currently, nuclear power is the only base load power that is emission free in operation including CO₂, NOₓ and SOₓ emissions. Growing demand for electricity, increasing concern over air quality, anxiety over greenhouse gas accumulation, and a domestic interest in a diverse energy supply has begun to re-solidify its future in the United States. Already, some utilities including Dominion, Entergy and Excelon are pursuing an early site permit in order to eventually build and order new plants [19]. Recent renewed interest in nuclear power has created motivation to research and develop new power plant designs. This interest has led to the Generation-IV program, an international consortium of scientists working to design power plants that are more economic, safe, proliferation resistant, and sustainable.
Six reactor designs were selected for Generation-IV development including the gas cooled fast reactor, the lead cooled fast reactor, the molten salt reactor, the sodium cooled fast reactor, the supercritical water reactor, and the very high temperature reactor.

![Diagram of the Supercritical Water Reactor (SCWR)](image)

**Figure 1.1:** A schematic of the SCWR [10].

One of the concepts of focus in the United States is the supercritical water reactor (SCWR). Compared to current LWRs, the SCWR is expected to have improved economics due to the simplicity of the plant (fewer coolant recirculation pumps, pressurizers and steam generators are needed and there is no need for steam separators or dryers) and improved thermodynamic efficiency (45% versus 35% for LWRs) [10]. The safety of the plant is expected to be better than the currently deployed generation (Generation-II) through the use of modern technologies and approaches such as passive
heat removal, which will eliminate the need for active safety systems for the first 24 hours following a severe accident [10].

Unlike other Generation-IV reactor models, the SCWR design leverages two current technologies, LWRs and the supercritical Rankine cycle used in some coal-fired power plants. Conceptually, the design is simply a supercritical coal power plant with a nuclear reactor used for the heat source. The design parameters are far more complicated due to issues such as neutron moderation with a low density supercritical fluid and material choice for high temperature and pressure that can withstand the corrosive conditions caused by water radiolysis and radiation damage.

At supercritical conditions, material selection is limited due to strength constraints of some materials such as zircaloy, which is currently used for fuel cladding. Nickel based alloys are problematic due to neutron irradiation induced helium embrittlement [66]. Stainless steels show promise, but iron also creates helium pores at high temperature and there is not enough data currently available to conclusively select an ideal alloy [89]. Studies at the University of Wisconsin have studied various candidate materials for supercritical water [2,76], studied the dependence of time, temperature and dissolved oxygen content in supercritical water corrosion and long term corrosion [87,89,90], and reported on specific candidate alloy results [15]. Before long-term studies can be run, neutron and gamma radiolysis yields must be known. When the data sets are complete, corrosion potential can be calculated through modeling, and accurate long term corrosion tests can be performed with different conditions. These tests will be essential to material choice for SCWRs.
1.2 Water Radiolysis

Radiolysis is the dissociation of water molecules as a result of radiation by neutrons, photons, and electrons and can be represented conceptually by

\[ H_2O \xrightarrow{\text{radiation}} e_{aq}, H, H_2, OH, H_2O_2, HO_2 (or O_2^-) \]

Eq. 1.1

Initially, reactive radicals are formed (H, OH, e\textsubscript{aq}), which can recombine to make either reducing or oxidizing species, react with unbroken water molecules, or react with the surroundings such as dissolved impurities or pipe walls if an event happens near a border. The effect on corrosion potential of the water can make material selection difficult for the transport or containment of water that is in a radiation flux.

The radiation-chemistry of water is a function of, among other factors, the linear energy transfer (LET) of the radiation. Since neutrons have a high LET, they will affect water differently than low LET radiation such as gammas (photon radiation). According to the track structure outlined in Spinks & Woods [75], radiation transfer of energy to electrons can be divided into four general groups: a transfer of 6-100 eV produces spurs, 100-500 eV produces blobs, 500-5000 eV produces short tracks, and >5000 eV produces branch tracks. Spurs are areas of ionization created when low energy electrons produced by gamma-electron interaction do not travel far from the secondary electrons that they produce. Blobs are groups of overlapped spurs; both spurs and blobs can be considered approximately spherical collections of both ground state and excited molecules and ions. Short tracks are comprised of overlapping clusters of events and are column shaped volumes containing a high proportion of ionized and excited molecules along the fast electron track. Branch tracks are a collection of all three types created by the highest energy electrons. Low LET radiation will produce low concentrations of radicals that
will most likely interact with the bulk water surroundings. High LET radiation will produce overlapping tracks that contain a higher concentration of radicals making second order inter-radical reactions favored [75]. Neutrons create high energy protons in collisions with hydrogen nuclei that produce dense tracks of electrons. Since photons produce lower energy electrons through Compton scattering, accurate extrapolation of neutron radiolysis data from gamma radiolysis is impossible. Experimental research into neutron radiolysis thus requires either a proton radiolysis experiment with knowledge of neutron-hydrogen interactions or actual neutron radiation experiments. Neutron radiation experiments are more difficult to perform than photon/electron and even proton studies due to radiation levels, activation of materials, and the difficulty of finding an appropriate neutron source. The use of actual neutrons is considered more accurate that proton radiolysis because it removes the necessity of neutron-proton collision simulation and proton radiolysis uses discreet energies of protons while neutron radiolysis, at least in this study, uses a full reactor spectrum of neutron radiation.

The chemical reaction most essential to reactor coolant chemistry is the reaction of the hydroxyl radical with molecular hydrogen to produce hydrogen atoms:

\[ H_2 + OH \rightarrow H + H_2O \]  

Eq. 1.2

This is a key reaction because it is the only reaction sufficiently fast to convert the oxidizing radical OH into a reducing radical H. Adding enough hydrogen to the water will consume OH radicals (Eq. 1.2) and reduce oxygen molecules (Eq. 1.3-1.5), essentially decreasing oxygen production to zero in a chemically homogenous medium (from low LET radiation). The concentration of hydrogen necessary to fully suppress the oxygen and hydrogen peroxide yield in the water is known as the critical hydrogen
concentration (CHC). A high ratio of high LET radiation will shift the balance of species in the water to molecular yields of H₂ and H₂O₂, reducing the amount of radicals needed to reconvert hydrogen peroxide and oxygen through Eq. 1.2 [22,58]. Interference by water impurities also becomes a greater factor as [OH]/[H₂O₂] decreases [58]. Increasing the relative dose of gamma to neutron radiation in a reactor core will thus lower the concentration of hydrogen necessary for CHC.

Other reactions of importance in reactor coolant include the following:

**Oxygen reducing reactions:**

\[ O_2 + e_{aq}^{-} \rightarrow O_2^- \]  
\[ O_2 + H \rightarrow HO_2 \]  
\[ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \]

**Hydrogen peroxide reducing reactions:**

\[ H + H_2O_2 \rightarrow OH + H_2O \]  
\[ H_2 + H_2O_2 \rightarrow 2H_2O \]

(along with Eq. 1.2)

**Oxygen producing reactions:**

\[ OH + O_2^- \rightarrow OH^- + O_2 \]  
\[ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \]  
\[ HO_2 + O_2^- \rightarrow HO_2^- + O_2 \]  
\[ H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \]

Where equation 1.8 is dominant at the core and thermal breakdown of hydrogen peroxide (1.11) is dominant outside of the core.

Other reactions of interest:
\( OH + OH \rightarrow H_2O_2 \)  
\[ \text{Eq. 1.12} \]

\( e_{aq}^- + e_{aq}^- (+2H_2O) \rightarrow H_2 + 2OH^- \)  
\[ \text{Eq. 1.13} \]

\( H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \)  
\[ \text{Eq. 1.14} \]

\( e_{aq}^- + OH \rightarrow OH^- \)  
\[ \text{Eq. 1.15} \]

\( e_{aq}^- + H_2O_2 \rightarrow OH + OH^- \)  
\[ \text{Eq. 1.16} \]

\( OH + H_2O_2 \rightarrow H_2O + HO_2 \)  
\[ \text{Eq. 1.17} \]

and at alkaline pH:

\( H + OH^- \rightarrow e_{aq}^- (+H_2O) \)  
\[ \text{Eq. 1.18} \]

The previous reactions work together to produce a complex system of water chemistry in a nuclear reactor. Chemical data is important because computer modeling, which is used to predict radiolysis and water chemistry in reactor piping, requires the following five factors:

1. Flow rates through the system
2. Temperature profiles within the system
3. Energy deposition patterns of fast neutrons and gamma radiation
4. Reaction rates for the species formed and any other chemicals in the system, and
5. Chemical yields of species from radiolysis, reported as a “g-value” or “G-value” (see appendix section 11.4, page 169) [29].

The first three factors are specific to the physical design of a reactor, and can be generated using core analysis simulations. The rate constants must be determined experimentally or extrapolated from known conditions to operational conditions. A G-value is the yield of species per unit energy and is reported in units of molecules/100eV.
or the SI unit of $10^{-7}$ moles/J. The yields also need to be determined through physical experimentation.
2 Previous Work on Radiolysis

Water radiolysis is an immense topic comprising many areas of study. This section is a brief summary of the history of water radiolysis and selected experiments and publications that relate to the work performed in this experiment. A collection of neutron G-values from various types of experiments is summarized in Table 2.1.

2.1 History of Radiolysis

In the early 1900s, the focus was on observations made with a radioactive source in or near water shortly after the discovery radium. In 1909, analyses of gases created in a sealed volume of water and a radium chloride source led Kernbaum to the assumption that water decomposition goes as $2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2$ [46,47]. Subsequent early experiments began to outline theories of the formation of oxidizing and reducing free radicals [22].

The advent of X-ray machines along with the interest in nuclear power research during and after World War II inspired a radical increase in radiation chemistry studies. As power producing plant ideas were proposed and studied, it was evident that water would be an essential piece of the power production puzzle. In this period, reactions involving free radicals reactions with water began to be investigated [22].

Subsequent efforts in research were aimed at finding formation rates of free radicals and reaction rates of the radicals at room temperature. Prior to 1980, LWR water chemistry simulations were based largely upon the extrapolation of chemistry data to high temperatures [11,13,29,38]. Between 1980 and 1994, sufficient data had been obtained to extrapolate complete data sets for modeling of LWRs [29]. Since then,
chemical data has been experimentally determined and simulated all the way up to (and in a few cases, beyond) PWR conditions [11,29,43,56,82,84,88].

Reaction rates for most reactions can be accessed via the NDRL-NIST Solution Kinetics Database along with Arrhenius factor frequencies and activation energies at sub-critical conditions. Modeling programs can take the data and predict chemistry in a radiation environment with sufficient accuracy for predicting material environments for conditions where the data applies. In the past, it has been found that these rates can be extrapolated to higher temperatures such as 300°C [29]. At supercritical temperatures however, it has been shown that radical recombination rates will not follow these lower temperature models and will instead have discontinuities near the critical point, since many properties change dramatically near the critical point such as density, dielectric constant and the self-ionization rate (Kw). For more information on the discontinuities of reaction rates, see section 2.5.

Elliot outlines results of previous research of G-values experimentally determined as a function of temperature from gamma radiation [28,29,45] as well as results as a function of LET of the radiation [3,12,29,49,50]. The G-values show a linear dependence on temperature from 25°C to 300°C for gamma radiolysis and a non-linear dependence on LET. In addition, the report shows linear dependence on temperature from 20°C to 190°C for G-values caused by different radiation sources including 23 MeV H⁺, 157 MeV Li³⁺, and 495 MeV C⁶⁺ [29].

A large portion of radiolysis yield and recombination rate experimentation done in the past has been for PWR or BWR conditions, that is, sub-critical conditions. Typically, these studies are performed at temperatures between 20°C and 300°C. The
four main types of radiation used are heavy ions, electrons, photons (both UV and photon), and reactor radiation. For high LET radiolysis, both protons (which are used to simulate neutron interactions) and actual neutrons are used. The advantage of protons is that there is little to no gamma interference, whereas neutrons are a better estimate of neutron radiolysis, although core gamma contribution (or prompt neutron gamma contribution if a non-fission source such as a fusion or spallation source is used) must be calculated and subtracted.

2.2 Ion Radiolysis

Ion radiolysis is used to obtain yields of primary and molecular species as a result of charged particles interaction, which generally have linear energy transfers (LET) orders of magnitude higher than electron and gamma radiation. Different ions used can include hydrogen, helium, carbon, oxygen, and other ions. Neutrons deposit energy from primary knock-on atoms (PKAs) or neutron born ions. PKA distributions (usually O$^+$ and H$^+$) can be computed via computer simulation and used in tandem with ion radiolysis experimental results to simulate radiolytic neutron yields. Generally, ion radiolysis is performed with pulse radiolysis, in which the dose is delivered in a relatively short period of time. Because of the dependence of radiolysis on pulse time, pulse radiolysis data may have to be manipulated to be compared to a constant radiation field (see Figure 2.1), but this will not be the case in this experiment.

As the LET of radiation increases in water, the chemistry is substantially different due to the track structure outlined in the introduction (section 1.2) of this paper. The work of Baldacchino et al. has studied hydrated electron yields with time resolved pulse radiolysis with $^{12}$C$^{6+}$ ions with LET of 30 keV/µm [4]. This study concludes that the
radiolytic yields of the hydrated electron decrease as the LET increases, and found a G-value of 0.26 molecule/100eV for 5µs pulses. A later study [5] further defined the hydrated electron results as a function of irradiation time and found G-values increase with lowering pulse time, as seen in Figure 2.1. The nanosecond time scale yielded G-values much higher than recent experiments with values as high as 4.3 molecules/100 eV. This data is important in the calibration and benchmarking of the Monte-Carlo codes used for simulation of ion radiolysis.

![Figure 2.1: A comparison for Monte Carlo simulation (-) of 10 averaged single tracks of $^{12}\text{C}^{6+}$ 1.1 GeV with experimental results as data points (●, ■, ▼, ◆). Note that the x-axis is the pulse time of the radiation [5].](image)

LaVerne et al. also did a study using heavy ion radiolysis in 2005 [51]. This study compared Monte Carlo track simulations to experimental data to determine the
effect of track structure on the initial yields of hydrated electrons. This experiment used glycylglycine as an aqueous electron scavenger that creates an ammonium cation detected with an ion chromatograph. The Monte Carlo track simulations matched the data well.

A summary of ion radiolysis and simulated G-values for neutrons is presented in the work of Elliot [29]. The study uses G-values for recoil protons from Gordon et al. [31] and 3 serial average collision energy transfer to protons (1.27, 0.485, 0.172 MeV transfers) from the average fast fission neutron (2.0 MeV). Lower energy protons are ignored since their contribution to radiolysis is not a large contribution according to Gordon et al. [31]. This data was used to calculate $G(e_{aq}^-, H, H_2, OH, H_2O_2, \text{and } HO_2)$ and a material balance is performed correcting the value of $g(H_2O_2)$, and the results of the study will be used to compare experimentally determined values from this experiment (Table 2.1). Elliot also discusses results for gamma radiolysis, which are discussed in section 2.4.

### 2.3 Mixed Field Radiolysis

The work that is most relevant to this study is reactor radiolysis research. In experimental studies, the mixed field chemical yields must be separated into gamma and neutron yields. Ibe et al. [35] studied mixed field radiolysis in BWR systems and used primary G-values from simulations by Burns and Moore [11], to examine hydrogen and oxygen formation. The Burns and Moore paper is one of the earliest calculations of neutron G-value at high temperature. It used the results with extrapolated rate constants of elementary equations up to $305^\circ C$ in order to simulate water chemistry for zircaloy corrosion studies. The experiment by Katsumura et al. [43] used Fricke and ceric
dosimeters at the YAYOI fast reactor in Japan to detect the quantity of \((e_{aq}^- + H)\), OH, H₂, H₂O₂, HO₂, and −H₂O. The G-values are calculated using a combination of the G-values of Fe³⁺ in both aerated and deaerated Fricke dosimeters and Ce³⁺ in ceric dosimeters, and neutron and gamma contribution was separated using combinations of dosimetry [43].

The work of Sunaryo et al. [78,79] has also utilized the YAYOI fast reactor in Japan. Products were measured by gas chromatography with argon carrier (H₂), Ghormley’s method (H₂O₂) [1,33], and the Nash method \((e_{aq}^-, H, OH)\) [65]. Two studies were performed, one at room temperature, and one up to 250°C. In the case of fast neutron experiments, the gamma dose is typically very small in comparison to the neutron dose, and can be either neglected or subtracted with little concern for error.

Most additional work such as the reports of Elliot [29] and McCracken et al. [58] report G-values calculated via simulations based upon ion radiolysis, although many also include critical hydrogen concentration results measured, such as the work at the Studsvik reactor [16,84], for which a neutron to gamma ratio was used to separate dose calculated with Monte-Carlo methods. In addition to this, experimental studies have used fast reactor spectrums, which have a different LET for neutrons. Results for these works can be seen in Table 2.1.
Table 2.1: A table of results for G-values for neutrons from different sources using different methods.

The Sunaryo et al. uses two different chemicals to determine OH and H₂O₂ G-values.
2.4 Low LET Radiolysis

Many studies have been performed for low LET radiolysis. These experiments are typically electron spur radiolysis experiments that use spectroscopy to detect the formation of radicals and depletion as a function of time to determine rate constants, but can also use a gamma source with a flow loop for yield calculation in longer energy deposition times. The experimental setup is much simpler than that of mixed field radiolysis because the radiation is easily aimed and there is no activation of materials (typically electrons or x-rays/gammas). In the work presented in this document, electron radiolysis will be essential to subtract the low LET yields from core gamma to determine pure neutron yields.

Electron radiolysis has typically been used for pulse radiolytic studies of reaction rates through real time analysis of radical concentration with spectroscopy. Work by Mezyk & Bartels [61,62,63] has focused on reactions between the hydrogen radical and different molecules. As typical with reaction rates, the general trend is that the data shows Arrhenius behavior up to high temperature (generally less than 300° C). Work by Shiraishi et al. also shows Arrhenius behavior in reaction rates between hydrated electrons and hydrogen atoms. Traditionally, values for temperatures higher than the range of experimental data have been extrapolated, but recent work [18] has shown that the sub-critical behavior, which has been Arrhenius, does not continue near the critical point (see section 2.5 and Figure 2.5 & Figure 2.6 for more detail).

Gamma radiolysis is typically studied for use in calculations of the gamma radiolysis contribution in nuclear reactors. One of the early studies by Draganić et al. showed that the G-values for gamma radiolysis are constant as a function of pH from 3-
13, while at a pH of 1.3, higher yields were seen including \( \text{H}_2\text{O}_2 \) and OH and \( e^{-}_{\text{aq}} \) [20]. These results are important because they show the stability of yields near neutral pH, where this research is conducted. Spinks & Woods show somewhat different results for pH dependence, although the yields are again constant near neutral pH [75]. The pH results can be seen in Figure 2.2 and Figure 2.3.

![Figure 2.2: Chemical yields (G-values, molecules/100 eV) as a function of pH. ●=H\textsubscript{2}O; ○=OH; □=e\textsubscript{aq}\; ; ×=H\textsubscript{2}O\textsubscript{2}; ▲=H\textsubscript{2}. [20]](image)
Early work by Elliot used ferrous sulphate solutions as well as methanol and methanol-D4 in 0.4 \( M \) sulphuric acid water solution de-aerated with a vacuum. Samples of size \( 10^{-2} \) dm\(^3\) were irradiated in sealed cylindrical Pyrex cells and heated in an autoclave. Upon reaching the desired temperature, they were irradiated with 7.8-8.2x10\(^{18}\) eV/kg-s gamma dose from an AECL gamma cell. Hydrogen yield was measured using gas chromatography. At 25\(^{\circ}\) C, molecular hydrogen yields in the de-aerated ferrous sulphate were reported as 4.13 ± 0.16 molecules/100 eV. The hydrogen yields for the methanol solution were reported as 4.33 ± 0.22, 4.73 ± 0.06, and 5.10 ± 0.16 for 25, 200 and 300\(^{\circ}\) C respectively. \( G[OH] \) is calculated via \( G(OH) = G(H) + G(e_{aq}) + g(H_2) - 3g(-Cr_2O_7^{2-}) \) using data from Kabakchi & Lebaddeva [39,40,41,42], giving the results in Figure 2.4. [27]
2.5 Supercritical Water Radiolysis

Before an analysis of supercritical water reactor chemistry can be simulated, reaction rates, gamma and neutron G-values must all be known. A pulse radiolysis experiment that uses an optical cell for supercritical water [81] has been the main source of published work on supercritical reaction rates. Work with this apparatus by Cline et
*al.* concludes that there is an effect on reaction rates due to the compressible solvent (supercritical water). Arrhenius plots that reach supercritical conditions can be seen in Figure 2.5 and Figure 2.6.

Figure 2.5: An Arrhenius plot of the reaction $e_{aq}^+ + O_2 \rightarrow O_2^-$ at 250 bar and other pressures. Note the dip and non-Arrhenius behavior around 380°C. [18]
Figure 2.6: An Arrhenius plot of the reaction $e^{-}_{aq} + SF_6 \rightarrow F + SF_5$ at pressures between 200 and 300 bar. Again, note the dip and non-Arrhenius behavior around 380°C. [18]

Other works of interest on pulse radiolysis results with the optical cell experiment include the work of Bartels et al. [8], Marin et al. [55], and Takahashi et al. [81,83]. Similar work has been performed in Japan such as the research of Wu et al. [88].

The final piece of information needed for water chemistry of SCWRs is the radiolytic yields for gamma and neutron radiation at supercritical conditions. Gamma chamber and electron experiments are already underway at the Notre Dame Radiation Laboratory. Supercritical neutron values do not currently exist and even lower temperatures neutron values have been measured with fast reactors or calculated with ion experiments. This project will create both sub-critical data for comparison to non-thermal neutron experimentation and supercritical data.

Radiolysis modeling will be one of the final steps in the determination of supercritical water chemistry. It will employ experimental data from all other steps.
mentioned in this overview. Usually, radiolysis simulation is done with a Monte Carlo technique, such as the work of Pimblott & LaVerne, and LaVerne et al. [69,51], who have contributed to the models used for this research. Other articles of interest on this topic include the information mentioned in Elliot [29] and McCracken et al. [58], as well as the work of Hervé du Penhoat et al. [32], Michalik et al. [64], and Meesungnoen et al. [60].

