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Extraction and Analysis of Leachates from Synthetic Corium Samples

And construction of a leaching apparatus

Master's thesis in Materials Science

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the Content of the Report**

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Extraction and Analysis of Leachates from Synthetic Corium Samples

A Subtitle that can be Very Much Longer if Necessary

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Abstract

The purpose of this project was to create synthetic corium samples and subsequently measure the leaching behaviour of these. The study aimed to see if different compositions affected the leaching behaviour and leaching rate. To accomplish this, corium samples were prepared using uranium dioxide (UO_2), Nd, Sr and Ce (as a surrogate for plutonium). These samples were divided into two groups: one to be leached and one to be pressed into pellets. The surface area of the powders was measured, and the water in which the powders leached was analysed using an ICP-MS. The pellets were analysed using a SEM and XRD. XRD, SEM, and ICP-MS indicated that corium was successfully synthesised; however, the leachate concentration was too high for the ICP-MS to measure, indicating significant elemental release, but this meant that the exact concentration of the element could not be quantified. In conclusion, corium was synthesised and leached, but further work is needed to accurately quantify the leaching behaviour and elemental release.

In addition, a leaching apparatus was developed to facilitate low-cost, accessible leaching experiments. This design, which is stackable and allows for simultaneous parallel testing, was made using CAD and can be 3D-printed, which removes reliance on specialised or expensive laboratory equipment.

Keywords: corium, nuclear, leaching behaviour, nuclear meltdown, uranium, strontium, cerium

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1

Introduction

Nuclear power is neither regarded as fossil nor renewable fuel but rather in a separate category, namely a low-carbon source, at least when referencing fission [1]. Fission means splitting nuclei of heavy atoms, which releases energy, and isotopes frequently used as fuel in nuclear reactors are U-235 and Pu-239. Technically, these isotopes are finite and are therefore not counted as renewable, but as they emit very little to no carbon dioxide and are not fossil fuels, they do not count in that category either. This places them in a special category - clean but not renewable.

In a nuclear disaster where the reactor core melts, a material called **corium** is formed. Corium usually consists of uranium oxide (or other nuclear fuel used), zirconium alloys (from the core-cladding) and steel and concrete which are just structural materials used surrounding the core [2]. Corium is dangerous due to its radioactive isotope content, making it difficult to handle and dispose of without risking contamination of nearby materials, equipment, and the surrounding environment. Its high temperature and chemical composition further complicate containment and mitigation efforts, as it can penetrate structural barriers and interact with other substances, potentially forming highly mobile radioactive compounds. Such mediums can be cooling water in which the corium can leach out radioactive compounds.

1.1 Scope

The aim of this project is to synthetically produce corium samples and subsequently analyse these samples and their leaching behaviour. In addition, design and construct a leaching apparatus suitable for similar purposes.

1.1.1 Limitations

Complex factors such as microbial activity or long-term material degradation will not be considered. This includes variations in parameters during the measurements, such as temperature, which could be done to simulate seasons or daily cycles. As it is not intended to create a real reactor meltdown due to safety risks, the corium samples will be very slightly active and cooled, meaning any temperature changes during the experiments will be externally induced rather than generated by the material itself.

1.1.2 Specification of the issue being investigated

- What role does the material composition of synthetic corium play in its leaching characteristics?
- Which elements or compounds are most prone to leach?
- How much will the synthetic creation of the samples affect the reliability of the experiment?
- How does the duration of exposure to water impact the extent of leaching? Will the leaching rate of different materials stagnate and if so, when and for which materials?
- How can a leaching apparatus be designed so that other parties can manufacture it as easily as possible

2

Theory

The following is basic information about the elements used, corium and its composition, ocean water properties, leaching and different analysis methods

2.1 Nuclear fuel

In Sweden, uranium oxide is used as nuclear fuel. Uranium oxide exists as a powder which is then compressed to small centimeter big pellets and heat treated to make the powder sinter to make the pellet more dense [3]. Uranium dioxide has a melting point of 2847°C and even if an accident would not cause that temperature it can still be hot enough to melt the surrounding structure such as steel, concrete and zirconium alloy which is what is often referred to as a "nuclear meltdown" [4].

The term "nuclear meltdown" is not formally defined by the International Atomic Energy Agency (IAEA); instead, more precise terms such as "severe accident" or "core damage" are used [5]. However, in this report, "nuclear meltdown" will refer to a scenario where the reactor core is partially or completely molten. While various factors can lead to such an event, the fundamental consequence remains the same — the core overheats and melts, hence the term.

2.2 Corium

Corium is formed when a nuclear power reactor core melts, creating a lava-like substance filled with everything inside and surrounding the core, such as uranium oxide, cladding and structural materials. The unique but unfortunate part about corium is that it produces its own heat through energy released by natural decay, making it very difficult, if not practically impossible, to stop once started. It is also hazardous for humans to approach the accident site due to the radiation, which further increases the difficulty of mitigating the hazards.

During this nuclear meltdown, the chain reaction stops due to a change in molecular geometry which fortunately prevents it from exploding. This also prevents further splitting of uranium keeping the composition relatively similar over time, of course disregarding the natural decay of radioactive nuclides, simplifying the experimental process.

Corium can, if a meltdown were to happen, come into contact with cooling water, groundwater or the sea in which case it could start to leach out potentially radioactive elements. Factors that can influence this are pH levels, temperature, salinity and/or ion presence.

2.3 Corium in previous nuclear accidents

As nuclear accidents are rare, corium is not often formed. There are two major accidents in which a reactor meltdown happened, namely the Chernobyl Nuclear Power Plant (ChNPP) and the Fukushima Daiichi Nuclear Power Plant (FDNPP) accidents. In the Chernobyl accident, the corium was prevented from coming into contact with the groundwater, avoiding a potentially catastrophic scenario; however, in the Fukushima accident, there was a tsunami which led to direct contact and interactions with the water.

2.3.1 The Chernobyl and Fukushima accidents

The Chernobyl accident happened in 1986 due to a mishandled safety test that caused a sudden power surge that led to an increased pressure, which, through a series of events, released fission products into the atmosphere [6].

