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Synthesis and Characterization of Simulated Corium Materials

Master's thesis in Materials Chemistry

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
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Cover: Wind visualization constructed in Matlab showing a surface of constant wind speed along with streamlines of the flow.

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Abstract

One part, of the massive undertaking that is risk management and accident prevention regarding nuclear power, is the study of corium. Corium, being the resulting material created during a nuclear meltdown, is an amalgamation of molten nuclear fuel combined with anything and everything it comes into contact with. Corium is not only dangerous during a meltdown when it risks causing further damage to the reactor and surrounding equipment. Due to it's high radioactivity, it stays dangerous for a significant amount of time after the accident as well. It is therefore important to study this material in order to better understand how to minimize any potential further damage, further contamination of surroundings and to find ways to safely carry out cleanup efforts. These studies however, are quite limited due to the hazardous nature of the corium. This project is therefore focused on exploring a way to safely synthesize small batches of low-activity corium, without requiring specialized equipment, to be used for smaller scale studies. This proof of conept was achieved by first synthesizing spent nuclear fuel consisting of UO_2 in the form of 238 U, as a lower activity replacement of enriched uranium, doped with several inactive elements for the purpose of simulating fission products. This powdered SIMfuel was then ground together with a selection of materials commonly found on the inside of a nuclear reactor and then fired in a reducing atmosphere at temperatures up to 1750°C to create a clump of material similar to corium. Analysis of this corium using powder-XRD and ICP-MS showed that the structure and properties of the synthesized corium varies significantly based on the composition and temperature it was created in. A leaching study was also carried out using the samples, but the results were inconclusive. The (justifiable) lack of real-world corium samples available for analysis means very little to compare these samples to, but this shows that a method of creating low activity samples it possible.

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Jesper Ozolins, Gothenburg, January 2025

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Introduction

An expansion of nuclear power around the world has the potential of providing incredible benefits to the world. Nuclear power plants have the potential to provide large amounts of electricity all while producing very low greenhouse gas emissions and working independent of time of day and weather conditions. In a nuclear reactor, heat is generated from the energy released by fission material in the fuel. The fission can happen in different ways depending on the isotope. For commercial power generation, reactors are normally of the type "LWR" (Light-Water Reactor) meaning they use (H_2O) as coolant and moderator. This also means they require enriched uranium as fuel, where the concentration of ^{235}U has been artificially increased in the fuel as compared to it's concentration in naturally occurring uranium. ^{235}U is what's known as a fissile material, meaning that if it absorbs a thermal, or "low energy" neutron, the isotope formed will then undergo fission. This is unlike ^{238}U which is known as a "fertile" material. A fertile material will not undergo fission upon absorbing a thermal neutron but will instead become a fissile material. In the case of ^{238}U it will become a ^{239}Pu atom through absorbing a neutron, becoming ^{239}U then through β^{-}-decay, ending up as ^{239}Pu which is a fissile material. It is through the fission of these fissile materials like ^{235}U and ^{239}Pu that majority of the energy in a nuclear reactor is produced. When the fissile nucleus absorbs a neutron it will then shortly after split into 2 smaller nuclei. This split releases energy as well as 2-4 neutrons. These new neutrons are what is being utilized to further the chain reaction. A moderator is used to control the energy of said neutrons, keeping them at a low enough energy for the reaction to continue. While control rods can be inserted to absorb neutrons in case the amount of neutrons becomes too high or the reactor needs to be shut down. This is how the primary production of heat is controlled in a nuclear reactor.

What is more difficult to control are the so called "fission products" (FPs.) These are the nuclei formed after fission and follow a bimodal distribution centered around half the mass of the original nucleus[1]. Many of these FPs are radioactive as well and will continue to decay independently of the state of the reactor which means they continue to generate energy. This heat, known as "decay heat" is why it is very important to keep cooling a reactor after shutdown as the fuel will continue to be heated through this decay heat for a long time. The decay heat is often what is responsible for any core damage in accidents where the control rods function but cooling does not. The meltdown occurring at Fukushima-Daichi nuclear power plant, Japan, in 2011 was a Loss-Of-Coolant Accident (LOCA) where the decay heat was enough to cause the core to begin melting, forming corium[2].

Corium is the collective name for the amalgamation of materials formed during a meltdown in a nuclear reactor. Containing for example the fuel and the structure holding it, control rods and in more severe cases it could also make its way down to the base of the reactor, melting a hole through the concrete and picking up that material as well. The properties of corium is of high interest with regard to disaster cleanup as these masses of highly radioactive material has to be safely managed and disposed of, or contained in order to avoid further contaminating the area. Properties such as leaching behavior of radioactive nuclides, primarily FPs, present in the corium in contact with water can be imperative to know in order to manage the safety of the local environment and limit any potential consumption or exposure to said potential contamination.

FPs also pose a problem once the accident has been brought under control. FPs present in the corium after a meltdown causes the mass to stay hot and radioactive, making it very dangerous to be near and therefore hindering cleanup efforts. Fission products like ^{131}I and ^{137}Cs are also volatile and can travel a long distance by wind if exposed to the open air and can therefore contaminate very large areas due to still being radioactive[8]. There is also a risk if the corium is in contact with water, that other active FPs might leach into said water and contaminating it. Understanding how FPs behave inside the corium and how they behave in contact with different mediums are important both in risk assessment and risk management both before and after an accident. However, due to the dangerous nature of corium as described previously in this section, it is not trivial to analyse.

Study of corium is being done at an extensive scale at facilities such as PLINIUS and PLINIUS 2 in France which are dedicated to the synthesis and research of corium formation and interaction[10] with research relevant to e.g. the corium formed during the Fukushima-Daichi meltdown[7]. But for for smaller scale experiments it is of interest to develop a method of corium synthesis applicable on a smaller scale. This has also been done before[4][5]. However the purpose of this project is to test a method of synthesizing similar corium-like materials leaching studies but without the use of active tracers. The goal of the method is synthesising corium on a laboratory scale for use in further research in leaching studies of various aqueous environments. The study will investigate a potential temperature dependence on the physical properties and solubility of corium formed in a reducing atmosphere, given a set ratios of elements.

2

Theory

2.1 The Simulated Nuclear Reactor

Due to the number of variables that can be changed regarding the synthesis of corium, baseline parameters have to be established. A standard design for many nuclear reactors usually consists of a reactor casing, coolant, control-rods and a fuel source. For this project, the reactor casing is chosen as the concrete constituents Calcium oxide CaO and Silicon dioxide SiO_2, keeping them as separate components to better maintain control over amount added and to avoid adding unknown compounds that could be present in premade concrete powder.

The coolant in most thermal power reactors used at the time of writing is water. Water will not be a component in the experiments although its effect on the fuel cladding is a relevant consideration. The cladding of the fuel rods is generally a Zirconium alloy which, under normal operating conditions (300c) does not react with water. But at temperatures of 1200c and above it reacts with the steam produced from the heat, forming Zirconium dioxide ZrO_2 and hydrogen gas H_2[12]. During a meltdown, the fuel reaches temperatures significantly higher than that of 1200c meaning the most likely material the fuel is going to come in contact with is Zirconium dioxide.

The simulated fuel is chosen as natural Uranium dioxide, meaning the uranium contains ca. 99.28% ^{238}U and 0.7% ^{235}U which is then doped with a selection of inactive elements to simulate fission products. This is to avoid working with any highly active materials such as the enriched uranium, where the concentration of the more active isotope ^{235}U has been artificially increased, found in most reactors. Or the active fission products formed from its decay. Instead choosing the higher concentration of the much less active ^{238}U and doping it with simulated fission products to imitate spent fuel. The dopants are selected from a set of elements shown to have worked well during previous experiments doping UO_2[6]. Dopants are also selected to try and represent multiple parts of the periodic table to try and represent the behaviour of different fission products. The dopants selected were: Sr, Ce, Nd, Pr and Pd. Ce, Nd and Pr were chosen to represent lanthanides, Sr to represent the alkali metals and Pd to represent transition metals.

The heat from the fuel rods will be simulated using a furnace. Starting temperature for the synthesis is chosen at 1200°C due to that being the failure point of the Zirconium cladding. The max temperature is chosen at 1750°C as that is the maximum temperature of the furnace. A third point is chosen at 1500°C as a point in the middle of the two extremes. The atmosphere in the oven is chosen as reducing with a composition of Nitrogen gas with 5% H_2. The formation of hydrogen gas from the oxidation of the zirconium alloy means that it is possible that at least part of the corium formation takes place in a reducing atmosphere. However, contact with water away from the zirconium alloy will have an oxidising effect. In the context of an accident, it is very likely that the reactor is no longer fully intact and is therefore leaking oxygen into the chamber. The reason for performing the experiments in a reducing environment was practicality. Because once Uranium oxidises higher than U(IV) there would be gaseous Uranium oxides contaminating the oven and tubing.

For real cases of corium formation, variations in conditions during formation such as area of contact, both between materials and atmosphere, local temperature and local atmosphere may induce variations in the same piece of corium. To avoid this during synthesis, the materials will be wet-milled together using a ball mill in order to achieve a homogeneous powder. Assuming the oven heats evenly and the gas is evenly distributed, very little variation should be observed in each individual sample.

2.2 Material selection

From the reactor materials selected, the final corium would consist of a mixture of: the doped UO_2, SiO_2, ZrO_2 and CaO, heated to the 3 temperatures mentioned: 1200°C, 1500°C and 1750°C. In order to study the effects of the individual materials on the uranium oxide, samples will be made using the individual materials mixed with uranium to use as references when analysing the corium. The final list of samples to synthesize is as follows: Corium, $UO_2 + ZrO_2$, $UO_2 + SiO_2$ and $UO_2 + CaO$ all fired at 1200, 1500 and 1750°C. A sample of the doped UO_2 will be used as a baseline from which any changes in properties will be compared to. For the different samples, a molar ratio of 1:4 of uranium to each of the different reactor materials was chosen, meaning for the corium, uranium makes up 1/17 of the amount of substance. This was chosen on the basis that there is very likely an excess of materials compared to uranium in a reactor. However, as it is unknown what ratios of elements are actually reacting, the specific ratio of 1:4 was chosen at random. It was later decided to also synthesize corium samples with an excess of UO_2, with these samples containing a molar ratio of 6:1 of uranium to reactor materials. Compared to the previous samples, uranium here makes up 6/10 of the total amount of substance.

2.3 Uranium Doping

The doped UO_2 is made using a method developed at the Nuclear Chemistry department at Chalmers University of Technology with the purpose of creating doped UO_2[9]. The method involves mixing solutions of uranyl nitrate and nitrate solutions of the desired dopants at desired ratios. Raising the pH will then allow all the metals to precipitate out of solution as a homogeneous slurry of metal hydroxides. The solid phase is then separated using a centrifuge, washed with ethanol to remove excess ammonium and dried in air in preparation for calcination. The calcination is done in a reducing atmosphere to remove any leftover water and nitrogen compounds present in the oxides and reduce the uranium to its desired U(IV) oxidation state. It is assumed that once added to the UO_2, the dopants are stable enough to not evaporate or escape during any of the heat treatments. This was shown to be the case up to 1200°C but not explicitly tested for higher temperatures.

2.4 Analysis

2.4.1 ICP-MS

To determine the composition of the samples after heating, ICP-MS is used. The ICP-MS, standing for Inductive Coupled Plasma Mass Spectrometer, is a highly sensitive mass spectrometer that utilizes plasma to ionize an atomized liquid that can then be accelerated into a mass spectrometer. This gives an output based on the mass of the ion over its charge, with an intensity proportional to the concentration of the ion in the sample. By calibrating based on known standards, the concentration of individual elements and even isotopes can be measured in the sample. This requires the samples to be dissolved and diluted to concentrations on the order of PPB ($10^{-9} g/g$) in order to not overload the detector. Nitric acid (HNO_3) is chosen as the solute due to uranium's high affinity for it. A solution of 8M nitric acid is used to try and dissolve the samples which is then diluted down to measurable levels using 0.5M nitric acid with the addition of 1PPB bismuth to serve as internal standard. This 1PPB bismuth internal standard will be present in all dissolved samples measured by ICP-MS but should not be present in any of the solid samples.

From the results of the ICP-MS, changes in composition between samples can be detected. These changes can, for example, occur due to phase changes where, a less soluble material becomes the dominant phase or vice versa, resulting in a change in how much material dissolves into the acid and how much material stays in the solid matrix. Concentrations of analytes are mainly interpreted using the instrument's software, giving the concentrations in [PPB] but concentrations can be calculated by fitting a linear intensity/concentration curve to the intensities from the known standards. Then fitting the results from the unknown samples to said curves and solving for the concentration.