2.6 Critical Hydrogen Concentration (CHC)

One of the main issues in a nuclear reactor is excess oxidation caused by radiolytically formed oxidizing species such as H$_2$O$_2$ and O$_2$. This can lead to enhanced stress corrosion cracking and other corrosion issues. The primary method used to control this effect is to add dissolved hydrogen gas to the water to change the oxidizing OH radical into a reducing H radical via Eq. 1.2. In the past, CHC has been measured experimentally in reactors after construction. If CHC behavior can be shown in this experiment, it can be used to predict CHC behavior in a reactor model.
Figure 2.7: CHC behavior with gamma and neutron radiation as modeled by McCracken et al. The modeling does not match measured values, leading to the conclusion that a model using escape yields and homogeneously overlapping neutron and gamma-ray tracks underestimates radiolysis and CHC behavior. [58]

The work of McCracken et al. uses G-values to model CHC behavior in a reactor system at 285º C. When neutrons and gammas were simulated with pure water and the G-value from set 1 (see Table 2.2) of the McCracken paper, the results showed a much lower CHC value (~6×10⁻⁷ M) than the lowest value of 3×10⁻⁶ M that had been measured in the NRU loop (see Figure 2.7) [58]. The study concluded that the overlapping gamma and neutron track model underestimates the CHC behavior. To further investigate, neutrons were simulated alone, and CHC occurred at 1×10⁻⁶ M H₂, which is still below the experimental value (Figure 2.8). McCracken et al. suggest that since gamma radiolysis suppression occurs at a lower concentration of hydrogen added, for an inhomogeneous case without track overlap, the neutron radiolysis can be considered independent of gamma radiolysis [58].
Table 2.2: Data sets used for CHC simulations from McCracken et al. [58]

<table>
<thead>
<tr>
<th>Set</th>
<th>Species</th>
<th>G [molec/100eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH 1 (bulk data)</td>
<td>2.73 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}O\textsubscript{2} 1 (material balance for OH 1)</td>
<td>0.39 ± 0.33</td>
</tr>
<tr>
<td>2</td>
<td>OH 2 (material balance for H2O2) PWR</td>
<td>1.79 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}O\textsubscript{2} 2 (fit to bulk data) PWR</td>
<td>0.86 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>OH (Sunaryo et al. 1995) [142]</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}O\textsubscript{2} (Sunaryo et al. 1995) [142]</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Figure 2.8: CHC behavior as modeled by McCracken et al. using neutrons only and revised G-values [58].

Additional modeling was performed using alternative G-values (set 2, Table 2.2) to model mixed field CHC behavior, giving a result of \( \sim 1.5 \times 10^{-6} \) \( M \) hydrogen for CHC. A neutron only study using the data of Sunaryo et al. [80] gave the result \( 3.0 \times 10^{-6} \) \( M \), which is within the range of values determined experimentally. McCracken mentions that this is not proof that the Sunaryo model is necessarily the “correct” model, but rather that limitations with the homogeneous chemistry model and escape yields for G-values under-predict the CHC chemistry at the low-scavenging powers used in NRU experiments. The study continues with simulations using low-efficiency scavenging and
impurity effects. Depending on conditions and G-values used, this resulted in simulated CHC values from $\sim 10^{-7}$ to $8.1 \times 10^{-6}$ $M$ $H_2$ added.

Figure 2.9: CHC behavior as modeled by McCracken et al. using an alternate set of G-values. The result of CHC at $\sim 1.5 \times 10^{-6}$ $M$ is much closer to the lowest experimental value as measured in the NRU loop of $3 \times 10^{-6}$ $M$, but is still low. [58]

Takiguchi et al. [84] performed an experimental study of dissolved hydrogen in reactor components to determine the necessary CHC for PWRs. The study chose temperatures higher than previously studied to determine if much hydrogen was being used in current reactors. A lower concentration of dissolved hydrogen has advantages including less nickel instability since nickel-oxide is harder to form in water with an excess of hydrogen and less hydriding on zirconium alloy fuel cladding [84]. Although zircaloy will not be used in the SCWR due to pressure and temperature, the nickel stability will be an issue since many of the newer high temperature and pressure resistant alloys are nickel based.
The Takiguchi study used two loops, the INCA Loop in the Studsvik R2 reactor and the in-core region of the Tsugura-2 reactor. Figure 2.10 shows the out-of-pile results for the INCA Loop, which illustrates the declining formation of oxygen as more hydrogen is added. The in-pile results can be seen in Figure 2.11, which is measured by a Pt electrode. Notice high hydrogen concentration shifts the water from an oxidizing agent, with 10 times as many oxidizing radicals, to a reducing agent, and shifts the electrochemical corrosion potential (ECP) from positive to negative. The study resulted in the conclusion that the DH threshold in-pile was higher by more than a factor of two, and that fully reducing conditions may have never been reached in-pile [84].
Figure 2.11: In-pile results from the INCA Loop showing the ratio of oxidizing to reducing species in the water and the calculated ratios as a function of dissolved hydrogen (DH) and electrochemical corrosion potential (ECP) via the equation \( \text{ECP} = 350 \times \log(\text{ox/red}) - 100 \) (1600 ppm B, 2 ppm Li). [84]

Christensen et al. also performed studies on CHC in the INCA loop of the Studsvik reactor [16]. The paper uses the values listed in Table 2.1 to simulate the CHC experiment. As seen in, Figure 2.12 at both 50 and 150° C, the calculated values of oxidizing species \([\text{H}_2\text{O}_2 + \frac{1}{2} \text{O}_2]\) approach zero much faster than the actual experimental results. The in-core calculation never truly approaches zero.
Figure 2.12: (A) Work by Christensen et al. on CHC both measured and calculated along with corrosion potential at 50° C. It can be seen that the concentration of H₂O₂ + O₂ does not approach zero in the experiment as it does in the simulation. (B) Similar work by Christensen et al. at 150° C.

Other work by Marin, Jonah and Bartels has looked at hydrogen radicals at higher temperatures, where evidence was seen that the reaction rate that drives CHC behavior begins to decrease near the critical point [57] (see Figure 2.13). The consequence of this decreased rate constant is that much more H₂ may be needed to successfully prevent the formation of oxidizing species; if more H₂ is required than can be dissolved in water, a CHC may not exist at all. Other effects, such as lower rates of OH to H₂O₂ production may decrease the CHC in supercritical water, making it easier to suppress oxidizing species. The overall combination of effects is currently unknown, but will be studied in this research.
Figure 2.13: An Arrhenius plot of the reaction $H_2 + OH \rightarrow H + H_2O$. Just as in the previous figures, the behavior is not Arrhenius at high temperature. [57]

Conclusions that can be drawn from the different CHC studies outlined here include the following:

1. CHC modeling is difficult to perform correctly

2. Different conditions such as impurities in water or scavenging power may affect CHC

3. Supercritical water may have higher CHC levels, due to lowering rate constants, or lower CHC levels, due to other factor such as lower G-values. The overall effect is unknown.
Because of these main conclusions, a study on CHC at supercritical conditions using a mixed gamma and neutron (thermal reactor spectrum) source will be essential. The ability of this project to change the neutron/gamma ratio will also offer further insight into how independent neutron and gamma tracks act with regards to oxidizing chemistry in reactor water.
3  Dissertation Goals

The goal of this experiment is to create neutron radiation water chemistry data sets from 25-400° C. Currently, data sets only exist up to 300° C and early evidence shows that these data sets cannot be reliably extrapolated to higher temperatures. The data must then be measured in experiments at high temperatures.

The first goal is to design and accurately characterize and calibrate an experiment to transport water near a reactor core and return it for measurement in a well controlled manner. The design will be for the beam port of the University of Wisconsin Nuclear Reactor.

The second goal is to measure radiolysis radical yields of aqueous electrons and the hydrogen radical. The data sets will be at 248 bar (3600 psi) and range in temperature from 25° C to 400° C. Data sets will also be measured at or near the critical temperature (pseudo-critical point of water at 248 bar is 383.8° C) as a function of density (pressure). These will be reported as G-values.

The third goal is to measure hydrogen molecular yield from radiolysis. This will be performed at the same conditions as the radical measurement and reported as g-values (see appendix for distinction between “g” and “G” values).

The final goal of the experiment is to measure the critical hydrogen concentration (CHC) at supercritical conditions. The purpose is to conclusively establish the existence of a CHC in supercritical water followed by the production of data sets of the CHC values as a function of temperature at 248 bar (3600 psi). This will be performed using two different ratios of neutron and gamma dose. If CHC behavior is found not to exist
above the critical point, it would be difficult to control oxygen concentration and thus water chemistry of an SCWR.
4 Experiment Outline

The experiment that was designed to measure neutron/gamma radiolysis product yields consists of a supercritical water loop apparatus inserted into the nuclear reactor at the University of Wisconsin, and associated chemical analysis equipment. Various pieces of equipment were used in the measurement system including a unique supercritical water apparatus that transported water near the core of the reactor for radiolysis, external support equipment, radiation shielding, and chemical measurement instrumentation. Prior to initial experimentation, a rigorous safety analysis was performed that included radioactive isotope production, a radiation level analysis, a radiation survey, and reactivity stability of the reactor. A similar experiment for low LET radiation (beta radiation) was implemented at the Notre Dame Radiation Laboratory and used for comparison and subtraction of low LET radiation yields in this experiment.

4.1 University of Wisconsin Reactor Lab

The University of Wisconsin Nuclear Reactor (UWNR) is a 1 MW TRIGA (Training, Research, Isotopes, General Atomic) reactor equipped with neutron irradiation experimental facilities including in-core sample positions, a pneumatic tube, three hydraulic irradiation tubes (“whale tubes”), a thermal column with an irradiation tube, and four beam ports. The beam ports are metal (aluminum in the pool, steel in the shield) tubes that go from the core grid box of the reactor, through the concrete shield, and to the edge of the beam port floor. They are made two separate coaxial sections, a 15.24 cm (6 in) diameter section from the core approximately 2.5 m long and a 20.32 cm (8 in) diameter section 0.9 m long to the outside of the shield. When not in use, the beam ports
are filled with high density concrete shielding plugs and a lead gamma shutter to limit radiation levels on the beam port floor. A cut-away diagram of the reactor can be seen in Figure 4.1 and a beam port drawing can be seen in Figure 4.2 [85].

![Diagram of the reactor](image)

Figure 4.1: A schematic drawing of the UWNR. Note the beam ports extend all the way to the edge of the core, but are cut away for viewing [85].

The reactor core consists of 23 fuel bundles (91 elements) with 5 graphite reflectors on each side. The fuel is TRIGA-FLIP fuel enriched at 70% U-235 in the form of U-ZrH$_{1.6}$ clad in 20 mill stainless steel and uses 1.5 wt% erbium as a burnable poison.
The core is cooled by natural convection with demineralized light water. The second beam port (second from the right on Figure 4.1) is the location of the supercritical water apparatus and connects to the core grid box opposite the north set of graphite reflectors at an angle of 60° and is aligned with the center of the core [85].

![Figure 4.2: A drawing of a reactor beam port. The outer section has a larger diameter to avoid streaming of radiation around the shielding in the inner section [85].](image)

In addition to the beam ports, the pneumatic tube system has been used as an experimental facility that transports samples to a position near the reactor core and directly below the beam port used for this experiment. It has the ability to deliver samples for precise irradiation times as short as one second. It is of interest due to its close proximity to the radiation location of the experiment [85].

Experimental data is normally desired at full power in the automatic mode of operation. In this mode, power level is maintained with a servo amplifier that compares a neutron signal from compensated ion chambers to the desired power level and moves a control blade to meet the demand. The neutron power level is accurate to approximately
1% error (see section 6.1). Typically, it takes 20 minutes for the reactor to reach a steady state of gamma radiation from startup.

**MCNP Model**

To further the understanding of the radiation inside of the experimental apparatus at full power, a model of the reactor has been constructed in MCNP5 [34,53]. This model includes the core, pool, reflectors, structural material, and the reactor shield including the beam ports and inserted apparatus. To obtain appropriate statistics, the irradiation volume was modeled as a cylinder of water. A cross section of the model can be seen below in Figure 4.3.
The MCNP model has been used to obtain certain physical quantities of the reactor such as flux, energy deposition and activation in the loop. MCNP results were used in the neutron energy deposition calibration (section 5.2). The model has been benchmarked with various methods such as critical bank height and blade worth [34] and beam port foils for gamma dose benchmarking [77]. Other work with the model has included a study of the burn-up of the core [73] and preliminary neutronic analysis of this experiment [23]. As the model continues to develop over time, additional benchmarking will likely be performed.
4.2 Water Loop Apparatus

The experimental apparatus used in the neutron radiolysis experiments is shown in Figure 4.4. The apparatus is designed for the second beam port of the University of Wisconsin Nuclear Reactor (UWNR). Several factors were considered in the design of the test loop; a high neutron flux requiring the irradiation volume to be as close as possible to the reactor core, constant temperature within 0.1°C during the irradiation time, and sufficient radiation shielding for personnel of the beam port floor. These criteria led to a fairly complex design including heating, temperature monitoring, pressure and chemistry control, graphite moderation, boral neutron absorption, lead gamma shielding and water radiation shielding.

Figure 4.4: The apparatus outside of the reactor.
Description

The apparatus can be divided into 4 main sections, (1) the irradiation volume/void and neutron shielding section, (2) the lead gamma shield section, (3) the voided heating section and (4) the water shielding section (Figure 4.5).

Figure 4.5: The apparatus design, not to scale.

Nearest the reactor core, section 1 is a voided section with the irradiation volume and neutron moderator and shielding (Figure 4.6 and Figure 4.7). In this portion four graphite blocks 7.62 cm (3 inches) long each and one 5.04 cm (2 inches) long were stacked to create a neutron moderator. The cylindrical blocks were machined to allow six feed-through ports in a helical pattern to prevent neutron streaming. Behind the graphite a 2.54 cm (1 inch) section of eight 0.318 cm thick boral plates are stacked to form a 2.54 cm (1 inch) neutron shield. One of the six feed-throughs allows a 0.159cm (1/16th inch) outer diameter (OD) 0.108 cm (0.05 inch) inner diameter (ID) hastelloy C276 tube to enter into the irradiation section. This tube carries preheated pressurized water from section three through a gamma shield (section two), into section one, and into the irradiation volume. The second of the six feed-throughs serves as an outlet for irradiated
water. The remaining feed-throughs allow wires to connect to E-type thermocouples that monitor the inlet and outlet temperature of the irradiation volume, current carrying aluminum wires for resistive heating of the irradiation volume and a vacuum connection for minimization of thermal convection from the irradiation volume to the inner walls of the aluminum tube.

Figure 4.6: A photograph of section 1 of the apparatus with the end cap removed.

Figure 4.7: A drawing of the Section 1 of the apparatus. This is the original design and was later adapted to include a lead shield as seen in Figure 4.15.

The outer structure of section 1 is constructed from a 91.7 cm long 6061T6 aluminum tube with an outer diameter of 12.7 cm (5 inch) and wall thickness of 0.635 cm (0.25 inch). The reactor side end is sealed with a 0.318 cm aluminum 6061T6 aluminum
plate welded to the tube end. The rear portion of this section is sealed to an aluminum junction piece which connects section 1 to section 2 with a 0.159 cm (1/16 inch) o-ring seal and series of 12¼ -20 – 316 stainless steel bolts. The rear half of this section was constructed with a slightly thicker aluminum tube 1.27 cm thick with an 11.43 cm (4.5 inch) ID.

Figure 4.8: Sections 2 and 3 of the apparatus.

Section 2 of the test loop is 48.3 cm long and contains a lead gamma shield with helical paths for the feed-throughs. This section is constructed with six 0.95 cm (3/8 inch) tubes welded to two end plates and then cast with lead. The joint in the front of section 2 (between sections 1 and 2) contains a small heater to recover heat lost in the lead section.
Section 3 (94.7 cm) contains the first stage of heating and first stage of water shielding (Figure 4.9). Section four is constructed out of a 19.8 cm (7.8 inches) OD 1.27 cm (0.5 inch) thick aluminum 6061T6 tube. The outside diameter change fits the change in the beam port diameter, which was designed to avoid streaming of radiation around the outside of shielding in the smaller diameter section. The end of the test loop is welded to a 1.27 cm (0.5 inch) thick flange and is sealed with a 0.318 cm (1/8 inch) o-ring face seal to the reactor beam port flange. This section is filled with distilled water to shield neutron and gamma radiation and to cool returning samples to room temperature for analysis.
Figure 4.10: Section 4 of the apparatus

**Thermo-hydraulics**

Water enters the apparatus at pressure in section 4 in 0.159 cm (1/16\textsuperscript{th} inch) OD, 0.108 cm (0.05 inch) ID hastelloy tubing and travels through the water shielding to the main cartridge heater in section 3, where it is preheated. After leaving the heater, it travels through the lead shielding section and into the secondary cartridge heater and heated slightly above irradiation temperature to account for heat lost in the final transport to the irradiation volume. It continues through the neutron shielding and into the 0.318 cm (1/8\textsuperscript{th} inch) OD, 0.155 cm ID titanium irradiation volume (see section 4.3). After irradiation, it returns to 0.159 cm OD hastelloy tubing, through neutron shielding, lead gamma shielding, and water shielding to the exit of the apparatus.

**Heaters**

The first stage of heating utilizes a cartridge heater with 1.5 cm diameter and approximately 20 cm long wound tightly with a 0.159 cm (1/16 inch) diameter hastelloy C276 tube. The tubing is wrapped around the heater about 80 times and has a straight length of 5 m. The heated water temperature is measured at the inlet, middle and outlet of the cartridge heater section, and is controlled to less than 570\degree C for water and 450\degree C for water with N\textsubscript{2}O to avoid thermal breakdown of water or N\textsubscript{2}O (the temperature limit
due to creep of the hastelloy is around 800° C [67]). To avoid conductive contact with the surroundings, the heater and tubing are wrapped with alumina-silica fiber insulation. This heater is controlled manually by adjusting a Sorensen DCR 150-6B DC power supply.

Depending on temperature, the water will lose up to 200° C between the first heater and the irradiation volume due to radiative heat loss. Originally, this heat loss was made up with ohmic (DC current) heating through the tubing between the lead and the irradiation volume, but since ohmic heating is also used in irradiation volume, the two DC currents would interfere with each other. The pre-irradiation DC current heating was removed and a small secondary cartridge heater was used. The second heater is approximately 1.5 cm in diameter and 3 cm in length. The outlet temperature is limited by thermal breakdown of water, not operational limits of the heater or the hastelloy tubing. The second heater is also wrapped with alumina-silica fiber insulation. The heater is controlled manually by adjusting a rheostat from 0-90% of 120V AC.

The final stage of heating is a DC current that runs through the tubing of the irradiation volume. For high temperature operation, currents of approximately 20A and voltages up to 15V were typical. Heating of the wiring has to be taken into account due to the high power loss caused by the high current, especially since aluminum wire was used near the irradiation volume to avoid neutron activation. Fluctuations in resistivity of the tubing caused by temperature changes in addition to power fluctuations tend to cause variations in the current and voltage through the tubing, even after a steady state temperature is reached. The DC current heating is controlled manually via a NJE SY 36-
30-M DC power supply. More detail on the irradiation volume can be found in section 4.3.

**Vacuum**

Within the apparatus where there is no shielding, a vacuum is pulled by a rotary vane pump. Pressure, measured at the inlet to the apparatus is normally kept below 250 Pa (2 torr). Without the vacuum, convective heat loss causes the water to cool substantially as it passes through the irradiation volume, making it impossible to keep water at a constant temperature.

**Safety Analysis**

A safety analysis assessed the production of radioactive isotopes, the shielding of the apparatus and the structural integrity and reactivity stability of the reactor. The specific stipulations of the safety analysis are listed below:

1. Less than 1.4% rho ($\Delta$) reactivity change for secured reactor experiment (Since this experiment is bolted to the shield, it is considered secured)

2. Sufficient shielding of gamma and neutron radiation from core during operation

3. Low enough activation of apparatus materials for safe storage and disposal

4. No possible damage to reactor system from high temperature and pressure of water

The details of this analysis can be found in the appendix (section 11.3).
4.3 Irradiation Volume

Irradiation volumes have consisted of different materials and dimensions. The first irradiation volume was one meter of hastelloy, 0.3175 cm OD, 0.2159 cm ID tubing wrapped in a single square shaped coil that extended to the end of the apparatus (no lead shield was planned at the time). This irradiation volume was limited to 24 MW-hours of irradiation due to activation of the high concentration of cobalt (<0.77% nominal).

The second irradiation volume was made of inconel, chosen for its strength and corrosion resistance at high temperatures and has a smaller concentration of cobalt. The dimensions of this irradiation volume were nearly identical to the hastelloy design. Later, it was replaced for the construction of a lead shield, which would further limit the space in the irradiation volume. Figure 4.11 shows the design of the first two irradiation volumes in, as well as the inlet and outlet thermocouples.

![Figure 4.11: The first irradiation volume design](image)

The third and fourth irradiation volume, designed to maximize the residence time of the sample water near the core and allow room for a lead shield, were made of 0.3175 cm OD, 0.155 cm ID titanium tube with 2 meters of length arranged in a 7 cm long double coil (shown in Figure 4.12). Titanium was chosen for the irradiation volume for three reasons, minimization of radiation induced chemical wall reactions, minimization of
neutron activation, and structural strength at high temperature and pressure. Since the
coil has a heating current running through it, it is formed so that the tubing does not
contact itself, causing a short circuit. Approximately 100 watts of power is used to
maintain the sample water at a constant temperature (less than a 0.1°C temperature
difference between thermocouples). The first titanium irradiation volume was replaced
because after maintenance, a short circuit formed between the coils, heating the contact
point to high temperature and causing a rupture in the irradiation volume. Photographs of
the irradiation volume can be seen in Figure 4.12 and Figure 4.13.

![Photographs of the second titanium irradiation volume.](image)

Figure 4.12: Photographs of the second titanium irradiation volume.

