

INVESTIGATION OF CORROSION MECHANISMS BETWEEN MOLTEN EUTECTIC  
FLINAK SALT AND 316L STAINLESS STEEL

BY

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THESIS

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## Abstract

When designing next generation nuclear reactors, material compatibility is a key component for safety and performance. One of these designs, the Molten Salt Reactor, can use molten eutectic LaF-NaF-KF (FLiNaK) salt as the heat transfer fluid and fuel carrier. Although a nickel-based alloy, Inconel, was originally used during the original Molten Salt Reactor Experiment, to become more economical and simplify material regulatory issues, using stainless steel as the primary containment material has gained interest. Much research has been done to identify the corrosive mechanisms within the stainless steel and FLiNaK system. In this work, the low carbon concentration stainless steel, 316L, was subjected to a static corrosion test of eutectic FLiNaK with varying carbon concentrations, salt purities, and atmospheric conditions for 72 hours at 600°C. The 316L samples were analyzed to determine severity of corrosive attack by measuring mass loss. ICP-OES was performed on each salt sample to identify the corrosion products within the salt and on the containment crucible. Optical Microscopy was used to illustrate differences in corrosive attack between each run. Due to the experimental conditions, many different corrosion mechanisms occurred concurrently. The corrosive mechanisms caused by salt purity, atmospheric purity, and galvanic coupling were observed and discussed in depth.

During the experiment, coupons of 316L stainless steel were contained in nickel crucibles and submerged in FLiNaK salt. To observe the effect metallic impurities have on corrosive intensity, two differently sourced salts were used. One set of samples used salt from Oak Ridge National Laboratory (ORNL) which contains impurity concentrations of calcium (180 ppm) and iron (25 ppm). The second set of samples used salt from Argonne National Laboratory (ANL) which contains larger impurity concentrations of iron (117 ppm) and nickel (179 ppm). Four samples of each salt were made with increasing graphite concentrations to observe the effect

graphite has on mass loss. This experiment was repeated with different furnace atmospheric conditions to establish the consequences of water and oxygen impurities within a fluoride salt system. Run 1 had an atmosphere with greater atmospheric impurities than Run 2. This was done by installing a bubbler on the tube furnace used in the static corrosion experiment for Run 2. Results showed the mass loss in Run 1 being significantly greater than Run 2 across all samples, with less of a disparity between the different purity salts. The no-carbon ORNL sample for Run 1 and Run 2 had a mass loss per square centimeter of  $6.05 \text{ mg/cm}^2$  and  $3.60 \text{ mg/cm}^2$  respectively. Within just the Run 2 samples, the 316L samples exposed to the more impure, ANL salt had an appreciably higher mass loss. The no-carbon ORNL sample and the no-carbon ANL sample had a mass loss per square centimeter of  $3.6 \text{ mg/cm}^2$  and  $5.45 \text{ mg/cm}^2$  respectively. These results provide a clear picture of impurity effects on 316L corrosion with water and oxygen impurities causing intense corrosive attack of 316L and metallic impurities contributing more within a pure atmosphere. Although no definitive conclusions could be drawn about carbon concentrations affecting corrosive attack, being able to see these mechanisms occurring during the same experiment had yet to be done in previous work. Seeing how these mechanisms behave together provides an important look into how the treatment of FLiNaK salt in the preparation and operation of Molten Salt Reactors can increase stainless steel lifetimes within these systems.

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# Chapter 1

## Introduction

As the Earth's population continues to increase, the consumption of energy will continue to rise. Due to the relative abundance and ease of extraction, this energy has historically been created from fossil fuels such as petroleum, natural gas, and coal. Consequently, the reliance on these fossil fuels has induced global climate change through the emission of carbon-based greenhouse gases. Steps are being taken today to reduce carbon emitting energy sources by diversifying the energy portfolio of the world into renewable and low emission sources. These sources can be solar, wind, geothermal, hydro, and nuclear. Nuclear energy is an attractive anchor to the modern low-carbon energy portfolio because of its consistency. A nuclear power plant doesn't need specific environmental conditions to operate at peak capacity, unlike solar and wind. They also are not as limited by geographical features like rivers for hydropower or geologic conditions for geothermal depending upon the design of the reactor. This consistency and versatility necessitate nuclear energy as the baseline for a successful low-carbon emitting energy portfolio. Modern society has seen these benefits and nuclear power is on the resurgence, with a large increase in research and development on novel reactors. These new reactors, Generation IV, will use new technology besides the boiling and pressurized water loops of the current nuclear fleet. One of these Generation IV designs is called the Molten Salt Reactor (MSR), as the name suggests, employs molten salt as a coolant and, within some designs, a fuel carrier. MSR technology has been around for many years, however it has yet to be implemented in a commercial capacity. Many of the early advancements needed to make MSRs viable were finding materials

that would survive long enough in the harsh environment of a molten salt fluid. Although Inconel was designed and found to be very resilient in MSR systems, the economics of creating a large system with Inconel is a roadblock in deploying an MSR reactor. Stainless steel is more economical and already has regulatory certifications needed to be used within a nuclear system. To confidently employ stainless steel into an MSR, the corrosive mechanism between the material and the fluoride salt medium needs to be understood. It has been shown that graphite can enhance corrosion in high carbon 316H stainless steel, but the same study has yet to be done with 316L, the low carbon composition stainless steel. By understanding the effect graphite concentration has on corrosion within 316L, carbon's influence on corrosion within the steel and within the salt medium can be found. This result may influence material choice moving forward in molten salt systems.

# Chapter 2

## Background

### 2.1 History of Molten Salt Reactors

The concept of a molten salt reactor has been around almost as long as nuclear technology. The motivating factor for researching molten salt reactors was the increase in thermodynamic efficiencies. For example, common boiling water reactors (BWRs) and pressurized water reactors (PWRs) operate around 300°C. BWRs and PWRs have operating pressures of around 7.5 MPa and 15 MPa respectively. These correspond to exit coolant temperatures of 286°C and 330°C respectively. Both water-cooled reactors operate in the Rankine cycle, in which a liquid undergoes a phase change into steam, thus expands, and does work on a turbine to create electricity. For BWRs this cycle results in 33% efficiency and for PWRs, this results in 34% efficiency [1]. Molten Salt Reactors operate with higher temperatures, a consequence of the higher melting and boiling temperatures the salts provide. These higher temperatures increase the thermodynamic efficiency of the cycle. MSR also can more easily employ the Brayton cycle within their secondary loops. The Brayton cycle is a single-phase thermodynamic process that utilizes a compressor and a turbine to create electricity. Because the Brayton cycle is single-phase, the temperatures the power-delivering fluid can reach are much higher compared to the Rankine cycle. A common fluid used is Helium. The combination of higher temperatures and Brayton cycle utilization can drive thermodynamic efficiencies up to 48% [2].

With the idea of a reactor that can provide high energy output in smaller infrastructure, in the early 1950s, the Air-Force commissioned Oak-Ridge National Lab to conduct the Aircraft

Reactor Experiment (ARE) with the goal of powering supersonic aircraft with a compact nuclear reactor [3]. The final design goal was for the reactor to generate between 100-300 MW, however the first design operated at 60 MW. The smaller power was to show the feasibility of these reactors and investigate the practical engineering concerns of a novel reactor [5]. A key design feature of the ARE was the use of a fluoride salt as the fuel carrier and as the heat transfer medium.

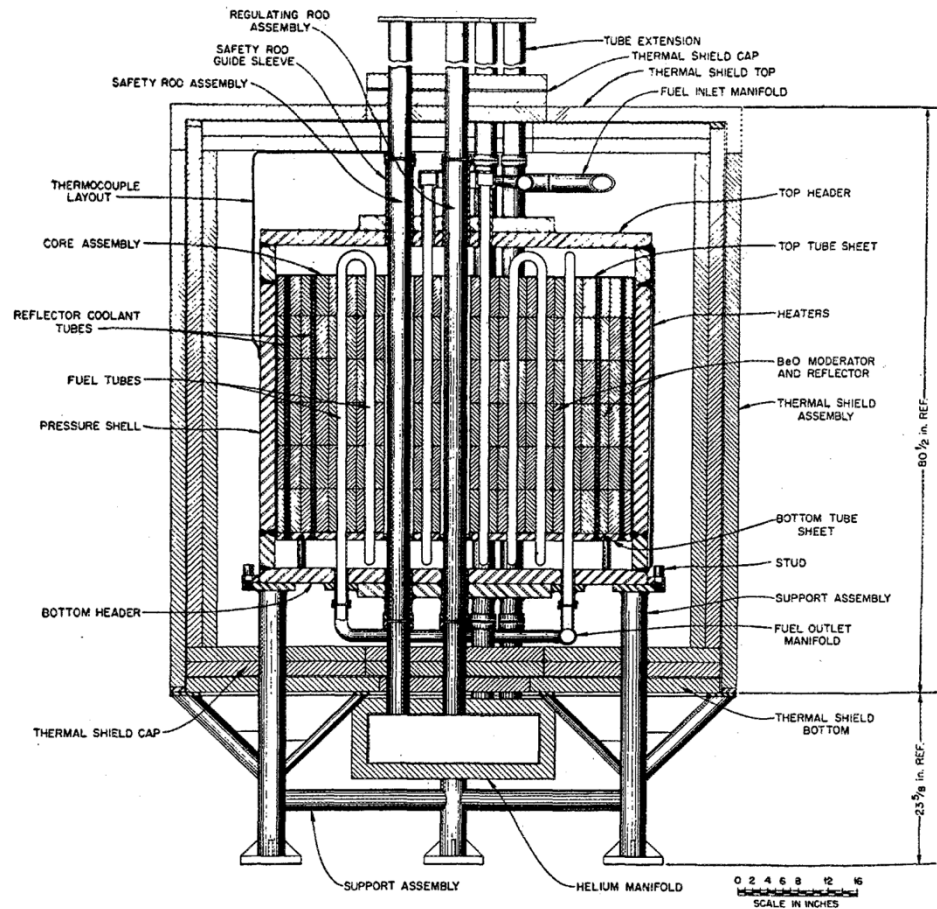


**Figure 1.** Schematic of the Aircraft Reactor Experiment core [4].

Uranium fluorides are highly soluble in fluoride salts [6]. With the fuel being dissolved within the molten salt, the design of the reactor can be simplified in terms of safety, refueling, and fission product removal. The safety of the system is simplified due to the operating pressures being

much lower, around 1 atm. With lower pressures, a breach of the coolant line would not cause a violent leak. This factor combined with the high melting point of the salts would also contribute to the passive safety measures of these reactors. If needed, the salt can be drained to a non-critical geometry storage tank where the salt can cool and solidify, trapping radioactive isotopes in one place. Refueling becomes simplified because the MSR can be refueled while the reactor is still in operation by injecting a freshly reprocessed salt with fissionable isotopes into the salt. Xenon and Krypton, common fission products, can also be removed much more easily because of their gaseous state and low solubility within the molten salt. These fission products can be bubbled out and collected or drawn out through other processes such as gas sparging [7]. With these benefits, the possibility of creating an aircraft fueled by this technology was intriguing. Therefore, the Air Force was eager to be at the leading edge of development for MSRs. The ARE was the original molten salt reactor, developed with a liquid fuel consisting of 53.09 mole % NaF, 40.73 mole %  $\text{ZrF}_4$ , and 6.18 mole %  $\text{UF}_4$  [4]. The ARE was operated at a temperature of around 850 °C. Much research was needed to determine and develop materials that would be up to the task of handling this high of temperature. One of the materials developed specifically for this purpose was Inconel, an austenitic nickel-chromium based superalloy. The inclusion of Inconel and other more resilient materials made these high operating temperatures feasible. After varied results from their experimental reactors, the Air Force shut down the ARE program in late 1954 for other power generation ideas. However, the ARE supplied the founding physics and design for researchers to take the next step in molten salt reactor experimentation, and the Molten Salt Reactor Experiment was ushered in on the literal and figural foundations of the ARE.

Throughout the late 50s and early 60s, ORNL researched, designed, and implemented a new molten salt reactor. This new reactor, dubbed the Molten Salt Reactor Experiment (MSRE),

was a two-loop reactor, with a fuel salt primary loop connected to a different salt secondary coolant loop through a heat exchanger.

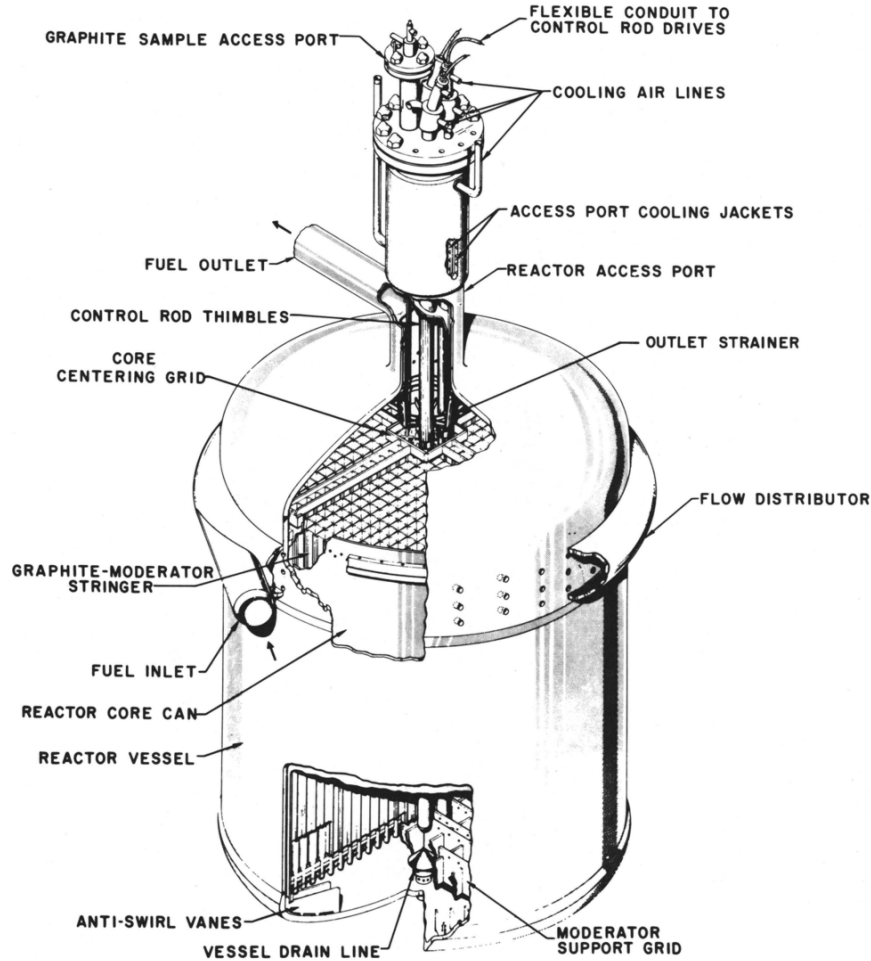


**Figure 2.** Molten Salt Reactor Experiment core design [8].

The fuel salt medium was composed of 65 mole % LiF, 29 mole % BeF<sub>2</sub>, 5 mole % ZrF<sub>4</sub>, and 1 mole % UF<sub>4</sub>. The choice of salt will be discussed in detail later. The coolant salt was composed of 66 mole % LiF and 34 mole % BeF<sub>2</sub> (FLiBe) [8]. Originally, the MSRE was fueled with <sup>235</sup>U. As the reactor continued operation, the curiosity of the researchers moved from just operating a critical MSR into operating a critical MSR with a novel fuel source. The MSRE was then transitioned to