2.4.2 Powder XRD

The above mentioned phase changes can be more easily detected using XRD. X-Ray Diffraction works by irradiating a sample with X-rays with a predetermined wavelength and from specific angles, utilizing Bragg's law:

$$n\lambda = 2d * sin(\theta) \tag{2.1}$$

Bragg's law says that for a certain wavelength λ that hits a sample where the distance between 2 planes in the crystal structure is d, then there will be constructive interference at angle θ. Constructive interference can only happen when the difference in distance traveled between rays hitting different planes is some multiple of λ, represented by n, as the rays otherwise would be out of phase.

This makes it possible to determine the length between crystalline planes given knowledge of the wavelength of the X-rays and the angle of incidence, which both are known when using an XRD machine. The diffractograms created by the instrument can also be cross-referenced to databases making it possible to match results to potential crystal structures.

This will be used to track where elements end up and to try and back up theories based of solubility mentioned in section 2.4.1.

3

Methods

3.1 Fuel Synthesis

Before the actual synthesis, a test batch of uranium was first synthesized in order to validate the method described in section 2.3. For the precipitation, a solution of 2.1M Uranyl nitrate in nitric acid was combined with 0.084M solutions of the individual dopants, also dissolved in nitric acid. To a glass beaker, 6ml of the 2.1M uranyl nitrate, equating to 12.6 mmol U, was added along with a magnetic stir bar. 1.5ml of each 0.084M dopant-nitrate solution, equating to 0.126 mmol each, was added to the beaker to achieve the doping ratio of 1:100 per dopant. The solution was then left to stir while centrifuge tubes were prepared for the precipitation. Large centrifuge tubes were filled with an excess of ammonium hydroxide along with a small stir bar in every tube. Multiple tubes were used per batch to ensure enough base was present to fully precipitate all the metal. Both the uranyl nitrate solution and the ammonium hydroxide in the tubes were kept under constant stirring as the nitrate solution was slowly and evenly dripped into the tubes. The tubes were then left to stir for 5 minutes to make sure the precipitation has finished after which, the tubes were centrifuged at 5000rpm for 5 minutes (Beckmann Coulter, Avanti J-26S XP centrifuge, JA-20 fixed angle rotor) to separate the liquid and solid phases.

In theory, all of the metals should have precipitated out and formed the solid phase. So to test if any uranium or dopants were left in the liquid phase after precipitation, half of the tubes were shaken to disperse the solid phase again. The re-dispersed suspension was then poured out into an clean, open beaker and the tubes were rinsed with 95% ethanol, removing anything stuck to the tube. This ethanol used to rinse was also poured into the same beaker as the suspension which was then left to evaporate and dry in the fume hood. The other half of the tubes were handled much more carefully as to keep the solid phase undisturbed. The liquid phase was discarded, and 95% ethanol was poured into the tubes instead. The tubes were then shaken to loosen the solid phase and the slurry was poured out into another open beaker, along with any additional ethanol used for rinsing the tubes. These beakers were also left to dry under the same conditions as the first half.

Once dry, the resulting powders were lightly crushed in a mortar and pestle to even the grain size and possibly preventing clumping. The powders were then calcinated in a tube furnace at 900°C in a reducing atmosphere of Ar + 5% H_2, to reduce the uranium down to U(IV), forming UO_2. The furnace used, was a tube furnace with an alumina tube and alumina crucibles. It was heated from room temperature up to 900°C, first at 3°C/min up to 150°C in order to avoid flash evaporation of any remaining water in the samples. Then, at 10°C/min up to 900°C where it dwelt for 3 hours. After which, it cooled down to room temperature at the same rate of 10°C/min. Once calcinated, the samples were stored in closed, plastic beakers, in room temperature and regular air.

The result of the ICP-MS showed that the composition of the calcinated powders corresponds with the amount of the solutions used. Which proved that this was a working method for doping uranium dioxide. It also showed that there were no significant difference between the samples that kept the liquid phase and the ones where it was discarded and washed with ethanol instead. This meant that discarding as much of the liquid phase as possible and rinsing with the much faster evaporating ethanol would be significantly faster: 24-36 hours to completely dry, compared to the liquid phase drying in 72+ hours. The temperature for calcination was also changed to 1200°C to ensure the time of 3 hours was enough to fully reduce the samples.

Two larger batches of doped uranium dioxide was then synthesized using the steps mentioned above. Both batches used 20ml 2.1M uranyl nitrate solution and 5ml of each dopant solution per batch, which resulted in 11.3 grams of powder per batch.

3.2 Corium Synthesis

The corium synthesis used the different materials mentioned in section 2.2 in powder form. Silica and zirconium dioxide were acquired from Sigma Aldrich as powders. As described by Krisishima et al.[5] CaO has a high hygroscopicity meaning weighing it accurately becomes very difficult so the choice was made to use $CaCO_3$ instead, letting it decompose to CaO once heated.

The molar ratios of 1:4 for the reference samples were weighed out for a target weight between 2 and 3g total, with accurate weights listed in table 3.1. The molar ratio of uranium in the corium was 1:4 per material, which meant a total ratio of 1:12 of uranium to the other metals and the ratios of reactor materials being 1:1. Later, samples containing a molar ratio of 6:1 uranium to dopant (meaning a total ratio of 6:3) was also made to test if an excess of uranium changes anything. Due to a calculation error regarding the sample of U + Zr 1200, the amount of ZrO_2 was calculated based on the molar mass of Uranium and not uranium dioxide, leading to a higher amount of ZrO_2.

As can be seen in table 3.1, some corium samples were placed in "Al + Ca" crucibles. This was due to the discovery that when above 1500°C, the Ca diffused into the alumina, resulting in an unusable sample. Therefore, some alumina crucibles were fired once with only $CaCO_3$ in the hopes of it saturating the alumina and preventing the sample from also diffusing in. Later however, the alumina crucibles were switched out for molybdenum crucibles due to seemingly, unavoidable reactions between the corium and the crucible. As molybdenum was found to work much better as material for the crucible, a final test was also conducted under much less controlled circumstances due to time constraints. Here, the same ratio of 1:4 of uranium to materials as used previously was mixed together by hand using a mortar and pestle and then placed in a molybdenum crucible, without further milling, to be fired at 1750℃ using the same conditions. The purpose of this test was only to see if it was possible to recover a sample at 1750℃ as there was no time to analyze it afterwards.

Sample	UO_2 [g]	ZrO_2 [g]	SiO_2 [g]	CaO [g]	**Total [g]**
U + Zr 1200	0.763	1.525			2.288
U + Zr 1500	1.201	2.193			3.393
U + Zr 1750	0.761	1.389			2.150
U + Si 1200	1,474		1,311		2,785
U + Si 1500	1.030		0.917		1.947
U + Si 1750	1.056		0.940		1.996
U + Ca 1200	1,007			1,493	2,500
U+ Ca 1500	0.873			1.294	2.567
U + Ca 1750	N/A			N/A	N/A
Corium 1200	0,575	1,031	0,502	0,840	2,948
Corium 1500	0,504	0,921	0,449	0,748	2,622
Corium 1500 Al + Ca crucible	0,508	0,928	0,452	0,753	2,614
Corium 1500 Mo crucible	0,578	1,033	0,504	0,840	2,955
Corium 1750	0,560	1,022	0,498	0,830	2,910
Corium 1750 Al + Ca crucible	0,563	1,027	0,501	0,834	2,925

Table 3.1: Table of all samples made and their compositions.

Once weighed, the powders were wet milled together using 95% etOH for 60 minutes at 500rpm with intervals of 3 minutes milling to 3 minutes rest, resulting in 30 minutes effective milling. The slurry was then poured into an open plastic beaker, the ball mill cup and lid were washed thoroughly with 95% ethanol, which was also poured into the same beaker. The ethanol slurry was then left to dry completely in the fume hood. Once dry, the sample mixture was placed in an alumina crucible and heated in the furnace in a reducing atmosphere of Ar + 5% H_2. Being heated from room temperature to the desired points of 1200℃, 1500℃ or 1750℃at 10℃/min, with a dwell time of 4 hours and then cooled back down to room temp at 10℃/min. A variation of this program was used for the samples containing calcium carbonate, where, to avoid carbon dioxide forming too quickly, some intermediate steps were used. First heating at 10℃/min up to 750℃, then from 750℃ to 900℃ at 3℃/min and dwelling at 900℃ for 60 minutes. Heating from 900℃ to the target temperature at 10℃/min, dwelling for 4 hours and cooling at the same rate as previously described. After heating, the samples were stored in sealed glass vials with regular air.

3.3 Analysis

3.3.1 XRD

The sample preparations for powder-XRD involved crushing 0.5 grams of the sample to a fine powder in a mortar and pestle. The powder was then transferred to a sample holder, gently flattened to height specified by holder and inserted into the Bruker D2 Phaser. Measurements were taken using a copper X-ray source with a wavelength of 1.54 Å, measuring with a 2θ from 20 to 90 degrees.

3.3.2 ICP-MS

Calibration standards had to be made for every analyte. Both standards and samples will all be diluted with a 0.5M solution of HNO_3 and MilliQ-water, with a 1PPB [g/g] concentration of Bismuth which served as the internal standard throughout all the samples. The standards were then prepared by diluting stock solutions of the analytes to set concentrations: 1, 5, 10, 25, 50, 100 PPB using the 0.5M HNO_3 + 1PPB Bi

To prepare the solid samples for ICP-MS analysis, a small amount of each sample, 0.1-0.2 grams, was added to 10 ml of 8M HNO_3 to dissolve, noting the exact mass of each sample taken. Samples that did not dissolve immediately were left for 24 hours before further dilution. The solutions were then diluted twice by a factor of 10^3 by taking $25 \mu l$ of the 8M acid solution and diluting with the 0.5M nitric acid with 1 PPB Bi, to a total weight of 25g. As the density of the diluted solution was very close to 1g/ml, the concentrations will be expressed in (grams of powder)/(weight of solution) [g/g]. After the first dilution, two separate solutions were made per sample. One which was used to analyze the uranium contents, which was diluted yet another factor 10^3 by repeating the same steps, giving a concentration of 10-20 PPB. The other solution was for analyzing dopants, which was diluted only by a factor 10, for a theoretical dopant concentration of 1-2 PPM. Note that the concentrations here are given in terms of sample weight and not the molar concentration of relevant analytes.

3.4 Leaching

Once the corium samples were all synthesised, a leaching study was started. The liquid chosen for the leaching was MilliQ-water with 20mM NaCl as an electrolyte. A limited amount of both samples and stirring plates restricted the study to only be able to have triplicates of a few samples. So it was decided that UO_2 and corium at 1200℃ and 1500℃ were going to be analyzed as triplicates, due to them being the most relevant samples to the project. Other samples were set up as singlets, meaning any data was not as statistically significant as the triplicates, but instead they served as preliminary references to help notice potential patterns in the triplicates. Every leaching sample contained 80ml of the 20mM NaCl MilliQ-water and a target weight of 0.1g of the solid samples. A tabular view of the leaching setup can be viewed in table 3.2. Note that samples heated to 1750°C were not considered for leaching as the corium samples only go up to 1500°C. For analysis, 2ml samples were taken from each sample on a weekly basis, first filtering the removed samples using a 0.45 μm syringe filter and then filtering again using Amicon Ultra-4 30000 NMWL centrifugal filters, to remove any solid particles that could have impacted the measurements. The samples were then diluted down to 1/10 concentration using 1ml of the filtered samples and 9ml of the 0.5M nitric acid with 1 PPB Bi and analyzed using ICP-MS. This dilution resulted in the samples containing 90% of the Bi of the standards, which meant the concentrations had to be calculated by hand, as the instrument expects the Bi concentration in all measurements to be the same and will therefore compensate for that in its calculations, overestimating the concentrations in this case.

UO_2 0.1040 g	Corium 1200 0.1021 g	Corium 1500 0.1040 g	U+Si 1200 0.0987 g	U+Si 1500 0.0993 g
UO_2 0.0995 g	Corium 1200 0.1018 g	Corium 1500 0.1025 g	U+Zr 1200 0.1006 g	U+Zr 1500 0.0991 g
UO_2 0.1024 g	Corium 1200 0.1022 g	Corium 1500 0.1045 g	U+Ca 1200 0.1031 g	

Table 3.2: Table of the leaching samples with exact amounts of each sample.