Temperature is monitored at the inlet and outlet of the irradiation volume with
two E-type thermocouples. These thermocouples were calibrated in a constant
temperature oil bath from 30-150 °C and a constant temperature lead bath from 350-600
°C with a N.I.S.T traceable 5699 platinum resistance thermometer to an accuracy and
resolution of ±0.2°C. A constant temperature was desired in the irradiation volume so
the inlet and outlet temperatures are kept to within 0.1°C. Irradiation temperature was
recorded as the average between the inlet and the outlet and should be considered ±0.2°C
due to the thermocouple accuracy.
Preliminary MCNP analysis suggested that there would be sufficient fast flux to produce detectable amounts of radiolysis for the experiment. Following experimentation, it was found that the gamma dose was also significant, and the neutron to gamma energy deposition ratio would have to be increased. The neutron flux determined by MCNP can be seen as a function of position in Figure 4.14. This result combined with the geometry of the irradiation volume showed that >99% of neutron fluence is experienced in the section of the temperature controlled irradiation volume.
Lead Shield

After preliminary experimentation, it became evident that a large portion of the radiation energy deposition was from gamma radiation. In order to reduce the gamma contribution to total energy deposition (and thus increase the neutron contribution), a lead gamma shield between the core and the irradiation volume was developed. Using MCNP analysis, an idealized model was designed with respect to shape, size, and thickness taking the irradiation volume size into account [34]. The final constructed design can be seen in Figure 4.15.
Further MCNP analysis predicted that the shield would reduce gamma energy deposition to 19.5% of the original value and neutron energy deposition to 69.9% of the original value. This resulted in a predicted 1.84 factor improvement in the neutron fraction of energy deposition. As can be seen in the energy deposition results section (sections 6.1 and 6.2), the physical results showed a 1.91 factor improvement, although the total energy depositions predicted by MCNP differ from measured values.
4.4 External Chemistry

Water Preparation Components

Water for the experiment is demineralized and organically filtered distilled water prepared by an Elga Purelab Classic Filter to produce 18.2 MΩ-cm water. This prevents unwanted impurities from interfering with desired reactions and minimizes the neutron activation of contaminants and the potential for flow obstruction in capillary tubing. Liquid and/or gaseous chemical scavengers such as nitrous oxide and ethanol-D6, which scavenge aqueous electrons and hydrogen radicals respectively, are added to the water to create stable chemical species to be measured at the outlet. Samples without a scavenger gas have dissolved air sparged out using gases that aren’t measured in analysis such as helium. Solutes that would activate to radioactive gases such as argon are avoided. Liquid scavengers are mixed into the water solution inside of glass or stainless steel bubbling reservoirs. All tubing in the system is stainless steel or hastelloy to avoid the infusion of oxygen that would occur with plastic tubing.

Pumps

Two constant flow rate high performance liquid chromatography (HPLC) pumps (Chrom Tech Inc P1100), capable of flow rates of 0.1-20.0 mL/min, are used to control the total flow rate through the system. The relative concentrations of the dissolved scavengers are controlled by adjusting the relative flow rates of these pumps, which are connected to different chemically prepared water reservoirs.

For low flow rates of water with dissolved N₂O, HPLC pump failure led to the addition of one syringe pump to the system, an ISCO 260D syringe pump capable of flow
rates of 0.001 mL/min to 107 mL/min at pressures up to 517 bar. The water reservoir for these pumps is 266.05 mL, meaning that they need to be refilled after every 266.05 mL of water, unlike the HPLC pumps that have two heads and are connected to an external reservoir. The syringe refill flow rate must be kept low to keep N₂O from being pulled out of the solution.

**Capillary Tubing and Pressure Control**

After water exits the irradiation volume, it returns to atmospheric pressure through stainless steel capillary tubing. The pressure is maintained by the viscous frictional pressure drop of the water in a coil of stainless steel capillary tubing, which is controlled by adjusting temperature in a constant temperature bath from approximately 12-42° C. The minimum pressure the system can achieve is with laminar flow at the laminar/turbulent transition point (42° C) [67]. In order to lower pressure beyond this point, capillary tubing must be removed, which can take up a large portion of irradiation time. Pressure in the system is measured at the inlet and outlet of the apparatus by two Siemens Sitrans P high accuracy diaphragm pressure transducers with accuracy of better than 0.1% (±0.25 bar). The typical pressure drop through the entire piping system at a flow rate of 10 mL/min is on the order of 2.40 bar, approximately 1% of system pressure (248 bar). The pressure in the irradiation volume is assumed to be a weighted average of the inlet and outlet pressures following pressure drop analysis and experimentation performed by Olson [67]. After the irradiated water is depressurized through the capillary tube back to atmospheric pressure the sample is sent to the chemical analysis system.
Sample Chamber

The sample chamber normally transports sample water from the inlet through the water valve and into the “water bypass” flow to radioactive water storage as seen in Figure 4.16. When a sample is taken, the water valve is simply turned to collection position, and sample water flows into the water sample collection volume, while the argon sparging gas is in bypass mode (so no Ar is bubbling through sample during collection). The sample volume is approximately 15 mL in volume, but typically, a 10 mL sample is taken as room is needed at the top of the volume for the bubbling caused by sparging. This sample is measured by timing the collection and using a calibrated flow rate.

When a sample is collected, the gases formed in the sample are removed by sparging with ultra high purity argon gas. The mixture is sparged until all gases are removed and the sample becomes saturated with argon. At this point, the gas flow is returned to bypass, and the water valve is turned to dump (this is a 3-way valve, and both “water flow in” and “water sample flow” go to waste). The sample is pushed out against the flow of water in by the pressure of the argon gas flow (both water in and sample are open to waste).
Following sparging, the gas mixture is separated from water vapor according to the reactivity of the gas in a gas chromatography (GC) column filled with molecular sieve A4 beads. This not only prevents water from entering the vacuum chamber, where it would interfere with hydrogen results, but also prevents nitrous oxide (N₂O) from reaching the chamber where it would interfere with nitrogen signal. The GC column must be baked out at high temperature with gas flowing through to remove water after every 50-100 samples or it will not delay water or nitrous oxide.

**Mass Spectrometer**

The gases flowing out of the GC column are collected through a 3 m long 0.05 mm ID flexible fused silica capillary tube (Alltech 602035) into a vacuum chamber. The capillary tube acts as the pressure boundary between the vacuum chamber...
and 3 m was chosen to keep the vacuum at approximately 7.5E-4 Pa (5.5E-6 torr). The sample gas flows around the capillary tubing collection point (only a small fraction is analyzed) and the gas that does not flow into the vacuum chamber instead goes through a flow meter (to assure constant flow throughout the day), and is released to atmosphere. A safety analysis was performed to assure that the gases would not be too radioactive to for release to the room. A Pfeiffer QMS 200 mass spectrometer is used to detect gases inside the chamber, and has sufficient resolution to separate isotope gases, but not different molecular gases of the same mass.
The data for this experiment is taken by measuring gaseous samples removed from liquid. The mass spectrometer ionizes gas and measures ion current of a particular gas by applying electric and magnetic fields. The physical quantity being measured is the mass/electric charge ratio, meaning water that is singly ionized would be measured in channel 18, and water that is doubly ionized would be measured in channel 9. The
ionization process also has the ability to break molecular bonds, which would thus measure a sub-product of the gas in the chamber.

**Spectrophotometer**

A spectrophotometer is used for ultraviolet (UV) and visible light (VIS) spectroscopy. It is a Hitachi model U-1800 190-1100 nm UV/VIS. Methacrylate cuvets measuring 1 cm square were used in the system. Wavelength scans were used to determine peaks of samples used, and a single wavelength was measured at the peak to acquire data. The photospectrometer and support equipment can be seen in Figure 4.18.

![Figure 4.18: The photospectrometer with 3 samples in it, along with support equipment.](image)

Samples are collected by flowing irradiated water into vials and using a pipette to move the required amount into the cuvets. In the hydrogen peroxide tests, 2 mL are
added to 1 mL of solution A and 1 mL of solution B, the reactive solutions that cause an absorption peak based upon the concentration of H$_2$O$_2$.

The hydrogen peroxide calibration is linear at H$_2$O$_2$ concentration ($M$) = absorbance/13043 for a 1 cm cuvet. The calibration curve can be seen in Figure 4.19. This corresponds to an optical density of 26,086 $M^{-1}cm^{-1}$ for I$_3^-$ at 350.2 based upon a 2:1 dilution with the reacting solution (A+B). This is within 1.4% of the value of 26,450 $M^{-1}cm^{-1}$ measured by Klassen et. al at 351 nm [48].

![Calibration for Absorbance of the Triiodide ion at 350.2 nm](image1.png)

**Figure 4.19:** The calibration curve for hydrogen peroxide.

**Fluoride Electrode**

An Accumet fluoride sensitive solid state combination electrode model 13-620-529 filled with Fisher saturated KCl filling solution (SP138) was used to measure fluoride ions. The electrode was calibrated using a 10 and 100mg/mL standard fluoride
solution from Ricca Chemical. Each sample was 50 mL and was mixed with a fluoride ionic strength adjustor powder pillows (Hach product #258999) and stirred at constant rate. Samples were insulated from the magnetic stirrer with expanded polystyrene to prevent heat transfer into the water. Temperature was measured with a thermometer. It was previously determined by collaborators at Notre Dame that SF₆ would interfere with fluoride readings on the electrode, so that any SF₆ in a sample would have to be bubbled out prior to the insertion of the electrode. The signal was measured on the LabVIEW board and values were recorded by waiting for linearity on a moving chart and taking the average of the last 100 data points. The electrode can be seen in Figure 4.20.

Calibrations fit the log₁₀ of fluoride concentration against the voltage potential created to a linear fit with R² values on the range of 0.999-0.999999. The calibration was stable from day to day as the standard deviation of fit coefficients m and b in Eq. 4.1 between 20 runs at slightly varying temperatures from day to day was 1.0% and 1.2% respectively.

\[ V(mV) = m \cdot \log_{10}[F^-] + b \]  
Eq. 4.1
4.5 Other Equipment

*Beam Port Floor External Lead Shield*

An external lead shield was constructed to limit dose on the beam port floor with the experiment installed and the reactor on. Without this shield, gamma exposure was measured to be up to 700mR/hr (~700 mrem/hr dose). This lead shield limited personnel dose to less than 5mR/hr at reasonable distances and 20mR/hr on contact. The shield was contained in steel and a photograph of it with the front sheet removed to show lead bricks is seen in Figure 4.21.
4.6 Notre Dame Radiation Loop

Low LET radiation experiments were performed at the Notre Dame Radiation Laboratory using 2.5 MeV electrons from a 3.0 MeV Van de Graaff (VdG) accelerator. The low LET apparatus was built similar to the neutron loop at UW, with similar pumps, transport tubing, and water preparation. The irradiation zone at Notre Dame was a 1/8\textsuperscript{th} inch titanium tubing section with a total volume of 0.06 mL. All chemical concentrations in the water were the same except that argon was used at Notre Dame where helium was used at UW and in the N\textsubscript{2}O/phenol tests discussed later, twice the concentration of N\textsubscript{2}O was used. More detail on the entire setup and chemistry can be seen in Janik \textit{et al.} [37].
Figure 4.22: A schematic of the Notre Dame water loop setup.
5 Methodologies

In order to measure a radiolysis product, it must form a stable product that can be directly measured at the outlet or react with a chemical at a fast enough rate to form a measurable product before it is consumed in some other process. The methodologies developed for measurement of different radiolytic species followed these guidelines. Techniques were developed for each instrument to properly measure a specific product. Each test used carefully chosen chemistry to react with radicals of interest and prevent other radicals from interfering with desired reactions. Experimental methods used are presented and explained in the following section.

5.1 Mass Spectrometer Techniques

Integration of Peaks

Data is acquired on the mass spectrometer by bubbling argon gas through water to sparge out gas formed by radiolysis. When the gases are measured by the mass spectrometer, the signal is a curve similar to the calibration curve shown in Figure 5.2. Data is analyzed by integration of the ion current trace with respect to the baseline. A LabVIEW program was written to perform this integration by choosing a baseline to be a zero signal for each signal, fitting a line to that baseline, subtracting the baseline from the signal, and integrating the difference. The integrated value has units of A-s, since it is an ion current (A) integrated over time (s). The process and output of the program can be seen in Figure 5.1.
Mass Spectrometer Calibrations

The mass spectrometer is calibrated by relating integrated current to total gas content contained in a known sample. This calibration is performed by running water saturated with a suitable gas such as a mixture of 90% nitrogen and 10% hydrogen (our N₂/H₂ calibration mixture) in samples of 10 mL. A series of 3 calibration peaks can be seen in Figure 5.2. Typically, 3 calibrations are averaged both at the beginning and the end of the day and linear interpolation is used to determine the calibration for each sample as a function of time. The calibration changes due mainly to the changing
conditions in the GC column and the decaying signal amplification of the electron multiplier, and will typically be 0-3% different between the beginning of a data run and the end (9 hours apart). The highest difference seen has been for H₂ and was measured to be 7.2% or 0.8%/hr. The highest difference for N₂ was 5.1%. The general trend of the calibrations is that the calibration coefficient goes up from day to day in a somewhat linear manner due to the electron multiplier.

Figure 5.2: A calibration run with hydrogen (black) and nitrogen (yellow) peaks.

Each day, the argon sparging flow rate is manually controlled, which can vary the calibration factor. Once the flow rate is set, it is checked before each sample is sparged and adjusted if necessary. The calibration factor will vary as a function of sparging gas flow rate because the gas in the sample is removed faster as flow rate goes up, but only a
fraction of the gas is sampled at any time. The result is that for a faster flow rate, there is a higher peak and a smaller integrated area while a slower flow rate will yield a broadened, lower peak with a larger integrated area. Ideally, a good signal to noise ratio yields the best signal, so a sharp peak is preferred. The value of 90-100 mL/min is preferred because it gives a sharp response, a large area and the sparging is a gentle bubbling (a violent bubbling should be avoided so that liquid sample does not enter the GC column).

The sparging gas flow rate was initially measured with a floating ball type flow meter. This flow meter was a 16 unit full scale glass tube, and the preferred argon flow of 100 mL/min was at 4 units, or about ¼ full scale. This did not give sufficient precision to keep the sparging gas at a constant flow rate for a constant calibration factor, which could change up to 10-20% without a significant response on the meter. The flow meter was replaced with an argon calibrated 110 mL/min full scale digital read out flow meter due to the necessity of a high precision and accuracy for this experiment. The variation of calibration factor as a function of the older flow meter reading can be seen in Figure 5.3 below. Typically, a flow rate of 3.8-4.2 may be read at 4, depending on conditions.
5.2 Radiation Energy Deposition Calibration

In order to obtain a final product for this project the energy deposition in the water by radiation must be well known. Since molecules of radicals formed per unit energy by neutrons alone is desired from data taken in a mixed field (neutrons and gammas), not only must the radiation energy deposition be well known, but also the separate energy deposition of both neutron and gamma radiation. The gamma energy deposition data can be used to subtract the radiolysis by gamma radiation with results from the Notre Dame Lab, and the remaining yield can be used to calculate G-values from neutron energy deposition. A flow chart of this necessary information can be seen in Figure 5.4.
Figure 5.4: The necessary inputs to determine neutron G-value, the quantity that is desired. Red hexagons are unknowns, turquoise squares are experimentally determined values, horizontally striped polygons are simulation results and gray ovals are intermediary values.

**Neutron Energy Deposition Calibration**

The MCNP5 model can tally neutron flux and energy deposition with different multipliers on a surface or through a volume. The results of the flux tally are in units of $\frac{\text{neutrons}}{\text{cm}^2 \text{source neutron}}$. The unit of $\frac{\text{neutrons}}{\text{cm}^3 \text{s}}$ is achieved by multiplying the MCNP result by total source neutrons/second in the entire reactor system. In the same manner, energy deposition from neutrons can be calculated as a function of position, and can be used to
develop total energy deposition in the water. In order to perform this analysis the position of the irradiation volume must be well known as well as the flow rate so that the energy deposition can be integrated over time and space. Since this is difficult to measure the exact position of the irradiation volume with good confidence, an experiment meant to incorporate actual geometry and flow time was chosen to calibrate neutron flux involving neutron activation analysis of sodium in the loop.

Neutron energy deposition is a strong function of fast neutron flux, which changes rapidly with the axial distance from the core. Sodium activation is a strong function of thermal flux, which also changes with the axial distance from the core. Since the ratio of fast neutron energy deposition and thermal activation was shown by MCNP to not change dramatically with position, it will be used for the neutron energy deposition calibration.

The neutron energy deposition measurement used a 0.0100 M Na2CO3 solution as a tracer for the thermal flux via the neutron capture reaction of the $^{23}$Na(n,$\gamma$)$^{24}$Na. After flowing through the loop at room temperature (25°C), a 10 mL sample of the sodium carbonate solution was collected in a polyethylene vial and the 1368 keV Na-24 gamma emission was counted on a high purity germanium detector (HPGe). The total number of sodium atoms activated in the irradiation loop was calculated using Eq. 5.1. In this equation, $\alpha_{Na-24}$ is the activity of Na-24 immediately after irradiation, $\lambda_{Na-24}$ is the decay constant of Na-24, CR is the count rate seen by the HPGe detector, $\eta_{detector}$ is the detector efficiency, and $t_{decay}$ is the decay time of the sample between irradiation and counting on the HPGe.

$$
N_{Na-24}^{Created \ per \ sample} = \frac{\alpha_{Na-24}}{\lambda_{Na-24}} = \frac{CR \cdot \exp(t_{decay} \cdot \lambda_{Na-24})}{\lambda_{Na-24} \cdot \eta_{det}}
$$

Eq. 5.1
MCNP calculations were used to calculate the neutron energy deposition ($E_{\text{dep}}$) rate in water in a number of energy ranges (all energies, >100 eV, and >15 keV), and the total activation rate constant ($<\sigma\phi>$) for the $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$ reaction. Again, the ratio of these quantities is independent of geometry and source strength. Multiplying the measured ratio of $^{24}\text{Na}/^{23}\text{Na}$ atoms by $E_{\text{dep}}/<\sigma\phi>$ gave the absolute energy deposition in the irradiation volume. A continuous energy dependant cross section was used for sodium from the ENDF/B-VI library and NJOY processed ENDF/B-VI data was used to calculate neutron heating [59].

**Gamma Energy Deposition Measurement**

Direct measurement of gamma energy deposition in a mixed field of high radiation is a challenging problem. Instruments such as ion chambers are expensive and will become activated by the neutron flux while thermoluminescent dosimeters (TLDs) will experience interference from the neutron energy deposition, giving errors that are larger than acceptable. Furthermore, using these techniques to measure the dose in the inaccessible and small space of the irradiation volume is not easy. Just as for neutrons, the gamma energy deposition is a strong function of geometry due to changing gamma flux, which means that it would be difficult to predict the energy deposition in a sample with good precision. Using a ratio of gamma energy deposition to neutron energy deposition from MCNP was ruled out because gamma benchmarks and preliminary experimentation have shown that MCNP has under-predicted gamma energy deposition [77]. Subsequent investigation revealed that MCNP only includes prompt core gamma in the KCODE calculation, meaning that approximately ½ of gamma energy deposition from the core is not included.
A radiolysis experiment has been devised to experimentally determine the gamma energy deposition and further benchmark MCNP for gamma radiation if the problem can be accounted for. The design flow of this experiment is outlined in Figure 5.5, where neutron and gamma G-values at room temperature are determined from simulations with known inputs at room temperature. Following the methodology described in section 5.3, the nitrogen gas yield was measured with the mass spectrometer.

Figure 5.5: The necessary changes from Figure 5.4 to determine gamma energy deposition at room temperature.
The water radiolysis simulation model has been described [68,69] and parameters have been updated and benchmarked [70,51] in several previous publications. The first step is a Monte Carlo (MC) track simulation, using inelastic scattering cross-sections derived from the differential dipole oscillator strength distribution for liquid water, vibrational and elastic cross-section measured in the gas phase, and electron scattering cross-sections for solid amorphous water. The primary particle and all secondary electrons are followed collision-by-collision until their energy drops below 25 eV energy at which point a “chemical action” algorithm apportions the energy between various excitation and ionization events. The most important parameterization of the model is to estimate the ultimate spatial distribution of solvated electrons, assuming a Gaussian probability function with standard deviation of 5.0 nm. This distance is chosen to correctly model the measured solvated electron spur recombination in ps pulse radiolysis experiments [6,7]. The kinetics of recombination is estimated employing the stochastic Independent Reaction Times (IRT) method, using the initial spatial distance distribution given by the track realization. Depending on the quality of information desired, between $10^3$ and $10^5$ tracks are typically averaged to arrive at a final yield.

The result for low LET gamma or electron radiation is easily and reliably calculated once the reaction rates are given, because the yields are quite insensitive to the initial energy. The basic chemical model for this calculation is given by Elliot [29]. The rate constants for H and for OH reaction with phenol are given in Bonin, et al. [9]. Other scavenging rate constants were taken from the review of Buxton, et al.[14]. The N$_2$ yield given at 25°C in this simulation of gamma radiolysis is 2.95x$10^{-7}$ moles/J of gamma energy.
Calculation of an average yield resulting from neutron radiolysis is more involved. The neutrons are stopped by both protons and oxygen nuclei, producing a spectrum of recoil ion energies. From MCNP simulations of the irradiation volume within the reactor we obtain a spectrum of neutron energies. This spectrum is used as input to the GROUPR module of NJOY99, a pointwise and multigroup neutron cross section program to produce a group spectrum of energy-weighted recoil events shown in Figure 5.6 [52] (Note that the chemical action of a single 1 MeV neutron is far more important than a million 1 eV neutrons). The greatest energies are deposited in the range of 0.5 to 5 MeV proton recoils. Adding over all events produces the result that 88% of energy is absorbed by protons, and 12% by oxygen atoms.

![Recoil Energy Spectrum](image)

**Figure 5.6: Energy-weighted recoil events created from NJOY.**

The rate of energy deposition by ions in the energy range below 10 MeV is strongly dependent on the energy. This in turn makes the density of reactive species in tracks change as the ion slows down. To solve the ion radiolysis problem, we calculate a
differential $G$ value for species $X$, $G_E(X)$, for 100 keV sections of tracks from ions whose initial energy is $E_0$. The integrated $G$ value for the entire track is then

$$G(X, E_0) = \frac{1}{E_0} \int_0^{E_0} dE G_E(X)$$

Eq. 5.2

In Figure 5.7, we plot the simulated results for differential $G_E(N_2)$, and for the track average $G(N_2, E_0)$ for protons of energy $E_0$. The differential results were interpolated on a log scale with a sixth order polynomial, and then integrated to give the solid curve displayed.

![Figure 5.7: Simulated results for differential $G_E(N_2)$ and track averaged yields.](image)

With the $G(N_2, E_0)$ results available for proton radiolysis, and the energy spectrum of proton recoil ions available, it is a simple matter to integrate over the energy distribution of Figure 5.7 to obtain a final average $G(N_2)$ from recoil protons. However, we still have 12% of the neutron energy to account for in oxygen recoil. Calculation of
chemistry induced by oxygen ions at these low energies is essentially impossible at this time. The problems are discussed in LaVerne et al. [51]. However, we can assert that the yield of hydrated electrons will be much smaller for oxygen ions than for protons. Based on the ion G value results of LaVerne et al. [51] and the recommended scaling by $MZ^2/E$ (where $M$ is ion mass and $Z$ is ion charge), it would seem that an upper limit for the yield from oxygen ions (assuming ca. $1 \times 10^7$ s$^{-1}$ scavenging rate) is $G(N_2)=0.2$.