The Elephant's Foot is a nickname given to the enormous mass of corium which was created during the disaster, which is the largest mass of corium known. During the accident, the corium had started to melt through different biological barriers, increasing the risk of it coming in contact with groundwater, contaminating the land. Fortunately, a concrete slab with a built-in cooling system was built, which prevented the melt from being able to leach dangerous radionuclides into the groundwater.

The Fukushima accident happened in 2011 at the Fukushima Daiichi Nuclear Power Plant in Japan. A 9.0-magnitude earthquake caused an automatic shutdown of the operating reactors and also a tsunami, which hit and flooded the plant. This caused the cooling and electrical systems to malfunction, leading to several reactor cores overheating and eventually melting, creating corium. These temperatures led to the release of hydrogen gas, which exploded and caused structural damage to several reactor units [7].

As the corium needed to be cooled, water was pumped onto the molten mixture. Still, in addition, some of the nuclear melt had fallen into water at the bottom of the reactor pressure vessel. There was also a high risk of debris generally coming into contact with the water, naturally, as there was a tsunami. Thus, a study investigating the leaching behaviour of prototypical corium samples was conducted to better understand the interactions between corium and water [8, 7]

Fortunately, corium from the Chernobyl accident did not contaminate the groundwater directly; however, the Fukushima accident did run the risk of creating a highly mobile radioactive mass, highlighting the risk associated with corium coming into contact with water. By analysing the leaching behaviour of corium, this study aims to simulate and understand these interactions and processes under a controlled lab environment.

2.3.2 Sample composition

When using UO_2 as fuel, PuO_2 will always be created due to the following reaction:



Instead of using plutonium, cerium will be used. Cerium has properties similar to those of plutonium because of its oxidation states, but is more attractive due to its heavily reduced toxicity.

Another element used will be strontium. As mentioned previously, strontium can also be found in corium due to it being a fission product split from uranium.

The study by Nakayoshi et al., as previously mentioned, estimated the composition of the molten corium to be as follows [8]:

	Mass (t)	Frac	Frac (corr.)
UO₂	75.77	0.538	0.96
F.P.*	2.49	0.018	0.04
Rest	62.546	0.444	-
Tot	140.806	1	1

Table 2.1: Mass and fraction distribution of materials.

*F.P. - Fission products which in this project will refer to e.g. Sr-90, Ce

Rest products include elements such as iron, nickel and zirconium, both as pure metals and in their oxide forms. These elements will not be present in the synthetic corium samples, as well as concrete. This is partly due to corium, naturally, being a relatively heterogeneous phase, and to produce as consistent and reliable results as possible, a homogeneous phase is desired.

The samples will thus consist of UO_2 , Nd, Sr and Ce in various proportions. The proportions will be loosely based on the study by Nakayoshi et al. [8]. However, variations will be introduced to achieve a more comprehensive result that can compensate for the local differences in the heterogeneous phase (see A.1).

2.4 Water properties

Different water properties affect the leaching rate. As mentioned previously, low salinity, for example increases leaching rate while high salinity lowers leaching rate.

Shiogama, a place near the FDNPP (≈ 100 km), has an average salinity of around 35 ppt (thousand) and a pH level of 8.1 [9, 10]. In contrast, water at nuclear power plants has to be very pure. This means that sodium and chloride levels have to be so low that they can exist below 1 ppb or even 0.1 ppb. These numbers are from nuclear power plant water chemistry guidelines from 2014; however, historically, such as in 1989, there were lower requirements, thus higher levels of ions accepted -

around 5 ppb, which is still magnitudes lower than the ocean [11].

By definition, H₂O has a pH of 7 (25 °C). However, carbon dioxide and other gases can be dissolved, which can affect pH levels.

While high pH can increase the leaching rate, acidic leaching is the quickest [12]. This indicates that lower pH is more critical than higher pH.

2.5 Elements present in the synthetic corium samples

The following is basic information about the elements used to create the synthetic corium samples.

Uranium

As mentioned previously, uranium is commonly used as fuel in nuclear reactors and is the most common radioactive element in corium. Uranium is most commonly found as the isotope U-238, which makes up over 99% of all uranium mined; however, U-235, which only makes up $\approx 0.72\%$, is the most desirable one for nuclear fuel. At neutral pH levels, uranium oxide is generally considered insoluble.

Neodymium

Neodymium is a lanthanide element and can be seen as representative of many lanthanides. It is also commonly found in corium as it is an abundant fission product. Most neodymium isotopes are stable, but some long-lived isotopes also exist. These can decay for long periods, making them a potential risk in leaching scenarios.

Strontium

Strontium-90 is a waste product found in spent nuclear fuel rods and is radioactive with a half-life of around 29 years. Strontium also has high solubility and mobility in water [13]. As strontium has similarities with calcium due to they both belong to the alkaline earth metals, this can make it extra hazardous as it can accumulate in the bones, causing damage to nearby tissue.

Cerium (plutonium)

Cerium in its tetravalent state is used as a surrogate for plutonium, a very toxic and radioactive actinide. Plutonium has a low leachability, however, still measurable [14].

2.6 Leaching properties

A study on the leaching behaviour of strontium in cement composites demonstrated that leaching rates increased with higher temperatures and lower water salinity. Additionally, greater permeability within the sample matrix was found to contribute

to a higher leaching rate [15]. However, since cement differs from corium in both composition and structure, these findings may not be directly applicable to our experiment.

In the following sections, examples of a figure, an equation, a table, a chemical structure, a list, a listing and a to-do note are shown.

2.7 Laboratory techniques

As it was desirable to ensure the sample's molecular structure, atom geometry and grain structure, analysis methods such as SEM, ICP-MS and XRD were used. Another technique used was spark plasma sintering to create pellets. Following is a short description of how they work and what can be read from each.

2.7.1 Scanning electron microscope (SEM)

A scanning electron microscope works by scanning a focused beam of electrons over a sample's surface. Images of the sample can then be produced by detecting different signals sent out by interactions between the sample and the electrons. Because a SEM works with electrons, it can achieve a much better resolution than a traditional optical microscope; 1 nm compared to approximately 500 nm. There are two modes frequently used on a SEM: secondary electrons (SEs) and backscattered electrons (BSEs). To generate SEs, primary electrons are shot at the sample and eject loosely bound electrons, which are of low energy and therefore can only escape from a volume close to the surface of the sample. This provides high-resolution images of the sample's topography. This is due to a high contrast caused by *edge effects* where the secondary electrons easier can escape from irregularities and edges, which causes the image to become clearer. In contrast, BSEs are elastically scattered primary electrons whose trajectories are influenced by interactions with atomic nuclei. Heavier atoms will scatter more electrons back toward the detector, resulting in brighter regions in the image. This provides information about the composition (i.e., atomic number contrast) rather than surface topography [16].