be fueled with  $^{233}\text{U}$  to observe this new fuel's characteristics [9]. The core was small, 54 inches in diameter, 64 inches in height, and moderated with graphite rods that are directly exposed to the salt. Graphite rods are used in molten salt systems due to the limited wetting interaction between the molten salt and the graphite surface. Corrosion on the graphite rods was then expected to be minimal due to the limited wetting of graphite from the MSRE fuel salt. The power was limited by the secondary heat exchanger and had a maximum power of 8 MW [8]. The reactor was critical for just over 15,000 hours, with roughly 11,000 hours fueled by  $\text{U}^{235}$  and 4,000 hours fueled by  $\text{U}^{233}$  (8). The experiment observed different aspects of interest including fuel chemistry, materials compatibility, reactor dynamics, and the equipment performance within the reactor. The observed materials compatibility is especially of interest to this literature review. The components of the reactor, besides the graphite moderator, were composed of Hastelloy-N (INCO), a nickel-based superalloy with a composition of 71 wt% nickel, 16 wt% molybdenum, 7 wt% chromium, 5 wt% iron, and 1 wt% other [10]. Material choice is vitally important to reactor lifetime, and with the environment with the MSRE being severe, much research was done to reach the choice of INCO [11]. INCO uses nickel as its base lattice structure and is solution strengthened with molybdenum. Solution strengthening of a metal adds lattice impurities to impede dislocation movement, thus increasing the yield strength [12]. The addition of chromium to INCO provides the alloy with oxidation protection. ORNL performed extensive corrosion tests on INCO to determine compatibility with molten salts. The tests had three phases: testing compatibility of INCO with beryllium-based salts, beryllium-based salts with large concentrations of thorium, and other coolant salts. The second and third phases used flowing loops, both convective and forced flow, to determine corrosion differences in hot and cold legs of systems. Beginning results of these flow tests showed that after 1000 hours of operation, the INCO components had no measurable

corrosion along the surface. Some small roughening or pitting of the surface was observed along with a minor deposition layer. Chromium concentration increased within the salt by roughly 50-100 ppm for reasons that will be discussed more in-depth in the corrosion section. Other metal concentrations within the salt remained unchanged. The researchers concluded that corrosion reached a limit at 5,000 hours at temperature and the depth of corrosion didn't reach deeper than 1 mm at 20,000 hours. Corrosion was hypothesized to be caused by impurities within the salt and did not worsen at temperatures higher than 815°C [11]. ORNL researchers also explored the effects of graphite exposure due to the graphite within the core of the MSRE. Their findings showed no carburization on the INCO surfaces or salt penetration within the graphite surface [11]. These studies used graphite containers to study interactions between the salt and graphite, not a graphite solution within the salt. These conclusions showed a large compatibility with INCO within the MSRE reactor system. During the MSRE, chromium levels rose within the salt from 35 ppm to 70 ppm after 3 months and then leveled off, increasing only to 85 ppm at the end of the 3-year experiment. According to the ORNL researchers, this was a result of iron-fluoride impurities within the salt reacting with the chromium of the INCO. Besides the increase in chromium concentrations, no corrosion was noticeable throughout the INCO components. The irradiation of the INCO also did not drastically change its material properties, with small changes in ultimate strength, yield strength, and secondary creep rate [8]. In general, this was seen as a success for the material technology of a molten salt reactor and provided confidence in INCO as a material that can survive a full 30 years within the reactor. The MSRE was decommissioned and shut down in 1969, with the cleanup of the salt ongoing until finishing in 2009. The experiment showed the viability of molten salt design and exposed the necessity for new research to make molten salt reactors commercially viable.

Although the MSRE was regarded as a success in determining the possibility of molten salt reactors, this was the last operating molten salt reactor at ORNL. The next step in MSR technological advancement would be to show the breeding potential of these liquid-fuel based reactors. Therefore, the Molten Salt Breeding Reactor (MSBR) was the obvious next step. The MSBR had a two-fluid core design with the core fluid containing the fissionable fuel, U235 or U233, and the blanket or breeding salt surrounding the core containing Th232 and a small amount of U233.

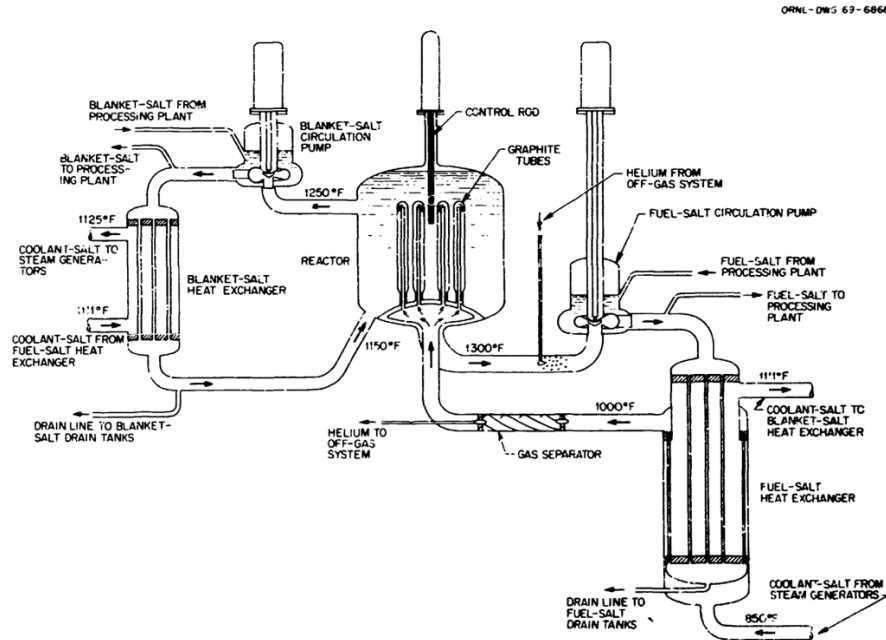


**Figure 3.** Design for Molten Salt Breeder Reactor Experiment. Designed as the next step in MSR technology after the MSRE [13].

The blanket salt experiences a high thermal neutron flux to facilitate the breeding of thorium into protactinium, which then decays into U233 [13]. Unfortunately, the MSBR competed directly with another project, the liquid-metal-fast-breeder reactor (LMFBR) [14]. The LMFBR had greater funding and support from governmental entities, pushing the new advancements towards these

fast-breeding reactors. Any large subsequent funding for the MSBR was shut down, citing three main concerns. The first being that Hastelloy N experiences radiation hardening due to a buildup of helium along the grain boundaries. The second concern being the containment of tritium. Tritium, a highly radioactive element, is created with the reaction of lithium and neutrons, which the core of an MSR would contain large quantities of. Tritium behaves very similar to hydrogen and can permeate metals, making containment difficult. This creates the possibility of a higher radiation concentration in the steam generators and subsequently the atmosphere. The last cited fault of MSR systems was the creation of small cracks in the Hastelloy N piping that are caused by the fission product tellurium [14]. Solutions to these problems were found with modified alloys to decrease helium diffusivity, an intermediate salt coolant to trap tritium, and adjusting the reductive chemistry of the fuel salt to keep tellurium attack to a minimum [14]. However, by the time these solutions were found, the momentum of development had shifted even further to other breeding reactors and MSR development stalled.

At the turn of the 21<sup>st</sup> century, with an increased urgency to develop zero-emission, high density energy, molten salt reactor research has a renewed interest. Especially considering MSR's inclusion into the Generation IV Reactor Forum, an international effort to develop advanced reactors to solve the concerns and problems of early-design reactors. The concerns addressed being safety, proliferation, waste, economics, and resource scarcity [15]. Groups such as the Thorium Molten-Salt Forum have been designing a molten salt reactor, thorium-based fuel cycle called Thorium molten-salt nuclear energy synergetics (THORIMS-NES). This idea builds upon the successes of the MSRE and the design studies of the MSBR to create a full thorium breeding fuel cycle. The group has proposed a three-facility design. The first being a molten salt reactor, FUJI, roughly designed like the MSRE, without breeding capabilities. The second, an accelerator-based

breeding facility called AMSB to use thorium to create fissile material that can be extracted using the third facility [15]. As of 2016, the process to implement any section of the THORIMS-NES system is still in the design and licensing phase [16].

Over the last 60 years, molten salt reactor research has been seemingly put aside for more lucrative energy generation ideas. However currently, an outspoken group of people and researchers have stuck by the technology, praising the many benefits that MSRs provide. Beginning with the impossibility of a fuel meltdown. MSRs don't contain solid fuel so the idea of a "melt down" cannot occur. Although telling the public that the fuel is already liquid, might influence public opinion away from MSRs. In terms of reactor physics, an MSR has low excess reactivity, decreasing the possibility of large power surges. The molten salt doesn't have violent reactions with air, water and is stable under irradiation. The high melting point of the salt creates much greater passive safety with freezing of the salt under accident conditions possible by draining the salt into non-critical geometry tanks. The high-melting and boiling point increases the thermodynamic efficiency of the system, as discussed above. The type of fissionable fuel is adjustable with U235, U233, Plutonium, and even trans-uranium elements (TRU) have been shown to be possible fuels. Decreasing nuclear waste storage needs and proliferation risk. The fuel also doesn't have to be fabricated, making the efficiency of the fuel cycle even greater [15]. These advantages are why MSR technology still has a place in research today, but there are still technological and political disadvantages that must be understood. For example, the idea of a liquid reactor is foreign to many and changing the minds of the public away from solid-fuel reactors would take massive convincing. Also, other reactors were tested besides the MSRE that were unsuccessful, stunting the growth of confidence for the technology. The material problems in the MSRE are also quoted as a large hindrance to moving forward with other experimental reactors,

instead focusing on other reactors without the same problems. Politically, because funding and research stalled in the 1970s, restarting and regaining the momentum of the research is difficult to do, especially with the large amount of funding needed for these projects [15]. The researchers above believe that public opinion and the energy needs have shifted enough for the benefits of MSR technology to outweigh these hindrances. This has been shown through U.S. Department of Energy awarding \$40 million towards MSR research in 2019 [17]. Along with multiple private energy companies declaring commercial MSR deployment by mid 2030s [17]. MSR research has expanded across many countries with the Gen IV initiative, with the culminating product, a TRU burning MSR called MOSART being deployed in the 2030s [17]. Overall, public and political opinion of nuclear energy around MSRs are improving, creating a bright outlook for MSR deployment over the coming decades.

## **2.2 Corrosion Fundamentals**

In general, corrosion is the degradation of a metal through some sort of reaction with the environment. A common example of corrosion is the reaction of iron with water and air, creating the recognizable dark-red film on the surface of iron alloys. These reactions are an electrochemical process, caused by either a reduction or oxidation of the metallic ions on the surface. Oxidation is an anodic reaction, where electrons are lost, and the metal goes into solution. The general form of the oxidation reaction is shown in Eq. 1.



Where M is a general metallic atom, e is an electron, and n is the number of electrons transferred. Reduction is the opposite process, where electrons are added to a metallic ion, ‘reducing’ the charge of the ion. The general form of the reduction reaction is shown in Eq. 2.



By combining these reactions together with an electrolyte, a potential difference, and a path for electrons to travel, a galvanic corrosion cell is formed. These reactions can even occur on the same metallic surface due to differing site energies, driving anodic and cathodic reactions at different sections of the heterogeneous surface. Some of the factors that affect these energies are dislocations, grain boundaries, point defects, or even surface impurities [18]. As seen above, corrosion follows the flow of electrons, therefore an energy change must occur for the reaction to proceed. A thermodynamic basis for this change in energy can provide a measure of whether the reaction can occur. This is determined by the Gibbs free energy of the reaction shown in Eq. 3.

$$\Delta G = -NFE \quad (\text{Eq. 3})$$

$\Delta G$  : Gibbs free energy [J]

N: number of electrons transferred per interaction [mole e]

F: Faraday’s constant [J/V\*mole e]

E: Standard emf potential =  $E_{ox} + E_{red}$  [V]

It should be noted that Gibb’s free energy does not determine the rate at which the reactions occur, just the possibility of them happening, with a more negative free energy, the more

thermodynamically likely the reaction will occur. Standard electromotive force (emf) potentials are an inherent property of the metal and have been determined for many different reactions. However, these potentials can be affected by the environment the reaction is occurring within. A higher concentration of the cathodic or anodic ions can either drive or halt the reaction. The change in potentials through the concentration of ions is determined by the Nernst equation shown in Eq. 4.

$$E_{cell} = E^o + 2.3 \frac{RT}{nF} \log_{10} \frac{[M^+]}{[M^-]} \quad (\text{Eq. 4})$$

R: Universal Gas Constant [J/mol\*K]

$M^+$  : Concentration of oxidized species [M]

$M^-$  : Concentration of reduced species [M]

The kinetics of these reactions can be determined by measuring the electric current from the anode to the cathode. After the current is found, a simple unit conversion can be used to calculate the number of ions reduced or oxidized per second. Corrosion can be broken up into two groups, localized and uniform. Uniform corrosion uses the galvanic half-cell reactions as shown above, but the location of where the reactions occur is constantly changing. Therefore, over a significant period, the metal surface is removed evenly, invariant of position. Localized corrosion also still uses the half-cell reactions, but the location at which the cathodic and anodic reactions occur are fixed. Inconsistencies on the surface can incite this type of reaction. Such as a breakdown of a protective oxide layer, small crevices, or even stress fields initiating local attack.

Another important corrosion mechanism is intergranular attack. Intergranular attack is the preferential corrosion of an alloy at or near the immediate vicinity of a grain boundary. 304 stainless steels have been shown to have large intergranular attack after being sensitized after heating to roughly 600°C. Sensitization of stainless steels is the process of carbon diffusion to grain boundaries where chromium carbides form [19]. Carbide formation depletes chromium concentrations around the grain boundary, changing the surface potential of the steel and increasing susceptibility of corrosion locally. The susceptibility is caused because the protective chromium oxide layer is no longer able to be formed. Many other mechanisms for corrosion can then occur. With examples being pitting, de-alloying, or erosion corrosion. The dominant mechanism of corrosion is determined by the material and type of environment the material is contained within. The above corrosion discussion is based around an aqueous environment, dissolved electrolytes in water. However, the environment that will be looked at in this thesis is with a molten-salt electrolyte, specifically, molten-fluoride based salts. Corrosion mitigation in alloys within an environment containing oxygen occurs by the formation of an oxide layer along the surface of the metal which acts as a diffusion barrier, reducing the rate of further oxidation [20]. In a fluoride salt system, there isn't any oxygen to create this layer and if oxygen contaminants are present, the oxide layer dissolves in the salt. Corrosion is then performed by the preferential leaching of the least noble, or most reactive, metal within the alloy [20]. The driving forces of the corrosion reaction are thermodynamic properties, contaminant effects, and thermal gradients. The thermodynamic properties that influence corrosion are the energies of formation of the possible fluoride compounds from the alloying elements compared to the energies of formation of the fluoride-salt constituents [21]. Free energies of common molten salt constituents and structural metals are shown in Table 1 [21].