Given the minor fraction of energy in oxygen recoil, and the small anticipated yield, the uncertainty represents a very small error on the order of 1-2%. Using this approximation, we can calculate the final $G_n(N_2)$ from neutrons as

$$
G_n(N_2) = \frac{\int_0^\infty E_o P(E_o) G(N_2, E_o) dE_o + 0.2 \int_0^\infty E_o O(E_o) dE_o}{\int_0^\infty E_o P(E_o) dE_o + \int_0^\infty E_o O(E_o) dE_o}
$$

Eq. 5.3

where $P(E_o)$ represents the recoil frequency spectrum for protons, and $O(E_o)$ is the recoil frequency spectrum of oxygen atoms. The integration is carried out as a rectangular integration using the energy-binned events from MCNP/NJOY times the $G(N_2, E_o)$ at the center energy of the bin, for energies from 0.01 MeV to 8 MeV, based on the energy spectrum of Figure 5.6. This accounts for virtually all of the neutron energy. The final result is $G_n(N_2) = 0.95 \times 10^{-7}$ moles/J in the phenol/N$_2$O scavenger solution used. This is to be compared with the calculation of $G(N_2)=2.95 \times 10^{-7}$ moles/J calculated for beta/gamma radiolysis of the same scavenger system. A chart of the total nitrogen G-value as a function of neutron energy deposition fraction can be seen in Figure 5.8.
Figure 5.8: MC/IRT results for G-values of nitrogen as a function of neutron dose fraction.

With a solution containing N$_2$O, the room temperature G-values, and neutron energy deposition, gamma energy deposition can be determined with the following steps (as outlined in Figure 5.5):

1. Experimentally measure concentration of N$_2$ formed by radiolysis
2. Calculate concentration of N$_2$ formed by neutron radiolysis with 100% neutron G-value and neutron energy deposition
3. Subtract concentration of N$_2$ formed by neutron radiolysis to get N$_2$ formed by gamma radiolysis
4. Use gamma G-value to get gamma energy deposition

These steps could be carried out with H$_2$ or HD also. Values for neutron dose fraction can be calculated by dividing the neutron dose by the total absorbed dose.

Another method of calculating the neutron dose fraction is to divide the G-values of N$_2$ by H$_2$ (or HD), and fit that ratio to the neutron dose fraction. A chart of these ratios can be seen in Figure 5.9. One of the problems with this method is the low slope of the
ratios. If there is a small error in $N_2/H_2$, it results in a large error in neutron fraction. Because of this error, the previous $N_2$ yield method will be the technique of choice.

![Figure 5.9: A chart of neutron energy fraction as a function of G-value ratios.](image)

### 5.3 Aqueous Electron Scavenging Reactions

Scavenging reactions are used to detect radicals formed by radiolysis, which must meet certain restrictions including the following: (1) they must quickly react with the radical, (2) they must be able to be dissolved in sufficient quantity, (3) they must not dissociate at supercritical temperatures, (4) they must not interfere with other reactions of interest, and (5) they must produce a stable product that is measurable and is not created by other reactions. All of these requirements are made to assure that all of the radical is consumed by the scavenger (not the surroundings) and produces a measurable 1:1 ratio.
product. Scavenging reactions that produce a measurable result for the aqueous electron include the following:

$$e^-_{aq} + N_2O \xrightarrow{H_2O} N_2 + OH^- + \bullet OH \quad k_{298K} = 9.1 \times 10^9 \text{ L/mol-s}^* \quad \text{Eq. 5.4}$$

$$e^-_{aq} + SF_6 \rightarrow SF_5 + F^- \quad k_{298K} = 1.6 \times 10^{10} \text{ L/mol-s} \quad \text{Eq. 5.5a}$$

$$SF_5 \xrightarrow{H_2O} SO_3^{2-} + 5F^- + 7H_3O^+ + OH^- \quad \text{Eq. 5.5b}$$

*Note: all reaction rate data not referenced explicitly was accessed via the NDRL Radiation Chemistry Data Center [http://www.rcdc.nd.edu/index.html](http://www.rcdc.nd.edu/index.html).*

The hydrogen radical can also react with nitrous oxide in the following reaction with reaction rate at non-alkaline pH:

$$H \bullet + N_2O \rightarrow \bullet OH + N_2 \quad k_{298K} = 2.1 \times 10^6 \text{ L/mol-s} \quad \text{Eq. 5.6}$$

Aqueous electrons are detected by measuring nitrogen gas created in Eq. 5.4. It is important that this is the only reaction in the system that is producing nitrogen so Eq. 5.6 should be avoided. Different chemicals were tested to scavenge the hydrogen radicals in the system without interfering with other reactions or breaking down. Cyclohexane [CH$_2$(CH$_2$)$_4$CH$_2$] was tested, but unrealistic yields of nitrogen gas were seen. Phenol (C$_6$H$_5$OH) was tested and worked to sufficiently scavenge hydrogen radicals as seen in Eq. 5.7.

$$H \bullet + PhOH \rightarrow \text{hydroxycyclohexadienyl radical} \quad \text{Eq. 5.7a}$$

$$\bullet OH + PhOH \rightarrow \text{dihydroxycyclohexadienyl radical} \quad \text{Eq. 5.7b}$$

The aqueous electron experiment was repeated using the reaction in Eq. 5.5 because of a large nitrogen background at high temperature. The electron will react with sulfur hexafluoride to release a fluoride ion and create SF$_5$, which will decay into 5 more fluoride ions, essentially releasing 6 F$^-$ for each aqueous electron. The fluoride ions
released can be measured using ion chromatography or a fluoride electrode. A fluoride electrode was used in this experiment due to the relatively low cost for use with potentially radioactive samples. Phenol was added again to remove hydrogen and hydroxide radicals. The methods for each of the separate scavenging experiments are described in this section.

Aqueous Electron $N_2O$ Experiment

The aqueous electron ($e^{-}_{aq}$) is detected via the reaction in Eq. 5.6 in the $N_2O$ experiment. For this experiment, two water reservoirs are prepared: one is pH=7 filtered water saturated with $N_2O$, and the other a pH=7 0.01 $M$ phenol solution saturated with helium gas (to sparge out other gases). The water flows are mixed at flow rates of 5\% $N_2O$ mixture and 95\% phenol solution, with final concentrations of 0.0012 $M$ $N_2O$ and 0.01 $M$ phenol. Typically, total flow rate is either 6 mL/min or 10 mL/min, and can be adjusted based upon desired energy deposition in the sample.

When the gaseous sample is analyzed, nitrogen (mass 28) and hydrogen (mass 2) levels are measured with the mass spectrometer. Other mass numbers of interest for this experiment include nitrous oxide (mass 44) and water (mass 18). If the nitrous oxide signal overlaps in time with nitrogen, there will be an effect on the nitrogen signal because $N_2$ will be formed during ionization by the mass spectrometer filament from $N_2O$. The same is true of hydrogen forming from water. As long as the GC column is working properly, the $N_2O$ and $H_2O$ will come out slow enough that they will produce a small slope in the baseline that can be easily subtracted out. If the GC column is not functioning, it may have to be baked out for a day before more data can be taken.
**Aqueous Electron SF₆ Experiment**

The aqueous electron was measured using Eq. 5.5 (a&b). A single source of water was prepared with saturated SF₆ \( (2.8 \times 10^{-4} \text{ M}) \) and phenol \( (0.0106 \text{ M}) \). Flow rates between 6 and 8 mL/min were used. The syringe pump was used to pump water at constant pressure while a sample was being irradiated and average flow rate was used to determine dose. The electrode was calibrated every two hours and 4-5 points surrounding the typical range expected in samples.

![Figure 5.10: A sample being bubbled with the argon sparge.](image)

A 50 mL sample was collected in a 50 mL beaker with a magnetic stir rod. The beaker was placed on a magnetic stirrer on a gentle stir. While being stirred, a total ionic strength adjustment buffer (TISAB) pillow was added (see section 4.4) and argon gas was bubbled into the sample to remove all remaining SF₆, which has been seen to poison electrodes by our collaborators. After approximately three minutes, the argon sparge was turned off, and the thermometer and electrode were lowered into the sample. Depending
on concentration of $F^-$, the signal would take between 60 and 240 seconds to stabilize.

An average of 100 sample points was used as the final data reading.

![Figure 5.11: A sample with the thermometer and electrode lowered into a reading position. The stir rod is still spinning during sample reading as recommended by the electrode manual.](image)

### 5.4 Hydrogen Radical

The hydrogen radical is measured in the same manner as the aqueous electron with HD as the stable product being measured via the reaction

$$H \bullet + CD_3CD_2OH \rightarrow HD + (CD_3CDOH) \bullet \quad k_{298K} = 2.7 \times 10^6 \text{ L/mol-s} \quad \text{Eq. 5.8}$$
In the case of mass HD, there is no interference on mass spectrometer channel 3 from other gasses as there is with N₂O on channel 28 and H₂O on channel 2. Two water reservoirs are prepared with demineralized and organically filtered water: one is pH=7 water saturated with N₂O and the other is a 0.021 M pH=7 ethanol-D6 solution saturated with helium gas (to sparge out air). The final solution is 0.02 M ethanol-D6 and 0.0012 M N₂O. It was the original plan to combine the reactions of Eq. 5.4 and Eq. 5.8 from the hydrogen radical section in to the same experiment. At high temperatures however (above 200° C), the ethanol radical formed in the reaction between ethanol-D6 and hydrogen radicals (Eq. 5.9) react with N₂O to create extremely high levels of nitrogen gas, interfering with the N₂ product. In this experiment, the N₂O is used to eliminate aqueous electrons from interfering with the alcohol.

\[
(CD₃CDOH)• + N₂O \rightarrow CD₂CDO + N₂ + •OH \quad \text{Eq. 5.9a}
\]

\[
•OH + C₂D₃OH \rightarrow HDO + (CD₃CDOH)• \quad k_{298K}=1.2x10^9 \text{ L/mol-s} \quad \text{Eq. 5.9b}
\]

### 5.5 H₂ Detection

Hydrogen gas is formed directly in a spur and is immediately stable. Because of this, no scavenger or additional chemistry is needed to detect H₂. The concentration of H₂ is read with the mass spectrometer in the same manner that HD and N₂ are read, with a daily calibration. It is read in the phenol/N₂O and the ethanol tests.

### 5.6 Critical Hydrogen Concentration

The products formed by radiation with the most effect on corrosion are hydrogen peroxide (OH) and oxygen (O₂). In order to control the formation of these oxidizing species, nuclear reactors have typically added hydrogen gas to the water as discussed in
The reaction in Eq. 1.2 will convert the oxidizing radical, OH, into the reducing radical, H, before OH reacts in an oxidizing reaction. When a sufficient quantity of excess hydrogen gas has been added to the reactor coolant, the net production of oxygen becomes essentially zero by the reactions in Eq. 1.3-1.7 and 1.12-1.18. It will become a key issue is whether or not rates of these reactions will be sufficiently fast in water at supercritical temperatures and pressures to consume the oxidizing species at any concentration of hydrogen.

The radicals produced in the irradiation of pure water will eventually recombine and breakdown to form hydrogen and oxygen gases dissolved in the water. The simplest method to measure the CHC in water is to take samples, adding more and more hydrogen to the feed until there is no oxygen production. In the apparatus used in this experiment, no oxygen was detected in the samples of pure water, likely due to oxidation of the internal walls of the transport tubing, which is appropriate behavior for transport through such large surface areas.

The lack of oxygen yield in the samples led to a different method of experimentation, the measurement of hydrogen formed by radiolysis. In this method, the total hydrogen yield is measured and the initial hydrogen concentration in the water is subtracted (see Figure 5.12). The main disadvantage of this method is that at high concentrations of hydrogen (50-100% saturated), the error in the measured hydrogen concentration is on the order of the hydrogen formed at zero hydrogen added. This creates values at high concentration (which should essentially be zero) with error bars as large as the values measured with pure water. Proving that these values are zero thus
becomes difficult, although critical hydrogen behavior has occurred in PWRs far before the water contains this much hydrogen.

Figure 5.12: A visual representation of CHC measurement procedure. The hydrogen produced is calculated by subtracting the added hydrogen concentration from the measured hydrogen concentration.

5.7 H₂O₂ Detection

An experiment was researched and used to detect H₂O₂ in the sample water commonly referred to as the Ghormley method [1,48]. This method uses detection of the triiodide ion at 350 nm with a spectrophotometer (Hitachi model U-1800) in 1 cm square methacrylate cuvets. A typical spectrum can be seen in Figure 5.13.

\[
H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \quad \text{Eq. 5.10a}
\]

\[
I_2 + I^- \leftrightarrow I_3^- \quad \text{Eq. 5.10b}
\]
Figure 5.13: A typical peak for a sample mixed with the H$_2$O$_2$ detection recipe. This spectrum shows data from 300 to 500 nm. This particular spectrum is of lower resolution than the one used to determine the location of the peak, and shows a peak at 350.5 nm. The actual peak was found at 350.2 nm.

Two solutions are created for the detection of H$_2$O$_2$, which are adapted from the recipes in Allen et al. and Klassen et al. to use LiOH·H$_2$O in place of NaOH: (A) 3.3 g KI (Sigma Aldrich 99.99+%), 0.105 g LiOH·H$_2$O, 0.01 g ammonium molybdate tetrahydrate (Sigma Aldrich Puratronic grade) with 50mL de-ionized water, (B) 1 g potassium acid phthalate (Sigma Aldrich ≥ 99.95%) mixed with 50 mL de-ionized water [1,48]. Hydrogen will react with the iodide in the system to form triiodide, which absorbs in the UV spectrum. A sample was prepared by adding 1 mL of solutions A and B to 2 mL of sample.
6 System Characterization

An energy deposition calibration was run in two steps: a neutron energy deposition calibration and a total energy deposition calibration. The gamma energy deposition was calculated by the difference between these two methods. The neutron energy deposition was a sodium activation analysis method and the total was a radiolysis experiment. Early experimentation provided the system characterization necessary to produce accurate results including the determination of what radiolysis products could and could not be measured, the exact chemical environments for each test, and a demonstration of the repeatability of radiolysis measurements.

6.1 Neutron Energy Deposition Calibration

The neutron energy deposition experiment was performed with a 0.0100 $M$ solution of 99.95% +/- 0.05% purity sodium carbonate solution. The sample was prepared by measuring 1.060 g of sodium bicarbonate (molar mass=1.0599 g/mole), and mixing it with 1.00 L of water in a volumetric flask. The solution was pumped through the apparatus for 25 minutes before the first data point was taken to reach steady state. Samples of approximately 10 mL were acquired by timing collection time in 15 mL (4 dram) polyethylene vials. The actual collection time was recorded and used for calculation of sample size. Before each calibration, the pumping speed was calibrated by measuring time to fill a 100 mL volumetric flask.

Samples were counted on two high purity germanium (HPGe) detectors. Count time was 300 seconds and the sample was positioned 3 cm away from the detector. Random counting error at this position for a 300 second count time was typically less
than 1%. The HPGe efficiency is calculated with a 10 mL liquid NIST standard europium source contained in a 4 dram vial, which is the same type of vial that is used for the sodium solution.

Multiple calibrations were taken. Each time the reactor power was calibrated or a significant change to the apparatus was made, the neutron energy deposition in the apparatus was re-calibrated. One radiation calibration will be presented here in detail followed by a summary of all recent energy deposition calibrations (using the most recent irradiation volume).

Repeatability

During a full day of operation, sodium calibrations were run to check the stability of the neutron dose rate. The repeatability and error involved with this experiment come from a variety of sources including pumping speeds, sample size error, reactor power error and sample counting positioning error. The most important result of this experiment (Figure 6.1) is the lack of a systematic drift in power throughout the day. The neutron dose is constant from the beginning of the day to the end.

The standard deviation of the data was found to be 1.13% and the counting error for the average count was 0.72% (1σ). This suggests that the error from sources other than counting error is approximately 0.87% using an RMS propagation of error.
Figure 6.1: Deviation from the mean in repeated counts during a full day of operation. The orange error bars are random counting error (0.72%) and the black error bars are the standard deviation (1.13%) of all 44 points. The propagation of this difference suggests that the total error outside of counting error to be on the order of 0.87%.

Results

The most recent energy calibration performed with the lead shield both on and off shows the difference in dose caused by the shield. A total of 3 data points were taken over one day with the lead shield installed, while 22 data points were taken over two separate days with the lead shield removed. Activity was calculated using Eq. 6.1 (CR=count rate). The ratio of Na-24 to Na-23 atoms was then calculated and the MCNP calibration factor (CalFac) was used to calculate energy deposition as in Eq. 6.2.
\[
N_{\text{Na-24}}^{\text{Created per sample}} = \frac{\alpha_{\text{Na-24}}}{\lambda_{\text{Na-24}}} = CR \cdot \exp \left( t_{\text{dec}} \lambda_{\text{Na-24}} \right) \frac{\lambda_{\text{Na-24}}}{\eta_{\text{det}}} \quad \text{Eq. 6.1}
\]

\[
E_{\text{dep}} \left[ \text{eV/g} \right] = N_{\text{Na-24}}^{\text{Created per sample}} \cdot \frac{\text{rxn/atom}}{N_{\text{Na-23}}} \times \text{CalFac} \cdot \frac{\text{eV/g}}{\text{rxn/atom}} \quad \text{Eq. 6.2}
\]

The results of the activation analysis can be seen in Table 6.1. The energy deposition with and without the lead shield from neutrons was calculated to be \(3.21 \times 10^{16} \pm 3.6\%\) and \(4.49 \times 10^{16} \pm 3.6\%\) \((100 \text{eV/g})\text{(mL/min)/(g/mL)}\) respectively. The total dose rate for a sample can be calculated from this number using the pump flow rate, density of the water in the irradiation volume, and total sample volume, as seen in Eq. 6.3. For a 10 mL sample at 22°C (density = 1.007 g/mL) pumped with a flow rate of 6 mL/min, the neutron dose would be \(5.39 \times 10^{15}\) and \(7.54 \times 10^{15}\) \((100\text{ eV/sample})\) with and without lead, creating \(1.16 \times 10^{-5}\) and \(8.30 \times 10^{-6}\) moles/L of nitrogen when using \(g=0.92\).

\[
E_{\text{dep, sample}}[100 \text{ eV}] = \frac{E_{\text{dep}}[100 \text{eV/g}]}{\text{Flow Rate}[\text{mL/min}]} \times \rho_{\text{water, irradiation}}[\text{g/mL}] \times \text{Vol}_{\text{sample}}[\text{mL}] \quad \text{Eq. 6.3}
\]

<table>
<thead>
<tr>
<th>Lead Shield</th>
<th>Ave. Activity (Bq/sample)</th>
<th>Count Error</th>
<th>Flow Rate</th>
<th>Samples Taken</th>
<th>MCNP Calibration Factor (100eV/g)/(rxn/atom)</th>
<th>Energy Deposition (100 eV/g)*(mL/min)/(g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed</td>
<td>9264.3</td>
<td>0.53%</td>
<td>9.950</td>
<td>3</td>
<td>(5.39 \times 10^{26})</td>
<td>(3.24 \times 10^{16}) (\pm 0.12 \times 10^{16})</td>
</tr>
<tr>
<td>Not Installed</td>
<td>19830.19</td>
<td>0.16%</td>
<td>6.009</td>
<td>22</td>
<td>(5.92 \times 10^{26})</td>
<td>(4.53 \times 10^{16}) (\pm 0.16 \times 10^{16})</td>
</tr>
</tbody>
</table>

Table 6.1: The results of the neutron activation analysis energy deposition calculation.

### 6.2 Gamma Energy Deposition Calibration

Following the neutron energy deposition calibration, a radiolysis experiment was performed to calculate the gamma energy deposition. In this experiment, nitrogen was
formed by a reaction between aqueous electrons and nitrous oxide as in Eq. 5.1. From
the data used to create the plot in Figure 5.8, the G-value for nitrogen formation via
neutron irradiation is 0.92 molecules/100 eV. Combining this with the flow rate of the
experiment (6.078 mL/min), the density of the water at 25°C (1.007 g/mL), the dose
rates, and the data from Table 6.1, it is expected that the neutron production of N₂ be 8.19
and 11.4 µM with and without lead respectively. In the experiment, 49.2 and 149 µM
nitrogen was formed with and without the lead shield respectively, meaning that 41.0 and
138 µM nitrogen was created from gamma radiation. Using a G-value for gamma
radiation of 2.85, gamma energy deposition can be calculated. The results can be seen in
Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>With Lead</th>
<th>Without Lead</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen Measured</td>
<td>49.2</td>
<td>149</td>
<td>µM</td>
</tr>
<tr>
<td>Neutron Energy Deposition</td>
<td>0.085</td>
<td>0.119</td>
<td>J/g (@6.1 mL/min)</td>
</tr>
<tr>
<td>Neutron G-value for Nitrogen</td>
<td>0.95</td>
<td>0.95</td>
<td>10-7 moles/J</td>
</tr>
<tr>
<td>Expected Neutron Contribution to Nitrogen</td>
<td>8.19</td>
<td>11.4</td>
<td>µM</td>
</tr>
<tr>
<td>Gamma Contribution to Nitrogen</td>
<td>41.0</td>
<td>138</td>
<td>µM</td>
</tr>
<tr>
<td>Gamma G-value for Nitrogen</td>
<td>2.95</td>
<td>2.95</td>
<td>10-7 moles/J</td>
</tr>
<tr>
<td>Gamma Energy Deposition</td>
<td>0.138</td>
<td>0.463</td>
<td>J/g (@6.1 mL/min)</td>
</tr>
<tr>
<td>Neutron Fraction of Energy Deposition</td>
<td>0.38</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Corresponding Neutron Flux</td>
<td>4.62x10¹¹</td>
<td>1.04x10¹²</td>
<td>n/cm²-s</td>
</tr>
</tbody>
</table>

Table 6.2: The results of the gamma dose calibration.

The results of the nitrogen calibration of the gamma energy deposition give a total
neutron contribution of total dose of 38% with lead and 21% without lead. Effectively,
the lead shield has doubled the neutron contribution to total dose, but has also reduced
total dose by a factor of approximately 3. Signals are thus smaller and noisier with the
lead shield on, but are easier to separate the product formed by gamma from the neutron
since the neutron contribution is larger.
Discussion

Hydrogen production could be also be used to calibrate the gamma dose in the same manner that the nitrogen production was. The nitrogen numbers are considered to be much better because the signals have less noise, more signal, and a lower background (since H$_2$ is hard to pump from a vacuum chamber). Also, the simulation of hydrogen production from radiolysis is more complicated and less work has been performed in benchmarking these tests to proton radiolysis. Most importantly, there has been evidence of a non-radiolysis source of hydrogen in the apparatus. This would give unrealistically high results for gamma energy deposition since the neutron energy deposition is calibrated separately and subtracted. The creation of hydrogen in the apparatus is discussed in more detail in section 7.4 on critical hydrogen concentration.