2.7.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS works by spraying a sample into a nebuliser, which turns it into a fine mist (aerosol). The aerosol is then exposed to plasma ($\approx 6000\text{-}10000\text{ }^\circ\text{C}$), which ionises the atoms. These ions are then transported to a detector, which can be detected with high precision and accuracy. ICP-MS can detect different isotopes of the same element with high precision, making it well-suited for isotope analysis even at very low concentrations, such as at the ppb level [17].

2.7.3 X-ray diffraction (XRD)

XRD is based on the principle that electrons can scatter X-rays. A beam of monochromatic X-rays (meaning the X-rays of the same wavelength) is directed toward the sample, and the rays are scattered by the electrons in the crystal lattice, which results in constructive interference at parallel crystal planes. At specific angles, constructive interference occurs, resulting in detectable diffraction peaks described by Bragg's Law. These peaks can give information about the phases present and lattice parameters [16].

2.7.4 Brauner Emmet-Teller (BET)

BET theory is used to measure surface area. It uses gas, in this case Kr, which adsorbs to the sample. This happens under vacuum under cryogenic temperatures, which can be accomplished using liquid nitrogen and a vacuum pump. The relative pressure is equalised, and the weight of the gas adsorbed is determined [18].

2.7.5 Spark plasma sintering (SPS)

SPS works by subjecting the sample to a current under uniaxial pressure to quickly heat it. The current is conducted directly through a graphite die, and in some cases, the sample itself, generating heat due to the Joule effect. The sample can be heated at up to ≈ 1000 °C/min and enables densification at lower temperatures and shorter times compared to conventional processes.

Technique	Description	Principle/output
XRD (X-ray Diffraction)	Phase identity	Crystalline phases, grains
SEM (Scanning Electron Microscopy)	Microstructure	Surface morphology, grains, pores
ICP-MS (Inductively Coupled Plasma Mass Spectrometry)	Element content	Determines elemental composition of samples
BET (Brunauer Emmett Teller)	Surface area	Measures specific surface area via gas adsorption

Table 2.2: Summarised explanation and comparison between the analysis methods used.

3

Method

This project consisted of a literature study and laboratory work. The literature study will focus on corium and leaching parameters from previous experiments. The laboratory work will consist of three parts.

3.1 Literature study

To obtain the best results possible, the experiments must be as effective as possible. The literature study served as a loose foundation for how the experiments would be carried out. This meant researching previous attempts and researching about the properties of corium, such as melt temperature, microstructure and chemical composition, i.e. the proportions of different elements in the material. For example, as mentioned earlier, it is not certain that the uranium dioxide will even melt, which means that the literature study would hopefully provide better information on how the project's corium samples should be constructed to make the results as reliable and useful as possible.

3.1.1 Experimental conditions

Parameters in the experiment were based on the ocean properties on the east coast of Japan, in the proximity of FDNPP and aim to simulate the environment of the characteristics of that sea water, but also reactor coolant, which in most cases is light water.

As for the composition of the corium samples, these were loosely based on the corium samples from the study done by Nakayoshi et al., with variations. See Appendix A.1.

Sources providing data on the quantity of fission products, such as Sr and Ce in this case, were difficult to find, as most references focused on alloys and the fuel itself. This may be due to fission products being assumed to be present by radioactive decay, and/or estimation/calculation of the specific amount is difficult and changes over time.

3.2 Laboratory part

The first part will focus on synthesising simulated corium samples, and the second part will focus on building a leaching apparatus.

The third part will consist of measurements and analysis methods of the samples. After having collected the data needed, a conclusion will be drawn, as well as various suggestions for improvement on both the sample synthesis and apparatus.

Due to many different steps, the laboratory process will be divided into sections.

3.2.1 Safety

Handling radioactive substances requires extreme precautions according to Strålsäkerhetsmyndigheten, and it is essential not to contaminate objects outside of the fume hood.

3.2.2 Weighing the elements

Strontium and neodymium in the form of $\text{Sr}(\text{NO}_3)_2$ and $\text{N}_3\text{NdO}_9 \cdot 6\text{H}_2\text{O}$ were weighed and then added to a $\text{UO}_2(\text{NO}_3)_2$ solution of 2.1 M, which was prepared by dissolving a rod of uranium in nitric acid.

The amount of dissolved uranium was measured using a scale. Because the stock solution could differ in density, a control sample of was weighed beforehand to account for that.

3.2.2.1 Precipitation and separation

After adding the Sr and Nd, the solution was stirred using a magnetic stirrer. In the case of slow dissolving of the Sr and Nd, distilled water was added to enhance the solubility. When fully dissolved, the solution was slowly dripped into a tube of ammonia to precipitate. The tube was put in a centrifuge to help separate the precipitate from the ammonia. The precipitate was then dried.

However, after some testing, this method changed, to save time, to use a polyester net as a filter, which was put in an ammonia bath. The uranium solution was then again slowly pipetted into the ammonia, and the polyester net was used to separate the precipitate from the ammonia.

But as that did not perform as desired, the method was then changed one more time to using large pipette tips lowered in a tube containing ammonia. The solution was then slowly pipetted into the pipette tip; the precipitate was solid enough not to exit the narrow opening while still allowing the ammonia to pass through and out when the pipette tip was removed from the ammonia bath. This showed to be the most efficient way, saving both time and consuming the least amount of ammonia. The precipitate, which due to some remaining ammonia, had a sludge-like consistency and had to be dried before being heat treated.

3.2.2.2 Heat treatment

After having dried off the remaining ammonia, the samples were transferred over into molybden crucibles and were heat-treated over the course of 8 hours.

Time (h)	Description
0-2	Heating to 1200°C
2-6	1200°C
6-8	Cooling to room temperature

Table 3.1: Temperature schedule

The heat treatment aimed to reduce the uranium oxide from U_3O_8 to UO_2 .

