

The Use of Sulfur Chloride Systems in the Digestion and Purification of Zircaloy[®] Nuclear Fuel Cladding

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Abstract

The overarching goal of this research has been to develop and understand a low temperature protocol for the digestion of zirconium nuclear fuel cladding. The basic goal will be to reduce the used cladding to low level radiological waste that can be disposed of more easily and at reduced cost. A “blue sky” goal will be to eventually recycle the cladding to reuse in industrial processes.

A hypothesis of this project is that by using various sulfur chloride compounds, Zircaloy[®] can be converted to zirconium(IV) tetrachloride (ZrCl_4) at low temperatures and the purification/decontamination can be accomplished through a crystallization using thionyl chloride or other sulfur chloride reagents. Three sulfur chloride reagents were investigated, thionyl chloride (SOCl_2), sulfur dichloride (SCl_2) and sulfur monochloride (S_2Cl_2). At 150 °C for each of these reactions the speed at which they digest the metal is very different. For SOCl_2 (2.937 g Zr, 1.3 times of excess SOCl_2), 30 – 40 hours; SCl_2 (3.033 g Zr), 28 hours; and S_2Cl_2 (2.950 g Zr, 2.5 times excess of S_2Cl_2), 3 hours.

Recrystallization of ZrCl_4 was accomplished using SOCl_2 and preliminary study of ZrCl_4 in SOCl_2 was conducted. A cloud point technique was used to determine the solubility. This was accomplished by dissolving ZrCl_4 in SOCl_2 then removing SOCl_2 at a specific temperature until crystallization occurred. The solubility was high at high temperature and was very temperature dependent over the range of 0 °C to 50 °C, the solubility increased by a factor of almost 4. Understanding the solubility will aid in the development of a purification strategy due to the high temperature dependence.

Table of Contents

Chapter One: Introduction	1
Chapter Two: Current Strategies.....	7
Chapter Three: Proposed Research	11
Chapter Four: Materials and Methods.....	24
Chapter Five: Results and Discussion	37
Chapter Six: Future Work.....	43
Chapter Seven: Conclusions	45
References	47
Vita	51

List of Figures

Figure 1. Diagram of pressurized water reactor (PWR).	2
Figure 2. Post fission waste includes uranium fuel, Zircaloy [®] cladding, hardware, transuranic and fission products.	3
Figure 3. Zircaloy-4 cladding oxide formation after 75 days in 360 °C water.	6
Figure 4. Simple cartoon of chemical passivation of a metal surface.	8
Figure 5. Schlenk reaction vessel with water condenser.	13
Figure 6. Calculated equilibrium of zirconium/SOCl ₂ digestion as a function of temperature. ..	15
Figure 7. Decomposition plot of SOCl ₂ as a function of temperature.	17
Figure 8. Mole fractions of decomposition products of SOCl ₂ as a function of temperature.	18
Figure 9. Digestion of Zircaloy [®] or zirconium metal in SOCl ₂	25
Figure 10. Digestion of Zircaloy [®] using sulfur and chlorine at 150 °C.	27
Figure 11. Digestion of Zircaloy [®] or Zr metal in sulfur monochloride.	28
Figure 12. Stages of air exposure to black-purple coating on cladding surface.	30
Figure 13. Stages of hydrolysis as a result of degassed water added to flask containing cladding with purple-black layer.	31
Figure 14. (A) Haake A82 recirculating bath, (B) jacketed flask used for temperature-controlled recrystallization.	33
Figure 15. (A) Fully dissolved ZrCl ₄ and (B) initial crystallization.	34
Figure 16. A plot showing the temperature dependence on the solubility of ZrCl ₄ in SOCl ₂	35

Chapter One: Introduction

As technology and industry advance, so does the energy needs of the world. The rate at which energy is consumed has continually increased and consequently the rate at which fossil fuels are burned and greenhouse gases are produced has increased. There is a growing concern about how these processes affect the environment and society is looking to more efficient ways for clean energy production. The nuclear industry is vital for the future of stable energy. While other means of sustainable energy production are investigated, for example, solar or wind power, these technologies are dependent on weather and other environmental factors. The effectiveness of solar and wind energy is dependent on the region, not all areas of the country have constant sunlight or wind. Nuclear power, however, also has its own drawbacks but as a source of constant and stable energy it is more superior to most other energy sources currently being developed. Traditional technologies to produce energy are coal, petroleum and natural gas. According to the EPA, the generation of electricity contributes 28% of the 6,511 million metric tons of CO₂ equivalent greenhouse gases produced annually in the United States.¹ Unlike energy generation from coal and natural gas, the generation of electricity using nuclear reactors is a green process where none to very little greenhouse gases are produced. Nearly 20% of the energy needs in the United States are currently fulfilled by nuclear energy.²

Typical reactors in the United States are either pressurized water reactors or boiling water reactors (Figure 1).³ These reactors utilize fuel rod bundles to facilitate the fission process which heats water, which then produces steam that drives a turbine. The fuel rods are comprised primarily of solid fuel (UO₂) and cladding. After the fission process is complete the waste is more complex than the starting fuel rod; it consists of the fuel, cladding, hardware, transuranic (TRU) waste and fission products (Figure 2).⁴ Twenty-five percent of the waste that

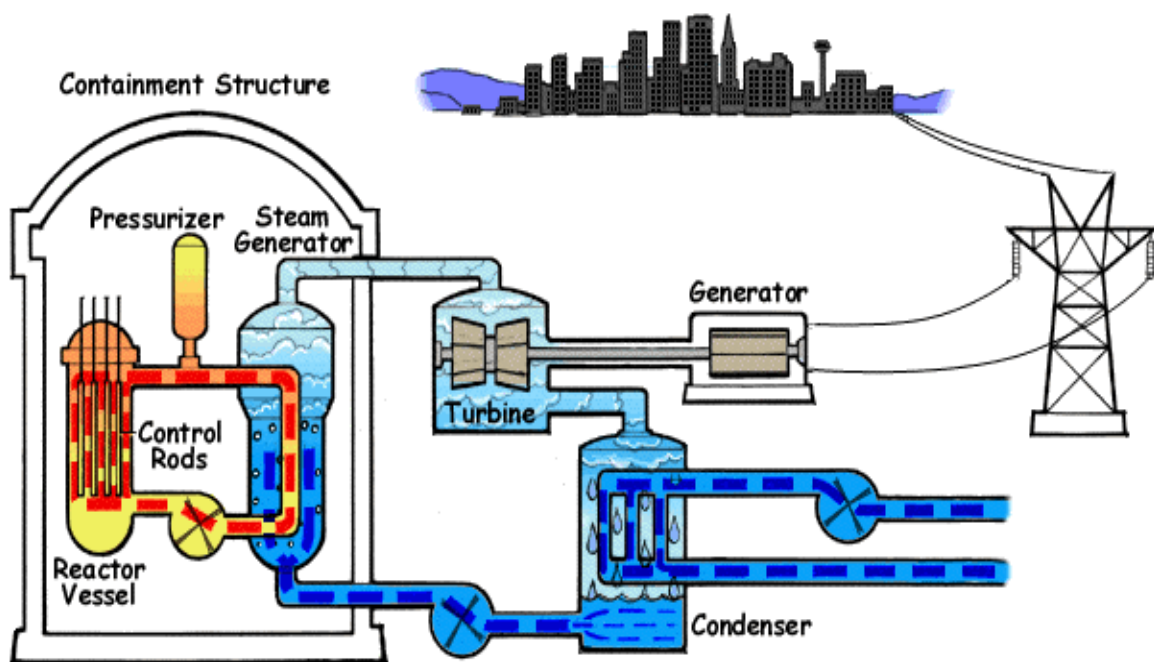


Figure 1. Diagram of pressurized water reactor (PWR).

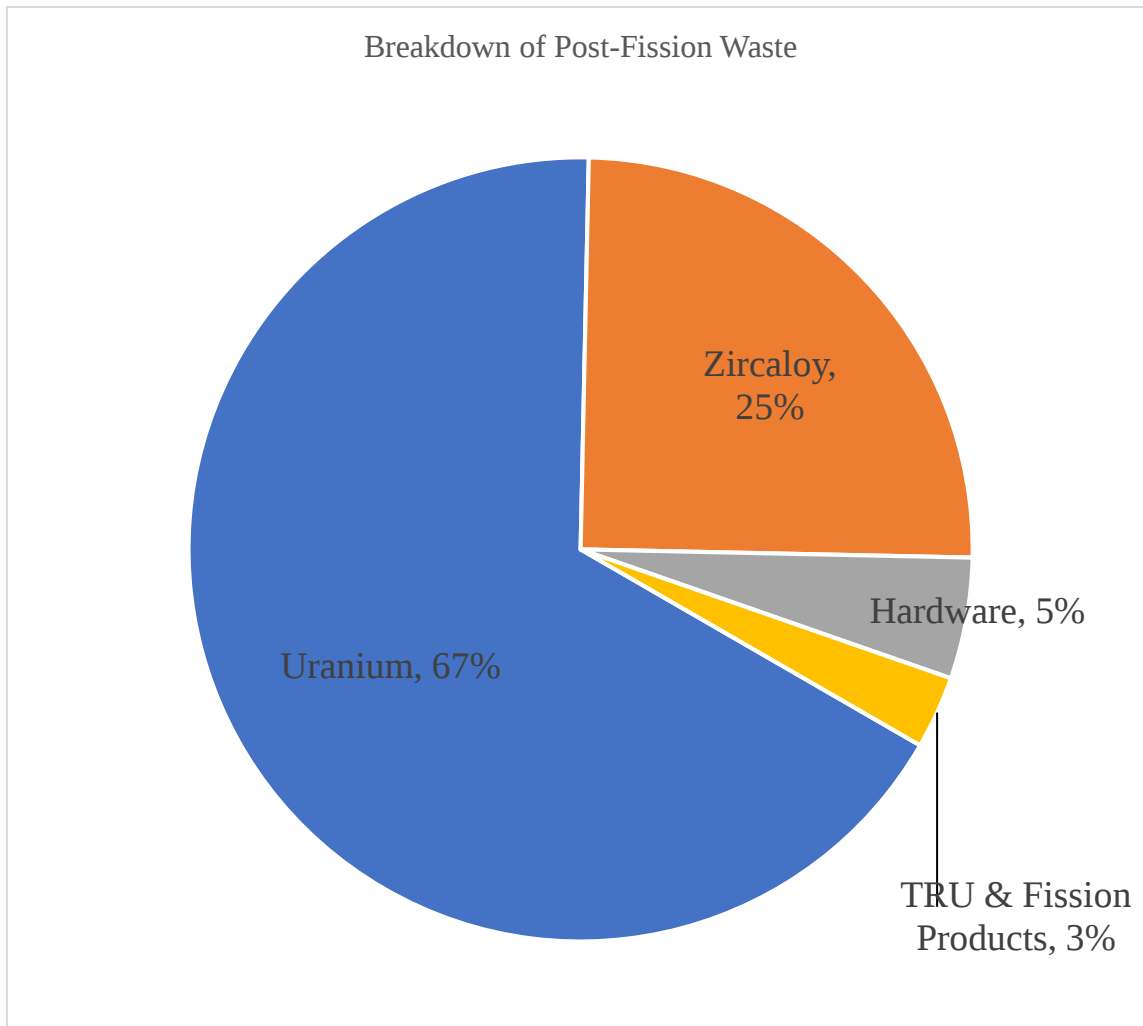


Figure 2. Post fission waste includes uranium fuel, Zircaloy[®] cladding, hardware, transuranic and fission products.

is produced is from used cladding. In 2012, it was estimated that 4000 MT of spent fuel rod waste was produced of which 1000 MT was just the cladding.