6.3 Results of Various Calibrations

No accurate radiation energy deposition calibration was performed for the hastelloy or inconel irradiation volumes. Because of this, only recent calibrations are reported, all for the second titanium irradiation volume. The most accurate radiation energy deposition for the earlier irradiation volume can be estimated with the total nitrogen yield at room temperature and an assumed neutron fraction of total energy deposition calculated without the lead shield.

Recent radiation calibrations are presented in Table 6.3. The difference between calibrations can be attributed to slight shifts in irradiation volume location and different reactor power calibrations.
Table 6.3: Results of different radiation calibrations

<table>
<thead>
<tr>
<th>Date</th>
<th>Lead?</th>
<th>Dose N</th>
<th>Dose G</th>
<th>Neutron Fraction</th>
<th>Dose N</th>
<th>Dose G</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/12/2006</td>
<td>no</td>
<td>4.49x10^{16}</td>
<td>1.74x10^{17}</td>
<td>20.5%</td>
<td>0.72</td>
<td>2.79</td>
</tr>
<tr>
<td>5/12/2006</td>
<td>yes</td>
<td>3.21x10^{16}</td>
<td>5.19x10^{16}</td>
<td>38.2%</td>
<td>0.51</td>
<td>0.83</td>
</tr>
<tr>
<td>10/30/2006</td>
<td>yes</td>
<td>2.74x10^{16}</td>
<td>5.07x10^{16}</td>
<td>35.0%</td>
<td>0.44</td>
<td>0.81</td>
</tr>
<tr>
<td>1/2/2007</td>
<td>yes</td>
<td>2.74x10^{16}</td>
<td>4.87x10^{16}</td>
<td>36.0%</td>
<td>0.44</td>
<td>0.78</td>
</tr>
<tr>
<td>2/2/2007</td>
<td>yes</td>
<td>2.91x10^{16}</td>
<td>4.97x10^{16}</td>
<td>36.9%</td>
<td>0.47</td>
<td>0.80</td>
</tr>
</tbody>
</table>

6.4 H2 Tests/Proof of Concept

The proof of concept radiolysis experiment used demineralized and organically filtered water saturated with nitrogen or helium to remove all other gases to show the formation of hydrogen from radiolysis. These experiments showed that there was radiolysis occurring in the system. A shifting baseline for gases in the system was seen and a determination of the effect of the shift on data was made.

Figure 6.2: Hydrogen yields in nitrogen saturated water. Runs 1-4 are at room temperature, runs 5-6 are at 185°C, runs 7&10 at 300°C and runs 8-9 at 400°C. The spread of the baseline can be seen in the data from one run to the next. A bar graph of the baselines can be seen in Figure 6.3.
The shifting baseline was caused by very small concentrations of test gases in the vacuum chamber building up during the day faster than they could be pumped out. An analysis was made for hydrogen runs taken at three different temperatures throughout the same day. The results of the 10 signals are shown in Figure 6.2. Notice the spread of the baseline from one run to the next. A graphical representation of each baseline level, seen in Figure 6.3, shows that the baseline is slowly increasing through the day up with a total increase of about 15%. Subsequent tests showed that this did not affect the results because it was properly subtracted out of the signal during peak integration.

Figure 6.3: The baseline of each run seen in Figure 6.2. Note the y-axis does not go to zero.
Figure 6.4: The concentration of hydrogen formed in nitrogen saturated water. This was one of the first feasibility tests for the SCW experiment.

Figure 6.4 shows the hydrogen yields in the proof of concept radiolysis test. In the experiment, no oxygen was seen corresponding to the produced hydrogen; although the mass spectrometer technique is quite sensitive to O₂ ($1 \times 10^{-6}$ M oxygen will produce a signal to noise ratio of 3). One would thus expect that a stoichiometric amount of H₂O₂ must be formed in the water corresponding to the H₂ produced. It is well known that this H₂O₂ should decompose on metal or metal oxide surfaces with the reaction $2 \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O}$. In the data from Figure 6.4, oxygen concentrations of $2.5 \times 10^{-6}$ to $1.7 \times 10^{-5}$ with signal to noise ratios of 7.5 to 50 would be expected.

6.5 Oxygen Results

Subsequent work would show that no oxygen was seen in the nitrous oxide, formed from the OH radical released in the reaction with the aqueous electron. Tests
performed specifically to look for oxygen saw none with the titanium irradiation volume. Tests with the reactor off showed that the oxygen measured at the outlet was the same as the oxygen going into the inlet. Injection of H₂O₂ with the reactor off produced the expected amount of O₂ at the outlet. Other tests designed to detect H₂O₂ did not yield a signal in water irradiated above 100⁰ C. The fate of the radiolysis-produced oxidizing species is the subject of ongoing research at Notre Dame.

The results of the hydrogen peroxide injection test are shown in Figure 6.5. At and above 200⁰ C, all hydrogen peroxide is breaking down into oxygen. At high temperature, something else must be happening to either the oxygen, hydrogen peroxide or the hydroxide in the system. Further work with hydrogen peroxide was performed later and the results of these tests can be seen in section 7.5.
Figure 6.5: The hydrogen peroxide concentration inserted divided by 2 and the total oxygen seen exiting the apparatus. At 195°C, there is more oxygen than hydrogen peroxide put in. It is thought that the hydrogen peroxide from the low temperature runs was oxidizing the walls of the tubing and the extra oxygen came out into solution at higher temperatures. It can be seen that at high temperature, all hydrogen peroxide is breaking down into oxygen.

### 6.6 Determination of Required N₂O Concentration

At 100% saturated nitrous oxide, a problem occurred because the GC column could not handle all the N₂O coming through. The N₂O in the vacuum chamber that split into N₂ during ionization created a false nitrogen “tail” at the end of the signal, and would continue to interfere with the shape of following data points by changing the manner in which the GC column held the nitrogen gas. The evidence for this can be seen in Figure 6.6.
Figure 6.6: Nitrogen results for two runs ran in sequence. Notice the “tail” at the end of the signal caused by the nitrous oxide making it through the GC column and breaking into nitrogen gas. Also, there is a broadening of peaks from one to the next due to poor GC column performance after being filled with N$_2$O.

The nitrogen tail was eliminated by reducing the nitrous oxide concentration to 0.0012 $M$ or 5% saturated. This eliminated the “tail” by allowing the GC column to properly hold nitrogen and nitrous oxide without being overwhelmed by high concentrations of nitrous oxide.

### 6.7 Selection of Alcohol

The first alcohol tests used methanol-D4. Initial hydrogen G-values would increase by 50 times from low to high temperature [24], but this was corrected by avoiding thermal breakdown of water due to high heater outlet temperatures. Subsequent tests were run to ensure enough methanol was in the solution so that the reaction between
hydrogen radicals was not limited by the concentration of alcohol. Because the reaction rate of ethanol with hydrogen radicals is higher than that of methanol, ethanol-D6 was chosen to lower the total cost of each experiment. It was determined that 0.02 \( M \) ethanol D6 was sufficient for all temperatures.

![Estimated G-values for preliminary data](image)

**Figure 6.7:** Estimated neutron G-values for methanol-D4 with the hastelloy irradiation volume. It is interesting to note that the nitrogen and HD yields get very high at high temperature due to a chain reaction between the alcohol radical and nitrous oxide as well as thermal breakdown of the alcohol.

Figure 6.7 shows neutron G-values calculated using an assumed neutron dose fraction, based on new data for the hastelloy irradiation volume. It is interesting to note that the room temperature hydrogen molecule yields are approximately \( 2 \times 10^{-7} \) moles/J, which is the same result that will be seen later in the N\(_2\)O phenol experiment. This result is approximately double what would be expected from neutrons and it is important in this case because the irradiation volume is hastelloy, not titanium (as in the later
experiments), there is a much shorter residence time in the irradiation volume due to a shorter length and faster flow, and yet the hydrogen yield differs by the same factor. This suggests that the excess hydrogen yield as discussed in section 7.1 and 7.4 is not a function of time spent in the irradiation volume, dose, or material of the irradiation volume. For more discussion of this, see section 8.4. Other preliminary data can be seen in Edwards et al. [26].

6.8 Repeatability Tests

Data was collected for over three days spanning the entire temperature range on each individual day. A plot of all data can be seen in Figure 6.8. The data shows the repeatability from one day to the next. A separate calibration for the mass spectrometer was performed on each day of operation.
Figure 6.8: Nitrogen and hydrogen yields from 3 separate days of experimentation in the N₂O/phenol experiment.
7 Chemical Yield Results

A variety of experiments were performed to acquire radiolysis yield results. Three main tests were performed to measure the three basic yields, a phenol/N$_2$O test that measured the yield of aqueous electrons and molecular hydrogen, a phenol/SF$_6$ test that re-measured the aqueous electron yields at high temperature, and an ethanol experiment that measured hydrogen radicals and again molecular hydrogen. CHC data was acquired that proved overall inconclusive due to problems with excess production of molecular hydrogen. Finally, to help determine why oxygen was not seen in the outlet water, a test was executed to measure hydrogen peroxide in the water.

7.1 Phenol/N$_2$O Experiment Results

In the phenol/N$_2$O experiment, nitrogen formed by aqueous electrons as in Eq. 5.1 is measured along with hydrogen formation as described in section 5.3. The flow rate was approximately 6 mL/min, and was calibrated before each series of experiments.
Background Fits of Nitrogen Formation for Low, Mid and High Temperatures

\[ y = 6.18E-09x + 1.42E-07 \quad R^2 = 9.94E-01 \]

\[ y = 6.88E-08x - 1.80E-05 \quad R^2 = 7.57E-01 \]

\[ y = 1.56E-06x - 6.04E-04 \quad R^2 = 8.88E-01 \]

Figure 7.1: The background levels of nitrogen formed with the reactor off vs. irradiation temperature. Generally, this data is taken at the same conditions as the irradiation data so that all internal temperatures are the same (for example, the highest heater outlet temperature).

A background level of nitrogen was measured with the reactor off, and a 3 regime approximately linear tendency was applied for nitrogen (see Figure 7.1). Because the background depends on variables such as heater exit temperatures and internal vacuum that can change, a background was performed at least each week. Two methods were used for background calculation, linear interpolation as seen in Figure 7.1, and simply repeating the experiment with the reactor off for each specific data point. It was assumed that the changing background would also change behavior (and deviate from a 3 regime linear fit), so the latter method became the method of choice. Above 400° C, nitrogen background will dominate the signal and determining the nitrogen produced from radiolysis becomes impossible.

Hydrogen gas did not show a background for the phenol test below 400° C and only had a small contribution at 400° C, making it easy to separate.
### Table 7.1: Phenol and Ethanol isothermal yields for low LET radiation from Notre Dame [37].

The isobar aqueous electron experiment was performed three times over a series of 2 or 3 days with multiple data points measured at each temperature. Gamma yields were used that were measured by the collaborators of this project in Notre Dame (Table 7.1) [37]. The concentration of hydrogen and nitrogen gas in the water from gamma radiation can be calculated by combining the G-value with the gamma dose of a particular sample. Individual gas concentration data points measured in the phenol experiment with the lead shield installed are compared to nitrogen backgrounds in Figure 7.2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (kg/dm³)</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.01 m PhOH</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.02 m EtOH-d6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>N₂</td>
</tr>
<tr>
<td>22</td>
<td>1.0000</td>
<td>0.45</td>
<td>3.02</td>
</tr>
<tr>
<td>100</td>
<td>0.9696</td>
<td>0.48</td>
<td>3.37</td>
</tr>
<tr>
<td>200</td>
<td>0.8813</td>
<td>0.54</td>
<td>3.62</td>
</tr>
<tr>
<td>225</td>
<td>0.8527</td>
<td>0.55</td>
<td>3.69</td>
</tr>
<tr>
<td>250</td>
<td>0.8209</td>
<td>0.57</td>
<td>3.74</td>
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<tr>
<td>275</td>
<td>0.7848</td>
<td>0.63</td>
<td>3.75</td>
</tr>
<tr>
<td>300</td>
<td>0.7430</td>
<td>0.67</td>
<td>3.64</td>
</tr>
<tr>
<td>325</td>
<td>0.6926</td>
<td>0.71</td>
<td>3.57</td>
</tr>
<tr>
<td>350</td>
<td>0.6271</td>
<td>0.75</td>
<td>3.40</td>
</tr>
<tr>
<td>380</td>
<td>0.4508</td>
<td>0.45</td>
<td>1.35</td>
</tr>
<tr>
<td>400</td>
<td>0.1665</td>
<td>1.09</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Table 7.1: Phenol and Ethanol isothermal yields for low LET radiation from Notre Dame [37].
Figure 7.2: Raw un-averaged nitrogen and hydrogen data with the reactor off measured nitrogen background.

Notice that the measured nitrogen gas yields approach the background signal, meaning the radiolysis production of nitrogen gas moves towards zero at high temperature. The hydrogen concentration also goes down, but when yield as a function of dose is calculated, the value will go up due to a much lower absorbed dose due of density effects. Even though the neutron + gamma production of nitrogen gas goes to zero at high temperatures, the gamma production does not, which will give negative yields in some cases. These negative values arise from the combined error in the experiment and likely mean the yield is very near zero, which makes it hard to measure. The nitrogen background is not such an issue in the Notre Dame loop because more is produced by radiolysis (low LET has higher yields), there is no subtraction of a specific
type of radiation (all beta radiation), and much less is thermally produced (smaller volume so less time at temperature).

Figure 7.3: Measured nitrogen and hydrogen production plotted with gamma expected production and neutron production calculated from the difference.

Neutron, gamma and net total (neutron+gamma) yields can be seen graphically in Figure 7.3. It is important to note how close the total yield of nitrogen is to the pure gamma yield. The neutron G-values are seen in Figure 7.4. The aqueous electron G-value is fairly constant for neutrons from 100-250º C, the yield goes down and exhibits a local minimum at 350º C, at 380º C, a local maximum occurs. The hydrogen produced by neutrons starts at 2x10⁻⁷ moles/J and increases to a value of 7x10⁻⁷ moles/J. The hydrogen values seem to be in excess of what was expected and will be further addressed in the discussion section of this document.
Isothermal data was also taken for the N\textsubscript{2}O experiment. Since the aqueous electron error increased to a high level at 400\textdegree C, only 380\textdegree C isothermal data was taken for neutron data. Data for both 380\textdegree C and 400\textdegree C for low LET radiation from Notre Dame can be seen in Table 7.2 and Table 7.3. To follow an isotherm, density was varied by modifying system pressure. According to the data shown in Figure 7.5, the hydrogen yield decreases as density increases. Nitrogen or aqueous electron yields begin by decreasing with density, then increasing and finally decreasing again, creating an s shaped curve. Many values of this curve are negative, which will be addressed in the discussion section. The fact that the error bars do not reach the zero on the y-axis is due to error that is not accounted for in the subtraction of the thermal background (see section
11.2). The maximum neutron aqueous electron G-value from this data, interestingly enough, is at 442 kg/m³, very near the pseudo-critical point.

Figure 7.5: Isothermal neutron phenol results. Note the error does not account for all of the error in the subtraction of the thermal background (see section 11.2).
### Table 7.2: Low LET data for the phenol and ethanol test at 380° C.

<table>
<thead>
<tr>
<th>Density (kg/dm³)</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.01 m PhOH</th>
<th>Density (kg/dm³)</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.02 m EtOH-d6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
<td>H₂</td>
</tr>
<tr>
<td>0.1229</td>
<td>0.75</td>
<td>2.31</td>
<td>0.1218</td>
</tr>
<tr>
<td>0.1542</td>
<td>0.74</td>
<td>2.08</td>
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</tr>
<tr>
<td>0.2045</td>
<td>0.65</td>
<td>1.73</td>
<td>0.1980</td>
</tr>
<tr>
<td>0.2501</td>
<td>0.51</td>
<td>1.43</td>
<td>0.2567</td>
</tr>
<tr>
<td>0.3116</td>
<td>0.44</td>
<td>1.12</td>
<td>0.2934</td>
</tr>
<tr>
<td>0.3599</td>
<td>0.32</td>
<td>1.16</td>
<td>0.3639</td>
</tr>
<tr>
<td>0.4004</td>
<td>0.34</td>
<td>1.05</td>
<td>0.4018</td>
</tr>
<tr>
<td>0.4524</td>
<td>0.38</td>
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<td>0.4540</td>
</tr>
<tr>
<td>0.4547</td>
<td>0.45</td>
<td>1.25</td>
<td>0.5126</td>
</tr>
<tr>
<td>0.5010</td>
<td>0.73</td>
<td>2.27</td>
<td>0.5430</td>
</tr>
<tr>
<td>0.5501</td>
<td>0.81</td>
<td>3.12</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 7.3: Low LET data for the phenol and ethanol test at 400° C.

<table>
<thead>
<tr>
<th>Density (kg/dm³)</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.01m PhOH</th>
<th>Density (kg/dm³)</th>
<th>G(X) ×10⁻⁷ (mol/J) in 0.02m EtOH-d6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
<td>H₂</td>
</tr>
<tr>
<td>0.1223</td>
<td>1.05</td>
<td>1.84</td>
<td>0.1211</td>
</tr>
<tr>
<td>0.1485</td>
<td>0.96</td>
<td>1.77</td>
<td>0.1518</td>
</tr>
<tr>
<td>0.2124</td>
<td>0.74</td>
<td>1.53</td>
<td>0.2124</td>
</tr>
<tr>
<td>0.2594</td>
<td>0.62</td>
<td>1.43</td>
<td>0.2594</td>
</tr>
<tr>
<td>0.3090</td>
<td>0.65</td>
<td>1.38</td>
<td>0.3090</td>
</tr>
<tr>
<td>0.3574</td>
<td>0.59</td>
<td>1.35</td>
<td>0.3574</td>
</tr>
<tr>
<td>0.4174</td>
<td>0.57</td>
<td>1.48</td>
<td>0.4094</td>
</tr>
</tbody>
</table>

### 7.2 Phenol/Sulfur Hexafluoride Results

Aqueous electron yields were measured with a reaction with sulfur hexafluoride as discussed in section 5.3 using SF₆ saturated 0.0106 M phenol solution. According to Eq. 5.5b, each aqueous electron that reacts with SF₆ will free 7 hydrogen ions forming hydronium (H₃O⁺). The aqueous electron will react with these H₃O⁺ ions as well as SF₆ and phenol. At low temperature where the dissociation constant of HF is high, hydronium will be present at high concentration in the water, consuming a significant
amount of aqueous electrons without forming the fluoride ion. At higher temperature, the
dissociation constant for HF and thus the total reaction rate (not rate constant) between
aqueous electrons and H$_3$O$^+$ will be lower, so that the ratio of aqueous electrons to
fluoride ions will be 6:1 as seen in Eq. 5.5b. High temperature kinetic data is not
accurate enough to determine if the supercritical aqueous electrons are being consumed
by hydronium. The best technique to collect this data for supercritical temperatures
would be to perform the experiment again with a base added at these conditions to
consume hydronium upon formation.

Raw data from the sulfur hexafluoride can be seen in Figure 7.6. It is important to
remember that this data was taken at different flow rates, meaning that the water was
exposed to different doses. The SF$_6$ experiment at 8 mL/min will have a dose that is
6/8ths the dose at 6 mL/min. Also, there is a small thermal breakdown background at
high temperatures (400-410°C). This background is lower for higher flow rate, which
makes the 410°C data converge to the same amount for different SF$_6$ tests. The data
converges at high temperature, and is nearly identical to N$_2$O data at 380 and 400°C.
Figure 7.6: Raw data for the sulfur hexafluoride tests. Note that this data is taken at different flow rates, which means that the water has been exposed to different doses. For example, the flow=8 condition will be exposed to less dose and should have lower values. In addition, there is a small background at high temperatures that is dependant on flow rate that converges the 410°C data to the same number.

Yield results reported as G-values can be seen in Figure 7.7. Notice that at 380°C, SF₆ and N₂O results are identical. At 400°C, SF₆ results much closer to zero than the N₂O results. At this temperature, F⁻ background is 7% of the total signal whereas N₂O background is 75-80% of the total signal. The value for SF₆ at 410°C uses extrapolated low LET data and should not be considered very accurate because of this. If 410°C data is produced for low LET radiation, an accurate neutron G-value could be calculated using raw data in the appendix to this document.
Figure 7.7: Neutron G-values for SF₆ and N₂O at high temperature. Notice a complete convergence of data at 380°C and a more realistic value at 400°C.

Assuming that most of the aqueous electrons react with the SF₆ at high temperature, the isothermal data presented in Figure 7.8 can be considered correct. This data shows different trends than the N₂O isothermal data, which will be discussed in the discussion section.
7.3 Ethanol Experiment Results

Hydrogen radical yields were measured at similar conditions to the phenol experiment. G-values were determined to be approximately 0.5 from 25-325°C as seen in Figure 7.9 and Figure 7.10. At 380°C, yields increase greatly until they are unrealistically high at 400°C. The behavior is currently unexplained since the yield with no radiation has been subtracted from this value. The hypothesis is that there must be some kind of radiation induced alcohol breakdown or chain reaction occurring independently from radiolysis reactions. Hydrogen yields also increase sharply with respect to temperature, increasing the calculation of the net dissociation of water well beyond realistic levels at high temperature.
Ethanol Results at 248 bar

Figure 7.9: Ethanol results with an expanded y-axis for better resolution of low temperature data.
Measuring critical hydrogen concentration (CHC) was a goal of this research. Ideally, one would measure the value by measuring oxygen concentration as described in section 5.5, but since no oxygen was detected in our experiment, the alternative method of measuring hydrogen gas described in the same section was used, which has given unrepeatable results. In many cases, the hydrogen production seems to increase instead of decrease at higher concentrations of initial hydrogen added.

A series of experiments were performed with the original hastelloy irradiation volume similar to pressurized water reactor (PWR) conditions (2250 psi, 300º C, pH=8). The results show that the critical hydrogen concentration for this setup occurs in the
range of $5 \times 10^{-5}$ and $8 \times 10^{-5} \, M$. This is too far above the results of $9.6 \times 10^{-6}$ to $1.7 \times 10^{-5} \, M$ (0.23 to 0.4 mL H$_2$/kg H$_2$O) that are reported for non-boiling water in EPRI report EPRI-TR-100789 [30].

![CHC (300 C, 2250 psi, pH=8, no lead)](image)

**Figure 7.11:** The first CHC data taken with the original hastelloy irradiation volume.

Following the initial PWR condition tests, the lead shield was added to the apparatus. Only one CHC at PWR condition (2250 psi, 300$^\circ$ C, pH=9) test was performed with the lead shield and the results can be seen in Figure 7.12. Two main features stand out on this chart are (1) The concentration of hydrogen produced never goes to zero and (2) more hydrogen is produced with less radiation. The major difference in the setup of the experiments was the pH.
Figure 7.12: The original test and a newer test, with the lead shield and the titanium irradiation volume.