4

Results and Discussion

4.1 Synthesis

The results from the synthesis and subsequent analysis show that it is possible to make corium-like materials in a lab setting. But difficulty increases with temperature. The method of doping uranium dioxide has now been shown to work reliably to produce a homogeneously doped simulated spent nuclear fuel. The corium synthesis itself becomes difficult once different material's melting temperatures are reached and side reactions begin involving the crucible and furnace tube. Under the conditions of this study, many of these issues seem to be avoidable by using a crucible made out of molybdenum instead of alumina. But it is still unknown what would happen as the temperatures continue to increase. Increased temperatures also mean increased vapor pressures from the different materials risking depositing inside the furnace and tubing, damaging equipment.

The synthesized corium also shows a change in characteristics depending both on temperature and the different materials it was mixed with. This suggests that the properties of corium is dependent on the conditions of the reactor during formation as well as exposure to different materials during the formation.

4.1.1 Visual Inspection

Observing the samples once they are out of the furnace reveals that changes have occurred on most of the samples. As seen in figure 4.1 all zirconium samples remained as powders after heat treatment although the color changed, darkening with temperature. This is not a surprise given uranium dioxides melting point of 2865°C and zirconium dioxides melting point of 2715°C. No phase change should be observed at any of the temperatures chosen in this experiment. When crushing samples for XRD, it became more difficult to crush the higher temperature sample suggesting some minor changes had taken place.

Figure 4.1: Samples of uranium dioxide and zirconium dioxide at different temperatures. From left to right: 1200, 1500 and 1750℃.

The samples of uranium dioxide and silica shown in in figure 4.2 also stayed as a powder for 1200℃ and 1500℃. But turned to a solid mass at 1750℃. The melting point of silica is just above 1700℃ so the melting and subsequent solidification is expected. The resulting sample was incredibly hard, and scraping it with a steel screwdriver barely made a scratch. The discoloration of the crucible could also point towards a reaction between the sample and the crucible. Silica and alumina reacting is not surprising as the existence of zeolites and alumino-silicates is well known[13]. It is however unknown whether the uranium is part of this reaction, and if so, to what extent? It has also made it impossible to non-destructively remove the sample from the crucible meaning, from a synthesis point of view it was a failure due to the sample not being accessible. The hardness of the sample also made further analysis difficult.

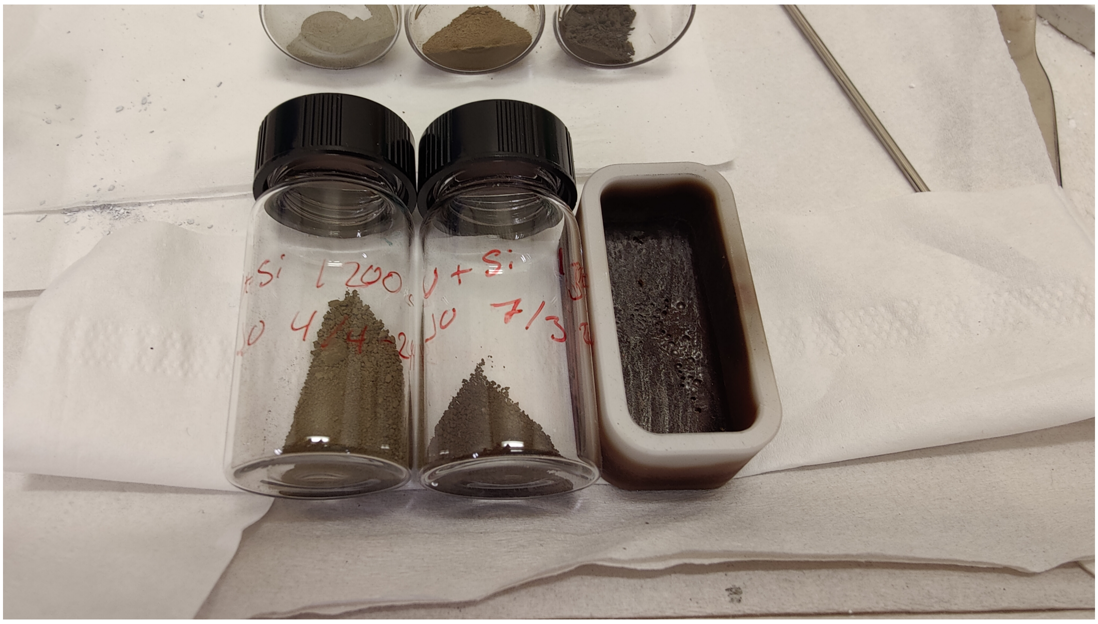

Figure 4.2: Samples of uranium dioxide and silica at different temperatures. From left to right: 1200, 1500 and 1750 stuck in the crucible

Figure 4.3a shows the doped uranium dioxide and the one sample of uranium dioxide and calcium carbonate that was made. Synthesis of the uranium dioxide and calcium oxide sample at 1200°C resulted in a dark powder like the other samples. At 1500°C the calcium carbonate seems to have reacted with the alumina, forming a coating on the bottom of the crucible as can be seen in figure 4.3b. The formation of calcium aluminates should be expected at these temperatures[11] but unfortunately, the coating was flush with the surface and it was not possible to safely obtain any samples for analysis. Therefore, this sample was never analyzed further and a sample at 1750°C was never made.

(a) Samples of the doped UO_2 and the sample of UO_2 + CaO heated to 1200°C.

(b) Alumina crucible with the coating of CaO and UO_2 after heating to 1500°C.

Figure 4.3: Doped UO_2 and the two U + Ca samples made.

Corium samples proved problematic during heat treatment. Figure 4.4 shows all surviving corium samples. Synthesis at 1200°C was no issue, no melting and no noticeable reactions with the alumina crucible. At 1500°C the sample looked to have begun melting, forming a solid mass compared to the powders both the Zr and Si samples formed. For both the Ca-pretreated and untreated alumina crucibles, this resulted in the sample also sticking to the crucible. There is no discoloration like the silica at 1750°C but the sample is still very stuck and difficult to damage. The Ca-treatment did not seem to prevent the corium from sticking to the crucible. However, comparing the samples visually, it seems to have had some effect. The sample in the treated crucible has risen from the bottom and parts of it is noticeably more porous. The sample in the untreated crucible instead looks to have formed a thin metallic piece covered by a clear glass.

At 1750°C, the alumina crucibles could not be removed from the alumina tube. Inspection of the bottom of the tube shows a large dark spot, not unlike how the melted silica crucible looked. The assumption is that the combination of calcium and silicon has migrated through the crucible and started reacting with the alumina in the tube, fusing everything together. It is also possible a spill might be the cause of it being stuck. But due to lack of ways to safely open the tube, it can't be investigated more at this time.

These results prompted the change to a less reactive material for the crucibles. Molybdenum crucibles were selected as the material of choice due to availability in the lab. The corium experiment was repeated at 1500°C for both the high and low ratio of uranium. This proved much more successful resulting in a black powder for the high U concentration sample. And a solid clump of material that could be removed from the crucible using very little force. However, due to how hard the clump was, the ball mill had to be used in order to break it for analysis. The improvised test for corium at 1750°C was a success as well. The sample had melted together into a homogeneous clump with a texture not unlike flint. This sample easily released from the bottom of the crucible and the edges were very sharp so care had to be taken when handling as it risked cutting through the protective gloves. Unfortunately, due to lack of time, no further analyses were done on this sample.

Figure 4.4: All samples of synthesized corium. Top row: Alumina crucible 1500°C. Left: Alumina crucible treated with calcium carbonate. Right: untreated crucible. Bottom row: Powdered Corium samples. From left to right: Standard corium in alumina crucible 1200°C, High U ratio in Mo crucible 1500°C, Regular corium in Mo crucible 1500°C.

4.1.2 XRD

The diffractograms from the powder XRD can give some more insight into what is happening. Figure 4.5 shows the diffractogram of the doped uranium dioxide matched with a reference of a slightly more oxidized UO_2 which makes sense considering the continuous exposure to air and the added dopants affecting the crystal structure. But not enough to change it from uranium dioxides default structure.

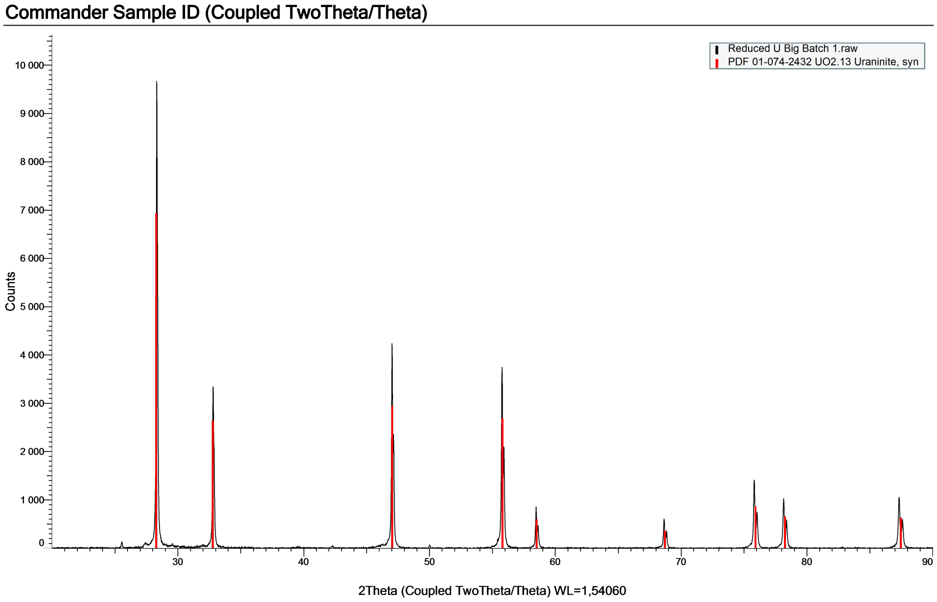

Figure 4.5: X-ray diffraction spectra of the doped uranium fuel

Figures 4.6, 4.7 and 4.8 show how the crystal structure changes in the UO_2/ZrO_2 matrix. Where it starts off as two separate phases of UO_2 and ZrO_2 and as temperature increases, the UO_2 diffuses into the zirconia structure forming a combined structure with little to none of the original UO_2 phase left.

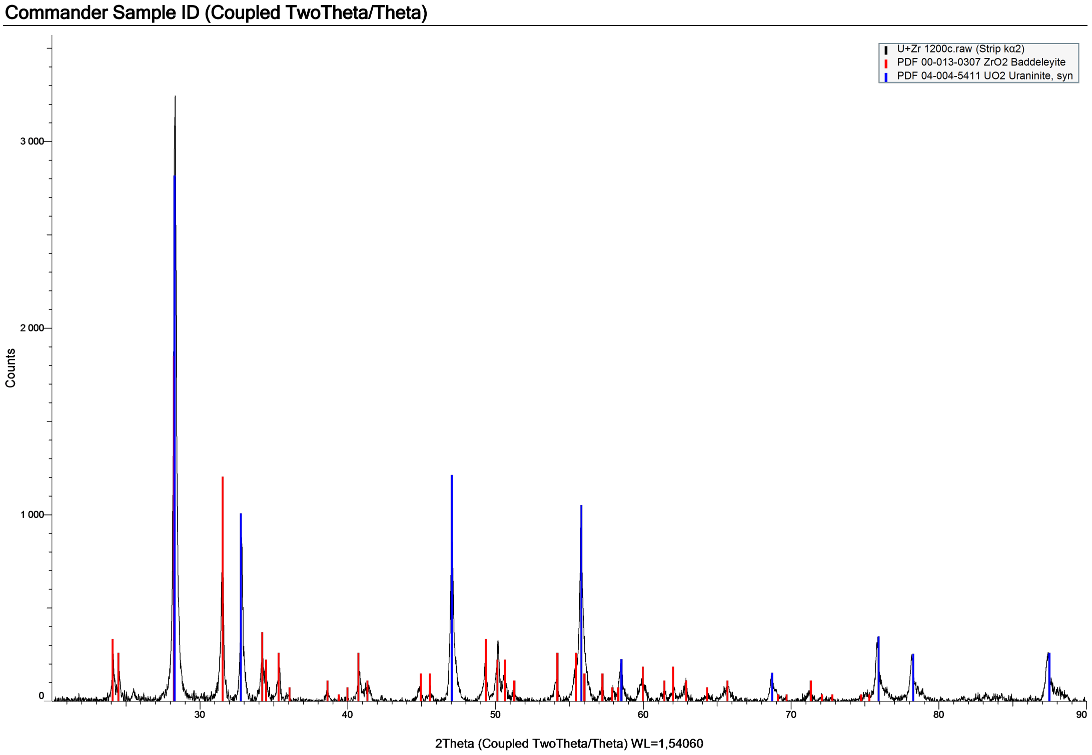

Figure 4.6: X-ray diffraction spectra of uranium and zirconium at 1200℃.