**Table 1.** Free energy of formation for common fluoride compounds of salt and structural material constituents. Taken at 727°C [21].

| Fluoride Compound | Free Energy of Formation (Kcal/mol-F) | Fluoride Compound | Free Energy of Formation (Kcal/mol-F) |
|-------------------|---------------------------------------|-------------------|---------------------------------------|
| LiF               | −125                                  | AlF <sub>3</sub>  | −90                                   |
| MgF <sub>2</sub>  | −113                                  | CrF <sub>2</sub>  | −75.2                                 |
| NaF               | −112                                  | CrF <sub>3</sub>  | −72.3                                 |
| Rb                | −112                                  | FeF <sub>2</sub>  | −66.5                                 |
| KF                | −109                                  | FeF <sub>3</sub>  | −60.6 (at 754 °C)                     |
| BeF <sub>2</sub>  | −104                                  | WF <sub>6</sub>   | −56.8                                 |
| ZrF <sub>4</sub>  | −94                                   | NiF <sub>2</sub>  | −55.3                                 |
| HF                | −66.2                                 | MoF <sub>3</sub>  | −52.5 (at 754 °C)                     |

Looking at Table 1 and taking the example of a simple FLiNaK salt, all components of the salt have free energies less than or equal to −109 Kcal/mol-F. These values are much more negative than the compounds formed with the common structural metals. Meaning that in a pure, clean, alkali-salt system corrosion should be minimal as soon as equilibrium is reached. A system without any corrosion is impossible, but because of these thermodynamic properties, there is a maximum limit of corrosion in pure conditions. Studies were done of ideal solutions and the equilibrium concentrations of common alloying components were found, with higher preference for attack increasing in the following order: Ni, Co, Fe, Cr, then Al [22]. This trend can also be inferred with the above table, with the free energies of the fluoride compounds becoming more negative in the same order. These thermodynamics are the basis of corrosion within alkali salts, with other driving forces introducing differing thermodynamic interactions or changing equilibrium concentrations.

Impurity driven corrosion is perhaps the greatest influence on severity in a molten salt system. Impurities such as moisture, oxides, and metallic ions greatly affect the corrosion mechanisms that occur. Moisture is a difficult impurity to control with these salts' high hygroscopic properties. Much care must be taken to minimize the absorption of water during synthesis and use. Common practices include using an inert atmosphere during synthesis, extensive vacuum drying process, and sparging of the salt with an HF/H<sup>2</sup> mixture. This is all needed because of the reaction water has with fluorine, creating highly corrosive hydrofluoric acid [21]. Hydrofluoric acid reacts readily with the metallic alloy constituents creating metallic fluorides that dissolve in the salt, and hydrogen gas. Water itself can also interact directly with the structural metals, creating oxides and hydrogen gas. Other impurities such as iron and nickel also contribute meaningfully to the corrosion process. Because of the favorable thermodynamics, these impurities create metallic fluorides that interact directly with the chromium in the alloy. Driving the leaching of chromium into the salt. This mechanism is described in detail in a subsequent chapter. This has a direct impact on determining container material during synthesis, where many impurities can be introduced. Also, nuclear fuel containing salts can instigate the same type of chromium leaching from uranium-tetrafluoride reduction. This reaction for chromium difluoride is shown below in Equation 5.



To control these types of reactions, the oxidation potential of the salt needs to be adjusted, possibly through the addition of beryllium. As shown in Equation 1, the chemical corrosion mechanism is driven by concentrations of UF<sub>4</sub> and UF<sub>3</sub> [42]. By adding the reducing agent beryllium, the concentration of UF<sub>4</sub> is increased due to the electron donation of the beryllium. In

turn, this reduces the corrosive potential of the molten salt. Impurity driven corrosion has been shown to be the main mechanism within the early stages of operation of a salt system [25]. Therefore, being able to control impurities is vital in inhibiting corrosive attack.

With these salts being usually deployed in some type of heat transfer loop, the effects of a thermal gradient on corrosion also need to be considered. The solubility of the metallic fluorides discussed above is dependent upon the temperature of the salt. Therefore, these corrosion products can be plated out onto the surfaces of the cold loop [26]. The concentration of metallic fluorides changes within the salt, consequently driving the hot loop out of equilibrium, inducing more corrosion. This mechanism is the dominant form of corrosion in long-running loops and consequently needs to be understood. Concerns about not only corrosion, but also the clogging of cold-leg components, such as the heat exchanger, need to be considered when thinking about salt system designs.

### **2.3 ICP-MS/OES Principles**

Inductively coupled plasma mass spectrometry (ICP-MS) is a common analytical technique to detect small concentrations of elements in a solution. ICP-MS uses ionization and magnetic fields to separate ions of specific mass to charge ratios. There are six main components of an ICP-MS instrument: sample introduction system, plasma, interface, ion optics, mass analyzer, and detector. The process begins with a sample introduction system. A sample is dissolved in usually an acidic or alkaline solution. Due to the sensitivity of the instrument, only a small amount of sample needs to be dissolved, with a total dissolved solid content of roughly 2g/L being a standard basis. The sample solution is pumped to a nebulizer which converts the liquid stream into tiny droplets. These droplets are then filtered to allow only the smallest diameter,  $\leq$

10 $\mu$ m, droplets to continue [27]. Only 1-2% of the sample stream will reach the plasma, therefore much care must be taken to not influence the introduction of sample to obtain consistent results [28]. The sample stream is then directed into the plasma. Argon plasma is primarily used. Plasma is used as a hard ionization technique which, if a sample contains molecular compounds, becomes completely atomized [29]. The ion stream is then passed through the interface, which consists of two cones, a sample cone and skimmer cone to accelerate the stream and more pointedly direct the sample into the ion optics and mass analyzer. The ion optics filter photon and neutral species away from the detector, decreasing noise and increasing sensitivity. After passing through the ion optics, the ionized sample goes into the mass analyzer. The most common mass analyzer used in ICP-MS is a quadrupole. A quadrupole is a series of four rods arranged in a rectangle that have AC or DC potential applied. When a certain combination of these potentials is applied, an electric field is created that only a certain mass to charge ratio can pass through to the detector. The potential can be changed quickly so that a range of ratios can be measured in fractions of a second. The ions that match the correct trajectory then hit the detector, commonly an electron multiplier, to induce a signal that can be observed and counted. An ICP-MS system can have sensitivities in the nmol/L range; however, the sensitivity varies with elements of interest, type of solution matrix, and dilution percentage. Calibration of the instrument also needs to be accurate to convert the given unit, counts per second, into a concentration.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is fundamentally similar to ICP-MS except for the mechanism that measures the different ions. The beginning of the sample introduction process is the same, with a peristaltic pump pumping a dilute solution of the sample into a nebulizer. The sample is then atomized and directed into an argon plasma. The argon plasma ionizes and excites the electrons of the sample atoms into higher energy states. As

these electrons relax back into their ground state, they emit characteristic photons that are collected and directed to a detector. Because each atom has unique wavelengths of emissions, the relative intensity of the signal corresponds to the concentration of that atom within the sample. Using calibration standards, the concentration of the atom of interest can be determined.

ICP-MS and ICP-OES both can determine concentrations of an analyte within a solution, however due to their different mechanisms, each technique has different advantages and disadvantages. Starting with detection limits, ICP-MS has an impressive lower detection limit of 1-10 parts per trillion (ppt) and ICP-OES has a detection limit about three orders of magnitude larger, 1-10 parts per billion (ppb). However, the detection limit of ICP-MS is greatly affected by the number of other atoms in the solution due to interference effects. The detection limit can be decreased by a factor of 50 depending upon the sample matrix. This is due to interference effects that the other ions can cause, especially if the matrix contains ions with a mass similar to that of the atom of interest. Usually, these spectral interferences are lessened by matrix matching of calibration standards, careful gas choice, and using a liquid chromatography separation technique before sample introduction. ICP-OES deals with spectral interferences as well. Instead of only having one possible characteristic detection for an atom, like ICP-MS, ICP-OES must deal with overlapping emission lines. This is a much more common interference because of the large amount of emission lines a single atom can have. A high-resolution spectrometer is necessary to be able to separate different emission lines of similar wavelengths [31]. The determination of technique to use for analysis is dependent upon detection limit, sample solubility, and analyte of interest.

## 2.4 316L Stainless Steel Application in Molten Salt Reactors

Although Hastelloy-N was invented and modified directly to withstand the corrosive environment of an MSR, stainless steel still has a use case within the MSR industry. 316 stainless steel is a type of steel containing at least 10.5% of chromium. Percent compositions of basic stainless steel are shown below in Table 2 along with the low carbon (316L) and high carbon (316H) modifications, with iron being the balance.

**Table 2.** Elemental compositions of different types of 316 stainless steel. All values are weight percent of total composition.

| Element | Cr    | Ni    | Mo  | C         | Mn | P     | S    | Si   | N   | Fe      |
|---------|-------|-------|-----|-----------|----|-------|------|------|-----|---------|
| 316     | 16-18 | 10-14 | 2-3 | 0.08      | 2  | 0.045 | 0.03 | 0.75 | 0.1 | Balance |
| 316H    | 16-18 | 10-14 | 2-3 | 0.04-0.10 | 2  | 0.045 | 0.03 | 0.75 | -   | Balance |
| 316L    | 16-18 | 10-14 | 2-3 | 0.03      | 2  | 0.045 | 0.03 | 0.75 | 0.1 | Balance |

The need to create 316L and 316H arises through different physical properties of the alloy that carbon exacerbates. For 316L, the lower concentration of carbon decreases the sensitization of the metal by reducing the amount of chromium carbides formed during high temperature exposures. Which, as discussed above, can increase the corrosion in stainless steel. 316H, while more prone to sensitization, has a higher resistance to creep effects at higher temperatures. Depending upon the specific component, each version of 316 has a use. With the corrosion of 316 being primarily driven by the loss of chromium at grain boundaries, 316L has been researched in MSR systems to determine its corrosive resistance. 316 also doesn't see the helium embrittlement that Hastelloy-N suffers from. A large reason 316 stainless steels are being looked at for MSR systems is that 316 is already fully qualified in the ASME Code. The ASME Code is a regulatory

design standard that oversees boilers and pressure vessels. By already being qualified, much less regulatory requirements would have to be researched for 316 systems [32].

Much research has been done on trying to quantify the severity of 316SS corrosion in molten salts. The Hastelloy-N (INCO) tests discussed in the history of MSRs section above were also performed concurrently upon stainless steel samples with FLiBe (LiF-BeF 66-34 mol%) salt. The salt had a significant impurity concentration of  $\text{FeF}_2$ . The iron impurity caused a significant mass loss in the first 500 hours the convective loop was operated [11]. To determine the effect of redox chemistry on corrosion, a beryllium rod was inserted into the salt to create a reducing potential. After the induction of the beryllium, the amount of corrosion was minimal. This experiment showed the importance of salt chemistry on corrosion intensity. As funding faded and motivation dwindled, minimal research of 316 compatibility with molten salts was done until a renewal in the early 2000s with the Gen IV initiative. In 2011, Sellers et al, used 316L crucibles and samples to determine if the modified alloy has any effect on the corrosion in a static eutectic FLiNaK system. While they did not compare directly to a higher carbon concentration 316, they still found significant corrosion through Cr depletion and, with an addition of a graphite rod, increased corrosion with graphite being introduced to the salt [33]. These findings have been observed by other laboratories, with graphite presence increasing the corrosive attack of stainless steel within a molten salt environment. Static experiments have been done with 316H samples in 316H crucibles with the addition of graphite particles roughly 200 microns in size [35]. They found that with an increase in graphite concentration, the corrosive attack increased. The proposed mechanism being that chromium was leached out at grain boundaries, then attached to the graphite particles to form carbides. This attachment drove the concentration of chromium atoms in the molten salt down, keeping the salt from reaching an equilibrium concentration of chromium ions.

Corrosion rate was kept high from the constant creation of carbides on the graphite particles [35]. By adding Zr to the molten salt, a preferential coating could be formed on the surface of stainless steel. Due to the diffusion coefficient being larger for Ni/Zr compared to Fe/Cr, a nickel-zirconium intermetallic phase was shown to appear on the surface of stainless steel. This coating is used as a diffusion barrier for the Fe and Cr atoms within the alloy, increasing corrosion resistance [33].

By performing a similar experiment with 316L, varying carbon concentration within a static corrosion crucible, the compatibility between 316L stainless steel and molten salt could be determined along with painting a clearer picture of the corrosion mechanisms.

# Chapter 3

## Static Corrosion of 316L Stainless Steel in Eutectic FLiNaK

### 3.1 Materials

Annealed 316L stainless steel foil was procured from Goodfellow Corporation. The foil was 12mm in width and 0.25mm thick. The material's composition, as reported by the supplier, is shown below in Tables 3 and 4.

**Table 3.** Primary element composition in procured 316L from Goodfellow Corporation used in FLiNaK corrosion experiment. Values are given in weight percent.

| Element              | Cr    | Mo   | Ni    |
|----------------------|-------|------|-------|
| Concentration (wt %) | 16.52 | 2.01 | 10.18 |

**Table 4.** Secondary element composition in procured 316L from Goodfellow Corporation used in FLiNaK corrosion experiment. Values are given in weight percent.

| Element              | C    | Cu   | Mn  | N     | P     | Si   | S     |
|----------------------|------|------|-----|-------|-------|------|-------|
| Concentration (wt %) | 0.03 | 0.56 | 1.2 | 0.024 | 0.072 | 1.18 | 0.002 |



**Figure 4.** Example sample of 316L stainless steel used in FLiNaK static corrosion experiment.

To compare salt purity's effect on corrosion, two different FLiNaK salt sources were procured. One was sourced from Oak Ridge National Laboratory (ORNL), and the other from Argonne National Laboratory (ANL). The composition of each is shown below, along with the trace elemental analysis. The trace element analysis was performed by Argonne National Laboratory using ICP-OES and ICP-MS. The results of this characterization are shown below in Table 5. Each salt has been stored in airtight jars and in an Argon glovebox since procurement to minimize air exposure [34].