CHC for the low LET loop in Notre Dame show similar results with increasing hydrogen as hydrogen is added. As seen below in Figure 7.13 and Figure 7.14 (A), hydrogen production increases as hydrogen is added to the water even though oxygen decreases. In other words, hydrogen is being produced by some reaction in the water such as a radiation catalyzed wall reaction or a radiation induced chain reaction. Mixed field results are presented in Figure 7.14 (B) that looks similar to the low LET results.
Figure 7.13: Oxygen out as a function of hydrogen added at the low LET loop. Notice CHC behavior is occurring (oxygen production goes to zero).

(a) Low LET Results (Notre Dame)  
(b) Mixed Field Results (UW)

Figure 7.14: Hydrogen output as a function of hydrogen added to the water pre-irradiation. Notice the hydrogen increases in (a) even though the oxygen decreases as seen in Figure 7.13. Also, notice the similarity in behavior between the low LET Notre Dame results (a) and the mixed field UW results (b).
7.5 $\text{H}_2\text{O}_2$ Results

The lack of oxygen measured at the outlet of the apparatus has led to the obvious question of where the oxygen is going. If hydrogen gas is being detected, there must be a stoichiometric concentration of $\text{H}_2\text{O}_2$ produced that should be breaking down into oxygen. It was hypothesized that perhaps the hydrogen peroxide breakdown, as a second order wall reaction, was not occurring in the loop, meaning that it would still be in the sample water as $\text{H}_2\text{O}_2$.

Aqueous hydrogen peroxide was measured in 1 cm path length cuvets in the photospectrometer. The absorption of each cuvet was measured without solution, then 1 mL of solution A, 1 mL of solution B (see section 4.4), and 2 mL of sample water was added. The absorption was calibrated using a 3% $\text{H}_2\text{O}_2$ standard diluted to concentrations between $1 \times 10^{-4}$ and $1 \times 10^{-6}$ $M$. A blank was created by mixing 2 mL of de-ionized water with solutions A and B in the same manner as a sample. Absorption was measured at 350.2 nm (with high resolution), which was measured to be the maximum of the peak for triiodide (versus 350.1 nm measured by Klassen et al.) [48].

The results of the tests were that hydrogen peroxide levels of $2.29 \times 10^{-6}$ $M$ at 25° C and $1.51 \times 10^{-6}$ $M$ at 100° C were detected. At and above 200° C, no $\text{H}_2\text{O}_2$ was detected, suggesting it was all breaking down into oxygen. The oxygen must thus be absorbed in the transport tubing since it was never detected in the mass spectrometer. Therefore, it is the conclusion that this particular setup will not be capable of detecting critical hydrogen concentration as first desired.

The measured concentration at room temperature is approximately one order of magnitude lower than the expected concentration based upon stoichiometry with $\text{H}_2$ gas.
formed. Since it is not detected at higher temperature, H$_2$O$_2$ must be completely breaking down at higher temperature. As stated in section 6.5, 1.0 µM oxygen will be detected by the mass spectrometer with a signal/noise ratio of 3, so even if only 2.3 µM hydrogen peroxide is produced, it should be detected by the mass spectrometer. Hydrogen peroxide is thus formed in the system, although at lower than expected concentrations at room temperature, and is breaking down at higher temperatures.
8 Discussion

The radiation calibration performed used neutron activation analysis as well as radiolysis to determine the independent neutron and gamma radiation energy deposition in sample water. This experiment was distinctive in that it measured high doses of neutron and gamma data separately. The unique methodology was adopted for various reasons that will be explained in this section.

Following the energy deposition calibration, experimental data was acquired and analyzed to create neutron G-values for different chemical species in water. Previous work has determined similar neutron data through various methods for sub-critical conditions as discussed in section 2. The sub-critical data from this experiment will be compared with that in previous publications where it exists. This comparison, along with physical limitations such as the maximum dissociation of water due to the strength of bonds in water and specific experimental behavior such as CHC results will be used to discuss what data acquired can be considered correct and what data should not be used.

8.1 Energy Deposition Calibration

The MCNP5 simulation package reports gamma energy deposition for the irradiation volume, similar to the results given for neutron energy deposition. The degree of gamma irradiation of the sample revealed by the calibration experiment is surprisingly large compared to the predictions from the MCNP5 simulations. The gamma energy deposition was predicted by MCNP5 to be only 0.191 J/g without the lead shield and 0.0391 J/g with the lead shield. These values are 40% and 28% of the values measured, respectively.
MCNP5 gamma energy deposition results for the UWNR model have also been compared to measurements from CaF₂:Mn thermoluminescent detectors (TLDs). In this experiment, the TLDs were irradiated in the pneumatic irradiation facility located near beam port #2. While both the simulation and measurements found a linear response with reactor power, the MCNP5 simulations under-predict the gamma energy deposition in the pneumatic irradiation facility by 23% [77]. In the absence of specific validation/calibration of the MCNP5 model for the gamma energy deposition in this irradiation volume, the simulated results are not considered reliable for this experiment.

The reason for the discrepancy in gamma energy deposition values is that MCNP only models prompt gammas from fission, which account for approximately half of total gamma energy from the core. In order to model the complete gamma spectrum, a separate simulation must be performed to calculate the burn-up of the core and the delayed gammas from fission products. Results from the current simulation and the burn-up delayed gamma simulation can be combined for total gamma energy deposition. Work is currently being performed to model fission product delayed gamma contribution for the UWNR.

Although the use of radiolysis yields for energy deposition calibration is well established [75], the methodology presented here allows these techniques to be used for measuring gamma energy deposition in a strong neutron field. This kind of measurement has been performed with TLDs in the past [77] but the present methodology permits such measurements using an aqueous dosimeter. It is possible that these results could lead to benchmarking of gamma dose simulations such as those discussed above to improve their reliability and credibility.
8.2 Aqueous Electron Results

Aqueous electron data was taken with two methods: the first method was with nitrous oxide and the second with sulfur hexafluoride. The nitrous oxide test was less accurate at high temperature due to a high thermal background of nitrogen gas. In the N$_2$O experiment at 380º C, 43% of the total nitrogen signal measured was thermal background and 48% of the signal was gamma production, leaving 11% of the total signal for calculation of the G-value. The SF$_6$ results had a 1% thermal background and 82% gamma production leaving 17% of the total signal for calculation of the G-value. The values calculated at 380º C were 0.43 and 0.52 for N$_2$O and SF$_6$ respectively, which is within the 1 standard deviation error bars. At 400º C, the thermal background of nitrogen was 84% of the total signal and the gamma contribution was 26% of the signal, giving a negative result. The sulfur hexafluoride experiment had a thermal background of 5% and a gamma production of 98% of the total signal, also giving a negative result, but much closer to zero and with much less error. An illustration of the extent of thermal background for the nitrous oxide test can be seen in Figure 8.1.
Figure 8.1: Raw data points for the N₂O test showing measured nitrogen gas concentration, thermal background, gamma contribution, and net neutron production. Notice how large the background is compared to the total signal at high temperature.

Thermal background of nitrogen gas is dependent on the hottest component of the apparatus, which is a heater outlet. In order to properly measure thermal background, the experiment must be performed with the reactor off with the same heater outlet temperature and irradiation temperature. Due to time constraints and the difficulty to cool the apparatus, this cannot be performed before a run. Because of decay and delayed gamma contribution, this is also not possible after a run, while still at temperature. The only way to measure the background is to repeat an experiment on a separate day with the reactor off, meaning there may be error associated with the background because the conditions are not completely repeatable. At and above 380°C, the error in the background for N₂O experiment is too high to accurately report a G-value, although the
380° C value is considered to be a reasonable estimate because it is the average of 20 separate data points taken with different background calculations.

At low temperature, aqueous electrons react with hydronium formed in Eq. 5.5 due to a higher dissociation constant of hydrofluoric acid, which gives low results. At higher temperature, this reaction is not a concern because most of the H₃O⁺ is consumed by HF, which has a low dissociation constant at these temperatures. Nitrous oxide results at low temperature will thus be reported with sulfur hexafluoride results at high temperature.

Results from the sulfur hexafluoride tests are too low at temperatures lower than 380° C. At the time of this writing, there is not proof that the 380° C and 400° C numbers are unaffected by H⁺ in the water, but data and kinetic data suggest this is the case. If so, these values would essentially complete the data set for aqueous electrons. The results of this combination can be seen in Figure 8.2.
Figure 8.2: Aqueous electron results from a combination of $\text{N}_2\text{O}$ and sulfur hexafluoride experiments.

Isobaric Results

The aqueous electron data shows different behavior for neutron and gamma radiation at high temperature. Specifically, neutron data decreases with temperature at low temperature, reaches a local minimum at $350^\circ \text{C}$, a maximum at $380^\circ \text{C}$, and is reduced again at $400^\circ \text{C}$. Gamma G-values increase with temperature at low temperature, reach a minimum at $380^\circ \text{C}$, and are increased again at $400^\circ \text{C}$. Above the pseudo-critical temperature ($383.8^\circ \text{C}$), the neutron production of aqueous electrons essentially reaches zero.

As far as we know, this data is the only experimental data that exists for neutron radiation at supercritical temperatures. Literature values exist for aqueous electron yields
at room and elevated temperatures. Works by different authors predict values of 0.16-0.96x10^{-7} moles/J for aqueous electron yield simulation [11,29,31,58] and 0.45x10^{-7} moles/J for fast reactor radiolysis [78] at 25°C. Our data gives a value of 0.86x10^{-7} moles/J.

A comparison at higher temperatures gives more insight to the agreement of the numbers. Sunyaro et al. predicted a G-value of 0.70x10^{-7} moles/J by simulation at 250°C [80]. Simulations from 285-305°C gave values from 0.42-1.05x10^{-7} moles/J with an average of 0.75x10^{-7} moles/J [11,16,29,58,72]. Our value at 250°C of 0.90±0.45x10^{-7} and at 300°C of 0.21±0.41x10^{-7} moles/J matches these within 1 standard deviation.

**Isothermal Aqueous Electron**

Isothermal results from both the nitrous oxide and sulfur hexafluoride can be compared as seen in Figure 8.3. Similarities exist for the 380°C data between 300 and 450 kg/m³, but do not extend to any other regime of the chart. As seen, the nitrous oxide data is an upside down “u”-shaped curve while the SF₆ data is a right side up “u”-shaped. In the case of the N₂O data, the background nitrogen was 40-80% of the measured signal. The predicted gamma contribution to the signal was then typically greater than the remaining signal, leaving extremely large errors and giving negative numbers. The SF₆ on the other hand had backgrounds of less than 10% and only yielded one negative number at 350 kg/m³. The 400°C data is also fairly close to the gamma G-values and actually matches the gamma G at 400 kg/m³. Since no error has yet been reported for the gamma data, it has not been taken into account for this data, although it should have a
relatively small effect considering the amount of error from the rest of the process of this experiment.

![Isothermal aqueous electron data for neutron and gamma](image)

**Figure 8.3:** G-values for isothermal data for neutrons and gammas. The neutron data is from both the SF$_6$ method and the N$_2$O method.

### 8.3 Hydrogen Radical

The hydrogen radical yield results were reasonable from room temperature up to about 350° C. Literature values suggest 0.35-0.60x10$^{-7}$ moles/J at 25° C [11,29,31,58,78] and 0.32-0.55x10$^{-7}$ moles/J at 250-305° C [11,16,29,58,72,80], consistent with our values of 0.46±0.02x10$^{-7}$ and 0.53±0.12x10$^{-7}$ moles/J at 25° C and 300° C respectively. Values above 300° C are questionable due to the hypothesized radiation catalyzed wall reaction breakdown of alcohol at high temperature, which does not occur under similar conditions with the reactor off.
The extremely high values at and above 350° C are important because they suggest that there may be excess HD and H₂ produced in the low LET experiment also, though to a much lesser extent.

### 8.4 Molecular Hydrogen and CHC

Hydrogen gas results are less reliable than aqueous electrons. All literature suggests that the yield of hydrogen gas should be approximately 1x10⁻⁷ moles/J at 25° C [11,29,31,43,58,78]. The error associated with this value is generally considered to be less than 10%, meaning that our value of 1.95x10⁻⁷ moles/J is far too high. Further evidence has been observed in other tests performed with the water loop that non-radiolysis hydrogen gas is being produced in the experiment that is not produced with the reactor off. At 400° C, the nitrous oxide molecular hydrogen production of 6.5x10⁻⁷ is approaching the limit for the energy deposition of radiation present of 1x10⁻⁶ moles/J due to net dissociation of water (section 8.5).

CHC experiments give more insight into the excess hydrogen formed in the system. The experimental method was to add hydrogen to the feed-water pre-irradiation and measure hydrogen post irradiation. Upon analysis, the added hydrogen pre-irradiation was subtracted from the measured hydrogen to give net radiolytic production of hydrogen in the loop. According to CHC behavior, net hydrogen production (and oxygen production) should constantly decrease with the addition of hydrogen until it is approaches zero [58]. In this experiment, hydrogen produced would lower slightly with small additions of hydrogen and then increased as more hydrogen was added as seen in Figure 7.14. Similar excess production of hydrogen in CHC tests was seen in the Notre Dame tests as well. The conclusion was that like ethanol breakdown, there must be some
kind of radiation induced wall reaction that may have been catalyzed by or involved hydrogen. Also curious was the lack of any oxygen in the post-irradiation water, meaning that the oxygen must also be reacting with the walls.

Low LET molecular hydrogen results from the nitrous oxide experiment are near expected values. Figure 7.14 shows that excess hydrogen is produced in the low LET CHC tests. This data is suggesting that the hypothesized catalytic reaction for the creation of molecular hydrogen needs H\(_2\) to occur, meaning it is a chain reaction. Since the low LET experiment at Notre Dame has a much smaller loop, a chain reaction may not be able to become established based on the speed of the steps and the mixing of hydrogen since the Notre Dame loop irradiation volume is 0.06 mL with a residence time of 0.6 s at 25\(^\circ\) C and 0.1 s at 400\(^\circ\) C (the UW irradiation volume is 7.3 mL with a residence time of 74 s at 25\(^\circ\) C and 12 s at 400\(^\circ\) C). In the case of CHC, hydrogen is in the feed-water of the low LET loop, so the chain reaction would be immediately established. This would explain why excess hydrogen is seen in both tests at UW and only in CHC in Notre Dame.

### 8.5 Net Dissociation of water

The net dissociation of water can be calculated through a summation of either all reducing or all oxidizing agents created by radiolysis. Since reducing agents have been measured in this experiment, the net dissociation of water can be calculated as seen in Eq. 8.1. The results, as a function of temperature from combined phenol and ethanol experiments, can be seen in Figure 8.4. Note the similarity of dissociation at low temperature between neutron and gamma radiation. Due to the hypothesized radiation
catalyzed thermal breakdown of ethanol at high temperature, the high temperature values are very high.

\[ G(-H_2O) = G(\text{oxy}) = G(\text{red}) = G(e^-_{eq}) + G(H) + 2G(H_2) \]

\[ = G(N_2) + G(H_2, \text{phenol}) + G(HD) + G(H_2, \text{ethanol}) \]

**Eq. 8.1**

**Net Dissociation of water at 24.8 bar**

![Net Dissociation of water at 24.8 bar](image)

**Figure 8.4**: The net dissociation of water calculated through summation of all reducing agents detected in the system.

Theoretical limits exist to the net dissociation of water. A value of 12.6 eV is needed to ionize one molecule of gaseous water. It takes 5.17 eV to dissociate one H$_2$O molecule into H and OH. Using the lesser energy for these two dissociation modes (5.17 eV), the absolute maximum dissociation of water is 2.0x10$^{-6}$ moles/J, assuming all energy goes into H-OH dissociation and assuming no recombination. From this, the absolute maximum hydrogen atom population contained in H$_2$ and HD would be 2.0x10$^{-6}$ moles/J. The high temperature ethanol data therefore must be incorrect since the total
dissociation of water is far above $2.0 \times 10^{-6}$ moles/J from $\text{H}_2$ and HD alone. The $\text{N}_2\text{O}$ experiment hydrogen molecule data also seems high, however, is not necessarily above these limits at $0.65 \times 10^{-6}$ moles/J.

**8.6 $\text{H}_2\text{O}_2$ Discussion**

Hydrogen peroxide detection tests showed that only $1.5 \times 10^{-6}$ molar $\text{H}_2\text{O}_2$ was being measured at $100^\circ \text{C}$. Assuming complete breakdown of this $\text{H}_2\text{O}_2$ to $\text{O}_2$ at higher temperature, the mass spectrometer would not be able to read the $0.75 \times 10^{-6}$ signal of oxygen. Therefore, the lack of oxygen in the system is due to some reaction with either the oxidizing radicals or the $\text{H}_2\text{O}_2$ itself, not oxygen.
9 Summary and Comments

9.1 Summary

An experiment was designed and deployed to measure neutron radiation water chemistry data sets from 25-400º C at high pressure. An apparatus was constructed and characterized that could transport water at variable temperature and pressure near the UWNR reactor core and return it for analysis in a controlled manner. Characterization included a radiation energy deposition calibration for neutron and gamma radiation, the specification of chemical conditions for measuring radiolytic species, and the determination of correct methodology for measurement.

Radical yields by spur radiolysis were measured using phenol/N₂O, phenol/SF₆ and ethanol/N₂O solutions. Isobaric data was acquired at 3600 psi (248 bar) from 25º C to 400º C and isothermal at 380º C and 400º C. Aqueous electron data was collected at all conditions. Hydrogen radical data was also collected at all conditions, although above 350º C, a radiation induced breakdown of experimental chemicals created an excess signal that was not indicative of true hydrogen radical yield.

Hydrogen molecular yields were measured in both the phenol/N₂O and the ethanol/N₂O experiments. In all cases, the molecular hydrogen seemed to be plagued by a radiation catalyzed reaction. A way to avoid this reaction and properly measure molecular hydrogen was not achieved in this experiment.

CHC behavior was investigated by measuring the molecular hydrogen produced as a function of hydrogen inserted in the water. This measurement of hydrogen suffered the same problems as the molecular hydrogen measurement. No method could be devised to properly measure CHC.
Excess hydrogen problems in this experiment could not be overcome with the experimental geometry and materials. Recommendations for overcoming these limitations for new designs are included in section 9.3. A summary of results can be seen in Table 9.1. Additional data tables can be found in the appendix, section 11.5.
Table 9.1: A summary of all results from the supercritical water loop experiment at the UWNR.

<table>
<thead>
<tr>
<th></th>
<th>25°C</th>
<th>300°C</th>
<th>380°C</th>
<th>400°C</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>Published Range</td>
<td>Measured</td>
<td>Published Range</td>
<td>Measured</td>
<td>Published Range</td>
</tr>
<tr>
<td>$e_{aq}^-$</td>
<td>0.86 ±0.40</td>
<td>0.16-0.97</td>
<td>0.21 ±0.42</td>
<td>0.43-1.05</td>
<td>0.52 ±0.11</td>
</tr>
<tr>
<td>$H^-$</td>
<td>0.45 ±0.02</td>
<td>0.36-0.61</td>
<td>0.48</td>
<td>0.31-0.52</td>
<td>5.71 None</td>
</tr>
<tr>
<td>$H_2$</td>
<td>1.94</td>
<td>0.86-1.11</td>
<td>2.30</td>
<td>0.92-2.10</td>
<td>3.33 None</td>
</tr>
<tr>
<td>CHC</td>
<td>Could not be measured, no published value above 300°C</td>
<td>Excess hydrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Isothermal: 380/400°C [all values 10⁻⁷ moles/J]

<table>
<thead>
<tr>
<th>Density (kg/m³)</th>
<th>533</th>
<th>516</th>
<th>501</th>
<th>476</th>
<th>443</th>
<th>348</th>
<th>169</th>
<th>Published Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>1.71 ±0.23</td>
<td>1.60 ±0.23</td>
<td>1.16 ±0.21</td>
<td>0.74 ±0.21</td>
<td>0.28 ±0.19</td>
<td>-0.5 ±0.20</td>
<td>0.45 ±0.29</td>
<td>None</td>
<td>380°C</td>
</tr>
<tr>
<td>$e_{aq}^+$</td>
<td>1.30 ±0.23</td>
<td>0.90 ±0.20</td>
<td>0.85 ±0.21</td>
<td>0.60 ±0.19</td>
<td>0.71 ±0.20</td>
<td>0.61 ±0.20</td>
<td>0.37 ±0.21</td>
<td>None</td>
<td>400°C</td>
</tr>
</tbody>
</table>

Table 9.1: A summary of all results from the supercritical water loop experiment at the UWNR.


9.2 Possible Extensions

Gamma Benchmarking

One of the byproducts of this experiment has been the creation of a new inexpensive method of gamma radiation measurement. The applications of the method described in section 5.2 go far beyond the scope of this project. Because of this, efforts are being made within the work performed here to make the analysis more robust, using transportable vials instead of a continuous flow loop so that neutron and gamma radiation information can be measured on other sites, such as research reactor irradiation facilities and any other vial accessible area with a high level of both neutron and gamma radiation.

One such experiment uses a combination of neutron activation analysis and MCNP as outlined in this document in combination with the radiolysis of methyl viologen [74]. This experiment attempted to find a robust dosimeter that could be packaged to measure and separate high doses of neutron and gamma radiation from reactor cores, and was created as a result of the SCW radiation calibration.

SCW Loop Experiments beyond the Scope of this Research

There is other work that could be performed with the SCW loop beyond the scope of this particular project. One such area could be the study of the effect of boric acid, which will exhibit different behavior due to alpha radiolysis, caused by alpha radiation formed by the boron/neutron reaction. If an indirect supercritical reactor design is investigated, boric acid treatment to supercritical water will become a very important experiment; the experiment has been performed for sub-critical water and is discussed in Spinks & Woods [75].
In addition to boric acid, there would be value in analyzing irradiation volume tubing after irradiations to compare the results to tests done in the absence of radiation. An irradiation loop could be designed that contained different test materials to be analyzed under a scanning electron microscope.

9.3 Recommendations for Further Experimentation

Recommendations for the construction of a similar experiment for similar research are as follows:

- It is essential to lower the gamma dose as much as possible and keep the neutron dose high.
- It is hypothesized that the radiation catalyzed molecular hydrogen chain reaction is a wall reaction. This could be minimized by keeping the surface/volume ratio as low as possible. A shorter irradiation volume with a larger diameter would achieve this goal. Ideally, a perfect irradiation volume would have a low surface/volume ratio and have no dead flow. This may also lead to a measurable oxygen concentration for the CHC experiment.
- Keeping the heater as close as possible to the irradiation volume is essential to reach high temperature since a lot of heat is lost in water transport. The further away the final heater is, the higher the maximum temperature in the system is for a given temperature. Of course, the closer the heater is, the more it is activated by the neutron flux, and the more radioactive it becomes.
- A different material such as glass lined tubing might limit wall effects in the irradiation volume
10 References


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27. Elliot, A.J., Ouellette, D.C., Reid, D., McCracken, D.R. (1989). “The g-values of the primary species in 0.4 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} irradiated at 300° C” *Radiat. Phys. Chem.* Vol. 34, No. 5, 747-751.