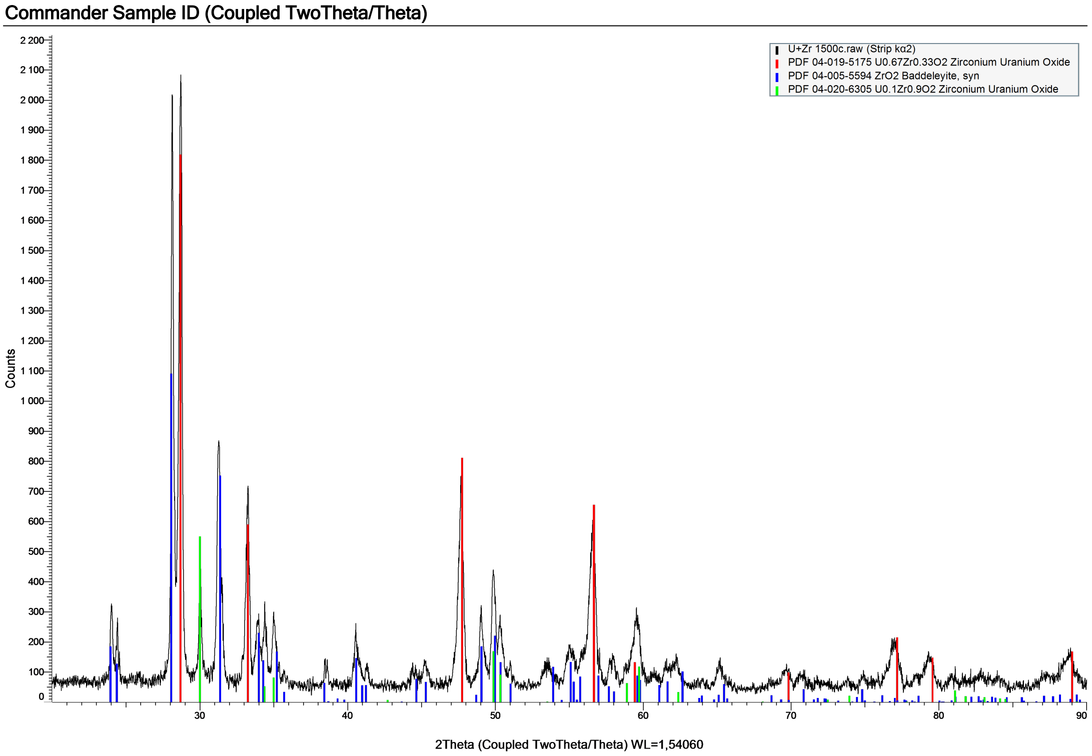

Figure 4.7: X-ray diffraction spectra of uranium and zirconium at 1500℃.

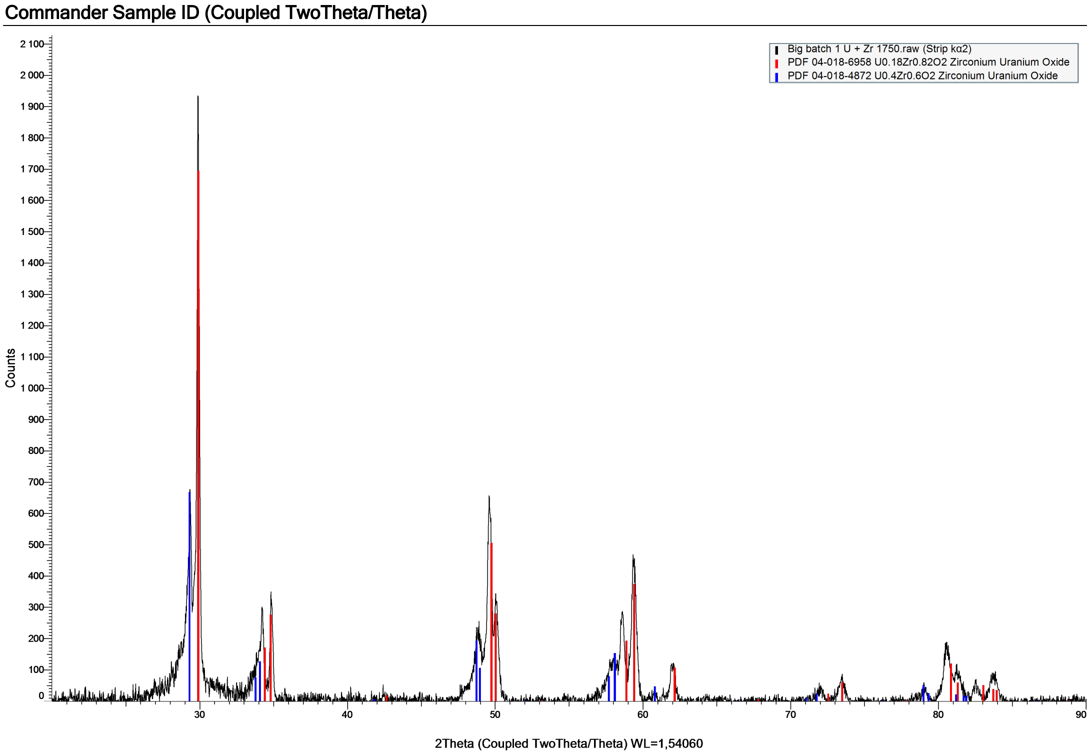

Figure 4.8: X-ray diffraction spectra of uranium and zirconium at 1750℃.

The silica and UO_2 samples seem to act noticeably different from the U + Zr mix. Figures 4.9 and 4.10 show separated phases of silica and UO_2, but as the temperature increases, the quartz structure seems to be reforming into a cristobalite structure instead and leaving the UO_2 untouched. Due to the variation in amount of powder used for each sample it's difficult to tell based on the measured intensities, if all of the silica turns from quartz to cristobalite or if there is some amorphous phase present as well. But from what can be detected, it's unlikely that the silica and uranium will react on their own.

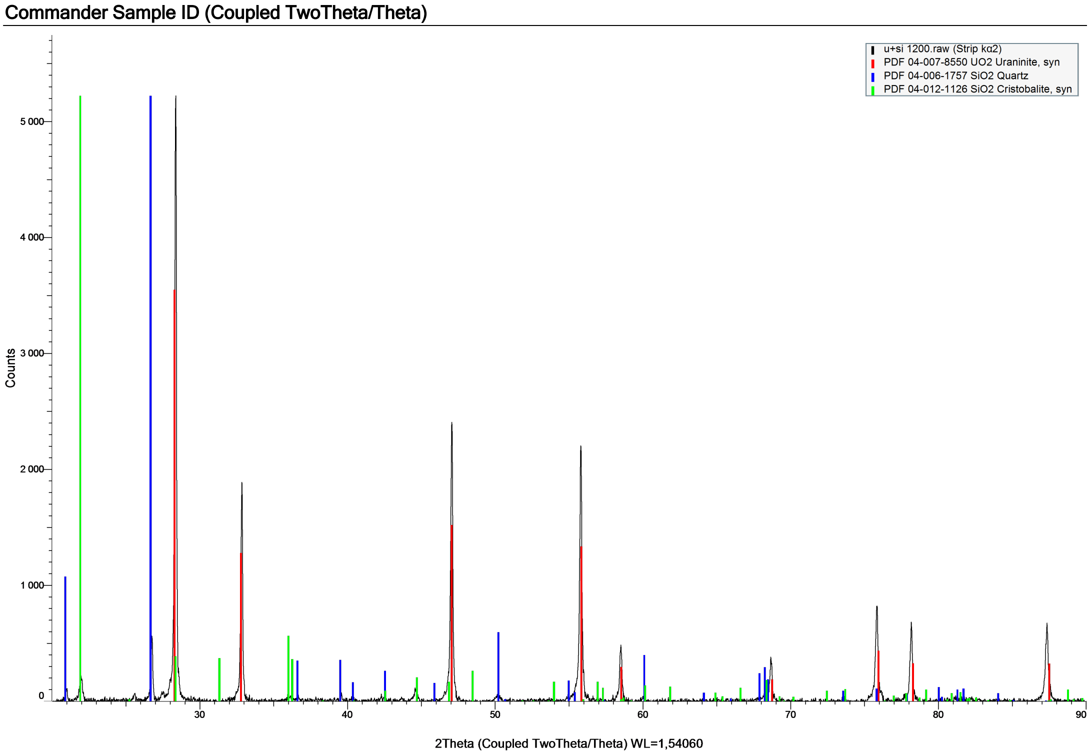

Figure 4.9: X-ray diffraction spectra of uranium and silica at 1200℃.

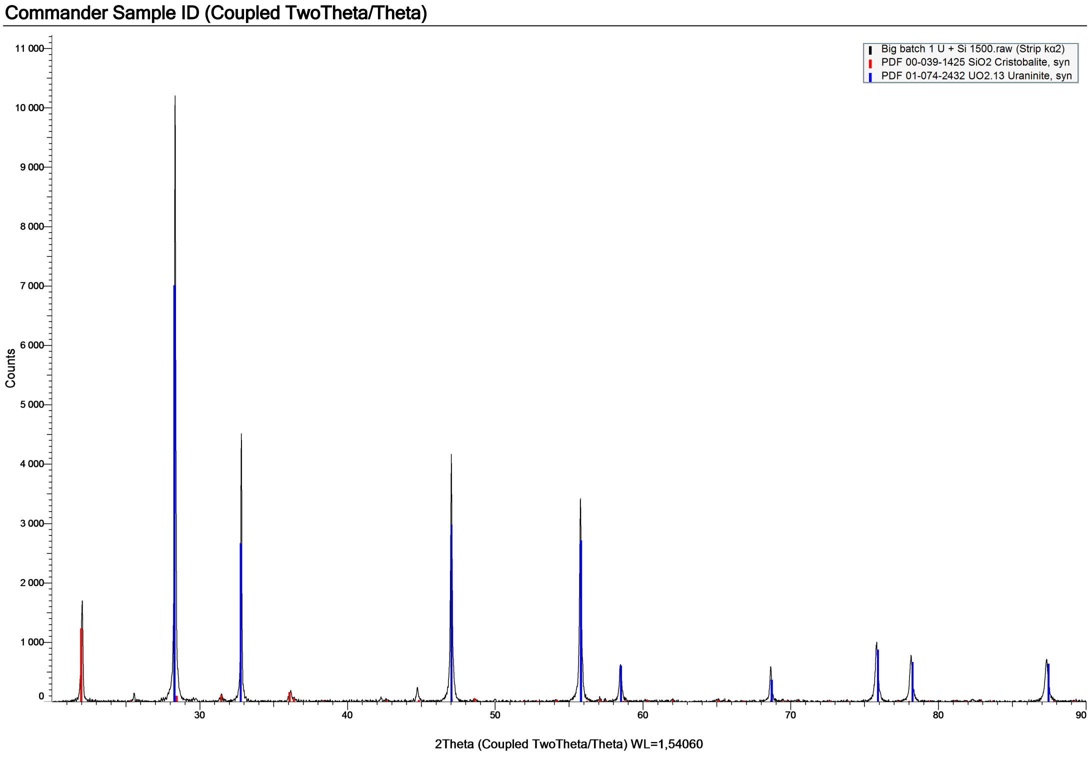

Figure 4.10: X-ray diffraction spectra of uranium and silica at 1500℃.

By not having any other temperature points to analyze than 1200, very few conclusions can be drawn from the diffractogram shown in figure 4.11. It does however show a phase of calcium oxide, meaning the calcium carbonate decomposed to calcium oxide during heating as theorized, with no other detectable phases present besides UO_2. No phase containing Al means that if any reaction between the Ca and Al would be taking place at this temperature, it would most likely be Ca diffusing into Al and not contaminating the sample. The lack of displacement of the UO_2 peaks also signifies that, at least at 1200°C, Ca and U also doesn't seem to react.