**Table 5.** Trace element analysis on ORNL and ANL sourced salts. All concentrations are in ppm by weight.

| Salt ID | Mg | Ca  | Cr  | Mn  | Fe  | Ni  | Rb | Cs  |
|---------|----|-----|-----|-----|-----|-----|----|-----|
| ORNL    | 32 | 180 | 2.7 | 2.1 | 25  | 1.3 | 13 | 0.1 |
| ANL     | 24 | 76  | 6   | 3   | 117 | 179 | 44 | 2   |

Graphite particles were sourced from Sigma-Aldrich and had a particle size of less than or equal to 20 microns. Pure nickel crucibles were sourced from Sigma-Aldrich and had a volume of 20ml, an example nickel crucible is shown in Figure 5.



**Figure 5.** Example nickel crucible used in FLiNaK static corrosion experiment for sample containment.

### 3.2 Static Corrosion Experiment

Two static corrosion experiments were set up to analyze the effects of graphite concentration on 316L stainless steel in eutectic FLiNaK. Stainless steel samples were created by cutting 1.5 cm lengths of foil. These samples were then sonically cleaned in ethanol and weighed to obtain their pre-exposure masses. The masses were measured with 0.01 mg accuracy with a Mettler Toledo XS105 Dual Range Balance. For the first run, the 316L strips were placed vertically within the nickel crucible, with some of the surface sticking out above the salt. For the second run, the 316L strips were bent into a ‘tent’ shape to ensure complete salt coverage of the strip and placed into the bottom of the nickel crucibles. Graphite particles were then added to the crucibles with amounts depending upon the wanted graphite concentration. Three different concentrations were made. A low graphite concentration of roughly 50 mg/kg, a medium concentration of roughly 100 mg/kg, and a high concentration of roughly 150 mg/kg. The actual masses of graphite weighed,

and the corresponding graphite concentrations for each run are shown in Tables 6 and 7. To be able to understand the effect of FLiNaK salt purity on corrosive intensity, two samples were made at each concentration and were filled with 30 grams of either the ORNL or ANL sourced FLiNaK. The sample setup is illustrated below in Figure 6.

**Table 6.** Run 1 sample compositions for 316L exposure in differing FLiNaK salt purity and graphite concentrations.

| Sample | Salt Source | Graphite Concentration (mg/kg) |
|--------|-------------|--------------------------------|
| 1      | ANL         | 0                              |
| 2      | ANL         | 45                             |
| 3      | ANL         | 85                             |
| 4      | ANL         | 135                            |
| 5      | ANL         | 709                            |
| 6      | ORNL        | 0                              |
| 7      | ORNL        | 45                             |
| 8      | ORNL        | 85                             |
| 9      | ORNL        | 135                            |

**Table 7.** Run 2 sample compositions for 316L exposure in differing FLiNaK salt purity and graphite concentrations.

| Sample | Salt Source | Graphite Concentration (mg/kg) |
|--------|-------------|--------------------------------|
| 1      | ORNL        | 0                              |
| 2      | ORNL        | 39                             |
| 3      | ORNL        | 120                            |
| 4      | ORNL        | 178                            |
| 5      | ANL         | 0                              |
| 6      | ANL         | 39                             |
| 7      | ANL         | 91                             |
| 8      | ANL         | 163                            |

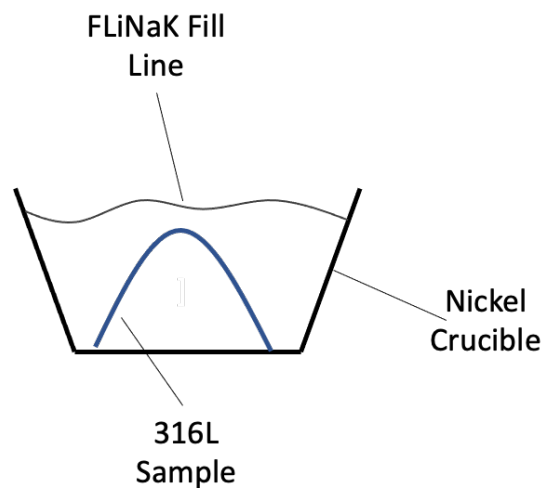


**Figure 6.** 316L FLiNaK Static Corrosion Sample setup in Nickel Crucibles.

For each run, the sample creation process was done in a glovebox to minimize the salts exposure to air. After creating each of the samples, they were sealed in airtight jars and left in the glovebox until ready to be moved into the furnace. The furnace used is a 6-inch quartz tube with three temperature zones. Argon gas was continuously flowed through the tube furnace to create an inert environment for corrosion. The furnace is shown below in Figure 7.



**Figure 7.** 6-Inch tube furnace located in the Materials Research Laboratory at UIUC.



**Figure 8.** Bubbler installed on the 6" tube furnace in the Materials Research Laboratory at UIUC.

A liner of stainless-steel foil was wrapped around the inside of the tube to protect the tube from possible FLiNaK evaporation and deposition. A 4.5" x 8" steel plate was procured to provide a flat surface for the samples to sit on while in the furnace. With the furnace ready to heat, the samples were taken out of the glovebox, while still in their airtight containers, and brought to the furnace lab in the Materials Research Laboratory. The samples were taken out of their containers, placed onto the steel plate, and inserted into the furnace with the center of the steel plate lining up with the center of the tube. This placement located the plate squarely inside the middle temperature

zone, ensuring even heating between each of the samples. As soon as the samples were in place, the lid on the tube furnace was replaced and the tube was purged with argon at a flow rate of 3 liters per minute for an hour. Before purging, the samples were not exposed to air for a time greater than 10 minutes. After purging, for the first experiment, the flow rate was lowered to 1 liter per minute and the furnace was turned on. During the second experiment, this flow rate was increased to 2 liters per minute for the duration of the exposure. The temperature program is shown in Figure 9.

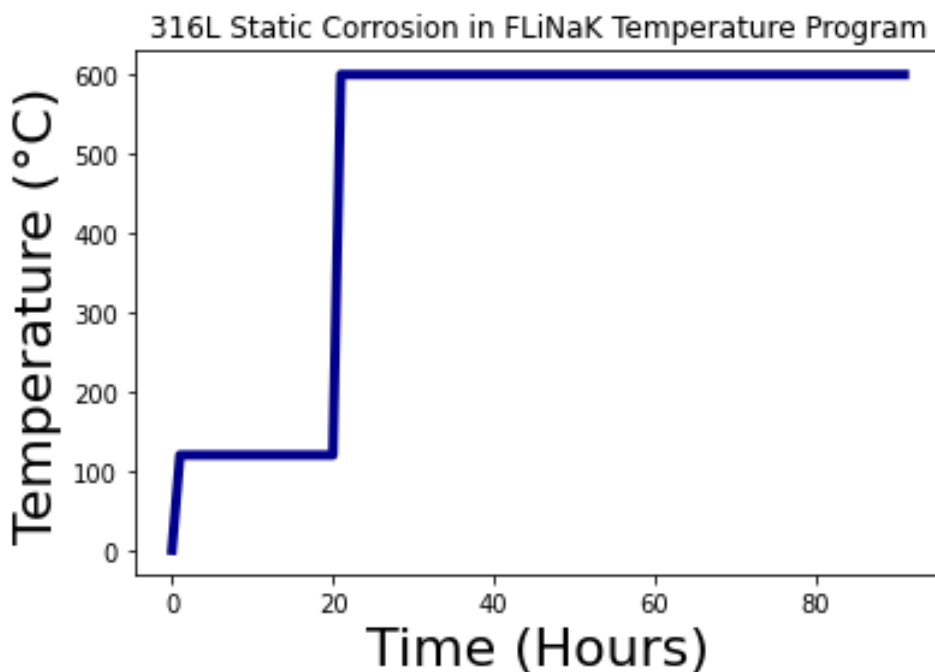


**Figure 9.** Temperature Program for static corrosion test.

This temperature program was used for both Run 1 and 2. The hold at 120°C is to dry the salt by hopefully expelling any water that could've been absorbed through the sample movement process. The time for corrosion begins as soon as the furnace reaches the upper temperature of 600°C and ends as soon as the furnace turns off. Each furnace zone was set to the same

temperature. As the test was ongoing, the temperature of each zone was checked. Uniformity of heating was confirmed with the temperature being the same across all three zones during each step of the experiment. The total time at 600°C was 72 hours with a total time above the melting point of eutectic FLiNaK of 75 hours.

After cooling down to 50°C, the plate with the samples was taken out of the furnace. The crucibles for the second run post-exposure are shown in Figure 10. The crucibles were quickly placed into their airtight containers and taken back to the argon filled glovebox. While in the glovebox, the salt was removed from the nickel crucibles by tapping the bottom of the crucible with a hammer. The salt from the second run was removed from around the stainless-steel samples and saved in airtight jars for further analysis. The 316L samples were cleaned in ethanol to remove any excess FLiNaK for analysis preparation.



**Figure 10.** Post exposure view of samples 1-10 from Run 2. Samples 1-4 are ORNL sourced salts with increasing graphite concentrations. Samples 5-8 are ANL sourced salts with increasing graphite concentrations. Samples 9 and 10 are empty nickel crucibles with ORNL and ANL salts respectively.



**Figure 11.** Clockwise from upper-left corner. Samples 2, 6, 8, 4 after removal of salt from the nickel crucibles. These samples are from Run 2.

For the Run 2, to ensure that the environment within the tube furnace is pure argon, a bubbler was installed on the exhaust port of the furnace to create an overpressure within the tube. The bubbler installation is shown in Figure 8. Other than the bubbler and the higher Argon flow rate, each corrosion run was identical. The results of these two runs will be compared in the next chapter.

# Chapter 4

## Analysis and Results

### 4.1 Mass Loss

After cleaning with ethanol, the 316L samples were weighed with a Metler Toledo XS105 Dual Range Balance to a precision of 0.01 mg. The samples were not sonically cleaned before weighing in case the cleaning process would dislodge loose grains from the steel, decreasing the accuracy of the mass loss measurement. Because mass loss due to corrosion is determined by the surface area of the sample, each sample's surface area was calculated by using the density of 316L Stainless Steel and the thickness of the steel foil. The density, as reported by the supplier, is 8.00 g/cm<sup>3</sup> and the thickness of the foil, as shown above, is 0.025mm. The mass loss metric used in this analysis is determined by the mass loss per surface area of each sample. The pre-exposure masses, post-exposure masses, and mass loss per surface area for each run are shown in Tables 8 and 9.

When preparing the analysis from Run 1, without the bubbler, the entire 316L sample was not exposed to the salt. To take this into account, the entire foil strip was weighed to determine total mass loss. Then the salt exposed side was cut off from the sample. This side was then weighed with the same balance as above and surface area was calculated using the exposed mass and given thickness and density. The assumption being that mass loss only occurs in the region exposed to the molten salt. Some error must be applied to the cutting process; however, this error did not exceed more than 5% due to the distinct line between regions and the precision saw used. The mass loss data for Run 1 is shown graphically in Figure 12. Mass loss is shown as a positive number for clarity.

**Table 8.** Run 1 mass analysis of samples pre and post FLiNaK exposure

| Sample | Pre-Exposure Mass (g) | Post-Exposure Mass (g) | Mass Loss/Surface Area (mg/cm <sup>2</sup> ) | Graphite Concentration (mg/kg) | Salt Source |
|--------|-----------------------|------------------------|----------------------------------------------|--------------------------------|-------------|
| 1      | 0.88938               | 0.86855                | 7.93                                         | 0                              | ANL         |
| 2      | 0.90561               | 0.8889                 | 5.48                                         | 45                             | ANL         |
| 3      | 0.92077               | 0.90007                | 7.88                                         | 709                            | ANL         |
| 4      | 0.88413               | 0.86009                | 8.99                                         | 85                             | ANL         |
| 5      | 0.9117                | 0.8938                 | 7.42                                         | 135                            | ANL         |
| 6      | 0.89144               | 0.87287                | 7.57                                         | 135                            | ORNL        |
| 7      | 0.88546               | 0.86624                | 6.34                                         | 45                             | ORNL        |
| 8      | 0.88387               | 0.87005                | 5.56                                         | 85                             | ORNL        |
| 9      | 0.89827               | 0.88272                | 6.05                                         | 0                              | ORNL        |

**Table 9.** Run 2 mass analysis of samples pre and post FLiNaK exposure

| Sample | Pre-Exposure Mass (g) | Post-Exposure Mass (g) | Mass Loss/Surface Area (mg/cm <sup>2</sup> ) | Graphite Concentration (mg/kg) | Salt Source |
|--------|-----------------------|------------------------|----------------------------------------------|--------------------------------|-------------|
| 1      | 0.64440               | 0.63280                | 3.60                                         | 0                              | ORNL        |
| 2      | 0.74024               | 0.72768                | 3.39                                         | 50                             | ORNL        |
| 3      | 0.73031               | 0.71789                | 3.40                                         | 100                            | ORNL        |
| 4      | 0.73547               | 0.72495                | 2.86                                         | 150                            | ORNL        |
| 5      | 0.69213               | 0.67325                | 5.45                                         | 0                              | ANL         |
| 6      | 0.70052               | 0.68152                | 5.43                                         | 50                             | ANL         |
| 7      | 0.65303               | 0.63760                | 4.73                                         | 100                            | ANL         |
| 8      | 0.71685               | 0.69725                | 5.47                                         | 150                            | ANL         |

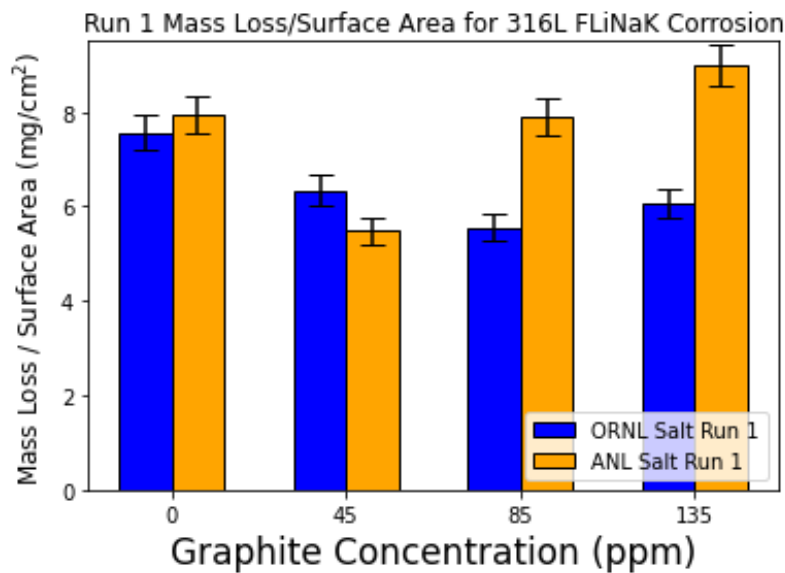


**Figure 12.** Mass loss per surface area of each sample separated by salt type for Run 1. The graphite concentrations are rough estimates grouped together to promote clarity.