73. Schmitt, B.J. (2006). *Accounting for core burnup in reactor analysis of the University of Wisconsin nuclear reactor*, University of Wisconsin Thesis (M.S.), Madison WI.
77. Staum, C.J. (2006). *Characterization of gamma radiation fields at the University of Wisconsin nuclear reactor*, University of Wisconsin Thesis (M.S.), Madison WI.


11 Appendix

The following appendix provides supporting material for aspects of this experiment.

11.1 Sodium Experiment Details

The sodium experiment was performed using a $0.01000 \, M$ solution of sodium carbonate ($\text{Na}_2\text{CO}_3$) prepared with solid sodium carbonate 99.95-100.05% pure. The sample was prepared by dissolving 1.0599 g of sodium bicarbonate (mm=1.0599) in 1.000 L of water in a volumetric flask. The solution was run through the apparatus continuously for approximately 25 minutes before the first sample was taken to reach a steady state and to assure the solution has flowed through the entire transport tubing. Samples of approximately 10 mL were taken by timing the collection. The actual sample size was recorded and used for calculation. The pumping speed was calibrated prior to the experiment and was typically 6±0.1 or 10±0.1 mL/min. The measurement was made by measuring the time to fill a 10 mL volumetric multiple times and averaging.

<table>
<thead>
<tr>
<th>Date</th>
<th>Lead Shield</th>
<th>Activity (Bq/sample)</th>
<th>Count Error</th>
<th>Flow Rate</th>
<th>Samples Taken</th>
<th>MCNP Calibration Factor (100eV/g)/(rxn/atom)</th>
<th>Energy Deposition (100 eV/g)* (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/17/2005</td>
<td>Installed</td>
<td>9.26E+03</td>
<td>0.53%</td>
<td>9.950</td>
<td>3</td>
<td>5.38E+26</td>
<td>4.26E+09</td>
</tr>
<tr>
<td>2/16/2006</td>
<td>Not Installed</td>
<td>1.99E+04</td>
<td>0.25%</td>
<td>5.918</td>
<td>10</td>
<td>5.53E+26</td>
<td>9.15E+09</td>
</tr>
<tr>
<td>3/10/2006</td>
<td>Not Installed</td>
<td>1.98E+04</td>
<td>0.20%</td>
<td>6.085</td>
<td>12</td>
<td>5.53E+26</td>
<td>9.33E+09</td>
</tr>
<tr>
<td>2/16 &amp; 3/10 Combined</td>
<td>Not Installed</td>
<td>1.98E+04</td>
<td>0.16%</td>
<td>6.009</td>
<td>22</td>
<td>5.53E+26</td>
<td>9.25E+09</td>
</tr>
</tbody>
</table>

Table 11.1: The results of multiple neutron energy deposition experiments.
Multiple calibrations were performed for neutron energy deposition. The result was that neutron energy deposition was 9.25x10^9 (100eV/g)*(mL/min) without the lead shield and 4.26x10^9 (100eV/g)*(mL/min) with the lead shield installed.

11.2 Error Analysis

**Calculated G-value Errors**

The MC/IRT calculation of G-values for nitrogen at room temperature carries with it error. The neutron G-value error has been estimated as a combination of MCNP error, proton recoil error, oxygen reaction uncertainty and other error to be 10%. Since the neutron subtraction in the gamma calibration is a small portion of the measured product (see section 5.2), total gamma calibration is less than the 10% error of the G-value uncertainty. The gamma G-values and theory is better known and the error has been estimated to be 3%.

**Mass Spectrometer Signal Integration Error**

The integration of the net signal from the mass spectrometer has error associated with it. In order to calculate this integration error, the noise in the signal was measured on a zero signal recording and identified as Gaussian noise. Standard deviations were found to be on the order of 1%.

Since the analyzed piece of data used for results is an integrated number (units=A-s) and the standard deviation is a non-integrated number (units=A), a simulation was used to create an error correlation that includes both the uncertainty of selecting the correct baseline and the uncertainty in the peak. This model created 1000 peaks with
Gaussian error added to an ideal signal with known integral and analyzed each one in the same manner that data is analyzed. The results were that error is a function of two separate factors, the ratio of signal height to baseline and the total integrated function (one relating to baseline noise, and the other to additional signal noise). Full width at half maximum also was a factor. The resulting equation for integration and signal noise error is seen in the following empirical relation:

\[
\text{Error} [%] = \frac{C_o}{\text{FWHM}[s]} \times \frac{\text{BaselineSig}[A]}{\text{MaxSig}[A] - \text{BaselineSig}[A]} \times \text{StDev} [%] + C_{\text{Specie}} \\
C_{\text{Specie}} = 0.179\% \quad (H_2, HD) \\
= 0.131\% \quad (N_2) \\
C_o = 48.3[s] \\
\text{For } \frac{(\text{MaxSig}[A] - \text{BaselineSig}[A])}{\text{BaselineSig}[A] \times \text{StDev} [%]} \geq 3
\]

Eq. 11.1

As expected, the smaller the signal in comparison to the baseline, the larger the error. This formula is only accurate for signal to noise ratios above 3. Below this, the error is underestimated. At S/N=2, the error is underestimated by 46% and at S/N=1, error is underestimated by 79% (Signal/StandardDeviation). Small signals like this are never used except in background subtractions, where a high percent error in the signal would translate to a very small total error in the final signal, as S/N<3 are deemed unacceptable for reported data.

**HPGe Calibration Error**

The high purity germanium detector is calibrated with a europium source in the same geometry that the sodium sample is counted. The calibration reports efficiency as a
function of gamma energy peak. Europium has peaks suitable for calibration at 122, 245, 344, 444, 778, 867, 964, 1112, and 1408 keV. In order to calculate the efficiency at 1368.8 keV, a 2nd order polynomial was used to interpolate between the points 964, 1112, and 1408 keV, which can be seen in the following figure:

![Efficiency curve for North HPGe detector 10mL 4 dram @ 4 cm](image)

**Figure 11.1:** A second order polynomial fit for the europium efficiency calculation curve final 3 points around 1368.6 keV

The values of the data points can be seen in Table 11.2:

<table>
<thead>
<tr>
<th>Peak (keV)</th>
<th>Energy</th>
<th>Efficiency</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>964</td>
<td>0.003889</td>
<td>0.62%</td>
</tr>
<tr>
<td>Eu</td>
<td>1112.05</td>
<td>0.003516</td>
<td>0.65%</td>
</tr>
<tr>
<td>Eu</td>
<td>1407.92</td>
<td>0.002905</td>
<td>0.38%</td>
</tr>
<tr>
<td>Na</td>
<td>1368.8</td>
<td>0.002976</td>
<td>1.26%</td>
</tr>
</tbody>
</table>

(Interpolated)

**Table 11.2:** The efficiency of each peak of the europium calibration and the interpolated value for sodium-24 at 1368.6 keV; counting error is included for the europium peaks and calculated error was included for sodium (Eq. 11.5)
The error for the 1368.6 peak was calculated as an addition of the errors of the three europium peaks (964, 1112.05, and 1407.92) and the interpolation error. The interpolation error calculation is shown in the next section.

**Interpolation Error**

Polynomial interpolation error is defined as

\[
\text{Error} = \left| \frac{f^{(n+1)}(\xi)}{(n+1)!} \prod_{i=0}^{n} (x - x_i) \right|
\]

Eq. 11.2

where \(n\) is the order of the polynomial interpolation, \(f\) is the continuous and \((n+1)\)th order continuous and differentiable equation for the data, \(\xi\) is some number on the smallest interval that contains all points \(x_i\), \(x\) is the interpolated value and \(x_i\) are the data points used. In this case, the former efficiency equation (Eq. 11.3), although not exact, will be used as \(f\), since it still defines the overall behavior of efficiency as a function of energy.

\[
\eta_{\text{HPGe}}(E) = 3.6854 \times 10^{-2} + \frac{3.6045 \times 10^{2}}{E(\text{keV})} + \frac{-2.0779 \times 10^{4}}{(E(\text{keV}))^2}
\]

Eq. 11.3

Therefore:

\[
\text{Error} = \left| \frac{4.987 \times 10^{5}}{\xi^5} - \frac{2.163 \times 10^{3}}{\xi^4} \right| \times \frac{1}{6} \times (1407.92 - 1368.6)(1368.6 - 1112.05)(1368.6 - 964)
\]

Eq. 11.4

The function is a maximum at \(\xi=964\) keV, which yields an error of 7.767x10^{-4}\% or fractional error of 7.767x10^{-6}, which is 0.44\% of the efficiency. The total combined error is calculated in the following equation:
\[
\text{Error} = \sqrt{\sum \text{Error}_i^2} = \sqrt{0.44\%^2 + 0.62\%^2 + 0.65\%^2 + 0.38\%^2} = 1.26\%
\]

Eq. 11.5

The total error of the efficiency of the 1368.6 keV photopeak or the RMS sum of the error of each peak used and the interpolation error has thus been calculated to be 1.26%.

Miscellaneous Error

Other error was estimated in the experiment. Sample size error in the mass spectrometer experiment was estimated to be a combination of 1% error in the pump speed (average error from pumps not always being constant) and 0.1% timing error associated with running the stopwatch to time sample size. This error does not apply to the SF₆ experiment as the electrode reads concentration and not total yield. Error from the MCNP calculation was also included in the final propagation of error.

Propagation of Error

Error was propagated by the sum of squares or RMS method. The dominant error in all signals is the error in the radiation calibration that stems from the error in the neutron G-value.

Error Not Accounted For

One of the complications involved with using a nuclear reactor for a neutron source is that it cannot instantly be turned on and off. Because of this, thermal background data must be taken on a different day than the data is acquired. This data is dependant on the maximum temperature in the system. As the temperature of the shielding increases through the day, the heater outlet temperatures decrease because less
heat is lost in the transport through shielding. The difference in ambient temperature between experimental days and background days causes error in the background subtraction that is extremely difficult to quantify. Because this error is only going to have a large effect in data that has been thrown out (the high temperature aqueous electron data), it was not accounted for. This is why negative values for the 380° C isotherm do not cross zero on the y-axis, even though negative values cannot exist for this experiment (Figure 7.5).

11.3 Safety Analysis

A safety analysis was made prior to running the experiment to show that there would not be issues related to stored energy, temperature, reactivity or radioactivity with respect to the reactor. Many of the numbers and ideas used in the safety analysis were not simplified in a conservative manner. The safety analysis was made for the first design of the experiment, for which many components have changed including, the irradiation volume material from cobalt containing hastelloy to highly pure titanium.

Thermodynamic Safety Analysis

A detailed analysis of the radiation heat loss in the apparatus was performed from the heater, through the lead, through the graphite and boral sections, to the irradiation volume and through half of the irradiation volume. The total heat loss in this transport can then be doubled to calculate the total heat loss outside of the water shielding.

The method was to use a formula from Icropera & DeWitt [36] for radiation heat loss between two concentric cylinders.
In the voided section, the tubing is treated as if it is in the center of the apparatus with no other tubing or device nearby. In reality, the return tubing will act as a thermal shield to a small percentage of the heat loss. The tubing in the lead and the carbon was treated as being in a 1 mm outer diameter tube. Emissivities were chosen for the tubing, the aluminum apparatus, the lead and the carbon as 0.1, 0.5, 0.5 and 1.0. The lead was given the same emissivity as the emissivity because it was poured around aluminum tubing. The hastelloy tubing was given an emissivity of 0.1 because it will be highly polished.

The analysis was performed by dividing up each section into ten subsections of equal temperature and assuming constant properties over that section. The total heat rejected to the apparatus according to this analysis was calculated to be 88 W. The remainder of the heat in the sample water will be transferred to the shielding water which will be cooled by an external heat rejection system.

In addition to the heat generated within the apparatus, there will be radiation heat generated in the shielding. In order to calculate this heating, MCNP tallies for gamma and neutron heating rates were added to the input file. The following gamma and neutron heating rates in Table 11.3 have been calculated in the shielding sections.
Heating at 1 MW

Heating at 1 MW

Heating at 1 MW

Heating at 1.25 MW

Energy for 20 MW-sec pulse

Delta T for pulse

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Mass</th>
<th>Heating at 1 MW</th>
<th>Heating at 1 MW</th>
<th>Heating at 1.25 MW</th>
<th>Energy for 20 MW-sec pulse</th>
<th>Delta T for pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Boral</td>
<td>MeV/g-s</td>
<td>kg</td>
<td>MeV/s</td>
<td>W</td>
<td>W</td>
<td>J/kg</td>
<td>°C</td>
</tr>
<tr>
<td>Neutron</td>
<td>1.50E+08</td>
<td>15.7</td>
<td>2.37x10^12</td>
<td>0.38</td>
<td>0.47</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>Lead</td>
<td>0</td>
<td>99.8</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Carbon/Boral</td>
<td>8.90E+09</td>
<td>15.7</td>
<td>1.40x10^14</td>
<td>22.43</td>
<td>28.04</td>
<td>35.64</td>
<td>0.05</td>
</tr>
<tr>
<td>Gamma</td>
<td>6.90E+06</td>
<td>99.8</td>
<td>6.88x10^11</td>
<td>0.11</td>
<td>0.14</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td></td>
<td>22.92</td>
<td>28.65</td>
<td>36.27</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 11.3: The radiation heating rates in the shielding close to the core. Note the minimal temperature rise in the shielding due to a 20 MW-s pulse

According to this and the section on radiation heat transfer, the maximum heat transferred to the apparatus (at 1.25MW) would be approximately 111 W.

A steady state analysis was done to find the maximum temperature in the lead. The assumptions made in this analysis are that all heat is through centerline of lead (conservative), there is no axial heat transfer, and linear heating (q') is evenly distributed. The inner radius is 0.159 cm and the outer radius is 6.67 cm. According to the results, the radiation heating was 10 W for each tube for a total of 20 W.

These thermodynamic results were determined to be much lower than acceptable limits for the heating of the reactor shield.

**Radioactivity Calculations**

**Apparatus Radioactivity**

There was no radioactivity in experiment before insertion. Radioactivity for one year was calculated using the following formula:

\[ A(t) = A_0 e^{-\lambda t} + \Phi \Sigma (1 - e^{-\lambda t}) \]

Eq. 11.6
The method of calculation was to turn the reactor on for 6 hours, off for 42 hours, on for 6 hours and off for 114 hours for the scheduled operation time (also, on for 8, off for 40, on for 8, off for 112 to simulate 8 hr runs). This was used to simulate a Tuesday/Thursday run schedule.

The values for $\lambda$ and $\Phi\Sigma$ were taken from an internal reactor laboratory document on pneumatic tube activity and can be seen in the following table. Pneumatic tube data was used because MCNP predicted flux at nearest the core to be $2.73 \times 10^{12}$ n/cm$^2$-s $[\pm 0.15\%]$, a value very close to the pneumatic tube value of approximately $3 \times 10^{12}$ n/cm$^2$-s. Also, the pneumatic tube is located immediately below the irradiation area of the apparatus.
Table 11.4: The isotope data used from the UWNR pneumatic tube book.

A sample calculation can for one week of six hour runs can be seen as the following:

$$\lambda = 1 \times 10^{-6} \text{ s}^{-1}; \quad \Phi \Sigma = 1 \times 10^{2} \text{ mCi/g}$$

Reactor on 6 hrs:

$$A(6) = 0 \times e^{-1E-6*(6*3600)} + 1E + 2 \times (1 - e^{1E-6*(6*3600)})$$

Reactor off 42 hrs:

$$A(48) = A(6) \times e^{-1E-6*(42*3600)} + 0 \times (1 - e^{1E-6*(42*3600)})$$

Reactor on 6 hrs:

$$A(54) = A(48) \times e^{-1E-6*(6*3600)} + 1E + 2 \times (1 - e^{1E-6*(6*3600)})$$

Reactor off 114 hrs:

$$A(168) = A(54) \times e^{-1E-6*(114*3600)} + 0 \times (1 - e^{1E-6*(114*3600)})$$

Eq. 11.7

These calculations will assume that the radioactivity produced beyond the neutron shield is negligible. The reasons for this assumption can be seen in Figure 4.14 showing
the flux in different sections. After the shield, the flux has dropped more than 4 orders of magnitude (a factor of 10000).

The analysis will assume $3 \times 10^{12}$ n/cm$^2$-s throughout the entire section of concern. This is considered a conservative value because it is the pneumatic tube flux which is closer to the core than the front of the beam port where the SCW loop components that will be activated are located.

All dose rates in this analysis were estimated using a correlation formula of $Dose(mrem/hr) = 6 \times Act(mCi) \times E_{decay}(MeV)$ formula except for the dose due to Na-24 and Co-60, the primary short and long lived contributors to dose. These were calculated using a more accurate formula from the NBS handbook 80 [86]. Upon final removal, materials will be stored and disposed of according to regulations.

In any run schedule, dose to the individual moving the experiment from activated materials would be minimized by minimizing time in contact with the apparatus, maximizing the distance to the highly radioactive part, and utilizing various shielding. The first method to limit dose is to only remove enough of the apparatus until beam port internal gamma shutter shield can be closed, utilizing the apparatus internal shielding to limit core gamma dose to personnel. Second, since the neutron flux is concentrated in the first meter of the apparatus (see Figure 4.14), the apparatus will be moved on a cart operated on the non-radioactive side to maximize distance from the irradiation volume into a lead shield. This shield is a cylindrical stainless steel structure filled with lead of sufficient size to roll the front end of the apparatus in. It is important to note that the inside of this lead shield could be a high radiation area, so it shall have appropriate signs
and meet requirements of accessibility of high radiation areas if it is over 100 mrem/hr at 30 cm.

Due to the large amount of aluminum in the structure and the cobalt in the hastelloy tubing, Na-24 and Co-60 will be dominating radioactive species within the apparatus. The following is the results of radioactivity for 3 different scenarios; one run per week on Thursday, one week of runs followed by one week off, and two weeks on followed by one week off. All three situations are analyzed because they will all be used together depending on the need for experiment time.

**Once a week schedule**

The once a week run schedule would consist of inserting the apparatus on Wednesday, running with the apparatus in on Thursday and removing it on Monday afternoon. After subsequent runs, the doses will be as seen in the following chart:
Dose on Monday SD time vs time (1 week schedule)

Figure 11.2: The doses from the aluminum and hastelloy at 1 foot in the apparatus on Monday from the Thursday run in rem/hr. This would be at Thursday’s shutdown time. Note the linear build-up due to the long lived Co-60.

The data from the chart can be seen in Table 11.5 below:

<table>
<thead>
<tr>
<th>Runs</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.19</td>
<td>0.12</td>
<td>1.31</td>
<td>1.52</td>
<td>0.16</td>
<td>1.68</td>
</tr>
<tr>
<td>2</td>
<td>1.19</td>
<td>0.18</td>
<td>1.37</td>
<td>1.52</td>
<td>0.24</td>
<td>1.76</td>
</tr>
<tr>
<td>3</td>
<td>1.19</td>
<td>0.24</td>
<td>1.43</td>
<td>1.52</td>
<td>0.31</td>
<td>1.83</td>
</tr>
<tr>
<td>4</td>
<td>1.19</td>
<td>0.29</td>
<td>1.48</td>
<td>1.52</td>
<td>0.38</td>
<td>1.9</td>
</tr>
<tr>
<td>8</td>
<td>1.19</td>
<td>0.48</td>
<td>1.67</td>
<td>1.52</td>
<td>0.64</td>
<td>2.16</td>
</tr>
<tr>
<td>26</td>
<td>1.19</td>
<td>1.2</td>
<td>2.39</td>
<td>1.52</td>
<td>1.6</td>
<td>3.12  (~6 months)</td>
</tr>
</tbody>
</table>

Table 11.5: The doses from the aluminum and hastelloy in the apparatus on Monday from the Thursday run in rem/hr. This would be at Thursday’s shutdown time.

The dose upon removal will be approximately that of the hastelloy tubing alone. This number is dominated by Co-60 that has a half life of over 5 years. It could be replaced at any chosen interval to be sure that radioactive material is kept to a low level.
One week on, one week off for analysis schedule

The one week on schedule will consist of inserting the apparatus on Monday, running Tuesday and Thursday, and removing it on the following Monday.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.19</td>
<td>0.21</td>
<td>1.4</td>
<td>1.52</td>
<td>0.28</td>
<td>1.8</td>
</tr>
<tr>
<td>4</td>
<td>1.19</td>
<td>0.32</td>
<td>1.51</td>
<td>1.52</td>
<td>0.42</td>
<td>1.94</td>
</tr>
<tr>
<td>6</td>
<td>1.19</td>
<td>0.42</td>
<td>1.61</td>
<td>1.52</td>
<td>0.56</td>
<td>2.08</td>
</tr>
<tr>
<td>8</td>
<td>1.19</td>
<td>0.51</td>
<td>1.7</td>
<td>1.52</td>
<td>0.68</td>
<td>2.2</td>
</tr>
<tr>
<td>16</td>
<td>1.19</td>
<td>0.85</td>
<td>2.04</td>
<td>1.52</td>
<td>1.3</td>
<td>2.66</td>
</tr>
<tr>
<td>26</td>
<td>1.19</td>
<td>1.24</td>
<td>2.43</td>
<td>1.52</td>
<td>1.66</td>
<td>3.17  (~6 months)</td>
</tr>
</tbody>
</table>

Table 11.6: The doses from the aluminum and hastelloy at 1 foot in the apparatus on Monday from the Thursday run in rem/hr. This would be at Thursday’s shutdown time.

Two weeks on, one or more weeks off for analysis schedule

The two week on schedule is the equivalent of insertion on Monday, running Tuesday and Thursday followed by running the Tuesday and Thursday of the following week, then removing the following Monday. This would be very similar to insertion on Monday, running Tuesday through Friday, and removing on the following Monday.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
<th>Aluminum</th>
<th>Hastelloy</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.19</td>
<td>0.34</td>
<td>1.53</td>
<td>1.52</td>
<td>0.45</td>
<td>1.97</td>
</tr>
<tr>
<td>8</td>
<td>1.19</td>
<td>0.51</td>
<td>1.7</td>
<td>1.52</td>
<td>0.68</td>
<td>2.20</td>
</tr>
<tr>
<td>16</td>
<td>1.19</td>
<td>0.85</td>
<td>2.04</td>
<td>1.52</td>
<td>1.14</td>
<td>2.66</td>
</tr>
<tr>
<td>26</td>
<td>1.19</td>
<td>1.24</td>
<td>2.43</td>
<td>1.52</td>
<td>1.66</td>
<td>3.18  (~6 months)</td>
</tr>
</tbody>
</table>

Table 11.7: The dose from the tubing at 1 foot in apparatus on Monday from the two weeks of running Tuesday and Thursday.
Analysis

It will be the goal of this project to run for as long as possible up to 2 weeks and remove the apparatus. Two goals will be made here, to run as many subsequent runs as possible (to limit dose to individuals) and to never leave the apparatus in idle (to limit radioactivity produced).