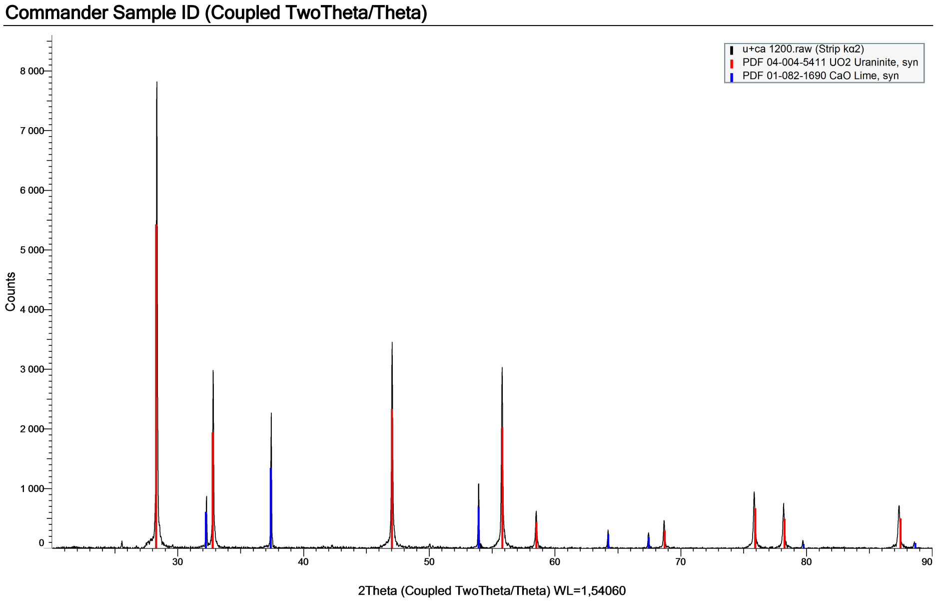

Figure 4.11: X-ray diffraction spectra of uranium and calcium oxide at 1200°C.

When combining the different elements in corium, multiple different reactions between the materials seem to take place. For corium heated to 1200°C shown in figure 4.12 there are the expected separate phases of UO_2 and ZrO_2. But it is very possible that silica and calcium oxide has started to combine into a separate phase together. The lack of a separate phase of calcium oxide as well as the only phase detected for silica is a phase that cannot exist under the conditions of the oven signifies most, if not all of the silica and calcium exists in a combined or amorphous phase.

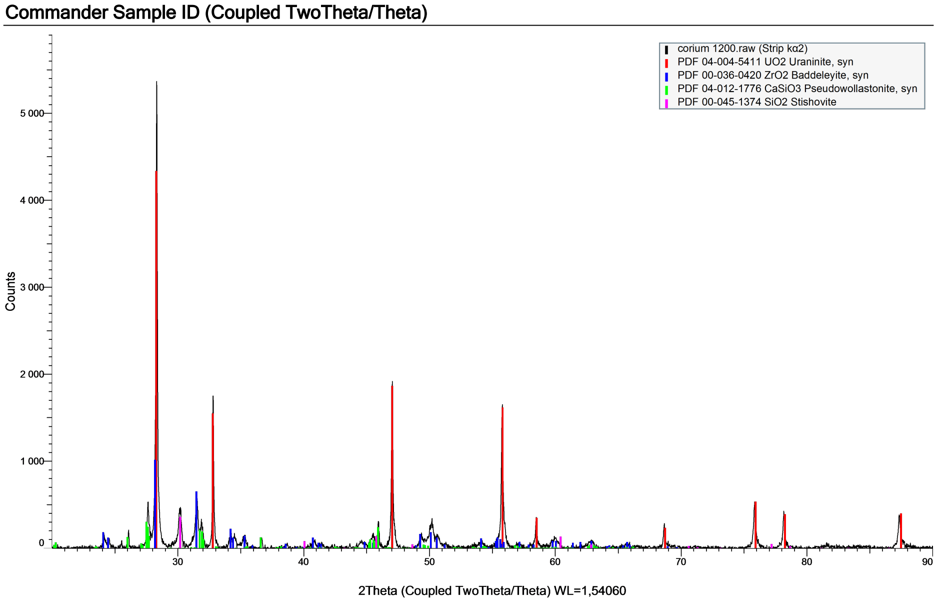

Figure 4.12: X-ray diffraction spectra of corium at 1200℃.

The corium samples made at 1500℃ all seem to display a common theme with a dominant zirconia phase swallowing up most of the UO_2, with calcium and silica forms their own separate phase. Shown in figure 4.13 the silica and calcium has formed a crystal structure with the Al from the crucible. Further reinforcing the theory that alumina is a poor choice of crucible to make corium in.

The corium made in a molybdenum crucible, shown in figure 4.14, show that it it pretty much exclusively a combination of zirconia and UO_2 forming a crystalline phase in the sample. With no real information about the structure of the silica, it is difficult to draw any significant conclusions about its impact on the structure. However, the difference between both 1200 and 1500℃ as well as between alumina and molybdenum is very noticeable from the powder XRD.

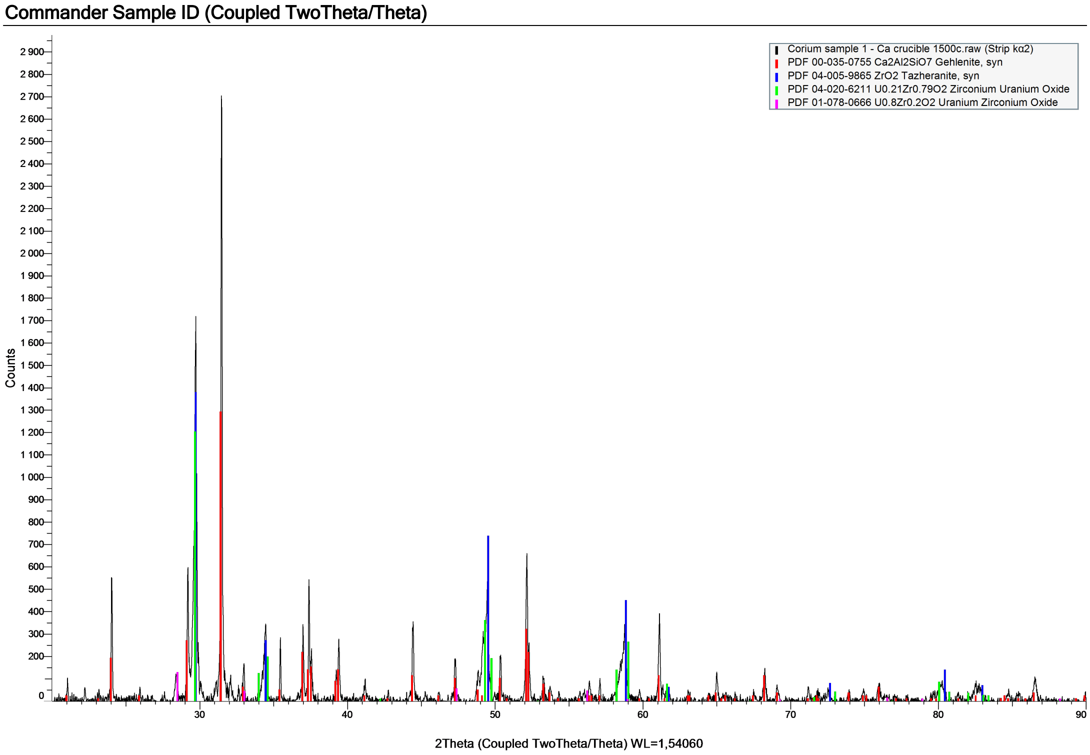

Figure 4.13: X-ray diffraction spectra of corium at 1500℃ using the alumina crucible

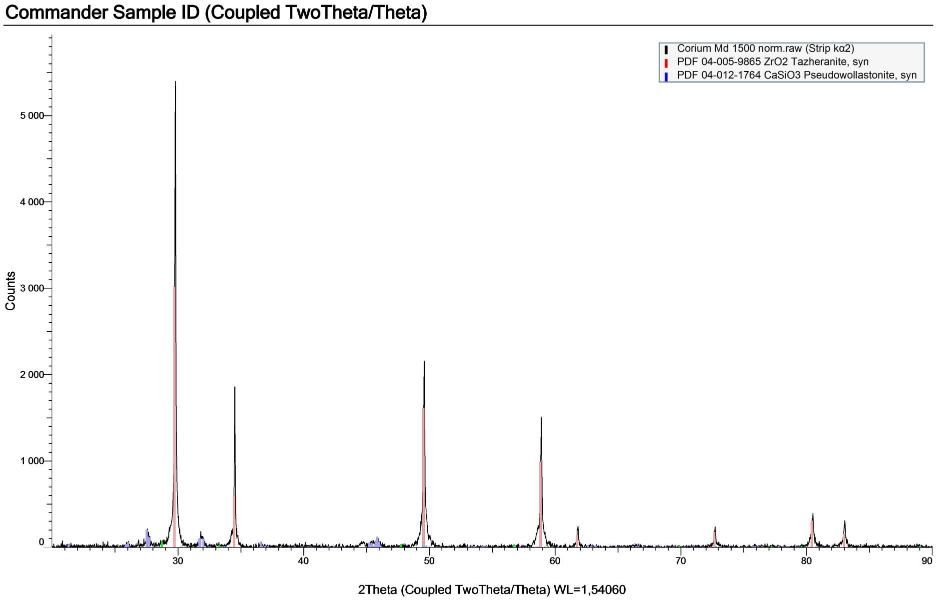

Figure 4.14: X-ray diffraction spectra of corium (1:4 U ratio) at 1500℃ using the molybdenum crucible

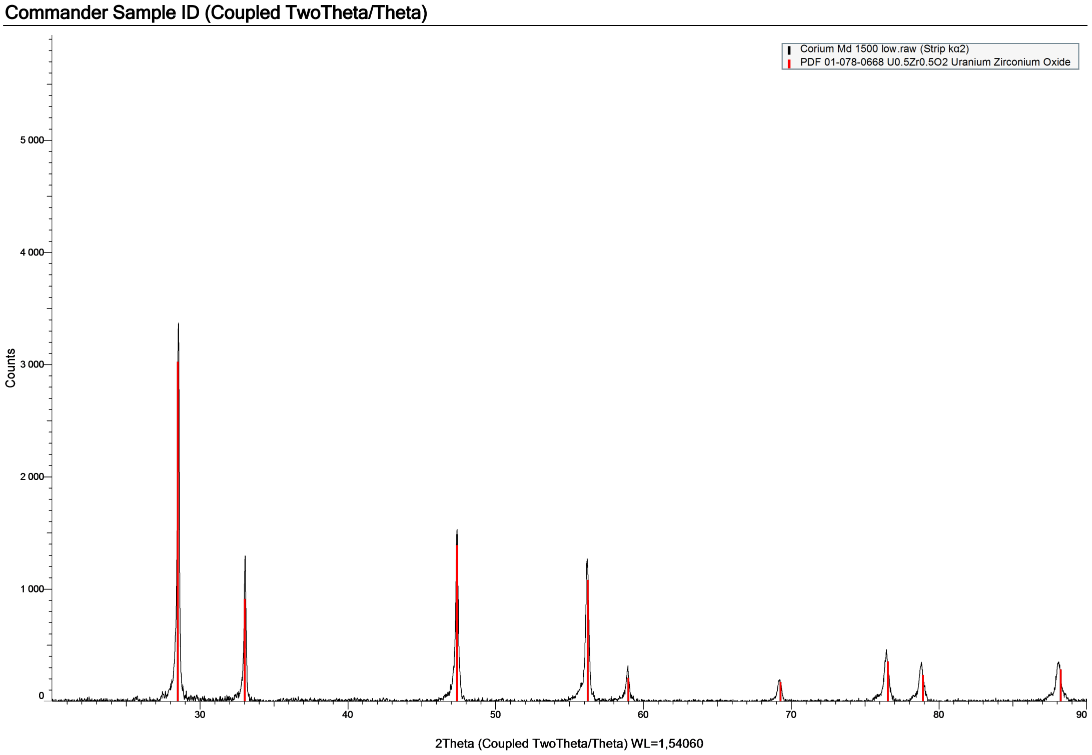

Figure 4.15: X-ray diffraction spectra of corium (6:1 U ratio) at 1500℃ using the molybdenum crucible

Based on the detected crystal structures in the previously shown samples, it can be assumed that the uranium has a significantly higher affinity for the zirconium compared to both the calcium and the silica. Of course, there might exist amorphous phases containing any mixture of the materials that can't be detected via this method of XRD but examining those are are outside the scope of this project. Table 4.1 shows the different samples along with their detected phases. Focusing on the U-Zr interactions, and comparing those peaks to the peaks of pure UO_2 and ZrO_2 shown in figure 4.16 and 4.17, created digitally using crystallographic data from Springer Materials and the program VESTA to generate the diffractograms. What's most immediately noticeable is the difference in amount of peaks and their relative intensity. UO_2 has a cubic structure while ZrO_2 is monoclinic with all sides having slightly different lengths. Based on that, the detectable U-Zr-O phases all have U as the dominant phase with different amounts of Zr diffusing into it.

That diffusion does not seem to occur uniformly throughout the sample however. In both figure 4.7 and 4.8 there were multiple variants of the U-Zr-O phases detected and the peak broadening in figure 4.8 specifically could indicate that the proportion of Zr to U in the crystal could vary continually throughout the sample and that the diffusion didn't have enough time to reach an equilibrium.