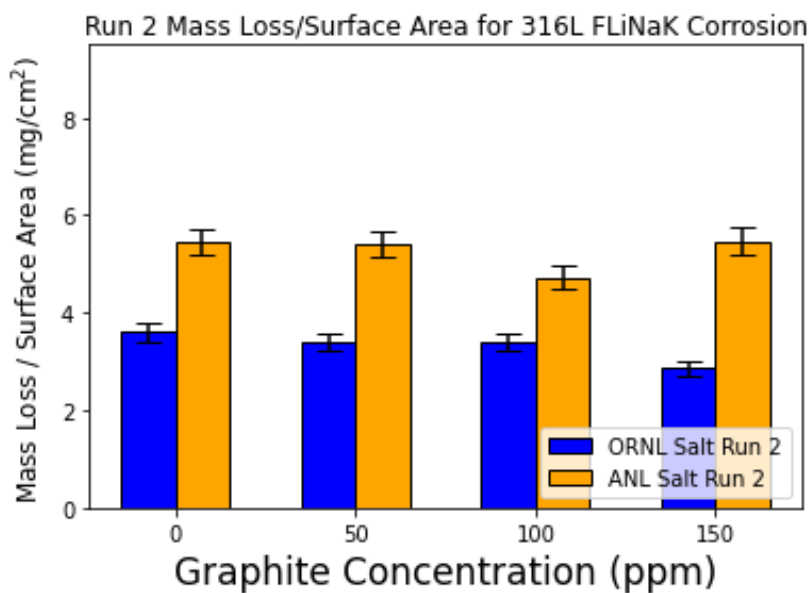


**Figure 13.** Mass loss per surface area of each sample separated by salt type for Run 2. The graphite concentrations are rough estimates grouped together to promote clarity.

There is a distinct difference between the mass loss from the ORNL salt and the ANL salt for Run 2, unlike that of Run 1. The 316L samples exposed to the purer, ORNL salt had significantly less mass loss than the ANL exposed 316L samples. With the ANL exposed 316L foil coupons having almost double the mass loss per surface area within the high-graphite salt mixture. A correlation between graphite concentration and corrosive intensity can be seen within the Run 1 ANL samples, besides the pure salt sample. The other samples do not show any distinct correlation. This observation will be discussed further in a later chapter.

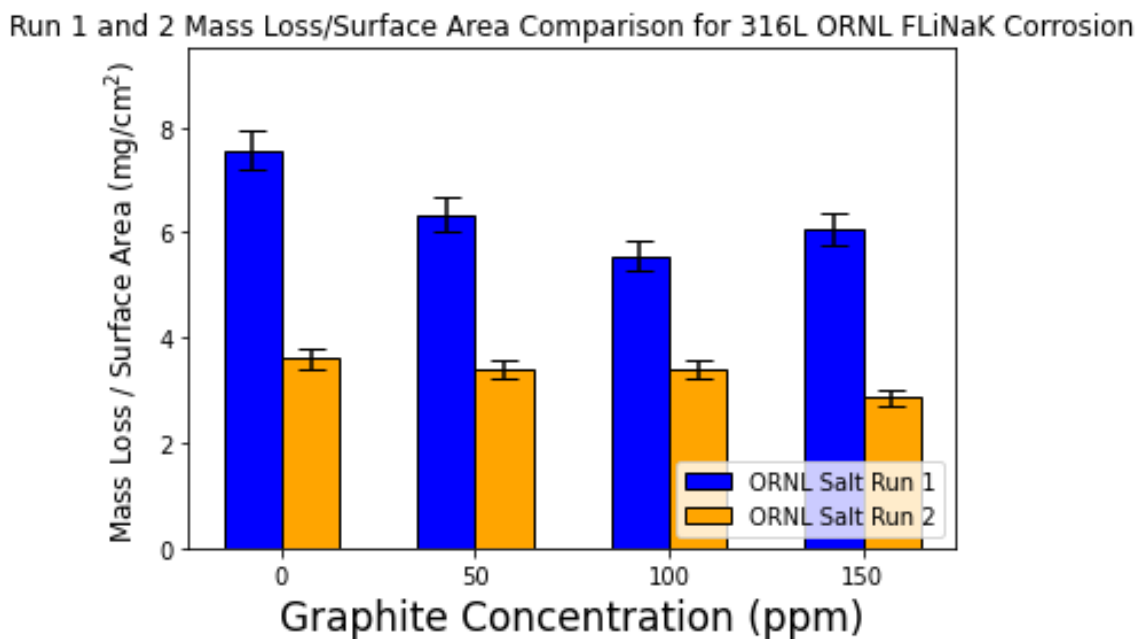


**Figure 14.** Mass loss per surface area of each sample for both runs of the ORNL salt.

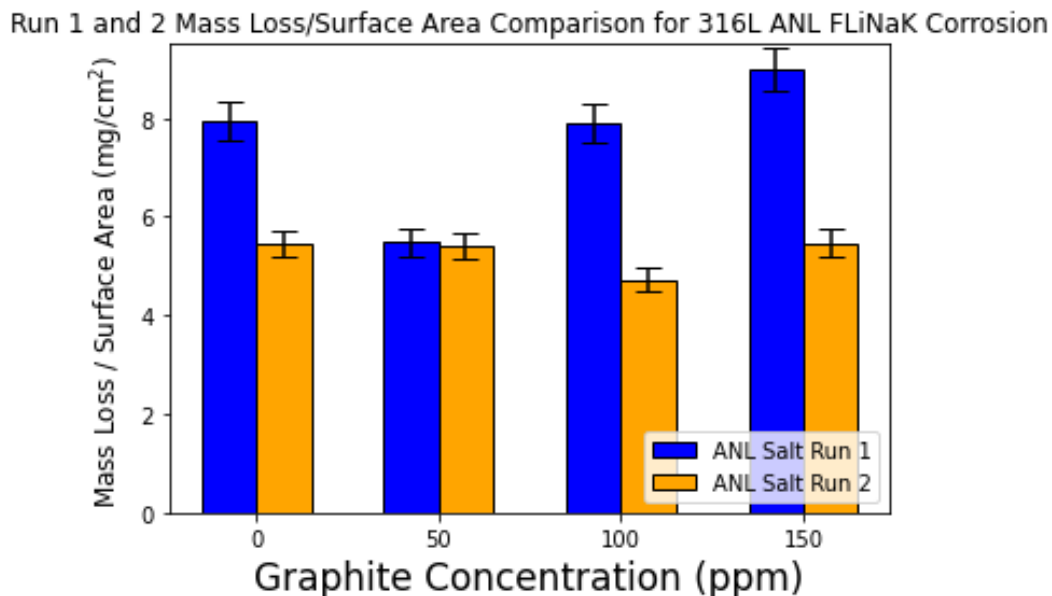


**Figure 15.** Mass loss per surface area of each sample for both runs of the ANL salt.

When comparing the two sets of corrosion data, mass loss, and thus corrosion, was much greater in the experiment without a bubbler and lower argon flow rate. Each corrosion experiment was done at the same temperature, time, and salt, with the only difference being the flow rate and the bubbler. When setting up the experiment without the bubbler, a flow rate was chosen to hopefully limit the amount of normal atmosphere backflow to a minimum. The outlet tube has a small diameter, restricting the flow enough to induce a positive pressure within the tube. The argon flow rate of just over one liter per minute was thought to be large enough to accomplish this. However, as seen in Figures 14 and 15, this is not the case. The corrosion being much greater in Run 1, the non-bubbler data. The reasoning for this will be looked at in a subsequent chapter. For Run 2, the purity of the atmosphere needed to be guaranteed, therefore the bubbler was installed. By installing the bubbler, it created large partial pressure between the tube furnace and the lab room, preventing air inflow from the lab, keeping the atmosphere pure within the furnace while the corrosion experiment was taking place. The mass loss results above imply that this was

successful with the corrosive attack being much greater in Run 1 than Run 2. The mechanism will be discussed in a later chapter.

## 4.2 Optical Microscopy

Each 316L sample was analyzed under an optical microscope at H-Lab in Talbot Laboratory at the University of Illinois at Urbana-Champaign to better understand the differences in corrosion between the two sets of salts and the two different runs. After cleaning, the plan view surface of each sample was analyzed at 20x magnification without polishing. Then, the samples were cut in half twice, mounted in epoxy, and polished to observe the cross-section of the stainless steel. An example of the mounted cross section samples is shown in Figure 16. These cross-section samples were analyzed in the same optical microscope to a maximum magnification of 20x. The plan view set of photos are shown in Figures 17 and 18 while the cross sections are shown in Figures 19 and 20.

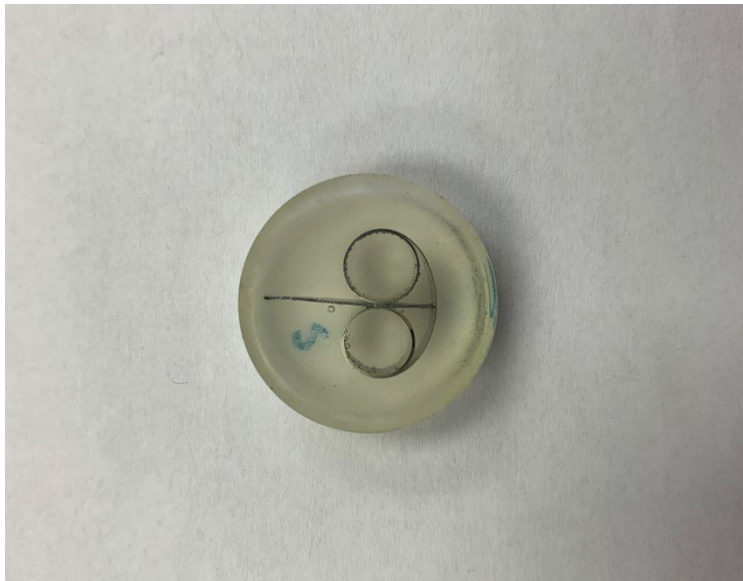


**Figure 16.** Sample 5 cross-section sample mounted in epoxy and polished.

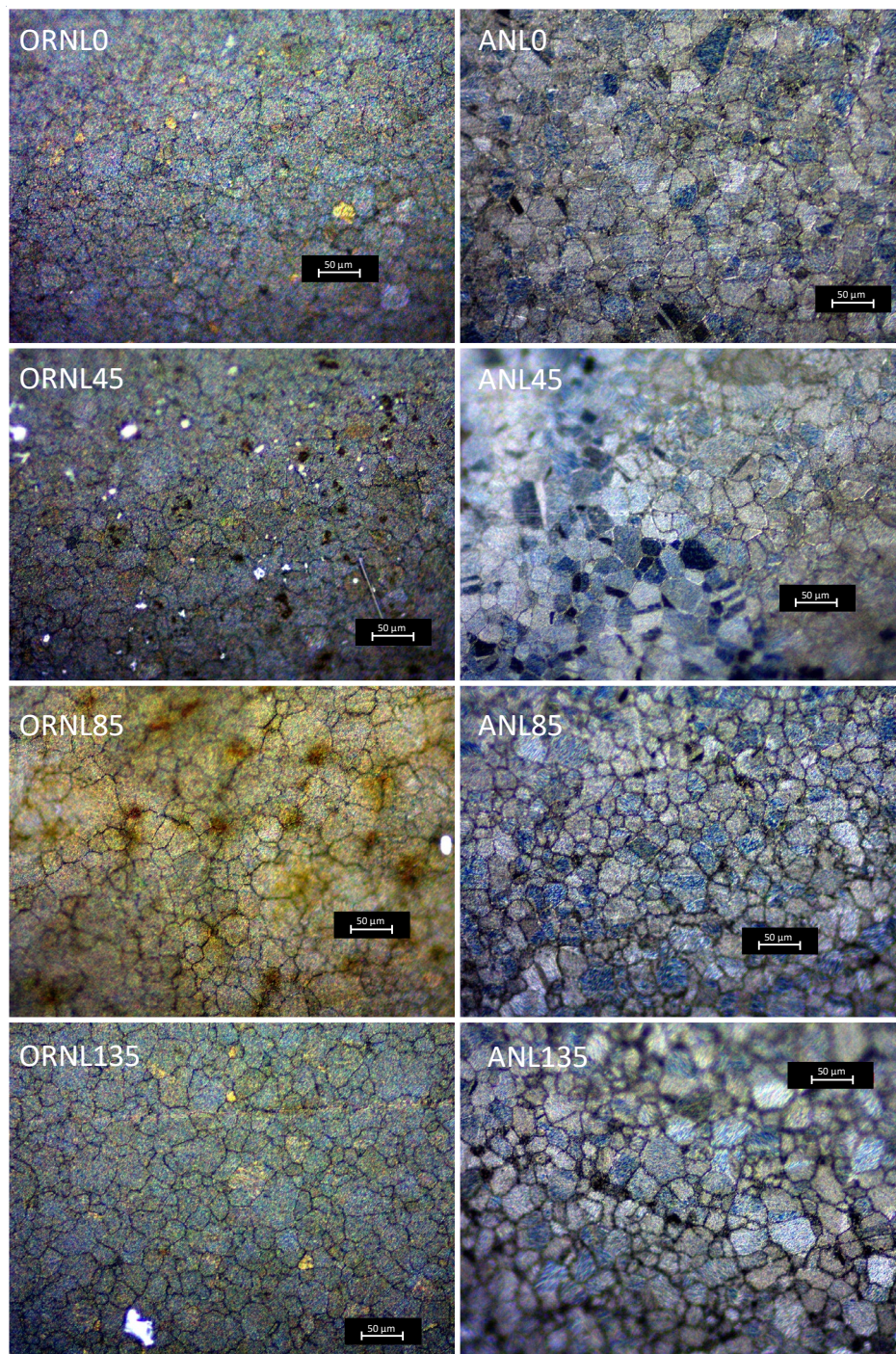


**Figure 17.** Plan View Optical Microscopy of each sample for Run 1 samples. ORNL salt with increasing graphite concentrations on the left and ANL with increasing graphite concentrations on the right. All graphite concentrations are estimates for simplicity.