An important issue that the nuclear industry has is disposing of its waste. The waste is typically stored on site in large concrete casks or stored underground in geological repositories. Eventually as more waste is produced these storage options will become limited. By developing a recycling strategy this waste can be reduced and its long-term storage avoided.

Recycled cladding could be disposed of as low-level waste or purified and used for a new feed stock for more cladding. Zirconium is used for cladding material due to its inherent corrosion resistivity and low neutron absorbing cross section.⁵ Zirconium is alloyed to improve properties that are useful in the high temperature, high pressure and corrosive environments of the various types of light-water reactors. This alloy is called Zircaloy®. The two main types of cladding are a newer cladding which has niobium and an older cladding with no niobium.⁶ In Table 1, a few of the common cladding compositions are described.⁷

Table 1. Compositions of various Zircaloy® cladding.

Alloys	Contents of elements (%)		
	Nb	Fe	Sn
M5	0.8 – 1.2	0.015 – 0.06	-
Zircaloy-4	-	0.18 – 0.24	1.2 – 1.7
Zirlo™	0.9 – 1.13	0.1	0.9 – 1.2

Zircaloy[®] cladding is produced from low (<100 ppm) hafnium content zirconium.⁷ This zirconium is referred to as nuclear grade zirconium or reactor grade zirconium. Mined zirconium ores has 1-3% hafnium. This hafnium content is due to the similar size and electronic properties of the two metals. The hafnium is undesirable because it has a high neutron absorbing cross section.⁵ The similarities of these two metals make their separation difficult. Producing nuclear grade zirconium is an expensive endeavor and if an effective recycling strategy could be developed, a new source of reactor grade cladding would be available.

After the cladding has been used in a reactor, its composition becomes more complex. Initially, there is only the zirconium and small amounts of alloying elements.⁸ However, after the fission process, typically 1-5 years, where the temperature is >300 °C, the cladding is a mix of the metal alloy and a metal oxide on the inner and outer surfaces, (Figure 3).^{4,9} Another consideration is that trace amounts of the radiologically active species are embedded in the cladding due to the fission process. These radiologically active components would have to be separated from the cladding, contained and then be disposed of properly during the recycling process. While establishing an effective recycling strategy both the metal alloy and metal oxide must be considered.

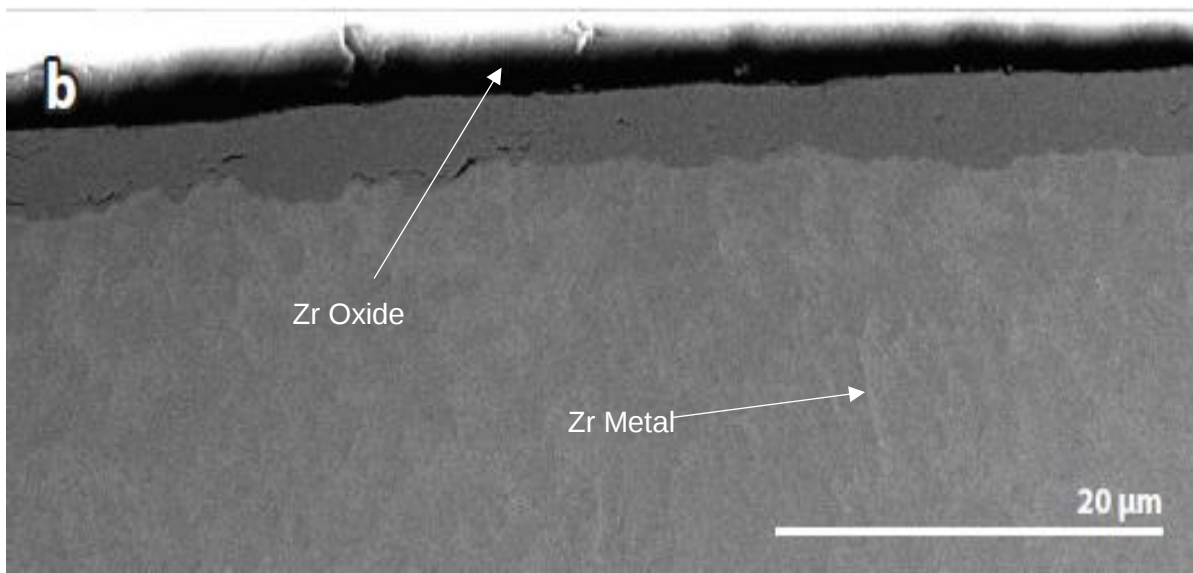
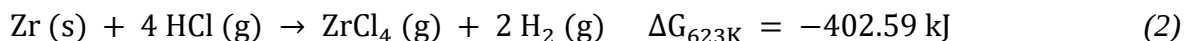
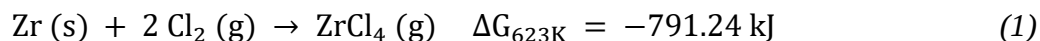


Figure 3. Zircaloy-4 cladding oxide formation after 75 days in 360 °C water.

Chapter Two: Current Strategies

Current strategies for the chlorination and purification involve a direct chlorination or hydrochlorination reaction, either by Cl_2 gas or HCl gas ($350\text{ }^\circ\text{C}$) as shown in Equation 1 and 2.²



Each reaction has its own complications. The Cl_2 reaction produces volatile impurities that can end up being collected with the desired product. In the hydrochlorination reaction, while it does not produce as many volatile impurities, H_2 gas is produced which is dangerous even in small concentrations. Corrosion of the reactor vessel is another complication associated with chlorination reactions conducted at elevated temperatures. The high temperatures of this reaction require that it be conducted in stainless steel reactors. The requirement of high temperature and a chlorine or HCl atmosphere could cause iron chloride contamination.

Another difficulty of the chlorination using Cl_2 or HCl is that the ZrCl_4 product must be purified further. The newly chlorinated Zircaloy[®] maybe purified through a sublimation. This method, while it purifies the material, represents an additional step that must be conducted at elevated temperatures ($>300\text{ }^\circ\text{C}$).

Chlorination reactions on a pristine metal surface proceed purely under thermodynamic considerations. However, pristine metal surfaces do not exist in nature. Most metal surfaces exposed to aerobic environments will have oxide layers present, a few exceptions being gold and silver surfaces. This oxidation of the metal surface could act as a chemical barrier that prevents further oxidation. Also, it could protect the surface from other types of chemical reactions, such as chlorination. A simple cartoon illustrates the passivation concept (Figure 4). Many types of

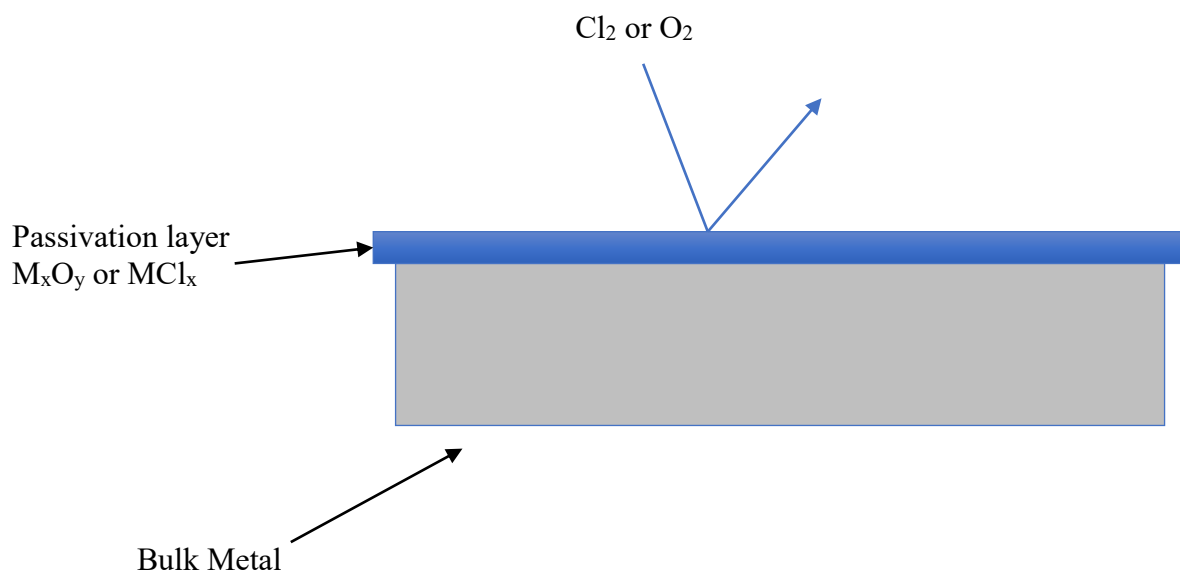
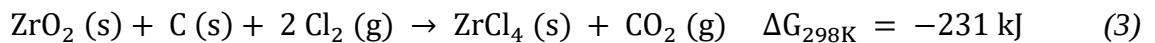


Figure 4. Simple cartoon of chemical passivation of a metal surface.

industrial materials and commercial products are passivated to protect them from harsh operating conditions. In the case of chlorination of Zircaloy[®] surfaces, one way to overcome this passivation is add enough thermal energy to overcome the reaction barrier. However, this increased temperature can increase corrosion to reactors and cause the sublimation of volatile metal chlorides. In the context of SNF cladding, this spread of volatile species that may be radiologically active is highly undesirable.