3.2.2.3 Surface area measurements

The powders were then weighed to approximately 0.050-0.100 g before having their surface areas measured using a Micromeritics ASAP 2020 Brunauer-Emmett-Teller (BET) analyser. The gas used was Kr, and the samples were degassed at 100°C for 2 hours prior to the analysis.

3.2.2.4 Producing of pellets

Approximately 1 g of all powders was pressed into pellets using graphite crucibles in spark plasma sintering. These were later sanded and polished with up to 0.2 μm fine particles to ensure a smooth surface.

3.2.2.5 SEM

The samples were analysed using a SEM. In order to prevent overcharging, a piece of copper tape was attached to the sample and the sample holder.

3.2.2.6 XRD

The pellets were also analysed using an XRD. In order to identify the phases present, the diffraction patterns were compared to a database of known materials and their characteristic patterns.

3.2.2.7 Leaching

To assess the leaching behaviours of the powders, they were weighed to 0.1 g and placed in vials with 20 mL of distilled water. These vials were placed in a water bath on top of a heat plate set to 80 °C. First, after 12 days and then, every 7 days, for up to 6 weeks, 1 mL of the water was collected from each vial to be analysed

using ICP-MS. Water level decreased over time at a rate greater than the 1 mL collected each week, indicating evaporation losses. To ensure water in the bath would always be present, a solution involved placing an inverted bottle in the basin, which functioned as a basic self-watering system.

3.2.2.8 ICP-MS

In order to ensure that the samples contained the correct elements, the powders were analysed using an ICP-MS. To analyse the samples, the powders had to be dissolved in 8M nitric acid and diluted to a reasonable ppb range. This was done by dissolving around 0.010-0.020g in approximately 5 ml of nitric acid (HNO_3) ($\approx 5\text{g}$) and then diluted (this time with 0.5 M nitric acid) by a factor of around 40,000 to reach circa 50-100 ppb. All samples also contained an internal standard of 1 ppb bismuth.

In order to quantify the elements, a similar process was done, but instead for the leaching water. The samples taken at a 7-day interval were diluted to a factor of ≈ 10 with 0.5M nitric acid while being weighed to account for the exact dilution factor. These also contain an internal standard of 1 ppb bismuth.

3.3 Statistical methodology and data treatment

The experimental design included 26 data points. To ensure robustness and ensure the evaluation of lack-of-fit, triplicates were placed at central and edge points of the ternary diagram. The data was then visualised using ternary contour plots, which could enhance the understanding of the behaviour and trends shown.

In order to understand the role that the elemental composition played, especially in relation to each other, the samples first had to be surface area normalised before they were used in a series of statistical models. The systems under investigation consisted of ternary mixtures of U, Sr and Nd. In another set of systems, U was partly replaced with Ce; however, it was still under constant proportions so as not to interfere with the cubic model. Analysis of variance (ANOVA) and regression modelling, exhibited using ternary contour plots, was used to analyse the leaching behaviour.

3.3.1 Leaching apparatus

A leaching apparatus prototype was designed using CAD. The model was subsequently printed, using a 3D printer, in PLA (polylactic acid). The aim for the apparatus was to be stackable to save space (in case of work in fume hoods, for example), with cable management channels and a place for a heating element as well as a stirring motor. Due to the low thermal stability of PLA, ABS (Acrylonitrile butadiene styrene) was considered, but the idea was rejected due to technical limitations with the 3D printer available.

4

Results

4.1 XRD

The graphs produced by XRD matched the standard reference data of uranium oxide, confirming its presence as the primary phase in the samples. There were also instances of cerium uranium oxide, neodymium uranium oxide and strontium uranium oxide, indicating interaction and incorporation of these elements in the UO_2 lattice. Full set of patterns is provided in Appendix A.2-A.9.

4.2 SEM

Images from SEM indicate a heterogeneous material with distinct grains and visible grain boundaries. Some samples showed a more defined morphology than others, and irregularities from polishing can be mistaken for grains or grain boundaries. Full set of images is provided in Appendix A.10-A.15.

4.3 ICP-MS

Leaching samples were taken, but many measurements were unfortunately not useful for quantification since the concentration of leachates was magnitudes higher than the measuring range of the device. This indicates that leaching had at least occurred and was significant. The measurements available were those in which the samples had been leached for 12 days.

4.4 Statistical methodology and data treatment

The surface area normalised leachate data were subjected to mixture regression modelling and ANOVA. The system without cerium (U-Nd-Sr) showed significant regression in the full cubic model, $P=0.008$; however, a low predicted R^2 value indicates that the model may fail to predict future observations reliably. A simplified quadratic model, including only the main effects, improved the predictability.

The interaction between uranium and strontium was found to be significant, suggesting a synergistic effect where Sr influences U leaching. Neodymium showed a passive role, with no significant contributions or interactions.

In the system where Ce partially replaced U (U+Ce-Nd-Sr), the regression model was not statistically significant ($P = 0.302$), and a significant lack-of-fit was observed. This indicates that either the substitution level (2%) was too low to have a measurable effect or the model was not able to capture more complex behaviours like redox changes or non-linear effects.

Uranium leaching was highest in U-rich regions, and Sr dominated the total dissolved mass. Neodymium remained largely insoluble across all compositions, while cerium displayed moderate mobility near the central compositional space.

The full set of ternary contour plots of surface area normalised leached elements is provided in A.16-A.25.

Table 4.1: Summary of statistical models for leaching behaviour

System	Model Type	R^2 (%)	Adj. R^2 (%)	Pred. R^2 (%)
U-Nd-Sr	Full cubic	69.02	51.59	11.31
U-Nd-Sr	Reduced quadratic	50.58	43.84	27.99
U+Ce-Nd-Sr	Quadratic (Ce=2%)	–	–	–

Table 4.2: Key interaction terms and significance

System	Interaction Term	P-value
U-Nd-Sr	$U \times Sr$	0.025
U-Nd-Sr	$U \times Sr$ (non-linear)	0.016
U-Nd-Sr	Nd-related terms	Not significant
U+Ce-Nd-Sr	All terms	Not significant

4.5 BET

The BET provided information about the surface area of the samples. The machine stopped working correctly before the last samples could be measured. No correlation between sample composition and surface area could be seen. For the samples measured, see Appendix A.26.