Based on the results in figure 4.15 it also seems likely that the uranium does react with other materials as well. The suggested ratio of U:Zr in the detected crystal structure, based on the computer evaluation is 2:1 of U:Zr. However, the starting ration was 6:1 for that sample, meaning that a minimum of 2/3 of the uranium is not detected via powder-XRD (assuming all of the Zr has diffused into the crystal.) This implies that the a large portion of the uranium in the corium 6:1 sample exists in some amorphous phase which cannot be investigated here. Which also opens up the possibility that phases could be present in the other samples as well.

Sample name	Temp [C]	U:mat	Dominant phase	Other phases
Doped UO2	N/A	N/A	UO2	None
U+Zr	1200	1:4	UO2	ZrO2
U+Zr	1500	1:4	U0.67Zr0.33O2	ZrO2, U0.1Zr0.9O2
U+Zr	1750	1:4	U0.18Zr0.8O2	U0.4Zr0.6O2
U+Si	1200	1:4	UO2	SiO2
U+Si	1500	1:4	UO2	SiO2
U+Ca	1200	1:4	UO2	CaO
Corium	1200	1:4	UO2	CaSiO3, SiO2
Corium Ca+Al crucible	1500	1:4	Ca2Al2SiO7	ZrO2,U0.XZr0.YO2
Corium Md crucible	1500	1:4	ZrO2	CaSiO3
Corium Md crucible	1500	6:1	U0.5Zr0.5O2	N/A

Table 4.1: Table summarizing the samples analyzed using XRD and their respective discovered phases.

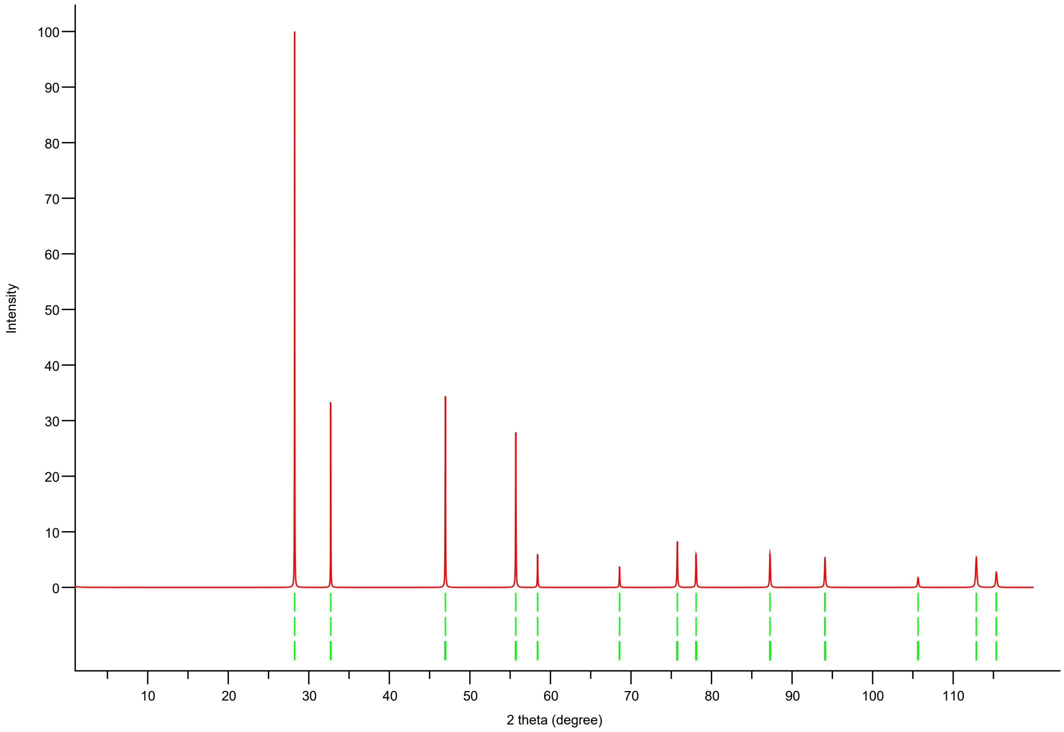

Figure 4.16: Simulated peaks for UO2

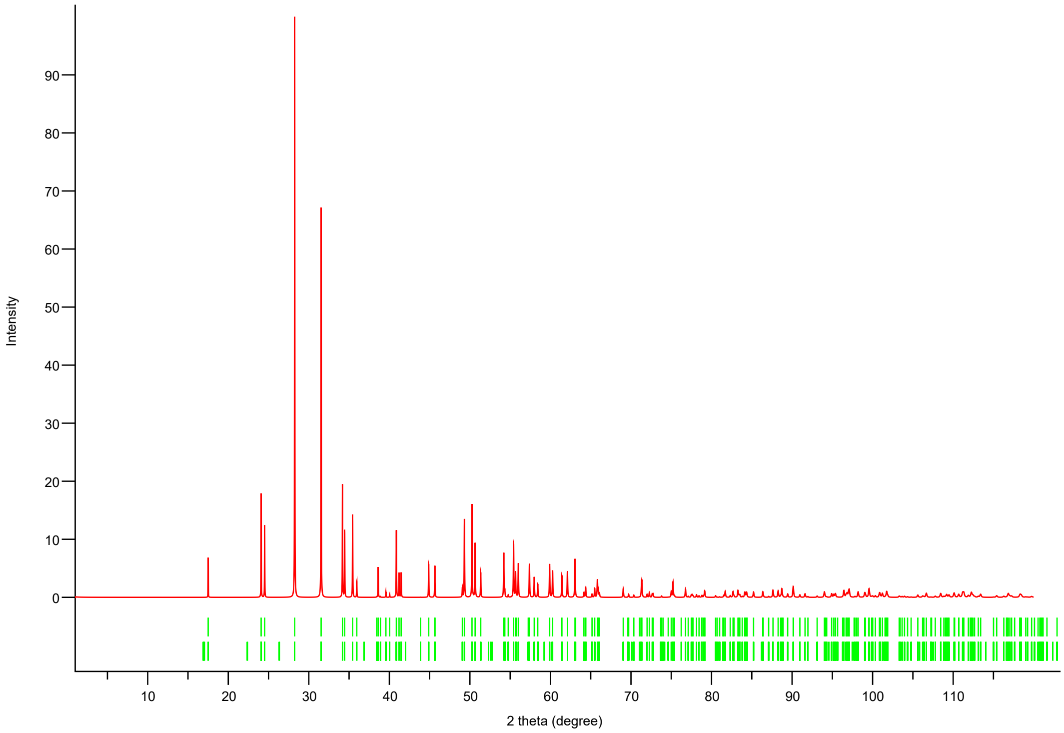

Figure 4.17: Simulated peaks for ZrO2

4.1.3 ICP-MS

Measured concentration of U and dopants are presented in table 4.2. Palladium was added as a dopant, but due to its standards requiring a separate acid for measurements it became too much of a hassle to try and measure in this project. The starting weight signifies the mass of powder added to 10 ml 8M nitric acid. The concentration of U and the dopants are calculated from the known ratios of every sample and the assumption that the ratio of dopants to uranium has stayed constant. Table 4.3 shows the ICP-MS signals converted to concentration while table 4.4 shows the ratio between the measured concentrations and the estimated maximum concentrations of the original samples.

Multiple samples show a measured concentration higher than the expected maximum. This is likely either due to contamination at some stage during the dilution and measuring process or user error during the dilution process. The two last corium samples using Mo crucibles were likely contaminated due to contaminated washing liquid.

However, looking at the ratios, some patterns can be discerned. For the zirconia samples, the solubility of both the uranium and the dopants decrease drastically with temperature. This is likely due to zirconias high resistance to acids, and as described from the XRD in figure 4.8, a Zr-U-O phase is dominating which likely affects the solubility. The silica samples seem to not hold on to uranium or the lanthanides very well but Sr has measured noticeably lower for both samples. Indicating that the dopants may not stay in the uranium once heated. This theory is reinforced by looking at the calcium sample, where the ratio of dissolved uranium is ten times higher than that of the dopants, and neither is very high.

Looking at the corium samples it is very likely there is some contamination present. Corium at 1200℃ stayed as a powder and was crushed before dissolving so the distribution of uranium and dopants should've been homogeneous. But there does not seem to be any difference between the dopants regarding which dissolve more easily. Corium made at 1500℃ in a Al crucible does not seem to dissolve at all. Samples of corium from the Mo crucibles are likely contaminated and no conclusions will be drawn from them.

Samples	Sample mass [mg]	UO2 [mol/l]	Dop. [mol/l]
Doped U	138.9	5.14E-02	5.14E-04
Zr 1200	164.3	2.16E-02	2.16E-04
Zr 1500	175.5	2.30E-02	2.30E-04
Zr 1750	100.7	1.32E-02	1.32E-04
Si 1200	139.6	2.74E-02	2.74E-04
Si 1500	119.6	2.35E-02	2.35E-04
Ca 1200	143.4	2.90E-02	2.90E-04
Cor 1200	80.9	6.60E-03	6.60E-05
Cor 1500 Al	58.7	4.79E-03	4.79E-05
1500 Mo	142	1.16E-02	1.16E-04

Table 4.2: Mass of powder dissolved in 8M nitric acid with theoretical max concentrations.

Measured conc. [mol/l]	238U	88Sr	140Ce	141Pr	143Nd
Doped U	5.68E-02	5.60E-04	6.07E-04	6.12E-04	6.41E-04
Zr 1200	1.96E-02	1.83E-04	2.16E-04	2.14E-04	2.23E-04
Zr 1500	1.60E-02	1.82E-04	1.97E-04	1.80E-04	1.77E-04
Zr 1750	9.99E-04	1.43E-05	1.94E-06	1.52E-06	1.39E-06
Si 1200	2.75E-02	1.82E-04	3.05E-04	3.07E-04	3.38E-04
Si 1500	2.18E-02	4.76E-05	1.72E-04	1.96E-04	2.36E-04
Ca 1200	4.91E-03	6.48E-06	2.72E-06	4.10E-06	4.71E-06
Corium 1200	6.68E-03	8.63E-05	8.40E-05	8.30E-05	8.55E-05
Corium 1500 Al	3.05E-04	5.60E-07	5.89E-07	6.10E-07	8.49E-08
1500 Mo	3.72E-04	1.10E-03	9.52E-05	8.00E-05	8.62E-05

Table 4.3: ICP-MS signals converted to concentration of starting sample.

Ratios	238U	88Sr	140Ce	141Pr	143Nd
Doped U	1.10	1.09	1.18	1.19	1.25
Zr 1200	0.91	0.85	1.00	0.99	1.03
Zr 1500	0.70	0.79	0.86	0.78	0.77
Zr 1750	0.08	0.11	0.01	0.01	0.01
Si 1200	1.01	0.67	1.12	1.12	1.23
Si 1500	0.93	0.20	0.73	0.84	1.01
Ca 1200	0.17	0.02	0.01	0.01	0.02
Corium 1200	1.01	1.31	1.27	1.26	1.30
Corium 1500 Al	0.06	0.01	0.01	0.01	0.00
Corium 1500 Mo	0.03	9.47	0.82	0.69	0.74
Cor 1500 6:1 Mo	1.02	2.05	5.61	5.26	5.53

Table 4.4: Ratios of measured concentrations/theoretical max concentrations.

4.2 Leaching

Due to a series of malfunctions both regarding filtering the samples and the ICP-MS not functioning once the samples were all filtered. Only the first three sets of samples could be analyzed before the writing of this report. There were also issues of what is currently believed to be solid particles of uranium making it through the different filters. The results of uranium leaching from each triplicate seen in figure 4.25-4.27 varied widely, leading to the conclusion that the problem does not stem from the leaching samples themselves. In that case each triplicate should individually behave somewhat consistently. The uncertainties in the measurements, which amounts to ±3% are also not enough to impact the results in a significant way.

The following plots show the data acquired by ICP-MS of the first three sets of samples. The data for the triplicates are shown as the average results of the three samples, with their individual measurements shown separately. The lack of further data points makes discerning any patterns very difficult, although some hypotheses can be formed. Comparing the concentration of Sr in the different samples, shown in figure 4.19, versus the concentrations of the other dopants in figure 4.20-4.24. Sr seems to leach out in significantly higher amounts compared to the other dopants. It also doesn't seem to follow the pattern of the other dopants and as Sr is the only measured dopant that isn't a lanthanide, it might not be too surprising that it behaves differently.