Understanding the formation of the zirconium oxide layer present on SNF cladding along with its reactions with chlorine will aid in the development of an effective recycling strategy. On the surface of Zircaloy[®] cladding there is typically 1 – 10% by weight of metal oxide present.⁹ After the fuel rod has been in a reactor for a couple of years the inner and outer surfaces form significant oxide layers. For every 1 µm of Zircaloy[®] consumed 1.56 µm of oxide layer is formed, which is called the Pilling-Bedworth ratio.⁹ Ultimately the amount of oxide corrosion present is based on the alloy being used. While different for each type of cladding alloy the oxide formation is constant. ZIRLO and other high niobium alloys show greater resistance to oxidation than claddings without niobium, such as Zircaloy-4. The oxide passivation on SNF cladding may present a challenge in the chlorination protocol for the recycling of Zircaloy[®].

Overcoming the passivation due to metal oxide formation may require different conditions than the chlorination of metal. While metals will chlorinate in the presence of chlorine gas, the reaction of metal oxide with chlorine is more complex. Typically, metal oxide chlorination is accomplished by subjecting the metal oxide to a chlorine stream at elevated temperatures in the presence of a coked carbon source, as shown in Equation 3.¹⁰



Another form of potential passivation is the formation of metal chlorides on a metal surface. This occurs in the preparation of some anhydrous metal chlorides using dry Cl_2 gas, such as cobalt(II) chloride.¹¹ The surface of cobalt becomes covered with a layer of CoCl_2 and the reaction stops. This could potentially occur in the dry chlorination of Zircaloy[®] where $(\text{ZrCl}_x)_n$ layers form on the metal surface and stop the reaction. However, current chlorination strategies are conducted at $>350\text{ }^\circ\text{C}$ where ZrCl_4 is formed and sublimates away presenting new surface for reaction. The high temperatures of these dry chlorination reactions increase the risk of impurities and contaminants being poorly contained. For an effective decontamination and purification recycling strategy the containment of the of radiologically contaminants is of extreme importance.

Chapter Three: Proposed Research

The overarching goal of this thesis is to develop and understand a low temperature protocol for recycling zirconium nuclear fuel cladding utilizing sulfur chloride reagents. This recycling strategy will have two desired outcomes: first, reduce the amount of high-level waste from nuclear reactors and second, provide a new source of nuclear grade zirconium that can be used in industry. A recycling protocol will be developed to reduce the cladding from a high-level waste to low level waste that can be disposed of more easily. Another goal will be the purification of the cladding, this could allow for the reuse of nuclear grade cladding.

A hypothesis of this thesis is that by using various sulfur chloride compounds, the digestion of Zircaloy[®] to form ZrCl_4 can be accomplished at low temperatures. Second, ZrCl_4 can be purified through crystallization using thionyl chloride. Establishing a recycling protocol is an engineering challenge, however understanding the fundamental chemistry taking place can provide further insight into metal-sulfur chloride reactions.

There are three overall aims for this work. The first is to determine which sulfur chloride compounds will be useful in the digestion of zirconium metal and zirconium oxide. These reactions will include thionyl chloride (SOCl_2), sulfur monochloride (S_2Cl_2) and sulfur dichloride (SCl_2) digesting Zr and ZrO_2 to produce ZrCl_4 . The reactions that show promise will be further studied. The second aim is to determine the reaction stoichiometry by which the chlorination occurs. The third aim is to determine the solubility of metal chlorides in S/Cl reagents which is a critical step in obtaining a pure ZrCl_4 product from the digested materials. This information will be used to obtain pure ZrCl_4 in high yields.

The proposed recycling strategy will be conducted at low ($<200\text{ }^{\circ}\text{C}$) temperatures in a gas-liquid phase reactor with the purpose of avoiding some complications in traditional chlorination methods. At the lower temperature the inherent sublimation of ZrCl_4 can be avoided.

Furthermore, conducting these reactions at lower temperatures can open up possibilities for other materials to be used as reaction vessels, such as Teflon based polymers. The use of polymers can limit the amount of contamination due to corrosion of metal-based reaction vessels. The use of a liquid media can aid in containing radiologically active species (Cs, Sb, Sr) that are initially embedded in the cladding surface as a result of the fission process but are released during the digestion reaction. These species presumably are chlorinated and can also sublime and end up in the product which is a serious risk for spread of contamination. The lower temperature of the sulfur chloride digestion should eliminate any sublimation of metal chloride species and the liquid phase zone of the reactor should aid in the better control of the radiologically active contaminants.

The digestion apparatus involves a Schlenk vessel and a simple water condenser Figure 5. The reactions are to be carried out at $200\text{ }^{\circ}\text{C}$. The boiling point of SOCl_2 is $74.6\text{ }^{\circ}\text{C}$, therefore the liquid flash vaporizes and then is condensed. This will create two zones in the vessel, a liquid zone in the bottom where solid products can be dissolved and a vapor zone where SOCl_2 vapor can react at high temperature ($200\text{ }^{\circ}\text{C}$) with the metal surface. When the SOCl_2 condenses then it can dissolve any ZrCl_4 that has formed on the metal surface.

When establishing the recycling protocol, the most effective reaction must be identified.

However, understanding the chemistry of each of the reactions is important. Preliminary results have shown that SOCl_2 , SCl_2 and S_2Cl_2 will digest Zircaloy[®] and zirconium metal. In the context of the recycling strategy we will establish which of these digestions are the “best”. The “best”

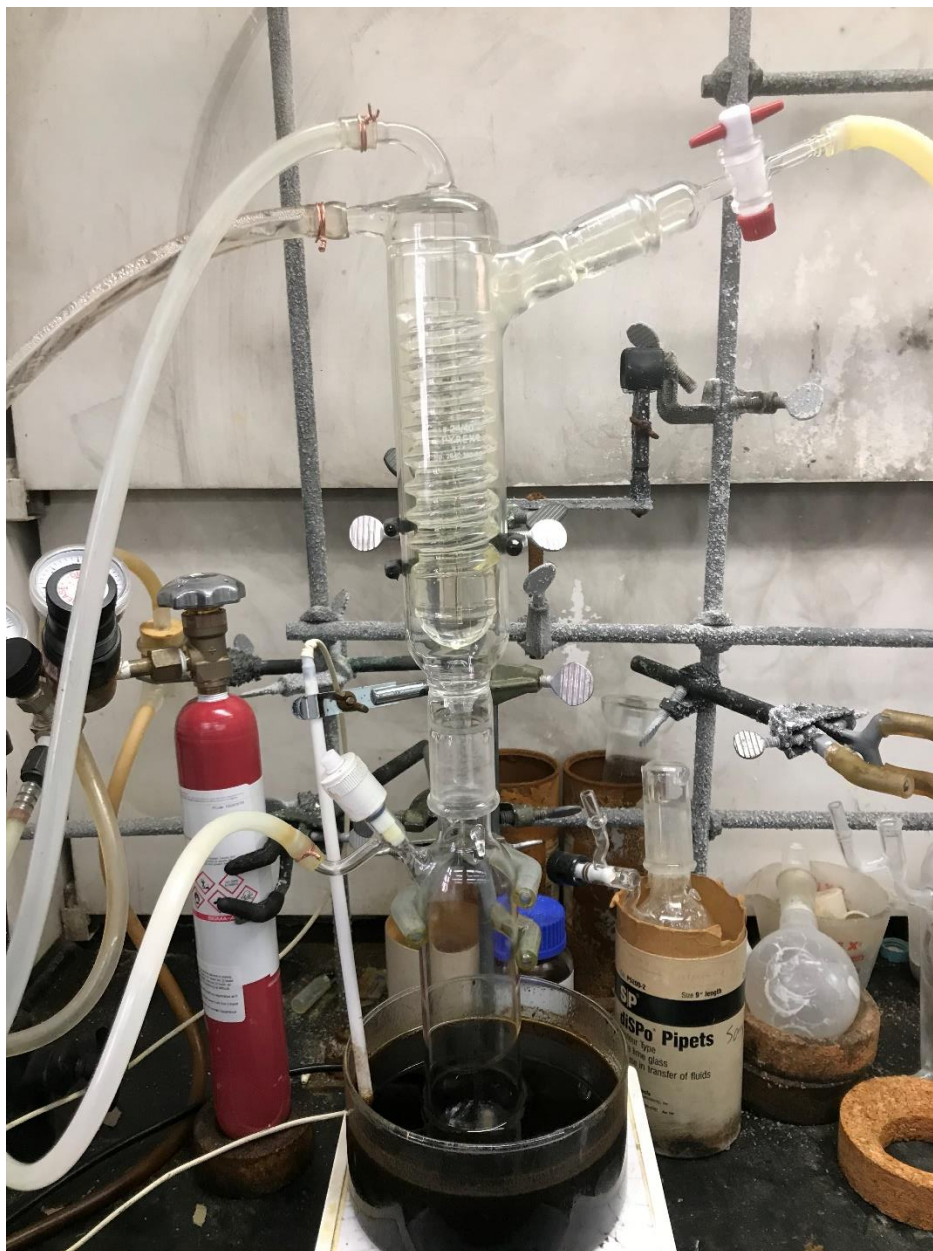
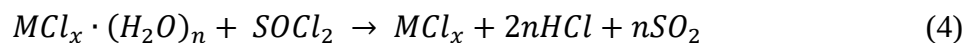


Figure 5. Schlenk reaction vessel with water condenser.

digestion is defined as the one that takes the least amount of time and can be conducted at a temperature at or lower than 200 °C. From an industrial standpoint the lower temperature can allow for other types of reactor materials and will reduce operational costs. The shorter digestion period will also reduce costs and allow for a higher throughput of materials. This best reaction will be the focus of our study, in that we will investigate the products formed and determine a balanced reaction equation.

The first reaction investigated involved thionyl chloride. While low temperature digestions with SOCl₂ should reduce corrosion to chlorination vessels there are other benefits to using SOCl₂. Thionyl chloride has been shown to be capable of dehydrating metal chlorides, shown in Equation 4.¹²



In the context of dehydrating metal chlorides there are some advantages to using SOCl₂. First, in the dehydration process any water in the system should be converted to HCl and SO₂. Therefore, in the chlorination of Zircaloy[®], SOCl₂ can act as a protectant, reducing the need for strict air-sensitive handling. Furthermore, thionyl chloride might prevent hydrolysis of ZrCl₄ to ZrOCl₂. In the preparation of dry metal chlorides, the only products are HCl and dry gases, such as SO₂, which can be easily managed.