<table>
<thead>
<tr>
<th>Runs</th>
<th>Once a week</th>
<th>One week on</th>
<th>Two weeks on</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.37</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.48</td>
<td>1.51</td>
<td>1.53</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.67</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 11.8: Doses after 4 days for different irradiation schedules according to number of runs.

After one year of decay, an irradiation section that has been in for 4 sessions under any schedule will have a dose rate of 136 mrem/hr (181 mrem/hr for 8 hour runs) at one foot. After one year, an irradiation section that has been in for 8 sessions under any schedule will have a dose rate of 270 mrem/hr (360 mrem/hr for 8 hour runs) at one foot.

The apparatus should not be removed before a 4 day period. The Na-24 dose will be on the order of 30 rem/hr after one day, and 10 rem/hr after two days. In fact, a further decay of two additional days would lower the dose to approximately the dose from the tubing alone.

Upon replacement of the irradiation volume with titanium, the apparatus could be installed for 100s of MW-hrs at a time, removing the limits brought about by the hastelloy. It was left in indefinitely for research and removed for each semi-annual reactor maintenance in order to survey the activation.
A storage facility was designed to be a lead brick housing to sit on casters in order to keep the housing at the same height as the apparatus. This is a stainless steel cylinder filled with lead. The apparatus will go in approximately 41 inches so that the internal lead will help shield the radioactivity. A picture of the shielding house can be seen in Figure 11.3 below:

Figure 11.3: The lead brick housing for the apparatus.

The apparatus cart will be chained to the housing in order to comply with the regulations in 10cfr20.1601 (subpart G) for control of a high radiation area. The total length of the building will be about 57” width of 22” and height of 18”.
According to a simple hand calculation, the flux will be cut down by a factor of more than 3000 taking into account buildup flux on the sides. On the top and bottom, gamma flux will be cut down by a factor 280.

Following the switch from the hastelloy irradiation volume to high purity titanium, there are no limits on irradiation time based on the irradiation volume. In addition to this, there is typically not a high radiation area upon removal of the apparatus from the reactor. The hastelloy analysis was kept in this report for documentation purposes.

**Water Activity**

The water activity was calculated in the same manner as the apparatus. Table 11.9 shows the flow times of the water through the system. The dose in this case was calculated using the \( D = 6 \times mCi \times MeV \) calculation because it was low.

<table>
<thead>
<tr>
<th>Flow (mL/min)</th>
<th>( T_{\text{rad}} ) (s)</th>
<th>( T_{\text{decay}} ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.53</td>
<td>19.31</td>
</tr>
<tr>
<td>3</td>
<td>11.78</td>
<td>64.37</td>
</tr>
<tr>
<td>1</td>
<td>35.33</td>
<td>193.11</td>
</tr>
<tr>
<td>0.3</td>
<td>117.77</td>
<td>643.70</td>
</tr>
<tr>
<td>0.1</td>
<td>353.30</td>
<td>1931.10</td>
</tr>
</tbody>
</table>

**Table 11.9: The flow times in different sections of the apparatus**

In order to estimate the activation, it was assumed that the water is irradiated only in the voided section and decays through the rest of the section. This analysis was done for flows from 0.1 to 10 mL/min, the flows that the system will operate through. Table 11.10 shows the activity produced in the apparatus per gram of water for immediately after irradiation and the decay time before it exits the apparatus.
Following this calculation, a calculation of dose per meter of tubing was made by using the 6*mCi*MeV approximation. These results can be seen in Table 11.11.

Since there will be less than 1 meter of tubing exposed near the experiment operator, dose to him or her will be less than 0.052 mrem/hr at any flow rate. Because of the extremely short half lives of N-16 and O-19, there will not be a problem with release of radioactivity in gaseous form to the environment due to a failure since there will be a long delay time between failure of tubing and release if any to the environment.

**Air Activity Analysis**

The calculation of the activity of the air saturated inside of the water assumed that all gases except N₂O will be saturated at $10^{-3} \, M$, a conservative estimate, and N₂O will be saturated at $2.5 \times 10^{-2} \, M$.

The irradiation and decay times will be the same as the preceding water analysis. The only difference is that there will be an additional time of about 5 minutes for sample
collection and a rejection delay of about 5 minutes due to at least 40 cm of ¼” OD SS tubing on the exit (or a comparable length and diameter combination) of the collection device (not all the water will be sampled at all times). In the analysis then, there will be an additional 5 minutes of decay time added before the gases may be released to the air (there is actually a longer delay time for flows of less than 10 mL/min). Note that if the gases are being sparged out, there will be an additional delay as it travels through the mass spectrometer tubing as well as an effect of becoming more diluted in the sparging gas. If the gas is not being sparged out, it will be released slowly into the air.

<table>
<thead>
<tr>
<th>Vol flow (mL/min)</th>
<th>Activity after irradiation (µCi/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 11.12: The immediate activity of the saturated gas in the water. There is a delay before the experiment operator comes into contact with this gas (see Table 11.13).

<table>
<thead>
<tr>
<th>Volumetric flow (mL/min)</th>
<th>Activity after delay time (µCi/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 11.13: The activity of the gas in the water in µCi/mL.

These values are low and conservative because of the delay for the gases to come out of water freely and the delay and dilution through the mass spectrometer tubing if being sampled.
The conclusion of this analysis is that there will be no issues with gaseous release. Although 10cfr20 has no limitations of N-16 or O-19 releases, the release of Ar-41 is limited to $1E-8 \mu$Ci/mL (which has a similar gamma+beta total energy). When this gas is released, it will be have a much larger volume than that of the volume of water it is contained in since it will become a gas. This will decrease its activity per unit volume.

**Other Concerns**

The eventual disposal was determined to be to keep the radioactive materials under the reactor lab license and store until they can be disposed of by other means (such as regular trash, low level waste disposal, etc). Since the material will stay under the reactor lab license, no authorization for transfer of materials was needed.

No materials in this experiment could off-gas, sublime, volatilize or produce aerosols. The hydrogen and oxygen will both be used at levels that cannot be ignited and will never enter the reactor shield in gaseous form, only in an aqueous form.

**Shielding**

**MCNP Calculation**

In order to calculate the effectiveness of the shielding, an MCNP tally was used. The two different tallies compared the flux of neutrons and gammas between having the apparatus in and having the plugs in. The results can be seen in the following table:
Table 11.14: The effectiveness of shielding according to MCNP calculations. Notice the worse attenuation with the apparatus and the acceptable attenuation levels of the beam stop shielding setup when compared to the shielding of the plugs.

The neutron attenuation of our shielding is better than that of the plugs.

The gamma flux is 2 orders of magnitude above the flux with the beam port plugs in. Because of this, an analysis was done using the shielding tank of water used for the neutron radiolysis experiments. According to this analysis, the hottest spot outside of the shielding is point 3, which is approximately four times hotter than the outside of the beam port plugs. All other points in the analysis have equal or less flux of gamma rays with the shielding. All points of gamma flux measurement can be seen in Figure 11.4 and Figure 11.5.

**Simple Hand Calculation**

Because the analysis of gamma radiation is important, a simple 1-D hand calculation was made. This analysis was meant to give a comparison between the flux outside of the plugs and the flux outside of the apparatus. Because it was a first approximation and build-up factors will be similar for both, build-up factors were not used and the gamma flux out was calculated simply with \( I = I_0 \exp(-\mu l) \). The results can be seen in Table 11.15 below (all fluxes are relative to an initial flux of 1):
Table 11.15: The results of a simple 1-D slab calculation of relative gamma flux.

<table>
<thead>
<tr>
<th>Gamma Energy In (MeV)</th>
<th>Plugs Flux</th>
<th>Apparatus Flux</th>
<th>% Plugs Flux</th>
<th>Shielding Flux</th>
<th>% Plugs Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.04x10^{-26}</td>
<td>9.33x10^{-26}</td>
<td>89.5%</td>
<td>1.89x10^{-47}</td>
<td>0.000%</td>
</tr>
<tr>
<td>1</td>
<td>2.91x10^{-18}</td>
<td>2.83x10^{-17}</td>
<td>97.2%</td>
<td>4.16x10^{-33}</td>
<td>0.000%</td>
</tr>
<tr>
<td>3</td>
<td>1.01x10^{-10}</td>
<td>2.89x10^{-10}</td>
<td>28.6%</td>
<td>3.71x10^{-19}</td>
<td>0.000%</td>
</tr>
<tr>
<td>6</td>
<td>2.14x10^{-08}</td>
<td>2.71x10^{-08}</td>
<td>127%</td>
<td>1.67x10^{-14}</td>
<td>0.008%</td>
</tr>
</tbody>
</table>

The results of the hand calculation support that of the MCNP calculation that the shielding inside of the apparatus will be worse that the shielding within the beam port plugs. It also supports the MCNP calculation that the water tank shielding will be more than sufficient to protect workers from the core gamma radiation.
Figure 11.5: The five different points of gamma flux measurement with the large shielding water tank.

Reactivity Changes Caused by Experiment

The experimental facility was constructed similar to the existing shielding structure for the beam port, therefore it is estimated that there will be little or no effect on reactivity. To ensure this, a calculation of $K_{\text{eff}}$ for the reactor with the existing plugs in and with the apparatus in for the same control rod position was conducted. $K_{\text{eff}}$ was calculated for the reactor with the plugs in and with the apparatus in for the same control rod position using MCNP. $K_{\text{eff}}$ was calculated to be 0.98506 (st err = 0.00005) for having the plugs in and 0.98501 (st err = 0.00005) for having the apparatus in. Table 11.16 below shows the confidence intervals for these results:
<table>
<thead>
<tr>
<th>Description</th>
<th>Confidence</th>
<th>Low</th>
<th>High</th>
<th>Low (%rho)</th>
<th>High (%rho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plugs in</td>
<td>68%</td>
<td>0.98501</td>
<td>0.98511</td>
<td>-0.01522</td>
<td>-0.01512</td>
</tr>
<tr>
<td>keff = 0.98506</td>
<td>95%</td>
<td>0.98495</td>
<td>0.98516</td>
<td>-0.01528</td>
<td>-0.01506</td>
</tr>
<tr>
<td>st err = 0.00005</td>
<td>99%</td>
<td>0.98492</td>
<td>0.9852</td>
<td>-0.01531</td>
<td>-0.01502</td>
</tr>
<tr>
<td>Apparatus in</td>
<td>68%</td>
<td>0.98495</td>
<td>0.98506</td>
<td>-0.01528</td>
<td>-0.01517</td>
</tr>
<tr>
<td>keff = 0.98501</td>
<td>95%</td>
<td>0.9849</td>
<td>0.98511</td>
<td>-0.01533</td>
<td>-0.01512</td>
</tr>
<tr>
<td>st err = 0.00005</td>
<td>99%</td>
<td>0.98487</td>
<td>0.98514</td>
<td>-0.01536</td>
<td>-0.01508</td>
</tr>
<tr>
<td>Water Flood</td>
<td>68%</td>
<td>0.98512</td>
<td>0.98523</td>
<td>-0.01510</td>
<td>-0.01499</td>
</tr>
<tr>
<td>keff = 0.98518</td>
<td>95%</td>
<td>0.98507</td>
<td>0.98528</td>
<td>-0.01516</td>
<td>-0.01494</td>
</tr>
<tr>
<td>st err = 0.00005</td>
<td>99%</td>
<td>0.98504</td>
<td>0.98532</td>
<td>-0.01519</td>
<td>-0.01490</td>
</tr>
</tbody>
</table>

Table 11.16: The $k_{eff}$ values as calculated by MCNP for the beam port plugs, the apparatus, and the apparatus flooded with water.

For a 99% confidence interval, the lowest and highest values of rho are -0.01502 and -0.01536 giving a 99% confidence that the change in reactivity is less than or equal to 0.00034 rho or 0.034% rho falling far below the upper limit of 1.4% rho for a secured experiment and also far below the 0.7% rho limit for any experiment.

In the case that the structure of the facility failed and water could leak in, it could feasibly replace all voided sections. The $k_{eff}$ value was calculated in the same manner as before to be 0.98518 with a standard deviation of 0.00005. Within a 99% confidence interval, this would at most add 0.046% rho and at most take out 0.011% rho of activity. This is much less than the 0.7% rho (the effective beta fraction of the reactor) allowed for a non-secured experiment, assuming the void is not secured.

Radiation Levels

Outside of Experiment

As discussed, the neutron shielding will be comparable to that of the concrete plugs and lead shutter shielding of the core. The gamma dose is expected to be 2 orders of magnitude higher than the theoretical non-streaming gamma dose with the plugs installed.
Because this flux may be at an unacceptable level, an analysis has also been made using the large beam stop shielding (a large tank of water to sit outside of the end of the beam port). This analysis showed that most areas around the beam stop would be much better shielded that with the beam port plugs. One hot spot off to the side of the beam stop is at a level of 4 times the flux with the plugs, which is an acceptable level since the plugs have less than 1 mrem/hr during full power radiation surveys.

Since measurements of flux outside of the beam port plugs during operation is in the region of noise, 100 times this flux may or may not be an acceptable level of radiation. During the first run, a radiation survey will be made without the additional beam stop shielding. This will be done by inserting the apparatus with no irradiation volume (to save on activation) and raising reactor power to 10 kW, 30 kW, 100 kW, 300 kW, and finally, 1000 kW. If the radiation level becomes nearing unacceptable limits at any power level, we will shut down and require the shielding for the design. Following this determination, we will remove the apparatus for the day and store it. This will not be performed on a full power 6 hour run, but instead as a separate run for this purpose only.

Following this initial power run, an external lead shield was constructed as described in section 4.

### 11.4 Note on G-values and g-values

The intra-spur recombination g-values are typically referred to with a lower case “g” and radical yields per energy deposition as “G”, although the terms have also been used interchangeably. In this document, the term “G-value” was used for all yields per energy deposition. Specific G-values were reported as g(species) for intra-spur recombination and G(species) for radicals.
11.5 Selected Tabulated Results

The following are tables of results from experimentation. Each table is likely to be graphically represented in the main text of this manuscript.
## Phenol/N₂O Results

<table>
<thead>
<tr>
<th>Pressure bar</th>
<th>Temp °C</th>
<th>Density kg/m³</th>
<th>$10^{-7}$ moles/J</th>
<th>Error g(H₂)</th>
<th>Error G(e⁻aq)</th>
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</thead>
<tbody>
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<td>1007</td>
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<td>0.86</td>
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Table 11.17: Phenol/N₂O Results
## Phenol/SF₆ Results

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<tr>
<th>Pressure (bar)</th>
<th>Temp (°C)</th>
<th>Density (kg/m³)</th>
<th>$10^{-2}$ moles/J</th>
<th>Error (G(e⁻aq))</th>
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</thead>
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Table 11.18: Phenol/SF₆ Results
## Ethanol Results

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<th>Pressure</th>
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<th>Density Kg/m³</th>
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<th>Error g(H₂)</th>
<th>Error G(H)</th>
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Table 11.19: Ethanol Results
11.6 Specific Equipment Challenges and Solutions

Various equipment failures led to challenging repairs or unusual solutions. Equipment failures that became routine or that could be avoided by a better choice of equipment are documented in the following sections.

HPLC Pump Failure

The HPLC pumps are designed to pump degassed water. Since it is in the nature of this experiment to use gas saturated water, the HPLC pump heads would often cavitate and stop pumping, causing the system to lose pressure. Typically, one head would stop pumping and system pressure would drop to approximately half of the working pressure. At high temperature, this could cause the water to flash from a supercritical liquid to subcritical vapor as it goes to a lower pressure. In order to fix this problem, the system typically had to be returned to atmospheric pressure so that the pumps could be reprimed. At high temperature, the system would have to be cooled first to below 100° C so that no water was boiling at 1 atmosphere. This process could take up to two hours to cool a hot system and reheat it. Since the data acquisition runs lasted only 6-7 hours, this could be up to 1/3 of a day of data lost each time it happened.

Different solutions were applied to fix this problem each time it happened. The first and most simple technique was (1) to tap the pump heads with a wrench to try to free any bubbles caught in the check valves or the head. This would fix the problem about 50% of the time, but the problem would often arise again in approximately one hour. A second fix would be (2) to double the flow rate, which would return the system to
operational pressure (the pressure trace would be noisy since only one head was pumping/refilling). After 30-60 minutes, the system would normally start pumping with both heads due to the higher flow rate, and pumps would have to be returned to optimal flow rate or else they would trip on a high pressure trip. More time consuming fixes included (3) re-priming the pump as mentioned previously, (4) flowing alcohol through the system, (5) ultrasonically cleaning or replacing check valves and most complicated, (6) rebuilding the entire pumps. During the last year of experimentation, a syringe pump was used in data acquisition. The syringe pump never had a failure like the HPLC pumps but the disadvantages included the increased cost, and the inability of one to refill online without a second pump connected to the same controller. A system with four syringe pumps and two controllers would have the ability to mix to water supplies and refill online indefinitely.

**DC Power Supply Failure**

The DC power supply that heated the irradiation volume would fail anytime it was turned on at power, blowing a 20A Bussmann fuse. This was solved by not allowing the machine to be turned on unless all power controls were at a minimum.

**GC Column Flooding**

At times, water would not drain properly from the sample chamber to the waste, causing water to fill in the chamber instead of drain due to increased friction from bubbles in the waste tubing. If not corrected, this would cause water to flow up the sample line and into the gas chromatography column, flooding it. When this happened, the system had to be shut down for the day and the GC column had to be baked out in
reverse. If a bake out in the same direction as water flow was attempted, the friction in the GC column would be too great and no flow would be moving. This created extremely high temperatures and pressures in the column, creating a slightly explosive release when the column became cleared. This was avoided especially because the water in the GC column was potentially radioactive. During a bake out, all of the water that came out was collected and released to the radioactive water hold tank. It would take more than a day to clear all the water from a flooded GC column.

**Mass Spectrometer Settings**

Hydrogen was especially hard to measure in the mass spectrometer because of the high background. A getter or cryogenic pump would have improved this background. An improvement that was made was the idealization of ion source settings, which are presented in Figure 11.6.
Figure 11.6: The ion source settings used to maximize the reading of hydrogen gas in the mass spectrometer

Vacuum Chamber to Atmosphere Accident

A specific accident occurred in the early phases of the experiment where a magnetic stirrer was dropped on a glass ion chamber while the vacuum system was at pressure, sucking glass into the chamber and into the turbo-pump. The turbo-pump needed to be inspected and cleaned, which was performed off-site by a vacuum pump specialist. The rest of the system was disassembled, cleaned and reassembled. The mass spectrometer needed a replacement filament as both the primary and backup burned out during the accident. One was ordered, installed and the cleaned with an ultrasonic
cleaner. A naked ion chamber was ordered as a replacement and inserted inside the stainless steel vacuum chamber so that the accident would not be repeated. Upon reassembly of all pieces, the vacuum system was returned to full working order.

Leaks in the vacuum chamber were detected with helium gas. It is important to note that helium was found to diffuse through Torr Seal ® vacuum epoxy during tests that lasted a long time. If the system was taped inside a bag and helium was added to the outside, the signal for helium would go up slowly, giving a false positive for a leak. Other gases did not leak through the epoxy.

**Sulfur Hexafluoride Poison**

Experience with the sulfur hexafluoride (99.9%) showed that if the gas was bubbled into the source water for more than an hour, the fluoride ion concentration would increase over time for irradiated water in the same condition. This was attributed to some sort of low concentration poison that must be in the sulfur hexafluoride bottle and building up in the water over time. The problem was solved when SF₆ was only bubbled into the water for the first 30 minutes, and a cover gas was left on top for the remainder of the day.

**Nitrogen Leak**

Different sources of nitrogen were found that gave unpredictable and un-repeatable results at times. The most severe of these was a leak in degassers used at one point that would let nitrogen into the feed-water that would slowly lower throughout the day. An example of the signals that were seen during this time can be seen in Figure
11.7. After the degassers were removed, the nitrogen signal was constant from day to day with no trend up or down with time.

![Molarity produced at room Temperature](image)

**Figure 11.7:** An example of unstable data due to a leak of nitrogen gas into the feed-water of the apparatus. The error in nitrogen is repeated over 2 days.

Ethanol data was acquired and analyzed on 380° C and 400° C isotherms. As is the case with the isobaric results, the yields are unrealistically high, giving more evidence of a breakdown of ethanol at high temperature in the water. The results are even more extreme at lower densities, giving results on the order of $3 \times 10^{-6}$ moles/J at 125 kg/m$^3$ at 400° C. Due to the bond strength of water molecules, $G(H) + G(H_2) + G(e^{-}_{aq})$ should be less than $2 \times 10^{-6}$ moles/J.
Figure 11.8: Ethanol Isothermal results for 380° C and 400° C.

11.7 Experimental Record

The following table is an irradiation record of the apparatus in MW-hrs as a function of time through the lifetime of the experiment. The total irradiation received was 910.43 MW-hrs over the lifetime of the experiment.
<table>
<thead>
<tr>
<th>Month</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>N/A</td>
<td>0.00</td>
<td>0.00</td>
<td>2.08</td>
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<tr>
<td>February</td>
<td>N/A</td>
<td>24.12</td>
<td>37.92</td>
<td>41.04</td>
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<tr>
<td>March</td>
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<td>31.80</td>
<td>29.55</td>
<td>30.07</td>
</tr>
<tr>
<td>April</td>
<td>14.40</td>
<td>0.00</td>
<td>68.22</td>
<td>21.93</td>
</tr>
<tr>
<td>May</td>
<td>6.00</td>
<td>24.00</td>
<td>18.56</td>
<td>38.00</td>
</tr>
<tr>
<td>June</td>
<td>3.98</td>
<td>21.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>July</td>
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<td>69.97</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>August</td>
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<td>53.00</td>
<td>0.00</td>
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</tr>
<tr>
<td>September</td>
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<td>35.00</td>
<td>0.00</td>
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<tr>
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<td>19.63</td>
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<tr>
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<td>49.55</td>
<td>40.50</td>
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</tr>
<tr>
<td>December</td>
<td>17.00</td>
<td>6.00</td>
<td>34.88</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>177.64</td>
<td>341.12</td>
<td>249.26</td>
<td>142.41</td>
</tr>
</tbody>
</table>

Table 11.20: The irradiation record of the apparatus as a function of time.