4.6 Leaching apparatus

The leaching apparatus was successfully designed and 3D-printed using PLA. The design of the apparatus allowed for stacking in 2 dimensions - height and width. The channels allow for easier cable management. See Appendix A.27.

5

Discussion

5.1 XRD

The XRD showed graphs matching the expected. In some tests, uraninite (pitchblende) was identified instead of the expected uranium dioxide. However, uraninite largely consists of uranium dioxide but sometimes with impurities and/or U_3O_8 (tr uranium octoxide), which could be the result of insufficient reduction in the sample preparation (too low temperature or insufficient time in the oven). There were also some findings indicating that the different materials had been incorporated into the uranium oxide lattice.

This supports the conclusion that corium samples were successfully synthesised. It also illustrates how different elements can interact with the uranium to form new compounds, such as mixed oxides. These interactions are likely to occur during the sintering process, where the temperature is very high. This can alter the composition in comparison with the powders, meaning that there is a possibility that the phases identified by the XRD do not fully represent what compounds participating in the leaching process.

5.2 SEM

The SEM images clearly showed a heterogeneous material with distinct grain boundaries, which coincides with the expected morphology of corium.

However, since the SEM scans the pellet samples, a similar limitation as in the case of XRD applies: the pellet may not fully represent the composition or phase distribution as in the powder used for leaching.

5.3 ICP-MS

Leachate concentrations were too high; it can be assumed that the concentration was at least 10 times higher than the maximum measurement limit of 200 ppb, which means at least 2000 ppb or 2 ppm since the sample was diluted by a factor of 10. Not great, not terrible.

5.4 BET

As the machine unfortunately stopped working, not all samples could be measured. As no correlation between the sample composition and surface area could be seen, it can be concluded that the surface area was more governed by the sample preparation rather than composition. If successful with the ICP-MS, the data could have been used to account for differences in leaching behaviour as surface area probably affects the leaching rate.

5.5 Statistical methodology and data treatment

As mentioned previously, some samples could not be analysed using BET, which meant that they could not be surface normalised. This essentially made those samples unusable for the cubic model. Moreover, the ICP-MS unfortunately malfunctioned multiple times, which caused delays, which, in the end, led to time running out, causing multiple measurements to be missed.

However, the ANOVA and regression model gave some insight into how different elements could affect the leaching behaviour, even though multiple measurements were desired to be able to understand the time evolution of the leaching behaviour. The predicative ability of the cubic model was low, indicating that, although the model would fit the existing data points, it may not necessarily fit newer points. The reduced quadratic model enhanced this somewhat but with limited generalisability. For the system where uranium was partially replaced by cerium, no significant statistical model could be identified. In the future, this could be improved by testing higher Ce levels or using other model types, such as non-linear regressions or machine learning.

Ternary contour plots proved to be an effective tool to visualise trends and interactions between components. They provided a clear picture of where leaching was highest and lowest and confirmed the results of ANOVA.

5.6 Conclusion

Despite some unforeseen, unfortunate events, there was still useful data to be studied. The results from the methods support that the corium synthesis was successful. The result of the analysis of the pellets may not fully represent what the powders consist of in terms of phases and compounds, though the elemental composition should still be the same. Further work may focus on leaching parameters such as high salinity, different pH, different temperature and/or continuous stirring. It may also include studies on other elements, such as Cs or replacing Ce with plutonium. The leaching apparatus could be designed to allow for pressurised leaching. It can also focus on developing an electronic controller to control temperature and stirring in each experiment.

5.6.1 Possible improvements

As the leaching was done using a water bath to place the vials in, it sometimes happened that the water evaporated, which could have affected the heat distribution by making it less homogeneous. To fix this, oil instead of water could have been used, or alternatively, pouring a thin layer of oil on top of the water to prevent evaporation.

Another problem encountered was the evaporation of water within the vials themselves. This was likely due to some vials not being completely sealed. One potential solution to this was to use parafilm and wrap it around the cap, or simply use higher-quality, better-sealing caps.

5.6.1.1 Leaching apparatus

As the leaching apparatus was in a very early stage, no testing of it was done. The apparatus was printed using PLA. As PLA has a relatively low glass transition and melting point, this is not suited for applications with significant heating. Instead, ABS or plastics with higher heat stability are recommended.

5.6 Final remarks

The synthesis and characterisation of synthetic corium was successful, as well as the production of a leaching apparatus, and the unexpected elemental release highlights the chemical mobility of uranium and fission products under simulated conditions. Although limitations were met, especially in the quantitative analysis, the work provides a solid foundation on which further studies in nuclear material degradation and post-accident behaviour can be made.

Bibliography

- [1] Vattenfall. Nuclear power, n.d. Accessed 2025-01-20.
- [2] ScienceDirect. Corium (nuclear reactor), n.d. Accessed 2025-01-12.
- [3] Strålsäkerhetsmyndigheten. Kärnbränsle, Last updated: 2023-01-23. Accessed 2025-01-27.
- [4] PubChem. Uranium dioxide, n.d. Accessed 2025-01-20.
- [5] International Atomic Energy Agency. Iaea nuclear safety and security glossary, 2022. Accessed 2025-01-20.
- [6] World Nuclear Association. Chernobyl accident, Last updated: 2024-12-03. Accessed 2025-01-28.
- [7] World Nuclear Association. Fukushima daiichi accident, Last updated: 2024-05-29. Accessed 2025-01-29.
- [8] A. Nakayoshi, C. Jegou, L. De Windt, S. Perrin, and T. Washiya. Leaching behavior of prototypical corium samples: A step to understand the interactions between the fuel debris and water at the fukushima daiichi reactors. *Nuclear Engineering and Design*, 360:110522, April 2020.
- [9] National Oceanic and Atmospheric Administration (NOAA). Sea water - jet-stream: An online school for weather, Last updated 2023-03-28. Accessed 2025-02-03.
- [10] National Oceanic and Atmospheric Administration (NOAA). Ocean acidification - education resource collection, 2020. Accessed 2025-02-04.
- [11] Electric Power Research Institute (EPRI). Nuclear plant makeup water chemistry guideline: Gap analysis. EPRI Report 3002003365, September 2014, 2014. Accessed 2025-06-14.
- [12] Shifeng Chen, Xuebin Wei, Jinhui Liu, Zhanxue Sun, Gongxin Chen, Mei Yang, Yuanyuan Liu, Duo Wang, Chengcui Ma, and Dexuan Kong. Weak acid leaching of uranium ore from a high carbonate uranium deposit. *Journal of Radioanalytical and Nuclear Chemistry*, 331(6):2583–2596, 2022. Accessed 2025-06-14.
- [13] Xiaoyuan Zhang and Yu Liu. Integrated forward osmosis-adsorption process for strontium-containing water treatment: Pre-concentration and solidification. *Journal of Hazardous Materials*, 414:125518, 2021. Accessed 2025-06-11.
- [14] Hye-Ryun Cho, Sangki Cho, Jueun Kim, Sangsoo Han, Hee-Kyung Kim, and Wooyong Um. Dissolution behaviors of puo(cr) in natural waters. *Frontiers in Nuclear Engineering*, 2, 2023. Accessed 2025-06-11.
- [15] Hideo Matsuzuru and Akihiko Ito. Leaching behaviour of strontium-90 in cement composites. *Annals of Nuclear Energy*, 4(9–10):465–470, January 1977.