The overall focus of our investigations of the reactions is to understand and establish a balanced reaction equation for each. This can be accomplished by investigating the products at the end of the reaction. The starting point for analysis of the SOCl₂ reaction began with a thermodynamic study conducted by a collaborator using NASA CEA software (Figure 6). The study showed the following reaction equation (Equation 5) to be thermodynamically favored at all temperatures

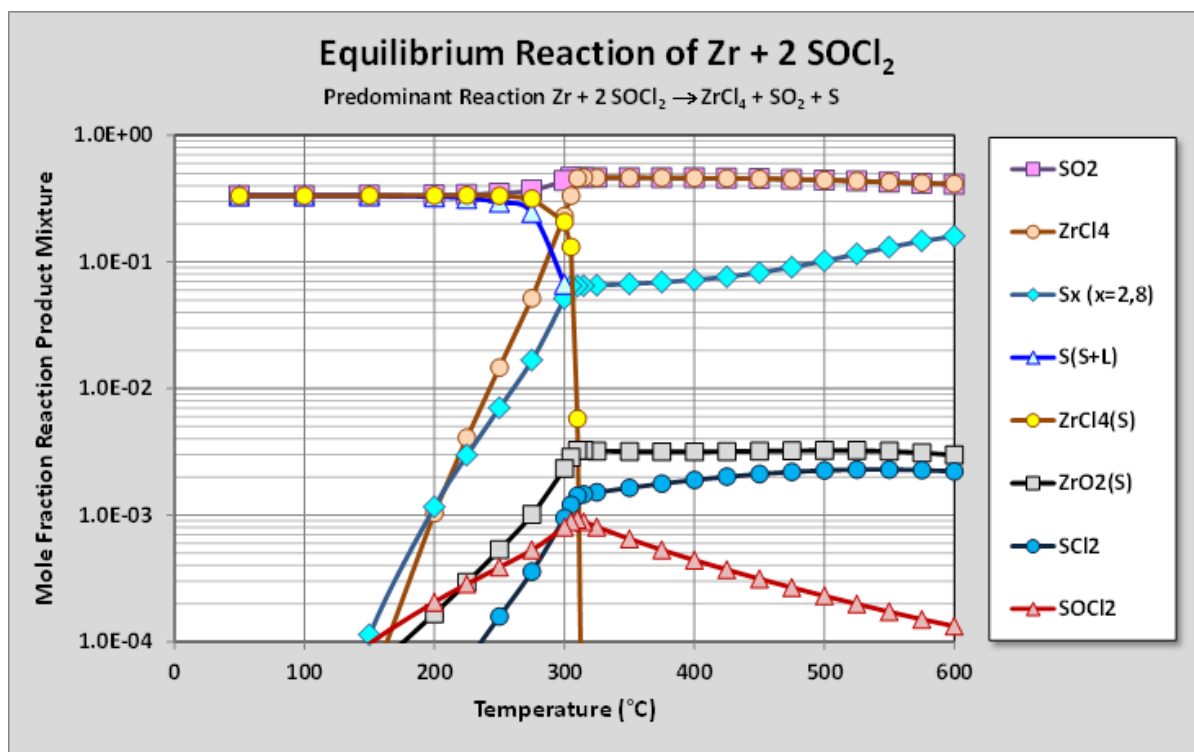
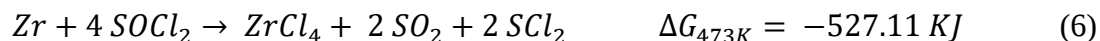


Figure 6. Calculated equilibrium of zirconium/SOCl₂ digestion as a function of temperature.

studied to form $ZrCl_4$. Experimental observations of this reaction show that a few days are required for the reaction to complete at the boiling point of $SOCl_2$ and months at room temperature. The $ZrCl_4$ product sublimes at 330 °C as shown in Figure 6. It is also shown that very small amounts of ZrO_2 and SCl_2 are formed at temperatures greater than 170 °C.



While the thermodynamic study showed one equation, others are also possible, most notably Equation 6.



Although the digestion of the cladding with $SOCl_2$ has been shown to work, its mechanism is unknown, and the specific reaction hasn't been confirmed.

Thionyl chloride is also known to decompose above its boiling point (74.5 °C). Equation 7 shows the decomposition equation and according to thermodynamic calculations, under 200 °C only a small fraction of $SOCl_2$ decomposes, (Figure 7 and Figure 8).

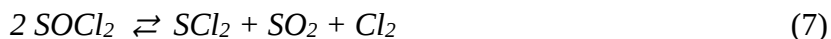


Figure 7 shows the total decomposition of $SOCl_2$ at a range of temperatures and Figure 8 shows the decomposition products.

The possible presence of these decomposition products at the temperatures that will be used in our studies brings into question whether they influence the reaction. It would be reasonable to assume that the presence of Cl_2 could play a role in the conversion of the cladding to $ZrCl_4$. However, the low mole fractions of Cl_2 under these conditions makes it difficult to investigate whether it plays a significant role in the bulk digestion. By combining the reactions of zirconium

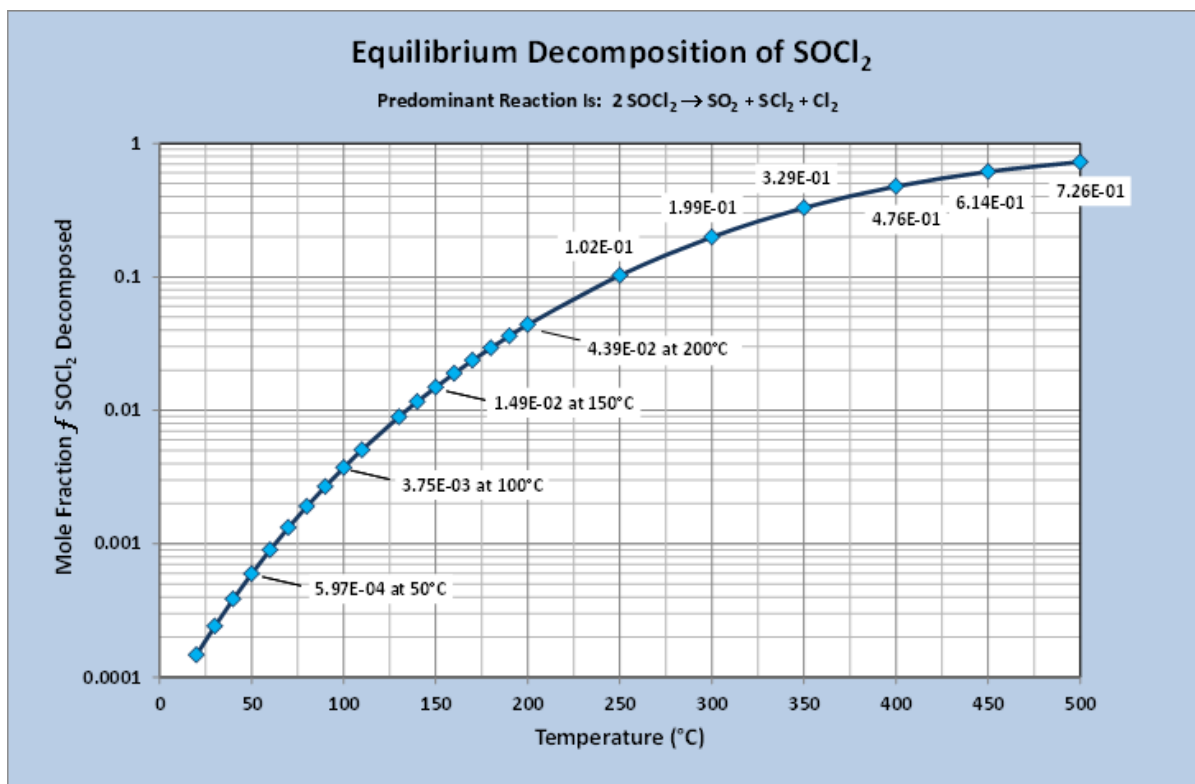


Figure 7. Decomposition plot of SOCl₂ as a function of temperature.

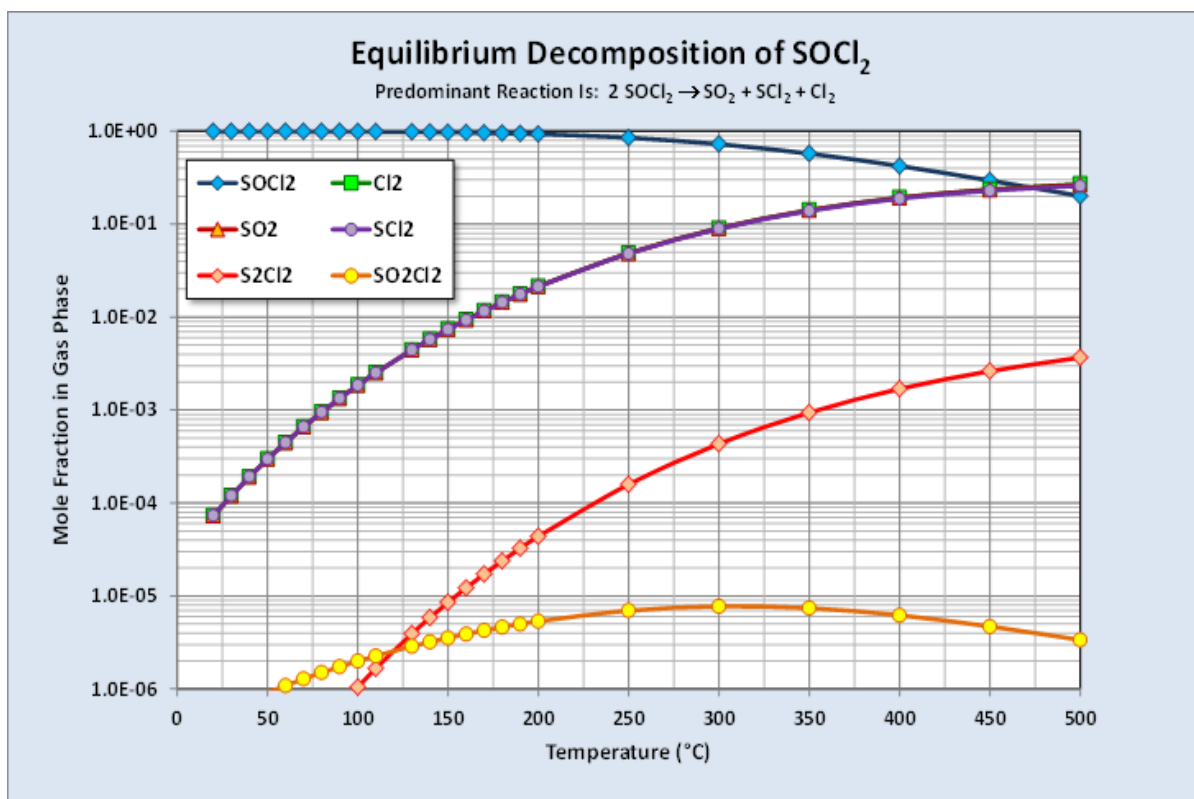
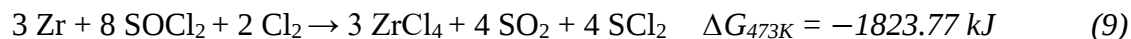


Figure 8. Mole fractions of decomposition products of SOCl_2 as a function of temperature.

metal with SOCl₂ and zirconium metal with Cl₂ (Equation 9), a more efficient digestion may be possible.