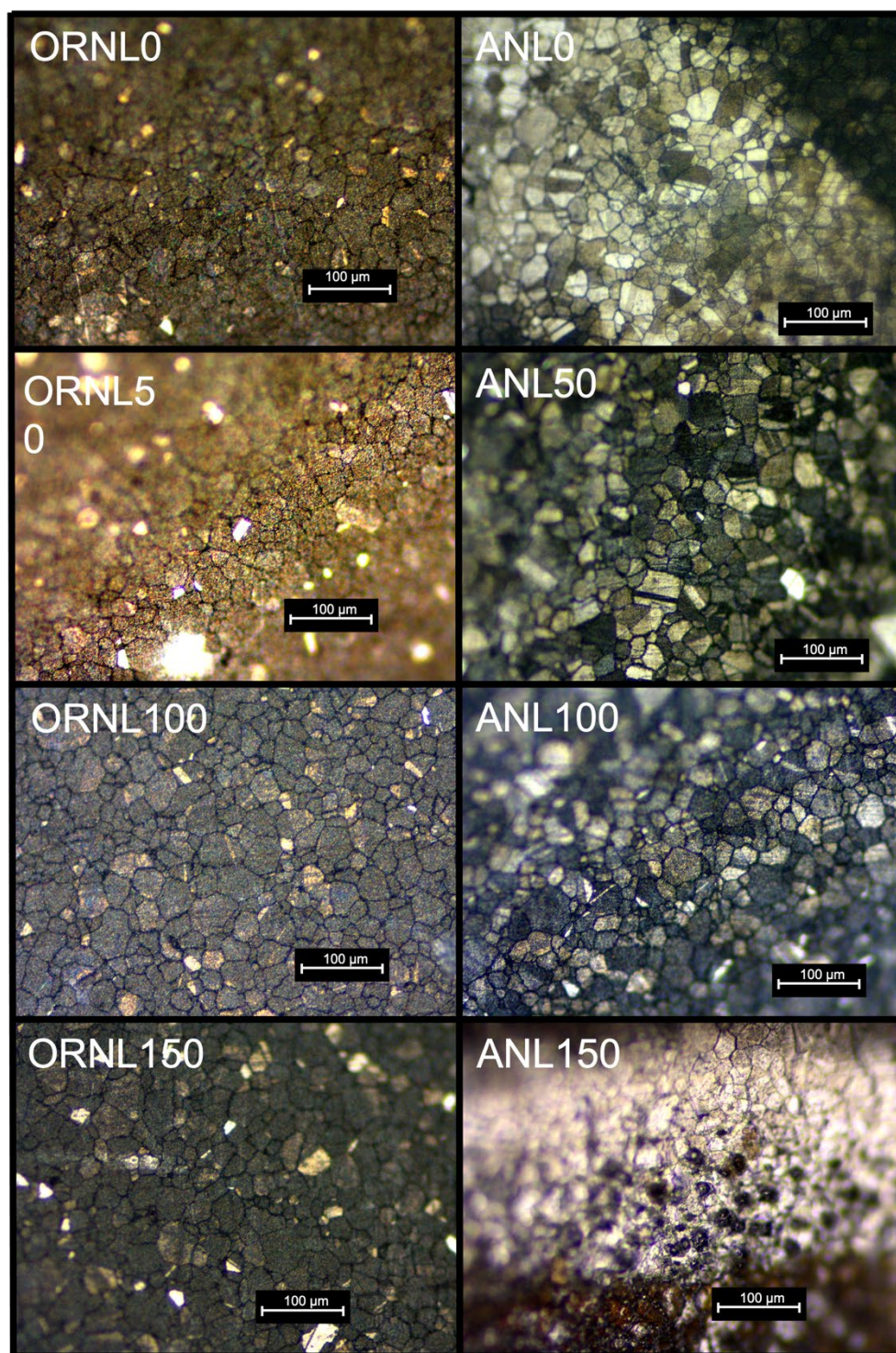


**Figure 18.** Optical Microscopy of each sample face for Run 2 samples. ORNL salt with increasing graphite concentrations on the left and ANL with increasing graphite concentrations on the right. All graphite concentrations are estimates for simplicity.

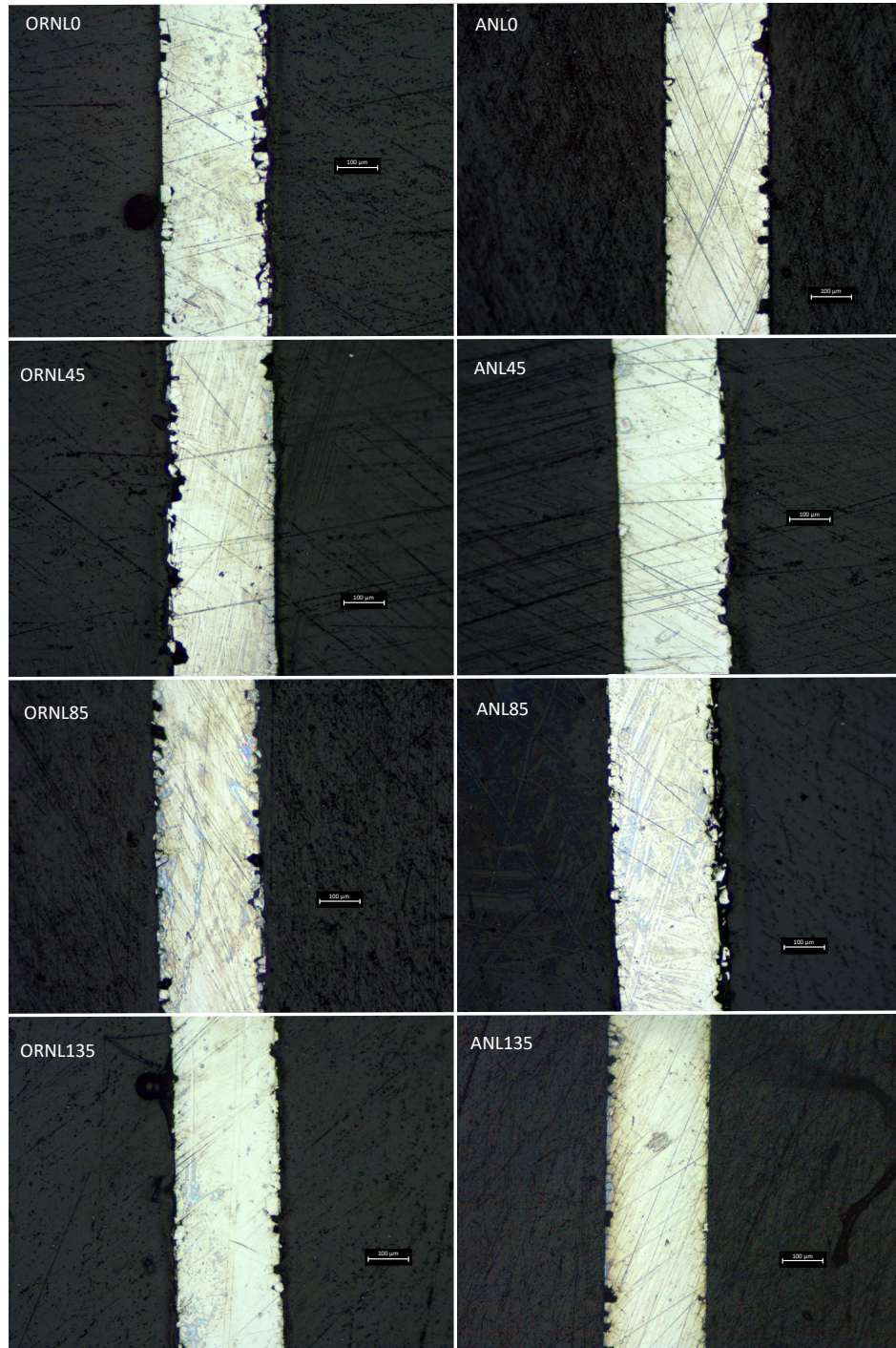


**Figure 19.** Run 1 Optical Microscopy of 316L sample cross-sections. ORNL salt with increasing graphite concentrations on the left and ANL with increasing graphite concentrations on the right. All graphite concentrations are estimates for simplicity.

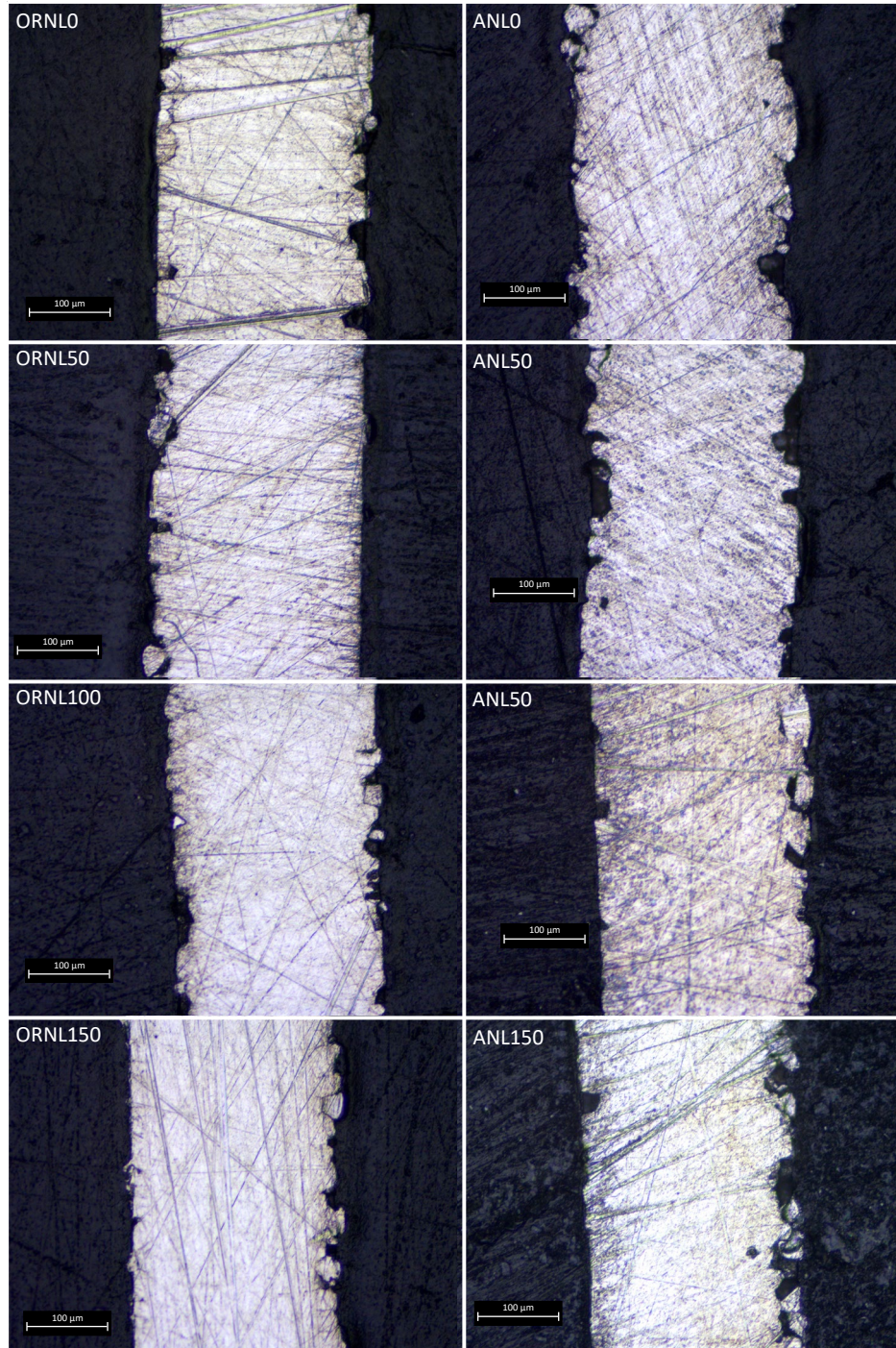


**Figure 20.** Run 2 Optical Microscopy of 316L sample cross-sections. ORNL salt with increasing graphite concentrations on the left and ANL with increasing graphite concentrations on the right. All graphite concentrations are estimates for simplicity.

A closer look at the grain boundaries can be useful to compare the depth of corrosive attack. Therefore, characteristic photos were taken at 50x magnification of Run 2 samples to show grain boundary attack, and thus, corrosive attack penetration. This is shown in Figure 21.

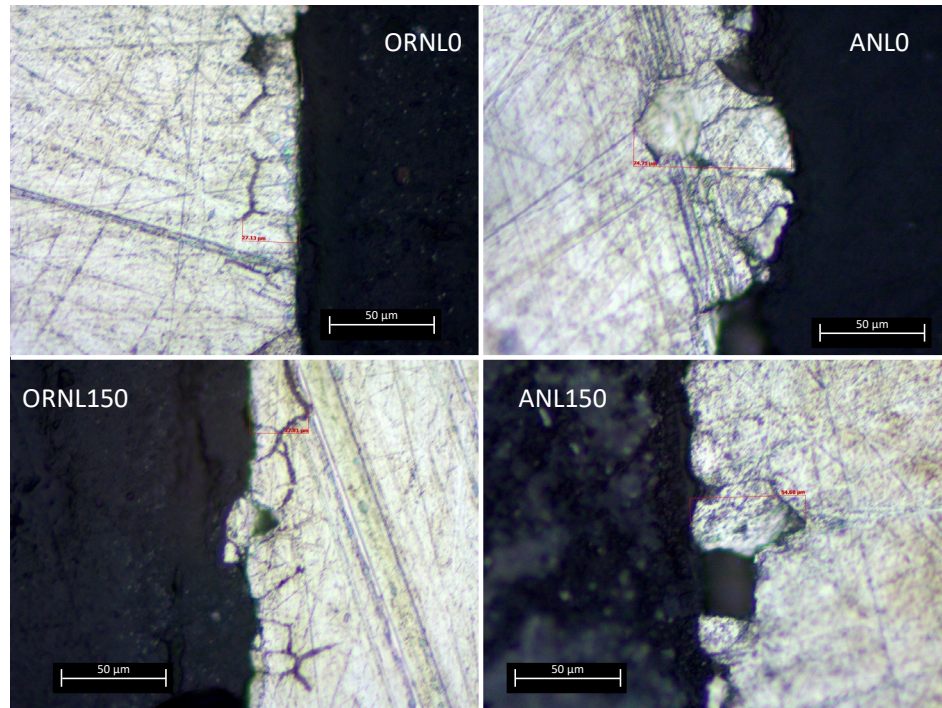


**Figure 21.** 50x magnification of the no-graphite and high-graphite concentrations of the ORNL and ANL salts.

The penetration depths were measured within the photo analysis software. The ORNL0 and ORNL150 penetration depths were 27.3 and 27.8 μm respectively. The ANL0 and ANL150 penetration depths were 74.7 and 54.7 μm respectively. Although these are only one measurement, they were chosen as characteristic points that roughly correspond to the average depth of corrosion throughout the sample.

Although optical microscopy does not give a highly detailed picture of what is happening on the surface of the 316L samples, these photos still give a visualization of the differences of the corrosion within the ORNL and ANL salt samples. The plan view Optical Microscopy images show an interesting difference between the salts. Although the differing graphite concentrations do not change much visually, the salt seems to have a large impact on the surface. The ORNL exposed 316L has a more uniform look between the grains, while the ANL exposed 316L has a more etched appearance, with a greater visual contrast between each grain. These observations are consistent across all graphite concentrations over both experiments. The cross-sectional differences are mostly defined by an increase in “missing” grains in the ANL exposed 316L, implying at greater grain boundary attack that leaves the grains susceptible to being broken off during the polishing process. The reasoning for this will be discussed in a later chapter.