- [16] Amanda Persdotter and Vincent Ssenteza. Labbmanual för mikroskopi-labb: Svepelelektronmikroskopi (sem) och röntgendiffraktion (xrd), 2024. Chalmers University of Technology, KBT290. Published March 9, 2024.
- [17] Wisconsin Department of Natural Resources. Icp-ms: Basic concepts and applications, 2003. Accessed 2025-06-11.
- [18] Virginia Tech NanoEarth. (bet) brunauer–emmett–teller, n.d. Accessed 2025-06-15.

A

Appendix 1

A. Appendix 1

Sample N	U(atomic %)	Ce atomic %	Nd (atomic %)	Sr (atomic%)
1	70	0	0	30
2	70	0	5	25
3	70	0	10	20
4	70	0	15	15
5	70	0	20	10
6	70	0	25	5
7	70	0	30	0
8	80	0	0	20
9	80	0	10	10
10	80	0	15	5
11	80	0	20	0
12	90	0	0	10
13	90	0	5	5
14	90	0	10	0
15	95	0	0	5
16	95	0	2,5	2,5
17	95	0	5	0
18	75	0	20	5
19	75	0	5	20
Ub1	100	0	0	0
Ub2	0	0	0	100
Ub3	0	0	100	0
A	68,627	1,373	0	30
B	68,627	1,373	5	25
C	68,627	1,373	10	20
D	68,627	1,373	15	15
E	68,627	1,373	20	10
F	68,627	1,373	25	5
G	68,627	1,373	30	0
H	78,431	1,569	0	20
I	78,431	1,569	10	10
J	78,431	1,569	15	5
K	78,431	1,569	20	0
L	88,235	1,765	0	10
M	88,235	1,765	5	5
N	88,235	1,765	10	0
O	93,137	1,863	0	5
P	93,137	1,863	2,5	2,5
Q	93,137	1,863	5	0
R	73,529	1,471	20	5
S	73,529	1,471	5	20
T	78,431	1,569	5	15
Uceb1	98,039	1,961	0	0
Uceb2	0	2	0	98
Uceb3	0	2	19,6	78,4