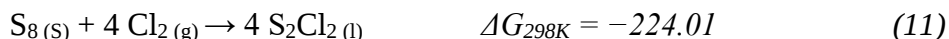


The second of the three sulfur chloride digestions is the reaction of SCl₂ and zirconium metal. Sulfur dichloride is another product of the decomposition of SOCl₂. A challenge in investigating the reaction of SCl₂ and Zr is that it must be conducted in an atmosphere of Cl₂ gas. The requirement of a Cl₂ atmosphere arises because of an equilibrium that exists between SCl₂ and S₂Cl₂ (Equation 10).¹³

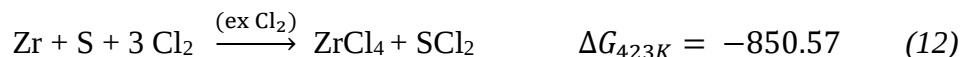


If the reaction were to be conducted in a nitrogen atmosphere, then the SCl₂ will form an equilibrium mixture with S₂Cl₂.

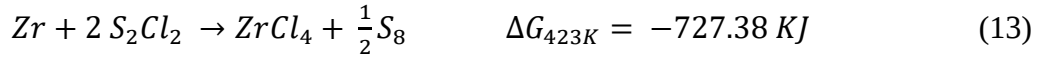
A simple method of testing the SCl₂ reaction will be to react elemental sulfur with Cl₂ above sulfur's melting point (115.2 °C). S₂Cl₂, initially formed, which upon continued exposure to Cl₂, forms SCl₂ (Equation 10 and 11).



The reaction of sulfur, chlorine and cladding will be another reaction that can aid in understanding the chlorination of zirconium metal. The overall reaction is shown in Equation 12, but there will be an intermediate step involving the formation of SCl₂ (Equations 10 and 11).



Finally, the third reaction involves S_2Cl_2 (Equation 13). This species is a result of decomposition of SCl_2 , the reverse of Equation 10. We surmise that if $SOCl_2$ decomposes into SCl_2 and chlorine is removed from the system it will further decompose into S_2Cl_2 . Its presence could also play a role in the digestion of zirconium and Zircaloy[®].



Each of these three reactions will be tested separately to understand how each species interacts with zirconium. Also, the “best” reaction can be determined from these experiments. If there are significant contributions due to decomposition products of $SOCl_2$ then the speeds of the reactions may provide some insight into what is occurring in the chlorination of zirconium in sulfur chloride reagents.

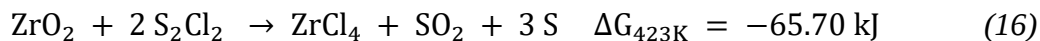
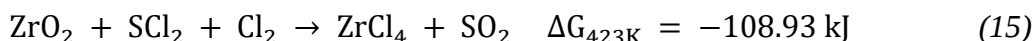
Metal Oxide Chlorination

Due to the complexity of the cladding composition after being in a nuclear reactor the reaction of the ZrO_2 surface is also involved rather than just pure metal chlorination. To chlorinate ZrO_2 there must be a species that binds to oxygen to act as a thermodynamic sink for a favorable reaction. The sulfur in $SOCl_2$ can potentially act as the oxygen binder producing SO_2 . The reactions of various metal oxides with $SOCl_2$ were investigated during the early 1900's.¹⁴ However, the techniques of analysis were not much more than color indication of a specific product. Furthermore, no insight into the mechanism by which $SOCl_2$ chlorinated the metal oxide was presented at that time. The chlorination of ZrO_2 using $SOCl_2$ is given in Equation 14.¹³



Hecht conducted chlorination reactions in sealed quartz tubes heated to 200-250 °C for several days.¹³ Therefore, there is a precedent for the chlorination of ZrO₂ using SOCl₂. However, we need to address how the reaction conditions would need to be altered to conduct the reaction at room pressure.

Other reactions of interest are using SCl₂ and S₂Cl₂ to chlorinate ZrO₂. Equation 15 shows the reaction of ZrO₂ with SCl₂ in the presence of Cl₂. Chlorine gas is required to prevent decomposition of SCl₂ to S₂Cl₂ and it may aid the reaction. The reactions with S₂Cl₂ and SCl₂ (Equation 15 and 16) will be investigated.



Analysis and Characterization

Analyzing these reactions will be challenging; care will need to be taken not to expose them to significant amounts of air or water. Also, the sulfur chloride compounds are rather toxic. The various methods of analysis include gravimetric analysis, ICP-OES, ICP-MS and IR spectroscopies. To analyze the radioactive species, cesium, strontium and antimony, surrogate materials comprised of stable isotope analogues will be used. Using gravimetric analysis, the various products can be estimated as well as when the reaction has reached its end point. Using the assumed reaction stoichiometry, the amounts of product can be predicted, and a mass balance can be obtained.

IR spectrometry will be used to analyze the liquid species during mid- and post-reaction. Each of the sulfur chloride species have differing boiling points, SCl₂ (56 °C), SOCl₂ (74.6 °C) and S₂Cl₂ (138 °C) which may make it possible to separate them by fractional distillation.

However, the decomposition of SCl_2 to S_2Cl_2 occurs readily above the boiling point of SCl_2 . This decomposition will have to be considered in analyzing the concentrations of each of these species. To stabilize SCl_2 during distillation a small amount of phosphorus pentachloride (PCl_5) can be added to the system. As a little as 0.1% PCl_5 has been reported to slow decomposition down to 2-3% after a week.¹⁵ These fractions can be analyzed using IR. Thionyl chloride has S-Cl symmetric and asymmetric stretches between 455-492 cm^{-1} and a S-O symmetric stretch at 1251 cm^{-1} .¹⁶ In SCl_2 samples there is a very strong absorption of S-Cl at 514 cm^{-1} and S_2Cl_2 shows absorptions at 445 cm^{-1} .¹⁷

Purification factors (PFs) will be used to analyze how well the protocol works in reducing impurities from the cladding. ICP-OES and ICP-MS analysis will be used to determine the PFs. By taking the weight percent from the starting material, digested crude Zircaloy[®], and comparing that weight percent to the weight percent of ZrCl_4 product a PF can be obtained (Equation 17).

$$\text{PF} = \frac{\text{wt \% starting material}}{\text{wt \% purified material}} \quad (17)$$

Elements such as zirconium, iron and niobium can be easily analyzed by ICP-OES; however, when using surrogates of the radiologically active species, cesium, strontium and antimony ICP-MS will have to be used. Knowing where each species is located whether it is in the mother liquor or crystal will be important in keeping track of radiologically active species. Also, zirconium tetrachloride's identity can be confirmed by comparing the weight percent of Zr to the weight percent of Cl in a crystal sample.

Purification and Decontamination

The proposed recycling strategy will utilize a crystallization method to purify and decontaminate the chlorinated Zircaloy[®]. The solubility of each of the species present will need to be studied in

each of the chlorinating solvents. The dangers of using radioactive materials will require surrogate materials be used as stand-ins for the radiologically active species: cesium, strontium and antimony. From these data an optimized protocol for the purification can be developed. Establishing solubility curves for each species will allow their yields to be tailored by adjusting a few parameters. Eventually, once purity data are obtained for each species at a given yield, a yield vs purity determination can be made. Of the known species in SNF cladding a few are reported to produce an adduct when dissolved in SOCl_2 . These species include ZrCl_4 , AlCl_3 , UCl_5 and SbCl_5 .^{13,18,19} The other alloying and contaminating species that do not form adducts are expected to either be insoluble, allowing hot filtration prior to crystallization, or soluble, therefore requiring no crystallization. If no crystallization occurs, the precipitated ZrCl_4 can be filtered and washed. The sensitivity of the crystals and solvents will require that various methods of air free and water free solubility experiments be developed.

Chapter Four: Materials and Methods

Materials

Zircaloy[®] cladding was obtained by collaborators from Oak Ridge National Laboratories, this included Zircaloy-4 and a high Nb Zircaloy[®], also used was Zr foil (0.2 mm thick, 99.8% purity) was obtained from Fisher Scientific.

Digestion Reactions

For each of the digestions of Zircaloy[®] or zirconium foil the observations were very similar regardless of the zirconium-based metal used. Photos of the digestions in SOCl₂ initially and when complete are shown in Figure 9.

Zirconium foil Digestion Using SOCl₂ Without Chlorine (200 °C): Zircaloy[®] cladding (2.937 grams, 0.03220 mols) and SOCl₂ (19.91 grams; 0.1674 moles, 1.3 times excess) were added to a Schlenk vessel with a stir bar. The reaction was conducted at 200 °C and took 30-40 hours to complete. The product was dried at room temperature under vacuum for 1-2 hours. After this drying period, the material was broken up and placed under vacuum for an additional 30 minutes. The product was a tan powder, 99.95% yield, based on the ZrCl₄:SOCl₂ adduct. Next, this material was heated in an oil bath at 60 °C under vacuum. This process was done to remove the SOCl₂ from the crystal adduct. The material was dried overnight, the next day the mass was found to be consistent with ZrCl₄ as the only product. The yield was ~100% based on a ZrCl₄ only product.

Zircaloy-4 Digestion Using SOCl₂ With Chlorine (150 °C): Zircaloy[®] cladding (2.783 grams, 0.03051 mols) and SOCl₂ (45.60 grams; 0.3833 moles, 3.1 times excess) were added to a Schlenk vessel with a stir bar. The reaction was carried out at 150 °C in a eutectic salt bath. Once the reaction vessel reached 150 °C a slow chlorine purge began. The reaction was continued until



Figure 9. Digestion of Zircaloy® or zirconium metal in SOCl_2 .

all the visible cladding disappeared and took 20-26 hours to complete. There was a red liquid that persisted while the Cl_2 was administered. The excess SOCl_2 was removed resulting in a tan residue (8.334 g). The mass of the residue exceeded what was expected based (1.225 g, 117%) on a ZrCl_4 only product, this could be a result of not all SOCl_2 removed from the crystal.