### **4.3 ICP-OES**

To better understand the corrosion mechanism difference between the different salts and graphite compositions, ICP-OES was performed on Run 2’s salt samples to obtain information about the corrosion product concentrations within each sample. After removing the stainless-steel samples from the salt, the Run 1 salt samples were not kept within the argon glovebox. Therefore, the Run 1 salt samples were contaminated post-corrosion through air exposure and were not analyzed with ICP-OES. To begin the ICP-OES process, pre-weighed tin capsules were obtained from the Microanalysis Laboratory in the School of Chemical Sciences at the University of Illinois at Urbana-Champaign. Tin capsules were used because tin is not found in either the 316L samples, salt, or crucibles. Each salt sample was broken apart, ground down into smaller particles that were then used to fill up each capsule. The tops of the capsules were crimped and placed in air-sensitive

jars. This process was completed within an argon-filled glovebox to minimize air exposure. An example of a filled tin capsule is shown in Figure 22.



**Figure 22.** Crimped tin capsule filled with FLiNaK salt used for ICP-OES analysis.

The capsules were transferred to a vacuum desiccator in the Microanalysis Lab and kept there until digestion was done on the sample. For digestion, each sample was weighed out and 5 mL of 70% nitric acid, 2 mL of 36% hydrochloric acid, and 2 mL of 18 M $\Omega$  Millipore water was added. The samples were digested in a CEM MARS6 microwave digestion system with the parameters shown below in Table 10.

**Table 10.** CEM MARS6 Digestion Parameters

|             |            |
|-------------|------------|
| Power       | 700-1800 W |
| Temperature | 240 °C     |
| Ramp Time   | 30 minutes |
| Hold Time   | 15 minutes |

After being digested, the sample solutions were diluted to a final volume of 25 ml. Analysis standards with Cr, Fe, Ni concentrations ranging from 0.5-10 ppm were prepared in 2% nitric acid. The samples and standards were analyzed on a Perkin Elmer Optima 8300 ICP-OES instrument with the operating parameters shown in Table 11.

**Table 11.** Perkin Elmer Optima 8300 ICP-OES Parameters

|                         |             |
|-------------------------|-------------|
| Plasma (Argon) gas flow | 10 L/min    |
| Auxiliary gas flow      | 0.20 L/min  |
| Nebulizer gas flow      | 0.80 L/min  |
| RF Power                | 1500 W      |
| Pump flow               | 1.50 mL/min |

Two emission lines were measured for each element of interest. The line that presented the highest precision was used for quantification. The elemental lines are shown below in Table 12. A quality control standard was run after the samples, which was within  $\pm 10\%$  of the expected concentration.

**Table 12.** Emission lines used for elemental analysis in ICP-OES

|    |            |            |
|----|------------|------------|
| Cr | 267.716 nm | 205.560 nm |
| Fe | 238.204 nm | 239.563 nm |
| Ni | 231.604 nm | 221.648 nm |

Chromium, Iron, and Nickel concentrations were measured for each FLiNaK sample, the results are shown below in Table 13.

**Table 13.** ICP-OES Results for Cr, Fe, and Ni Concentrations

| Sample | Cr (ppm) | Fe (ppm) | Ni (ppm) | Salt Type | Carbon Concentration (mg/kg) |
|--------|----------|----------|----------|-----------|------------------------------|
| 1      | 200      | 2440     | 0        | ORNL      | 0                            |
| 2      | 0        | 2030     | 0        | ORNL      | 50                           |
| 3      | 270      | 1910     | 0        | ORNL      | 100                          |
| 4      | 210      | 2640     | 0        | ORNL      | 150                          |
| 5      | 0        | 1960     | 0        | ANL       | 0                            |
| 6      | 0        | 2070     | 0        | ANL       | 50                           |
| 7      | 0        | 2400     | 0        | ANL       | 100                          |
| 8      | 0        | 2730     | 0        | ANL       | 150                          |
| 9      | 0        | 2660     | 0        | ORNL      | 0                            |
| 10     | 0        | 2830     | 0        | ANL       | 0                            |

Looking at this data on the surface, it is problematic. The iron concentration is elevated much higher beyond the chromium levels. This would imply that the primary mechanism of corrosion uses iron instead of chromium, which is a direct contradiction to what the literature has said. The largest red flag of the iron data is samples 9 and 10. These samples did not contain any 316L foil. Without having an outside source of iron, these salts should not contain any concentration of chromium or iron. After looking at the stainless-steel foil used to line the furnace, it was determined that there wasn't any flaking of the foil caused by oxidation or evaporating FLiNaK, that could contaminate the salt. Therefore, the elevated iron content must be coming from the ICP experimental procedure. After counseling with the ICP staff scientist, two samples were to be re-run, mid-graphite (100 ppm) FLiNaK of both ANL and ORNL. Sample numbers 3 and 7 from Run 2. The samples were to be ground into a finer powder, hopefully homogenizing the

mixture, and more salt was to be used. The staff scientist also realized that there is a spectral overlap of emission lines between iron and tin. Tin has a spectral line at 238.204, which coincidentally overlaps directly with the iron spectral line shown in Table 12. The new salt samples were then not put into tin capsules, instead digested directly into the acid solution described above. Because each sample is no longer digested and contained within a tin sample, the 238.204 wavelength of iron was used again, along with the same wavelengths for chromium. The results of this experiment are shown below in Table 14.

**Table 14.** ICP-OES Results for Cr and Fe Concentrations

|    | Sample 3 Concentration (ppm) | Sample 7 Concentration (ppm) |
|----|------------------------------|------------------------------|
| Cr | 30                           | 20                           |
| Fe | 10                           | 0                            |

The data from the second experiment is much less contradictory. With concentrations of the corrosion products being within expected levels.

The chromium concentrations within Table 13 are also troubling. From the mass loss data, the ANL samples showed a greater amount of corrosion which would imply a larger concentration of chromium and iron within the salt. However, as seen above in Table 13, no chromium was found within the salt. This could be a consequence of the non-uniformity of the salt and the small amount of sample salt used for the measurements. Yet the possibility of missing the chromium four times is unlikely, as is shown in the ORNL salts. Three out of four samples contain chromium while the fourth does not. The combination of a higher corrosion rate and lower chromium and iron content within the salt brings about the need to find where the corrosion products are located. A look at the nickel crucibles post-exposure may provide the answer. Within the ORNL salt crucibles, the

sides where the FLiNaK salt are touching the nickel, the sides are clean, only with a small amount of salt still attached. The nickel crucibles containing the ANL salt contain a black scale, covering the inside of the crucible where the salt was in contact with the crucible. The comparison between the ORNL and ANL nickel crucibles is shown in Figure 23. The photo is representative of the entire set of crucibles. Every ORNL crucible was clean while every ANL crucible had a black deposit along the inside.

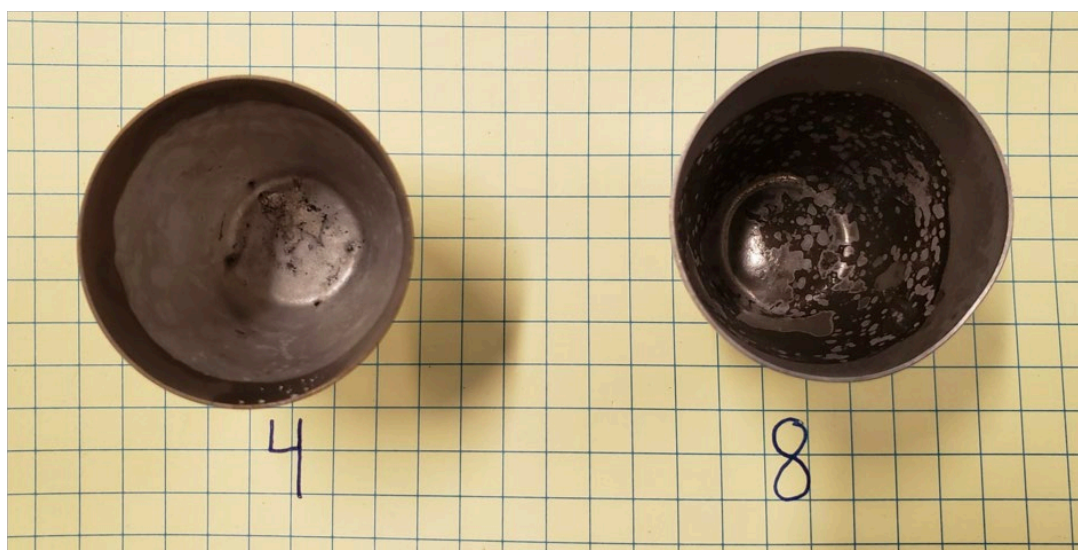


**Figure 23.** Nickel crucible from Run 2 for samples 4 (ORNL high graphite) left and 8 (ANL high graphite) right. Crucible 8 shows deposition along the FLiNaK contact surface while crucible 4 does not. Black deposit in the bottom of sample 4 is loose graphite, not deposited on the surface.

To determine what this deposit is, another ICP experiment was conducted. Sample crucible 6 was taken and a considerable amount of the black deposit was scraped off. The deposit was

contained in an air-tight vial and transported to the ICP-OES laboratory. The deposit was put through the same procedure as the second round of ICP samples. Without the tin container, the black scale was digested in the acid solution and ran under the same instrument conditions as described in Table 11. The intent was to determine what atoms were making up the deposit. It was hypothesized that the corrosion products were being plated out onto the nickel crucible. Therefore, chromium and iron atoms were to be screened for during ICP-OES. Concentration values wouldn't be of much use; however, a percentage of each atom could help determine where and what element is being corroded. Because tin is not a factor in these sample matrixes, the wavelengths given above in Table 12 were used for analysis. The results are shown in Table 15.

**Table 15.** ICP-OES results for deposit on the ANL sample 6 nickel crucible.

|        |        |
|--------|--------|
| FLiNaK | 98.08% |
| Cr     | 0.29%  |
| Fe     | 1.63%  |

Most of the black deposit is FLiNaK. This is to be expected as the crucible wasn't washed prior to scraping the surface as to preserve the deposit. Even with the large amount of FLiNaK within the sample, the amount of chromium and iron was elevated, with those metallic atoms being just under 2% of the entire sample. Compared to ppm levels in the sample salt itself, this shows that the deposit is primarily the missing corrosion products. Chromium levels look to be much smaller than iron levels. With chromium being 0.29% of the sample and iron being 1.63%. Unfortunately, this result nullifies much of the comparisons that can be made from the ICP-OES data between the ORNL and ANL salt samples because most of the corrosion products are on the walls of the crucible and not contained within the salt. However, the ICP-OES data combined with

the mass loss data can provide sound reasoning for differing corrosion mechanisms between the ORNL and ANL salts which will be discussed in the next chapter.

# Chapter 5

## Discussion and Conclusions

Corrosion within a molten salt system is a complicated process, with many variables affecting the severity and mechanisms. Some of these variables include salt purity and crucible material. The experiment above was designed to study the effect graphite concentration has on corrosion kinetics. The work in this thesis is building on the study done by Liu et al that found an increase in corrosion severity with higher graphite concentrations in eutectic FLiNaK of 316H stainless steel [36]. With the lower concentration of carbon in 316L, understanding if 316L is susceptible to corrosion could provide some insight to possible structural material choices in systems containing molten salt or supply more details on the corrosion mechanisms within molten salts. Unfortunately, the data from the 316L experiment did not show a meaningful correlation between graphite concentration and mass loss, as seen in Figures 12 and 13. With an increase in graphite concentrations over both runs and within each salt not substantially increasing corrosion, and in some cases, lowering mass loss. However, this does not mean that graphite has no effect on corrosion. The 316H and 316L experiments were very similar but had a few key differences. The 316H samples were suspended in a 316H crucible. The suspension was accomplished by attaching foil coupons to a ceramic lid with a wire. The choice of 316H as the crucible nullified the amount of galvanic corrosion within the system. The graphite particles were also mixed into the FLiNaK uniformly by grinding them together. The exposure time for the 316H experiment was 50 hours, comparable to the exposure time of 72 hours for the 316L. Nickel crucibles were chosen for the 316L experiment due to the known resistance to FLiNaK attack, limiting impurities leached

into the salt by crucible corrosion. When comparing mass loss normalized to surface area between the 316L and 316H experiments, the difference is substantial. The highest mass loss in the 316H occurred with the highest graphite concentration of 130 mg/kg, and was small, with a weight change of roughly 0.22 mg/cm<sup>2</sup>. The mass loss in every single one of the 316L samples for either experiment was larger by over a factor of 10. With the smallest amount of mass change being around 3 mg/cm<sup>2</sup> for the ORNL salt samples from the second run. The mechanism described by Liu et al hypothesizes that when chromium is leached out of stainless steels, it will react with the surface of the graphite particles creating chromium carbides. Carbide creation draws chromium ions out of solution, increasing the concentration gradient between sample and salt. Thus, increasing the rate of corrosion. This mechanism was shown to increase mass loss from 0.12 to 0.22 mg/cm<sup>2</sup> from pure FLiNaK salt to a concentration of 130 mg/kg of graphite. The effect of graphite concentration looked to saturate around 80 mg/kg. This saturation is thought to be an effect of carbon from the graphite particles dissolving into the surface of the steel. As carbon concentration grows within the surface, chromium mobility decreases due to in-sample carbide formation, making corrosion slower. The mechanism that graphite increases corrosion kinetics is fragile, by increasing corrosion rates by adjusting concentration gradients of corrosion products within the salt. This is shown by the small mass change of 316H after exposure. This mechanism is applicable to the general surface corrosion of stainless steel. Instead of primarily attacking at the grain boundaries, the corrosive attack is spread across the surface. This broad attack is not shown in Figures 19, 20, and 21. In these figures, grain boundaries are being attacked more preferentially than the surface, indicating a different mechanism is responsible for the larger mass loss in this experiment. Liu et al, successfully isolated this mechanism through their experimental design. Comparatively, the 316L experiment above has multiple corrosion mechanisms observed due to

the much larger mass change data gathered. These other mechanisms may be overwhelming the small effect that graphite concentration has.

Although no conclusion can be drawn about 316L sensitivity to corrosion in relation to carbon concentration, understanding the other corrosion mechanisms can provide other meaningful observations. A key piece of the experimental setup that contributed to the elevated corrosion was the choice of nickel for the crucible. When two metals with different electrical resistances are connected by contact or an electrolyte, electrons will flow between each metal surface. The difference in potentials drives the electron movement, causing the oxidation and reduction corrosion reactions discussed in the corrosion chapter. Electronegativity is a way to quantify these potentials. Electronegativity can be defined as the ability for an atom to attract neighboring electrons and the ability for an atom to hold on to its own electrons. Linus Pauling developed a scale to qualitatively scale the electronegativity of elements, with the higher the electronegativity, the higher the number on his scale. The highest number is fluorine with a value of 3.98. Within our corrosion system, nickel, iron, and chromium have values of 1.91, 1.83, and 1.66 respectively. Because of nickel's electronegativity value, the nickel surface becomes cathodic, accepting electrons from the anodic stainless steel. The effect that nickel has on corrosion has been studied by Olson et al [36]. In the study, mass loss per surface area of Incoloy-800H due to corrosion within eutectic FLiNaK was compared with different crucible material. The crucible materials used were nickel, graphite, and Incoloy-800H. The exposure time was 500 hours. It was found that corrosion within nickel and graphite crucibles was 30x greater than corrosion within the Incoloy-800H crucible. Although this is a study of an Incoloy, the leaching of chromium was still the main cause of mass loss, in which we can draw similarities between our experiment. The chromium concentration increases being shown in the ICP-OES data in Tables 13 and 14 along

with the deposition layer data in Table 15. Chromium, being the least electronegative constituent of 316L, will leach out quicker. The graphite particles and nickel crucible surface act as sinks for the chromium to precipitate out of solution. Keeping the chemical activity of the salt high. This galvanic effect is an important factor in the severity of corrosion and may be the reason for the high mass change within our system. By using nickel as our crucible, the effect carbon had on the corrosion process was drowned out.