Figure A.1: Atomic composition of all samples synthesised

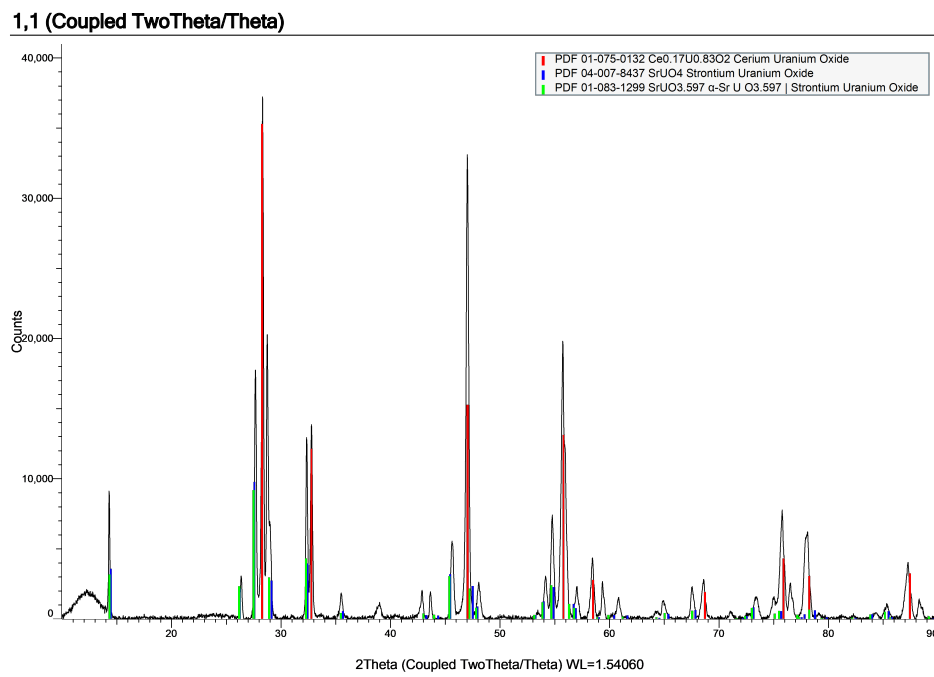


Figure A.2: XRD on sample 1,1

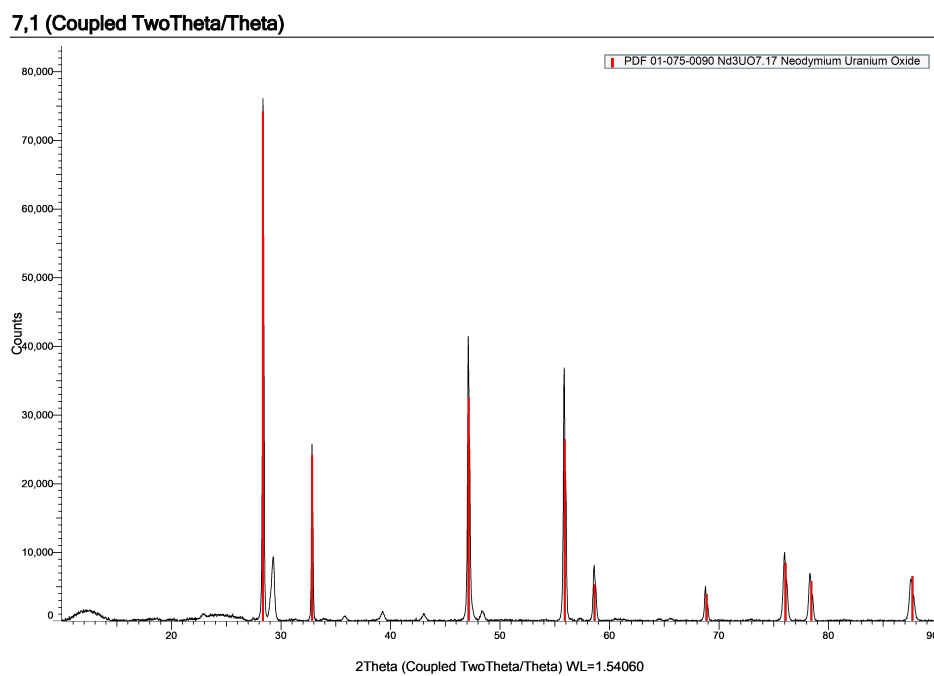


Figure A.3: XRD on sample 7,1

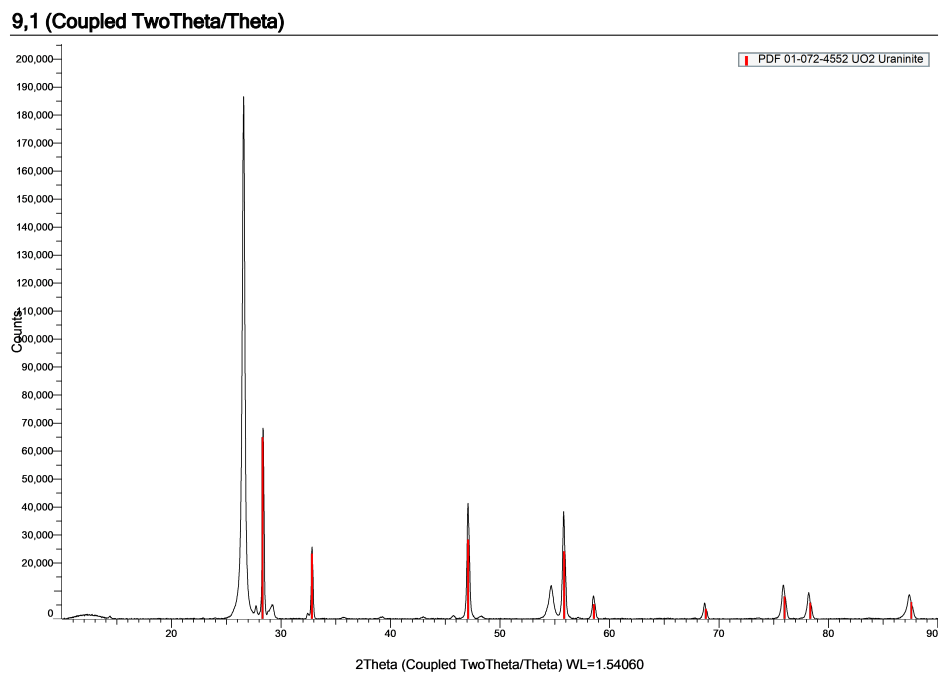


Figure A.4: XRD on sample 9,1