Zircaloy® Digestion Using SCl_2 With Chlorine (150 °C): Zircaloy® cladding (3.033 grams, 0.03325 moles) and sulfur (10.145 grams, 0.040 moles) were added to a Schlenk vessel with a stir bar. The reaction was carried out at 150 °C with a slow chlorine purge. The reaction continued until all of the visible cladding disappeared which required 28 hours. The volatiles were removed, resulting in a tan residue (8.825 grams). The mass of the residue exceeded what was expected based on a ZrCl_4 only product. This could be a result of either unreacted sulfur remaining or SCl_2 decomposing into sulfur. The stages of reaction are shown in Figure 10.

As with the digestions in SOCl_2 the observations remained the same between the two S_2Cl_2 digestions and a general figure is shown in Figure 11.

Zircaloy® Digestion Using S_2Cl_2 Without Chlorine (150 °C): Zircaloy® cladding (3.031 grams; 0.03323 moles) and S_2Cl_2 (22.33 grams; 0.1654 moles, 2.5 times excess) were added to a Schlenk vessel with a stir bar. The reaction was carried out at 150 °C. The reaction continued until all the visible cladding disappeared and took approximately 3 hours to complete, each step of the reaction is shown in Figure 11.

Zircaloy® Digestion Using S_2Cl_2 Without Chlorine (200 °C): Zircaloy® cladding (2.950 grams, 0.03234) and S_2Cl_2 (30.980 grams, 0.2294 moles, 3.5 times excess) were added to a Schlenk vessel with a stir bar. The reaction was carried out at 150 °C. The reaction continued when all the visible cladding disappeared and took approximately 3 hours to complete. The

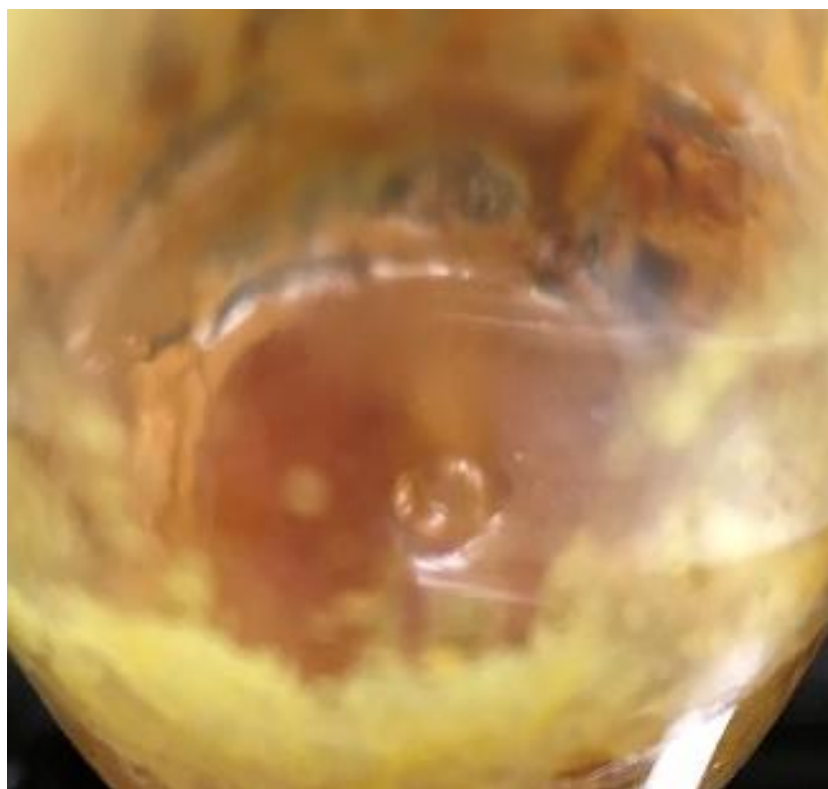


Figure 10. Digestion of Zircaloy® using sulfur and chlorine at 150 °C.



Figure 11. Digestion of Zircaloy® or Zr metal in sulfur monochloride.

excess S_2Cl_2 was removed the residue was dried *in vacuo* at 50 °C resulting in a red residue (11.986 grams). The predicted mass of the residue which we assume contained both ZrCl_4 and sulfur was 11.684 grams. Under the assumption, the yield of this reaction was 102.6%.

ZrO₂ conversion to ZrCl₄ in S₂Cl₂: To a Schlenk flask ~3 grams of ZrO_2 was added to ~20 grams of S_2Cl_2 . The reaction is being conducted at 200 °C. After six hours there did not appear to be any reaction occurring. The reaction was allowed to continue for 3-days then a gravimetric determination was made. According to gravimetric analysis it appeared that no reaction occurred as the mass did not change from the starting mass.

Partial digestion, air exposure: Cladding material (3.192 grams) was digested in S_2Cl_2 (20.73 grams) for ~ 30 minutes then the reaction was stopped. This produced a dark brown black surface coating on the metal. The piece of cladding was then placed on a watch glass and exposed to air. The dark colored material was scraped off using a spatula exposing the surface as shown in Figure 12A. The removed material began to change to a white color and the surface also began to turn white as shown in Figure 12B. This white material on the surface was then scraped off exposing more cladding underneath, as before the cladding surface began to turn a white color. After air exposure for over 30 minutes the white material took on a yellow color as shown in Figure 12C.

Partial digestion then dried under vacuum exposed to degassed DI water: Zirconium metal (3.031 grams) was partially digested in S_2Cl_2 (20.76 grams) for ~30 minutes, a significant purple-black coating was present on cladding surface. A piece of the metal was transferred to a new Schlenk flask and solvent removed *in vacuo* as shown in Figure 13A. While the Schlenk flask was under a flow of nitrogen a small portion of degassed water was added. The reaction of the surface material and water occurred rapidly, and a white material



Figure 12. Stages of air exposure to black-purple coating on cladding surface.

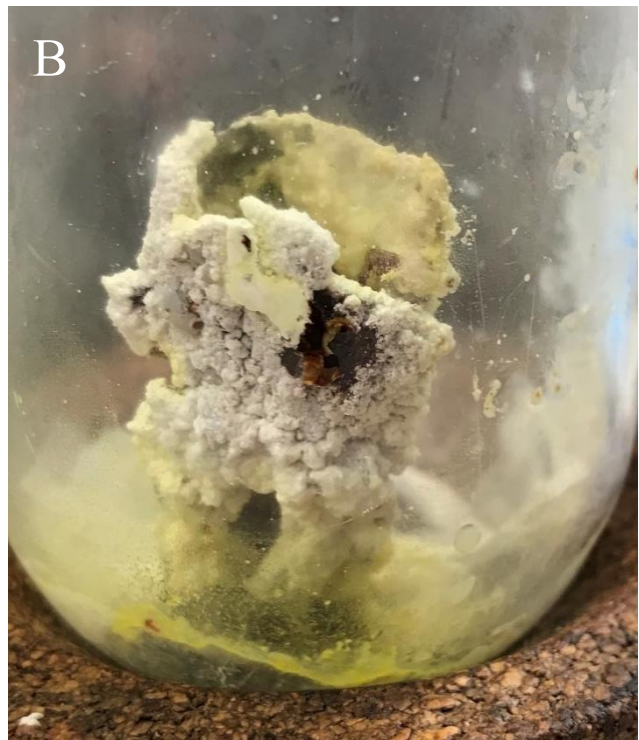


Figure 13. Stages of hydrolysis as a result of degassed water added to flask containing cladding with purple-black layer.

formed show in Figure 13B. After a few more minutes of reaction the purple-black material was converted to a white solid, a yellow solid also formed as shown in Figure 13C.

Preliminary Solubility Studies

Zirconium tetrachloride (9.40 grams) was added to a jacketed Schlenk flask. To this flask SOCl_2 (194.61 grams) was added. A constant temperature recirculating bath using iPOH was connected to the flask shown in Figure 14. After the ZrCl_4 was dissolved then the temperature of the jacket was set to 0 °C. After reaching 0 C the solution was allowed to equilibrate for 10 minutes, shown in Figure 15A. At this temperature and each following temperature, SOCl_2 was removed until crystallization was noticed, shown in Figure 15B. The removed SOCl_2 was weighed for each temperature. For 0 and 10 °C apparent crystallization occurred. For the range of temperatures, 16 to 47.5 °C, a cloud point was observed. In these cases, there was less a less noticeable point of crystallization. The temperature was cycled over a few degrees to determine the range of temperatures at which this cloud point persisted.

Two sets of data are shown in the plot are shown in Figure 16. The blue points reflect the cloud point determination. The red point was determined by saturating SOCl_2 with ZrCl_4 and decanting over some of the solution. This was then dried under vacuum and weighed. Table 2 summarizes the solubility values for both sets of data.

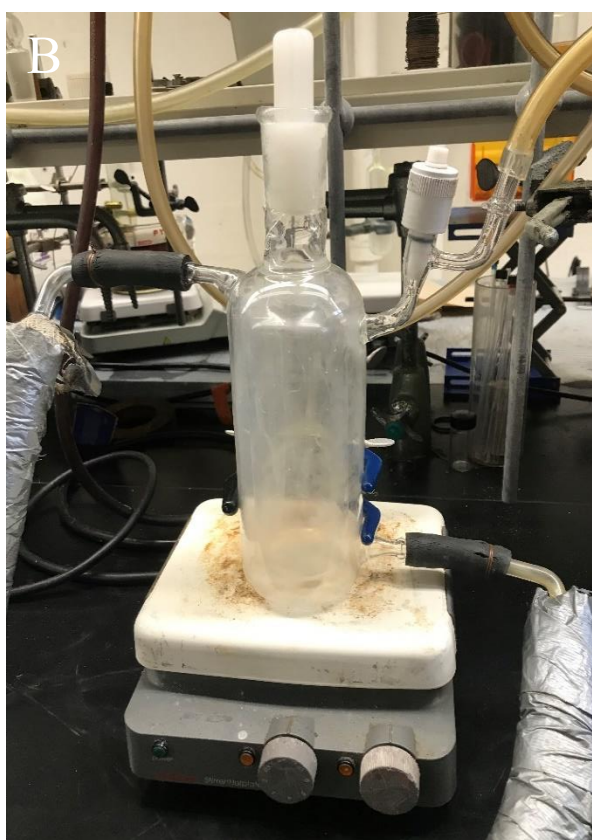


Figure 14. (A) Haake A82 recirculating bath, (B) jacketed flask used for temperature-controlled recrystallization.