The galvanic coupling between 316L and nickel was shown not only by the mass change, but also by the location of corrosion products within the system. Within the ANL salt, the chromium and iron concentrations should be much higher than the ORNL salt, just based on the amount of corrosion of the sample. This is not the case, with the ANL salt containing similar or even smaller amounts of iron and chromium. The missing corrosion products were found plated out on the surface of the nickel crucible. The obvious question is then why the plating only occurred on the crucibles that contained the ANL salt. Each sample within the second run was subjected to the exact same experimental conditions, with the only changing variable being the salt composition. Looking back at Table 5, the ANL salt's primary impurities were iron and nickel and the ORNL salt's main impurity was calcium. One idea could be the solubility limit of chromium and iron was reached within the ANL salt and not in the ORNL salt because of the higher rate of corrosion. The solubilities of chromium, iron, and nickel in FLiNaK have been studied and are determined to be at roughly 600 °C; 0.061, 0.39, and 0.73 wt% respectively [37]. Every sample salt had around 30 grams of FLiNaK. Using these values, the maximum amount of chromium, iron, and nickel this amount of FLiNaK can have in solution would be: 54, 58, and 61 mg respectively. Without normalizing to surface area, the greatest mass loss in the 316L samples exposed to the ANL salt was roughly 20 mg. Even if this value was only chromium, it would not

be enough to surpass the solubility limit. The only other obvious culprit is the calcium within the ORNL salt. Calcium does have a lower electronegativity value than that of chromium, so it is possible that the calcium interacts first with the nickel crucible instead of chromium. This could make a protective layer on the nickel surface that would inhibit the reaction of chromium or iron with the nickel crucible. The calcium content of both salts is still quite high, in the 100-ppm range, therefore the calcium concentration cannot singlehandedly account for the plating of the corrosion products. However, the different starting nickel and iron impurity concentrations between the ANL and ORNL salt may influence the way constituents are plated onto the nickel crucible. More work would have to be done to test the hypothesis on this subject.

While galvanic coupling could be the reason the baseline corrosion severity was high for both FLiNaK salts, the differences between corrosion severity between the ORNL and ANL exposed samples within the second experiment were considerable. And likely a consequence of salt purity. A study done by Raiman et al. analyzed every corrosion experiment done with chlorinated and fluorinated salts [38]. The goal of the study was to create a condensed library of each experiment and determine a correlation between the most prevalent factors for corrosion severity in molten salts. It was found that salt purity had the highest correlation coefficient with corrosion severity.

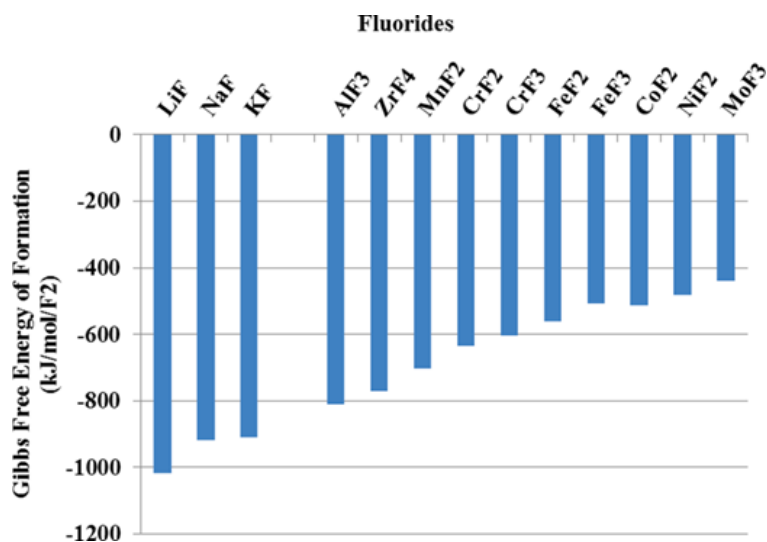


**Figure 24.** Gibbs free energy of formation for fluorides. Separated by salt constituents and common impurity fluorides [36].

The reason for the strong correlation between impurity and corrosion is illustrated above in Figure 24. The individual components of FLiNaK: LiF, NaF, and KF, all have vastly more negative free energy of formations than that of the constituents of 316L. Therefore, the thermodynamic energy barrier for the salt compounds to disassociate, react with a sample surface atom, and create a fluoride compound is substantial. Consequently, in pure fluorine salt, corrosion of chromium, iron, and nickel would be slow or nonexistent. Whenever impurities are found in the salt, however, new reactions occur that are thermodynamically favorable. For example, the ANL salt above has a considerable amount of iron and nickel impurities that were introduced into the salt from its synthesis. These iron and nickel impurities create fluoride compounds that are relatively unstable compared to the salt components. Once the corrosion experiment begins, these impurity fluorides can encounter the sample surface. Either chromium fluoride compound shown in Figure 24 is

avored thermodynamically more than both nickel and iron fluorides. This reaction is shown below.



Similar reactions can be undergone by  $NiF_2$ ,  $FeF_3$ , and even  $CrF_3$ . This reaction drives corrosion within the early stages of salt exposure until solubility is reached. The ORNL salt above had minimal impurities, with averages of 25 ppm for iron and 1 ppm for nickel. The ANL salt contained 117 ppm of iron and 179 ppm of nickel atoms. The effect of the impurities was drastic, with the mass loss of the ANL salt exposed samples being almost double that of the ORNL salt samples within the second experiment. One observation that may need to be looked at further is a decrease in corrosion severity with greater graphite concentrations in the ORNL salt exposed samples. Shown in Figure 14. This effect may be due to the carbon reacting with the impurities within the salt, creating iron and nickel carbides. The carbide formation could decrease the reactivity of the salt with the chromium of the 316L, decreasing mass loss with an increase in graphite concentration. The effect this would have depends upon the stability of the carbides in FLiNaK at elevated temperatures. According to studies about the stability of nickel and iron carbides,  $NiC_3$  is stable above 500°C and  $FeC_3$  is stable above 700°C [39,40]. The instability of the carbides may be why graphite lowering corrosive attack effect doesn't counter impurity driven corrosion fully. If these carbides are formed at lower temperatures, the concentration of free metallic impurities would decrease. As the temperature is raised into a standard operating temperature of a molten salt reactor, these carbides decompose, increasing the concentration of these metallic impurities. More work would have to be done to test this hypothesis. In any case, small concentrations of metal

impurities, specifically nickel and iron, increase corrosive attack in the early stages of exposure drastically. This is evident in the data gathered in this work.

Metallic impurities are not the only factors that can have an impact on corrosion within a fluoride salt. Atmospheric impurities such as oxygen and water can create an environment that induces greater corrosion chemistry. The impact that atmospheric impurities can have is illustrated when comparing the mass loss of the 316L samples between Run 1 and Run 2. FLiNaK salt is highly hygroscopic and will readily absorb water. Water absorption is mainly caused by the hydration of KF. At high temperatures, this absorbed water hydrolyzes the salt creating HF. HF will then react with chromium using the same mechanism and chemistry as shown above in equation 5 [23]. Sona et al showed the importance of drying the salt before starting exposure [41]. Drying was accomplished by heating the salt to 130 °C for three hours. Corrosive attack was lessened in the salt that underwent this drying process, determined by lesser mass loss after exposure. For the work in this thesis, care was taken when storing and transferring both ANL and ORNL salts to minimize exposure to air. Both salts were stored in an argon filled glovebox in airtight containers until ready to be used. Also, before the tube furnace was heated to 600 °C, the furnace was held at 120 °C for 24 hours. Compared to the Sona experiment, this was more than enough time to thoroughly dry the salt. Minimizing the water contamination and HF formation within the salt during exposure. During Run 2, while at temperature, the bubbler kept an overpressure of argon within the tube, keeping atmospheric contamination to a minimum. Compared to the experiment without the bubbler installed, mass loss was significantly less with the bubbler. When comparing mass loss data between the two different experiments, the mass loss between the ORNL and ANL salts without the bubbler is much more similar than with the bubbler. This is illustrated in Figures 14 and 15. The similar corrosion intensity implies the corrosion

mechanism is shifting from metallic impurity driven to water impurity driven in the impure environment. Chemically this would make sense, HF is much more oxidative than the fluoride compounds created with metallic impurities. The assumed continuous flow of water and oxygen into the system would be a stronger driving force in the corrosion process. Ouyang et al showed that even a small amount of water absorbed into the salt would increase the oxidative potential of the salt immensely [43]. A 3.19 wt % concentration of water in FLiNaK would increase corrosion by an order of magnitude over a time period of 100 hours. Between the two experiments shown here, corrosion without the bubbler caused an increase in mass loss by about a factor of two. Although the concentration of water was unable to be obtained in either of these experiments, by using the mass loss as an indicator, atmospheric impurities were controlled during the test with the bubbler. Isolating at least one corrosion mechanism from the 316L samples within Run 2.

Corrosion susceptibility within the microstructure of 316L is also illustrated above within the optical microscopy photographs. It is well known that corrosion is more likely to occur at grain boundaries. When two different grains connect, vacancies are created by imperfect contact. The vacancies enhance diffusion through the grain boundary. Within stainless steels, carbon diffusion into the grain boundaries creates chromium carbides. Chromium provides corrosion resistance to stainless steel, as it is depleted through this carbidization process, the entire sample becomes more sensitive to corrosion. 316L has a lower carbon content than 316H, making it less susceptible to this sensitization, an effect we had hoped to observe within this experiment. This process would have to be looked at with a different experimental setup to decrease the galvanic corrosion mechanism. The grain boundary depletion described above is seen clearly in the optical microscopy figures. In both the plan-view and cross-sectional photos for both runs, the grain boundaries are distinctly defined, much more than that of non-corroded 316L. The cross-sectional

view illustrates the depth of the corrosive attack, another merit of corrosion intensity. The ORNL exposed Run 2 316L sample shows moderate penetration depth, while the ANL exposed Run 2 sample has a penetration depth almost double. Reaffirming the difference in corrosive attack between the purer ORNL salt and the contaminated ANL salt. The preference for corrosion to occur at the grain boundaries also suggests that microstructure control is important for corrosion resistance. A study from Maric et al. observed the correlation between cold-working 316L stainless steel and the effect it had on corrosion susceptibility. They found that as more cold work was done on the steel, grain boundary length increased. The difference in corrosive attack between a plate of 316L stainless steel with 0% thickness change and a plate that was 30% thinner changed from 1.75 mg/mm<sup>2</sup>/year to 2.75 mg/mm<sup>2</sup>/year [42]. The 316L samples were cold rolled during manufacturing to obtain their thickness, however they were annealed afterward to remove dislocations. Although no cold rolling was done to decrease the thickness of the 316L samples during this experiment's sample preparation, it still is worth it to note the possibility that the bending of the 316L coupons can have an impact on corrosion severity in a more sensitive test. Because each sample was bent the same way, the comparisons between the different salts are still valid.

In general, corrosion is a complicated process with many factors influencing severity. 316L corrosion in molten FLiNaK is no different. Each mechanism needs to be understood completely to be able to isolate a single factor and study it. Although the systematic study of the effect that graphite concentration has on corrosion severity in 316L stainless steel was inconclusive, other mechanistic observations were able to be observed. Experimentally, the successful implementation of a bubbler to confirm atmospheric purity while undergoing exposure within a 6" tube furnace. This confirmation also showed the primary mechanism of corrosion being water contamination

even when other possible driving factors are around, such as metallic impurities or galvanic corrosion. Making atmospheric control a high priority for corrosion control in FLiNaK systems. Once atmospheric purity is controlled, the biggest finding of this research is the importance of metallic impurities impacting corrosion severity. 316L exposed to ORNL sourced salt, in which the main impurity being calcium, showed significantly less mass loss after 72 hours than 316L exposed to ANL sourced salt, which had significant concentrations of iron and nickel impurities. Accelerated corrosion was caused by the thermodynamically favored reaction of iron and nickel fluorides in the salt solution with chromium atoms in the stainless steel. In the case of the ANL salt, chromium and iron corrosion products were then plated out onto the nickel crucible, keeping the concentration gradient higher between the 316L and the FLiNaK salt. The plating of corrosion products was not seen on the ORNL sample crucibles. The magnitude of corrosion severity cannot be quantitatively determined, only qualitatively, due to the other corrosion mechanisms at work such as galvanic corrosion and graphite addition. However, the observation of mass loss decreasing with increasing graphite concentrations for the ORNL salt could have merit. More work would have to be done to prove this hypothesis. The work in this thesis provides a solid framework for subsequent experiments in 316L corrosion in FLiNaK through the illustration and understanding of multiple mechanisms that affect the corrosion reactions present in molten salt systems.

# Chapter 6

## Recommendations for Future Work

This work was unsuccessful in determining the impact of graphite on 316L stainless steel; however, it did provide meaningful insights into how this could be measured. The same test should be redone in 316L crucibles with a lid where the 316L coupon should be attached to, keeping the sample and crucible from contacting. Only the ORNL FLiNaK salt should be used but the same concentrations of graphite should be used, 0, 45, 90 and 135 mg/kg of graphite. The ORNL salt should be ground down into a powder and mixed evenly with the graphite. This experimental setup should isolate the carbon corrosion mechanism well enough to determine sensitivity to graphite. A mirrored experiment with 316H samples and crucibles could be done to compare the corrosion robustness between the two alloys. The idea that graphite can become a sink for impurities, lessening the corrosive attack in impure salts can also be looked at. A systematic study, starting with pure salt and adding increasing concentrations of iron and nickel, of an alloy of choice would be beneficial in determining if graphite can lessen the impact of impurities on corrosion. In the context of nuclear reactors, little research has been done on the impact of radiation damage in FLiNaK corrosion. Radiation induced segregation within an alloy may have a significant impact on corrosion susceptibility. A study on microstructure and mechanical properties on unirradiated and irradiated samples of 316SS and Inconel after exposure to a molten salt would be beneficial in helping determine engineering concerns when designing the next generation of nuclear reactors. This work mentioned here could help understand more of the complexities in molten salt corrosion and add to the engineering arsenal for molten salt reactors.

# Chapter 7

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