Another strange behavior can be noted regarding the dopant analysis. The calibration of the ICP-Ms instrument was done using standards which mimic the most common composition of isotopes found for any given element and based of the measured concentration of any isotope, calculates backwards to a total concentration of said element including all its isotopes. This means that the difference in concentration between 143Nd and 146Nd seen in the graphs below, where the concentrations of Ce and 146Nd seem to follow each other closely. Even stranger is the U + SiO_2 samples plotted in figure 4.21 where it no longers follows that pattern as both Nd isotopes show just about the same concentrations and the concentration of Ce is notably higher. This indicates it might not be a systematic error in the measurements as all samples were analyzed at the same time and calculated the same way. The actual cause of this phenomena is however unknown.

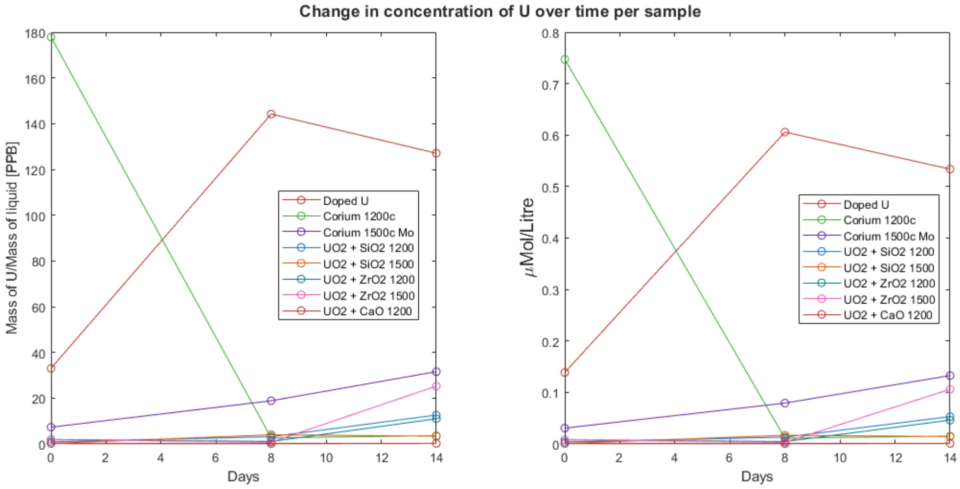

Figure 4.18: Change in uranium concentration for all leaching samples

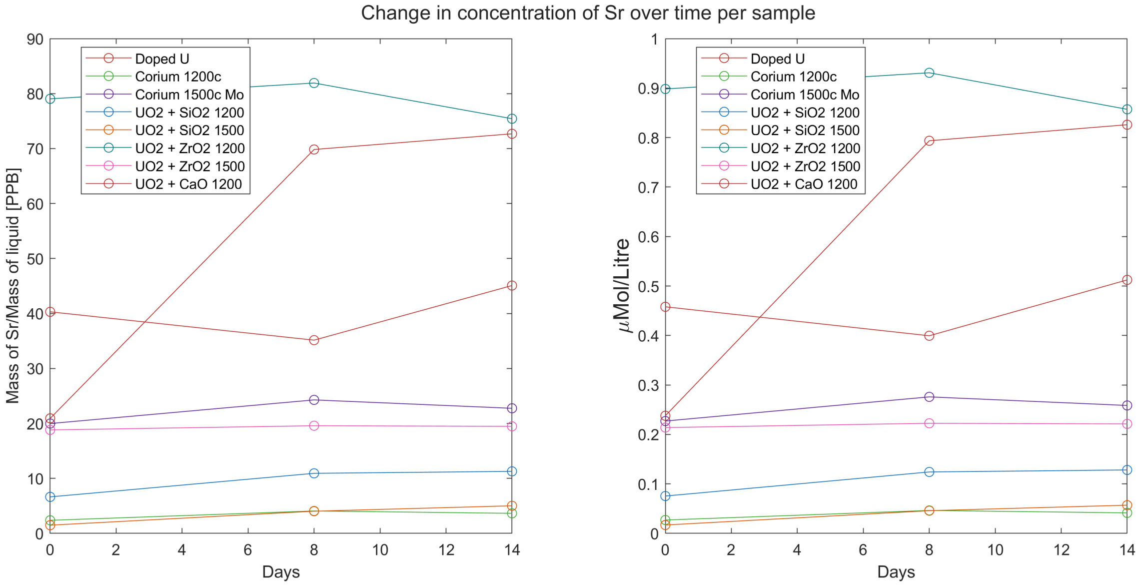

Figure 4.19: Change in strontium concentration for all leaching samples

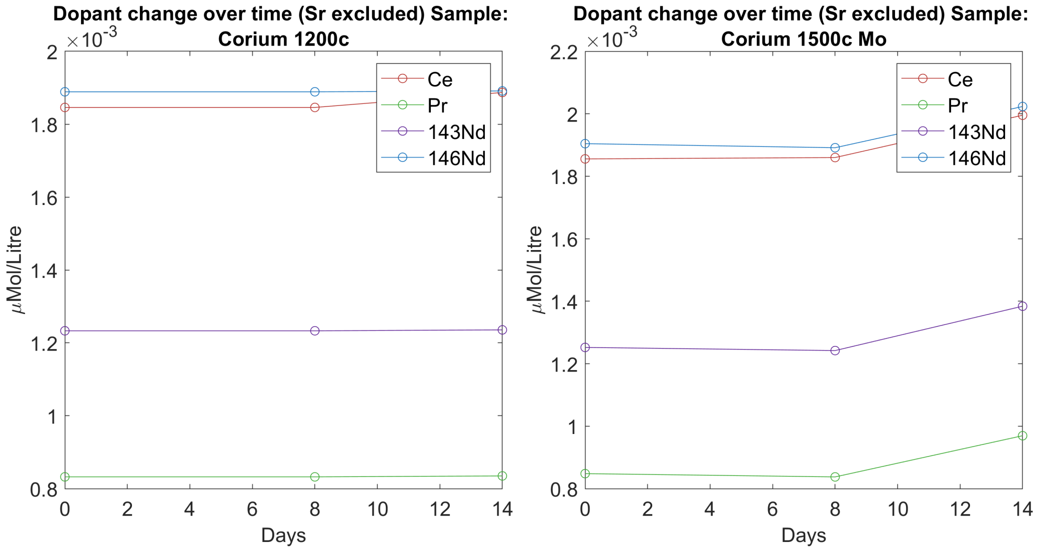

Figure 4.20: The average change in dopant concentration over time for the corium triplicates

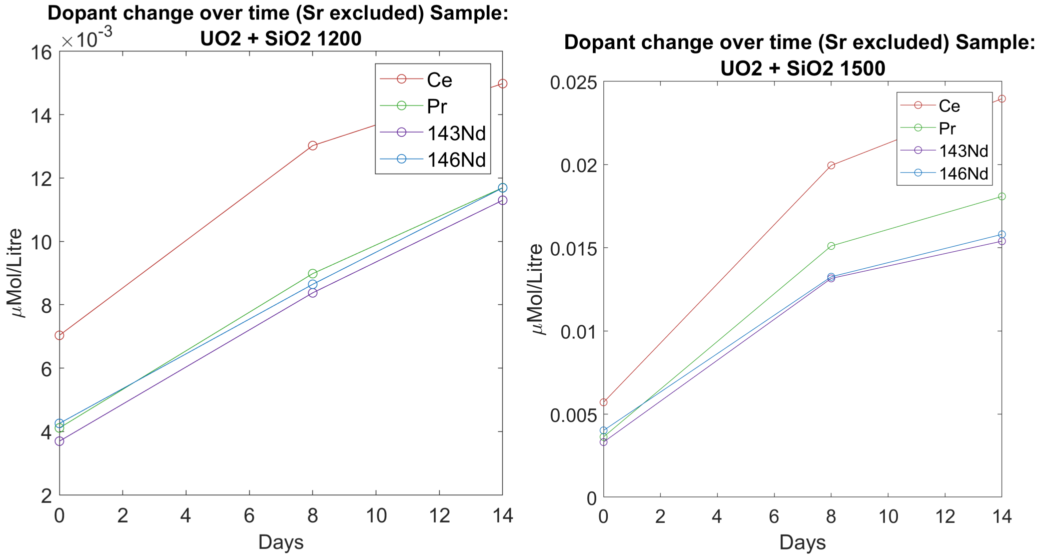

Figure 4.21: The average change in dopant concentration over time for the Silica samples

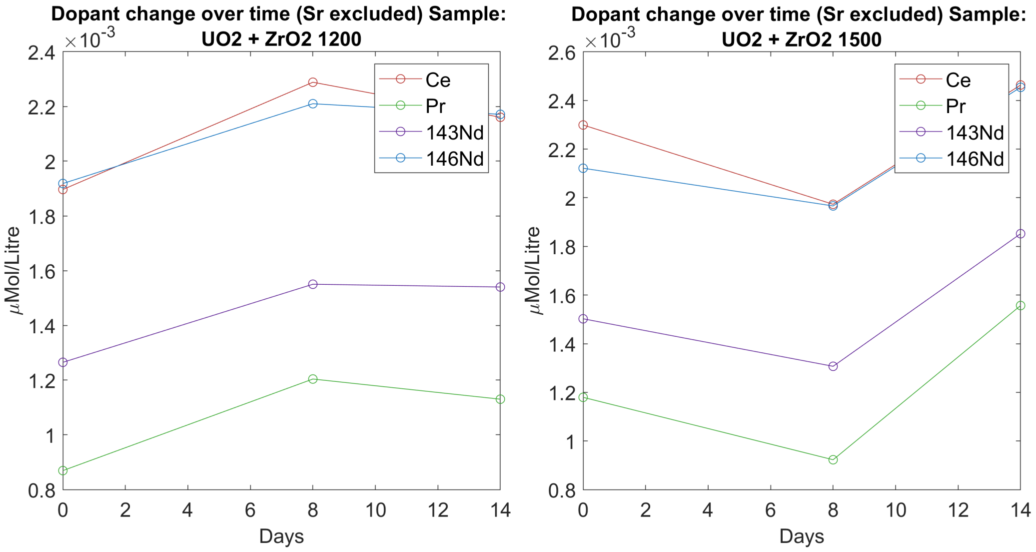

Figure 4.22: The average change in dopant concentration over time for the Zr samples

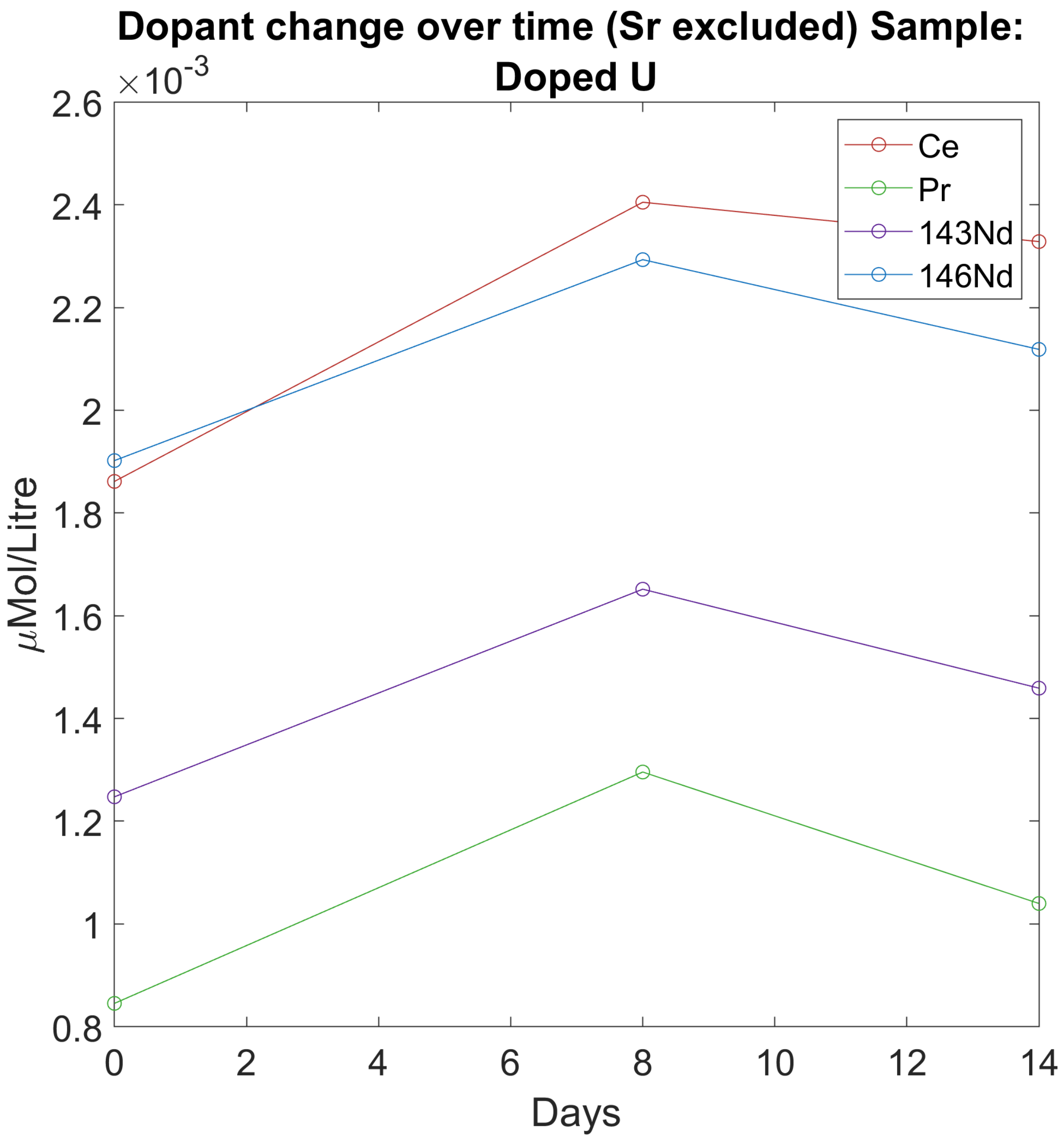

Figure 4.23: Average change in dopant concentration from the doped uranium triplicates