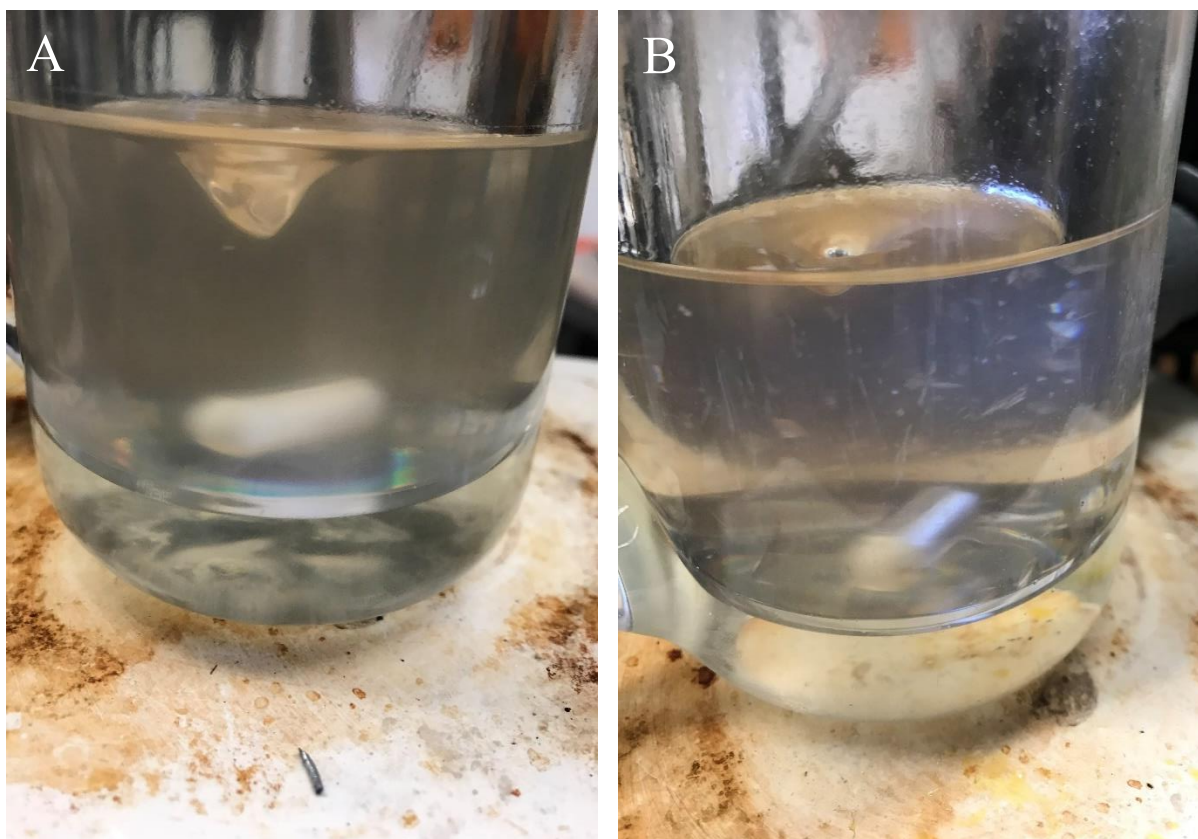


Figure 15. (A) Fully dissolved ZrCl_4 and (B) initial crystallization.

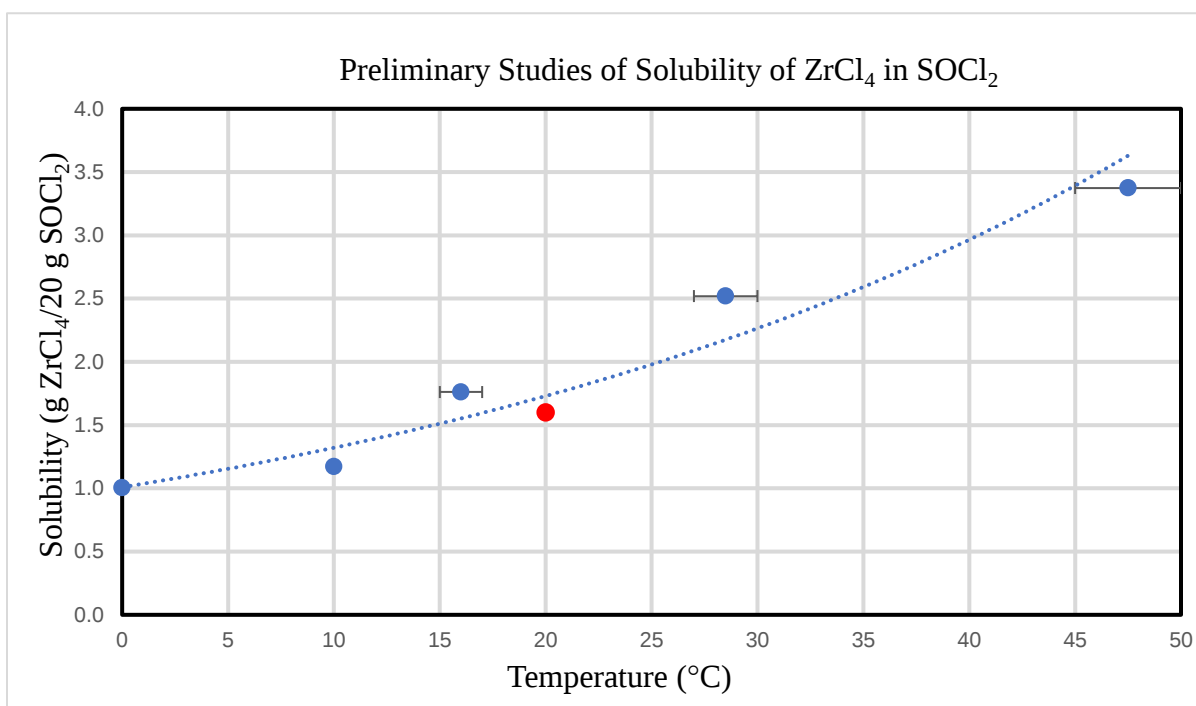


Figure 16. A plot showing the temperature dependence on the solubility of ZrCl_4 in SOCl_2 .

Table 2. Data for the temperature dependent solubility of ZrCl_4 in SOCl_2 .

Temperature	Solubility (grams Zr in 20 grams SOCl_2)	Determination method
0	1.005	Cloud Point
10	1.172	Cloud Point
16	1.761	Cloud Point
20	1.600	Saturation/Gravimetric
28.5	2.520	Cloud Point
47.5	3.374	Cloud Point

Chapter Five: Results and Discussion

Digestions

The initial goal of this research was to identify which of the sulfur chloride digestion reactions could be done the quickest and at a temperature lower than 200 °C. Another goal included identifying the balanced chemical equation for each digestion reaction. All of the initial experiments were conducted using a Zircaloy[®] alloy. This was replaced with a zirconium foil, due to colored iron and niobium chloride species present in Zircaloy[®]. Comparing the digestions of Zircaloy[®] and zirconium foil, no significant differences were observed.

Three digestions in different solvents were investigated at 150 °C; SOCl₂, SCl₂ and S₂Cl₂. The SOCl₂ digestion was the slowest of the three requiring 30 – 40 hours for completion. This reaction was also conducted in the presence of chlorine gas and the speed of the reaction increased slightly, 20 – 26 hours. Using SCl₂ the reaction time decreased further, to about 28 hours. Finally, the reaction involving S₂Cl₂ was the fastest, the total time of digestion was approximately 3 hours. The thionyl chloride and sulfur monochloride reactions were conducted at 200 °C as well. There was not a noticeable decrease in the time for either the SOCl₂ or S₂Cl₂ reactions. The reaction of SOCl₂ at 200 °C was not done in the presence of Cl₂.

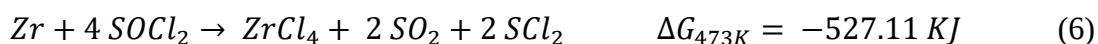
The SOCl₂ and S₂Cl₂ reactions were chosen to study further at 200 °C. The thionyl chloride reaction was chosen because the products were simpler to study compared to the other reactions. For SOCl₂, the only apparent reaction products were ZrCl₄ and volatile species which were easily removed during the reaction and post reaction by drying *in vacuo*. The S₂Cl₂ reaction was chosen because it was the fastest and would be the most viable for industrial processes. The SCl₂ reaction was not chosen for further study because of its intermediate time and possible

complications of post reaction products. Aside from $ZrCl_4$ there were other non-volatile species that are not as easily separated.

Zirconium Metal Digestion in Thionyl Chloride

The thionyl chloride reaction was studied further because of its apparently simple reaction products. One of the products, SO_2 will not condense in a water condenser and therefore leaves through a bubbler. The other potential product, SCl_2 , decomposes at the temperature that the reaction is conducted at and forms Cl_2 and S_2Cl_2 . The Cl_2 leaves the same way as the SO_2 . The S_2Cl_2 remains but is easily removed with the excess $SOCl_2$ when the $ZrCl_4$ is dried.

Based on a thermodynamic analysis of the thionyl chloride reaction sulfur was thought to be a reaction product, possibly from decomposition or reaction. However gravimetrically there is no evidence that sulfur is present. When the $ZrCl_4$ product was dried its weight was compared to that of the weight predicted by the assumed stoichiometry. In this digestion $SOCl_2$ was used and easily forms an adduct. When the excess $SOCl_2$ is removed at room temperature then the $ZrCl_4 \cdot SOCl_2$ adduct remains intact. Gravimetrically this matched what was expected. The $SOCl_2$ can be gently removed by heating to $60\text{ }^\circ\text{C}$ and pulling vacuum on the Schlenk flask. After removing the thionyl chloride from the crystal adduct the mass of the crude $ZrCl_4$ matched that of the mass predicted by the assumed reaction stoichiometry. These results are evidence of two things. First, if sulfur was present then it would show in the gravimetric analysis, because sulfur does not sublime at this temperature and under vacuum. Second, these results support the proposed reaction stoichiometry shown below (Equation 6).



Identification of the ZrCl_4 product was limited to gravimetric analysis and ICP-OES at this stage in the project. Of three potential zirconium species; ZrCl_4 , $\text{ZrOCl}_2 \cdot \text{H}_2\text{O}$ and ZrO_2 , ZrCl_4 is the most likely. One reason for this is that $\text{ZrOCl}_2 \cdot \text{H}_2\text{O}$ has not been reported to exist as a stable species. Upon removal the final water, ZrOCl_2 converts to ZrO_2 releasing HCl . For the formation of ZrO_2 from zirconium metal there would have to be sufficient oxygen present and the only source of oxygen atoms would be from SOCl_2 . However, while the conditions are different, the reaction of ZrO_2 and SOCl_2 produces ZrCl_4 . The final reason for why ZrO_2 and ZrOCl_2 are not formed is that comparing their molar masses the molar mass of ZrCl_4 is greater than the other two species. If there were a mixture of the three species, then the final product mass would be lower than if it were 100% ZrCl_4 . This was not observed to be the case; the final mass is consistent with 100% ZrCl_4 .

ICP-OES compares weight percent of elements analyzed. The relative weight percentage of zirconium and chloride are analyzed to compared to what would be expected for a ZrCl_4 or $\text{ZrCl}_4 \cdot \text{SOCl}_2$ species. For ZrCl_4 , the relative weight percentage of Zr and Cl is 39.2% and 60.9% respectively. For the $\text{ZrCl}_4 \cdot \text{SOCl}_2$ species, the relative weight percentage of Zr and Cl is 25.9% and 60.4% respectively. If ZrO_2 were the product then the mass percent in a sample would be 74.03% and if ZrOCl_2 were the product the mass percent of Zr would be 51.21%. The analysis of ZrCl_4 from a SOCl_2 digestion was inconclusive at this time.

One issue that arose from analyzing the reaction products was separating the excess SOCl_2 from the assumed S_2Cl_2 present. The volatiles removed were a yellow color which is most consistent with S_2Cl_2 , as SCl_2 is red and SOCl_2 is colorless.

Distillation was attempted however there were some complications. Distilling the volatiles using a fractionating column did not separate the SOCl_2 from the species that was giving the yellow

color. A possible explanation for the two liquids co-distilling is due to the two possibly forming an azeotrope. This will make their separation difficult as well as quantifying the amount of possible S_2Cl_2 formed.

There are a few methods for “breaking” an azeotrope. One way is to add an entrainer, this will change the volatility of one of the components of the azeotrope. In some organic synthetic procedures benzene or toluene is added to aid in distilling SOCl_2 post reaction.²⁰ Another method is to distill the thionyl chloride in the presence of diterpene then another distillation using linseed oil.²¹ Ultimately if the SOCl_2 and S_2Cl_2 can be separated in the post digestion volatiles then proposed reaction equation can be supported through gravimetric analysis.

Other forms of analysis such as GC-MS are difficult due to the need for air sensitive handling. There are other complications for various analytical methods. Another useful technique would be ^{91}Zr or ^{33}S NMR, however each of these nuclei have a spin of 3/2 and a quadrupolar moment.

Zirconium Metal Digestion in Sulfur Monochloride

Past digestions of Zircaloy[®] cladding and zirconium metal using S_2Cl_2 have provided interesting results. The most exciting result is that the digestion occurs more rapidly than the digestions in SOCl_2 and SCl_2 . However, the reaction is also interesting due to the products formed post digestion. A volatile red species is observed which can be separated from the rest of the products using vacuum sublimation at low (<60 °C) temperatures. The sublimation of ZrCl_4 occurs readily under vacuum around 80 – 90 °C.

The gravimetric analysis of this reaction showed that the product residue was consistent with the assumption that only ZrCl_4 and S_8 forming. The mass of the dried residue was 11.986 g. Of this mass ZrCl_4 accounts for 7.536 g. The remaining 4.450 g of residue is assumed to be the sulfur

product. The mass of the residue was 102.6% of what was expected. ICP-OES was used to analyze the products from the S_2Cl_2 digestion. While the product residue contains sulfur, the mass percent of Zr remains 39.2 % as the sulfur is insoluble in water. Using ICP-OES the weight percent of zirconium in ZrCl_4 from the S_2Cl_2 digestion was 36.44%. This is further evidence that only ZrCl_4 is formed and helps in confirming the reaction stoichiometry.

Another interesting observation in the S_2Cl_2 digestion is that the surface of the cladding takes on a black-purple color during the digestion. The identity of this black-purple solid is of interest. Our first guess was that it was a zirconium disulfide (ZrS_2). ZrS_2 is a violet-brown solid when dry. Possibly the zirconium is oxidized to zirconium sulfide and then is converted to the chloride. Another possibility is that the black-purple layer is a mixed valent $(\text{ZrCl}_x)_n$ intermediate. Fully oxidized ZrCl_4 has no d electrons therefore it is a white solid. If a partially oxidized Zr-Cl intermediate was present it would have electrons that could allow for a color to be present hence the purple coloring. The colors of partially oxidized ZrCl_x have been reported: ZrCl , metallic grey; ZrCl_2 , brown; and ZrCl_3 , blue-black.²² The behavior and physical properties of a mixed valent $(\text{ZrCl}_x)_n$ intermediate may be different and represent a mixture of all four metal valences.

Two tests were done to understand the black-purple species' reactivity. First, the cladding was removed about 30 minutes after the reaction began, at this point there was a noticeable amount of the black-purple solid on the cladding surface. The cladding was removed from the Schlenk flask exposing it to air and the surface was scraped off using a spatula. After a few minutes the removed material started to turn white and the surface of the cladding began to turn white as well. A yellow solid also formed, this is sulfur from hydrolyzed S_2Cl_2 remaining on the surface.

Second, another partial digestion was conducted, but this time the metal was exposed to degassed H_2O . The metal with the black coating was removed and placed in the Schlenk flask under vacuum to remove any volatile species at room temperature. Then a few milliliters of water was added to the Schlenk flask with the purple-black metal. A reaction forming a white solid and evolving a gas ensued. A yellow solid also formed, this could be due to any remaining S_2Cl_2 on the metal surface.

The observations from both tests do not support the presence of ZrS_2 . Zirconium disulfide has similar stability to that of ZrO_2 and most likely would not react with water. However, these observations would support hydrolysis of a metal chloride to its oxide.

Zirconium dioxide reaction with S_2Cl_2

The digestion of ZrO_2 with hot ($200\text{ }^\circ\text{C}$) S_2Cl_2 was investigated over 3-days gave no sign of reaction. The mass of starting ZrO_2 was similar to that of the solid material after the 3-day period. This suggests that the ZrO_2 remained “untouched” by the S_2Cl_2 . More forcing conditions may be needed to accomplish this conversion at ambient pressure.

Chapter Six: Future Work

The fastest reaction, Zr in S₂Cl₂ (200 °C), was identified and the possible balanced equation (Equation 13) was determined.



Accurately identifying the reaction products of each of these reactions will be a future focus.

Utilizing various techniques and instrumentation the currently unknown species can be identified. This will aid in better understanding the fundamental chemistry of these digestion reactions.

Preliminary solubility studies show that the saturation concentration of ZrCl₄ shows a high temperature coefficient. These solubility experiments will be extended to other metal chlorides, such as those present in virgin cladding and post-fission cladding. The study will continue with SOCl₂ and investigations will also be conducted in other sulfur chloride reagents.

As a part of the overall proposal funded by the DOE the process of digesting cladding will extend to the whole fuel rod. This is where a difference in the kinetic and thermodynamic digestion is expected to occur. The cladding has been shown to chlorinate readily using S₂Cl₂ and taking only a short amount of time. However, a metal oxide, ZrO₂, did not chlorinate readily and under the conditions applied. By taking advantage of the different rates and conditions by which, the total fuel rod is chlorinated; the whole fuel rod can be subjected to a once through chlorination procedure. The total chlorination of the rod would be completed by changing reaction parameters and selectively chlorinating and removing the different species. Another future work is to investigate metal oxide reactions with the sulfur chloride media and apply this to UO_x solid fuel. The chlorination of the solid fuel can lead to decontamination and allow for

lower level of storage. It could also lead to a new reactor fuels used in GEN IV reactors. By taking the used UO_x fuel and converting it to UCl_y the fuel cycle of nuclear reactors can be a closed cycle rather than the open cycle that is currently used today.

Chapter Seven: Conclusions

These initial results show that Zircaloy[®] fuel rod cladding can be chlorinated using sulfur chloride media and the reaction can be accomplished at low (<200 C) temperatures. This will be beneficial compared to the current strategies for the chlorination of this fuel rod cladding. Currently the reaction is done at elevated temperatures and uses chlorine or hydrogen chloride gas. While these methods are effective at the chlorination of metals, in the context of SNF cladding these methods are not ideal. The spread of radionuclides is possible due to sublimation of the metal chloride species at these temperatures. These species must be handled in a controlled and safe manner. Another issue is the damage the steel reaction vessels take from corrosion by Cl₂ and HCl gas. This both introduces increased cost in replacements as well as reintroduces benign contaminated such as iron and chromium.

The work that has begun in this thesis will possible circumvent the issues of the classical chlorination. By conducting the reactions in liquid media, the radiologically active metals can be better handled in liquid waste streams rather than in vapor streams that can be carried to other parts of the chlorination system thereby spreading radioactive contamination. The lower temperatures of the sulfur chloride digestions will reduce sublimation and will allow for chlorination vessels to be made of less reactive materials, such as polymers.

A benefit of using SOCl₂ in these procedures is that it easily forms an adduct with the ZrCl₄ and readily crystallizes. Using crystallization can yield high purity material in high yield. The initial solubility data shows that the ZrCl₄ product can be obtained in high yields just by changing the temperature. Also, the removal of the SOCl₂ adduct is simply accomplished.

By using these protocols, a closed cycle for the cladding can be achieved whereby the used cladding is chlorinated, crystalized and then can be reused in further industrial processes. The

material already contains very low amounts of hafnium and therefore could be used to produce more cladding. This closed cycle can be beneficial to the nuclear industry by reducing costs and making available a new source of cladding. This protocol may also lead to the conversion of HLW to LLW by taking highly contaminated cladding then removing all the radioactive species. This can allow the newly chlorinated Zircaloy[®] to be disposed of in less expensive manners than the high-level Zircaloy[®]. These initial results are encouraging in that a technology may be developed for the purpose of recycling spent nuclear fuel rod cladding.

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Vita

Jordan Travis was born in Frederick, MD to the parents Robert and Kimberly Travis and is the second oldest of fifteen children. He has three children of his own. He graduated high school from the Mason-Dixon Homeschoolers Association in Marion PA. After high school Jordan served in the United States Marine Corps for five years as an Infantryman. After military service he attended Shippensburg University and earned a Bachelor of Science degree in Chemistry in 2017. He then attended the University of Tennessee and work in the Barnes Lab. Jordan Graduated in 2019 with a Master of Science in Inorganic Chemistry then pursued a career in industry.