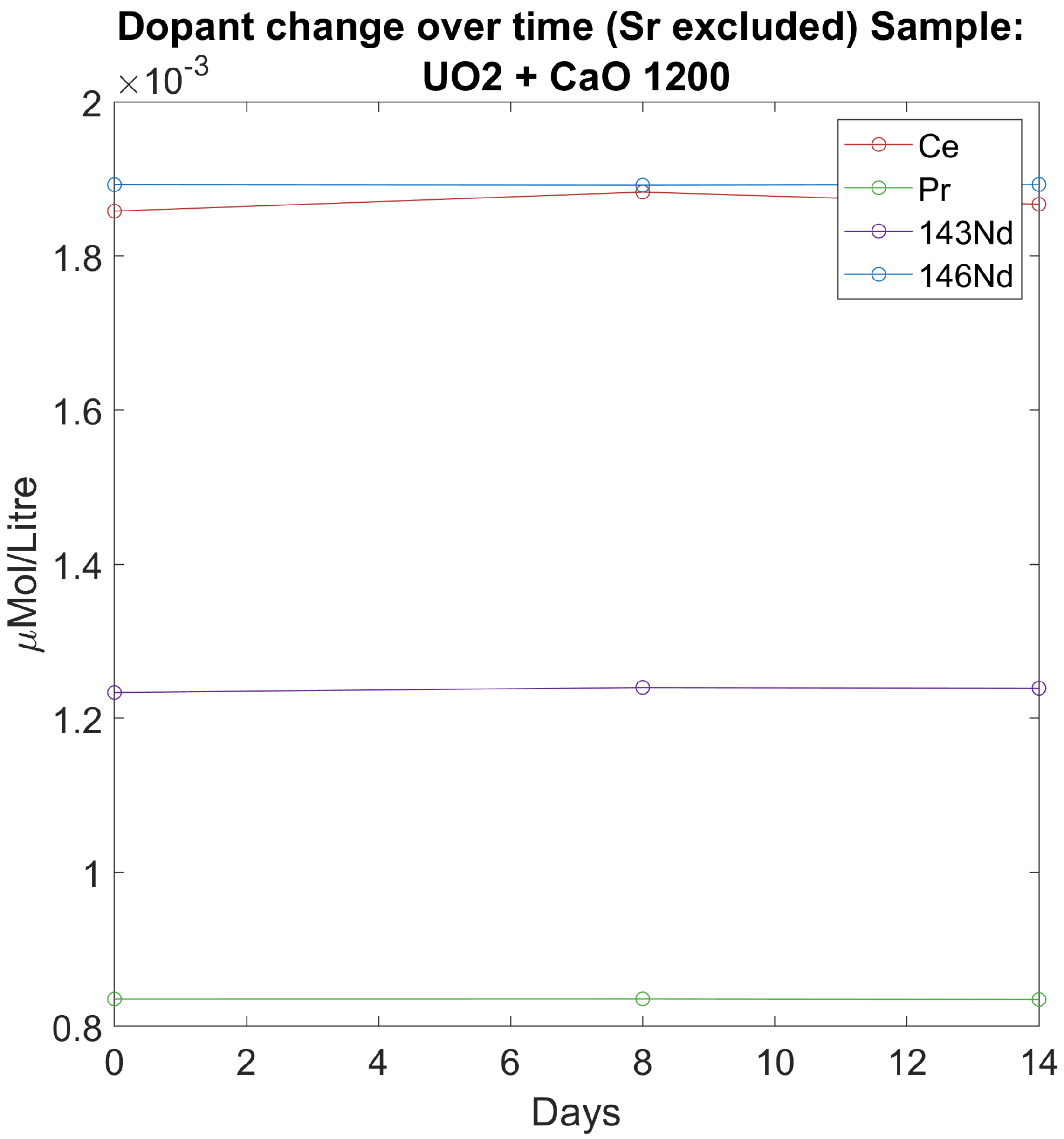

Figure 4.24: The average change in dopant concentration over time for the calcium sample

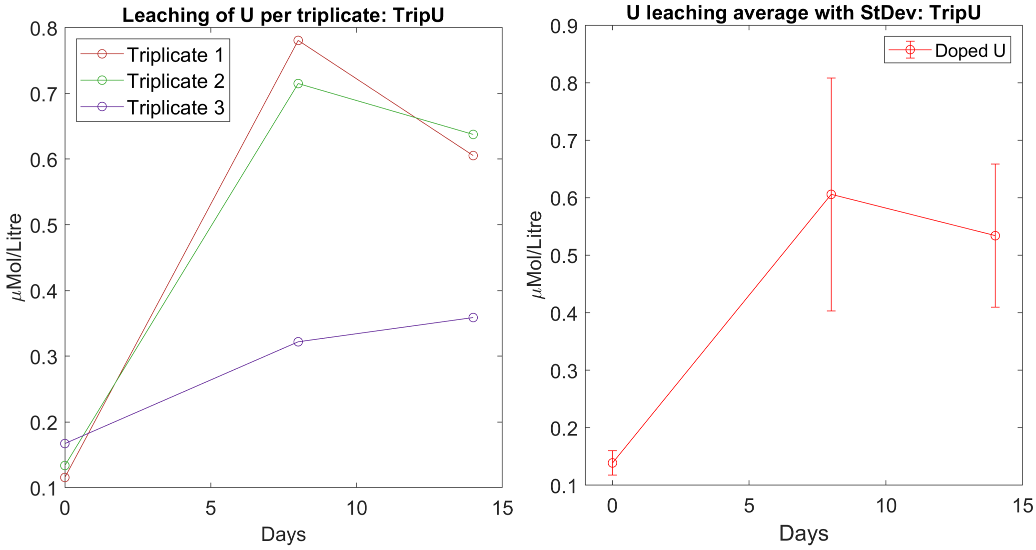

Figure 4.25: Change in uranium concentration for each UO_2 triplicate along with mean concentration and standard deviation.

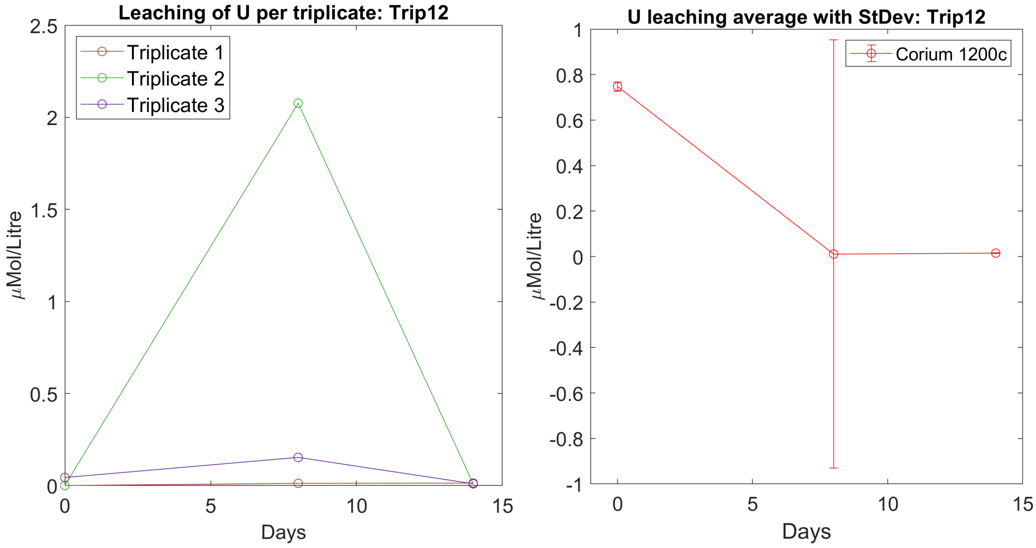

Figure 4.26: Change in uranium concentration for each Corium 1200℃ triplicate along with mean concentration and standard deviation.

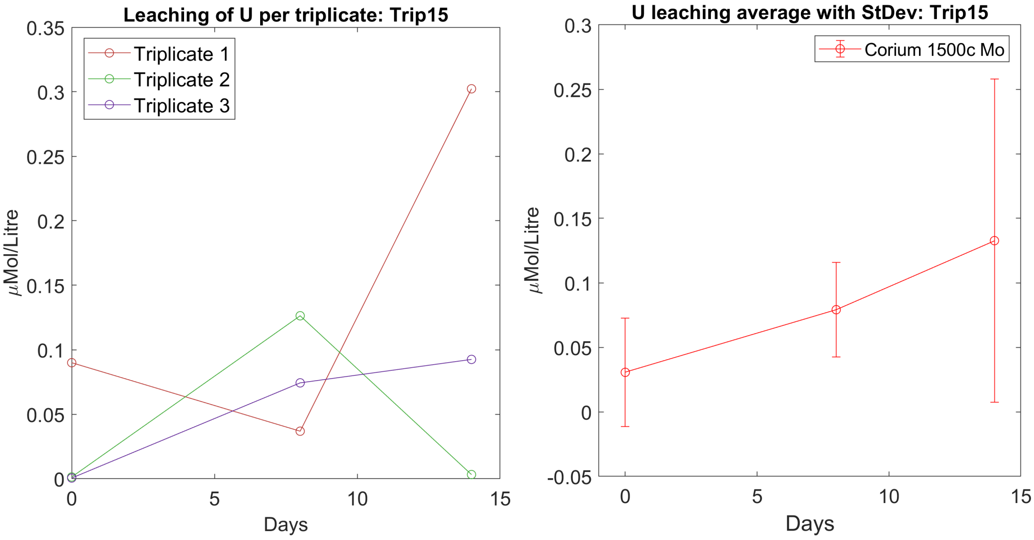

Figure 4.27: Change in uranium concentration for each Corium 1500℃ triplicate along with mean concentration and standard deviation.

5

Conclusion

This study has tested one method of synthesising corium debris from a nuclear meltdown in a small-scale lab setting. The method was shown to successfully create usable samples up to at least 1500℃. It becomes difficult once the melting point of silica is reached and the mass begins to react with its surroundings. Alumina was shown to not be a good material for the crucible due to it's affinity for silica and calcium. Leading to a reaction between the crucible and the corium, the rate of which seems to increase with temperature. Molybdenum crucibles seemed to work a lot better in preventing the corium from reacting and sticking to anything, making the process of accessing the corium after heating much simpler. Molybdenum working so well as a crucible means that is likely the way to go as alumina is just too reactive with the materials in the corium. Molybdenum also has a significantly higher melting point than alumina (2072℃ vs. 2623℃)[3] which could be useful as the temperature of a meltdown can still go much higher than the 1750℃ used in these experiments.

If the corium that was synthesized during this project is a realistic representation of actual corium found in meltdowns is difficult to tell. There has been assumptions regarding the composition of the materials, heat, atmosphere, homogeneity, time, etc. This means that it may only be representative of a very specific case and other conditions could vary the final result significantly. But as a proof of concept, a mass of inactive or low activity substitutes of the materials found in corium has been created on a small scale, meaning the method works and can be further built upon as necessary.

The leaching unfortunately gave little to no significant results. The very varying concentrations of uranium in the triplicate samples and no apparent explanation as to why, means that those results cannot be interpreted and it is also unknown whether that affects analytes other than the uranium.

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