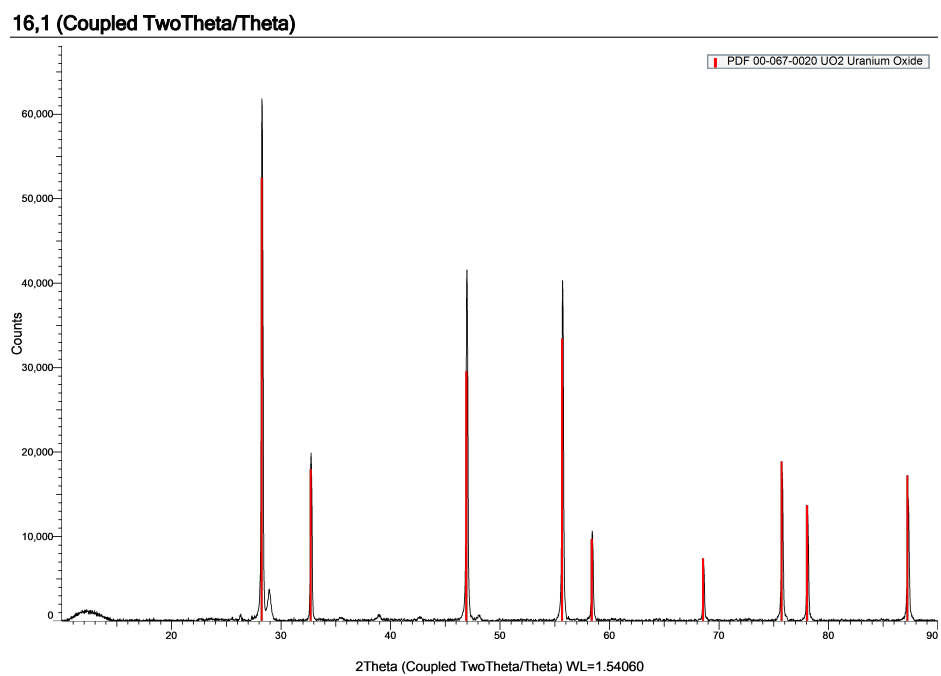


Figure A.5: XRD on sample 16,1

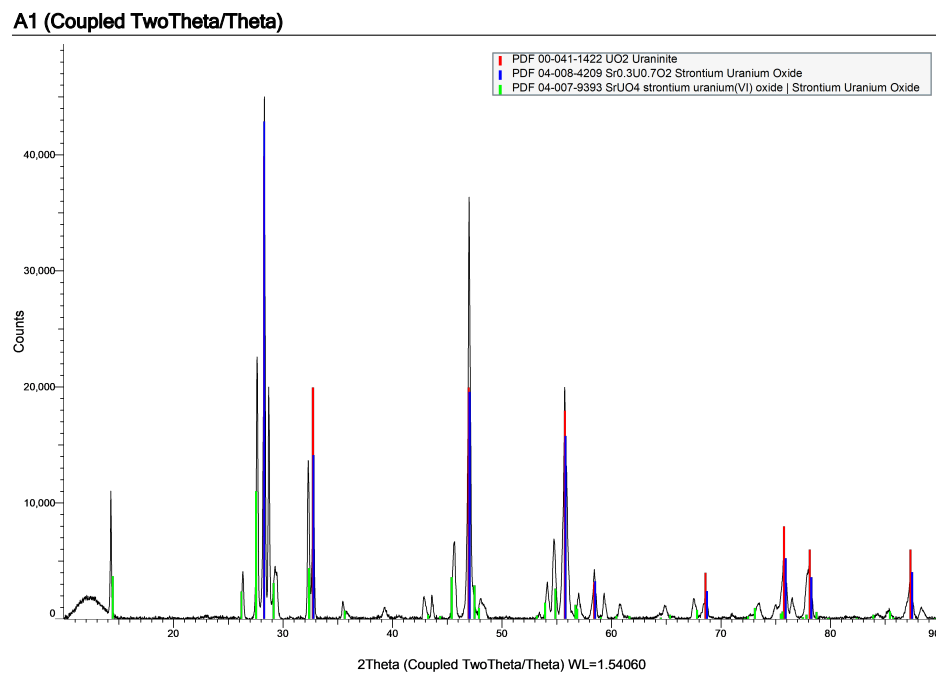


Figure A.6: XRD on sample A1

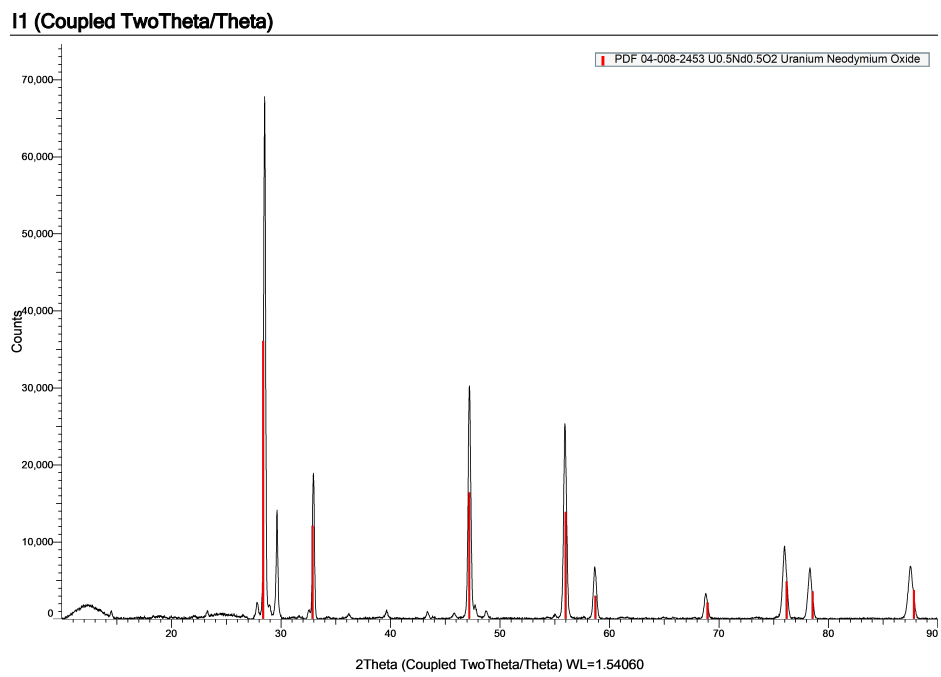


Figure A.7: XRD on sample I1

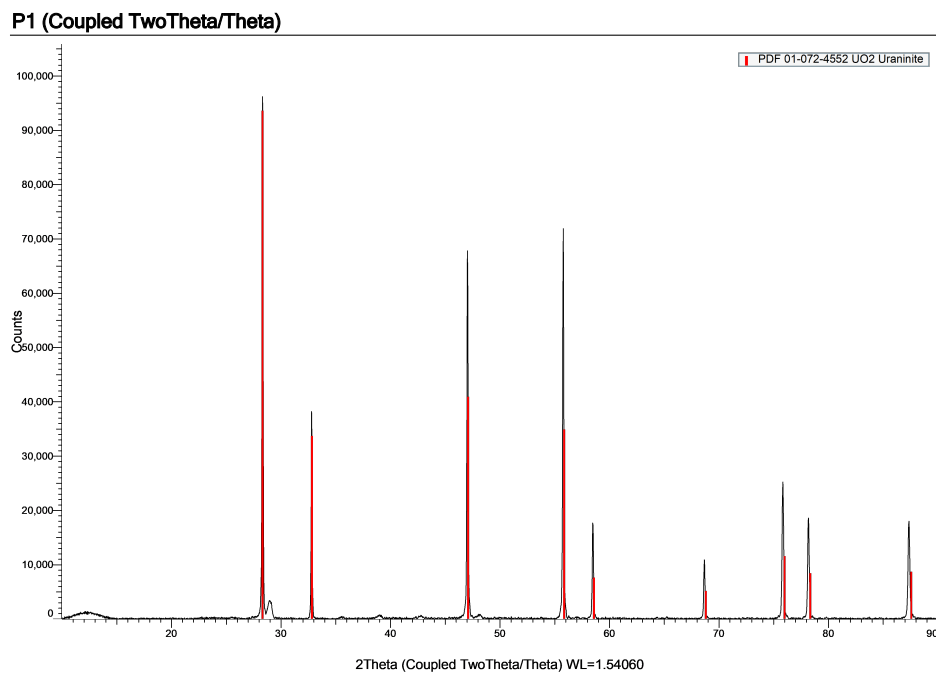


Figure A.8: XRD on sample P1

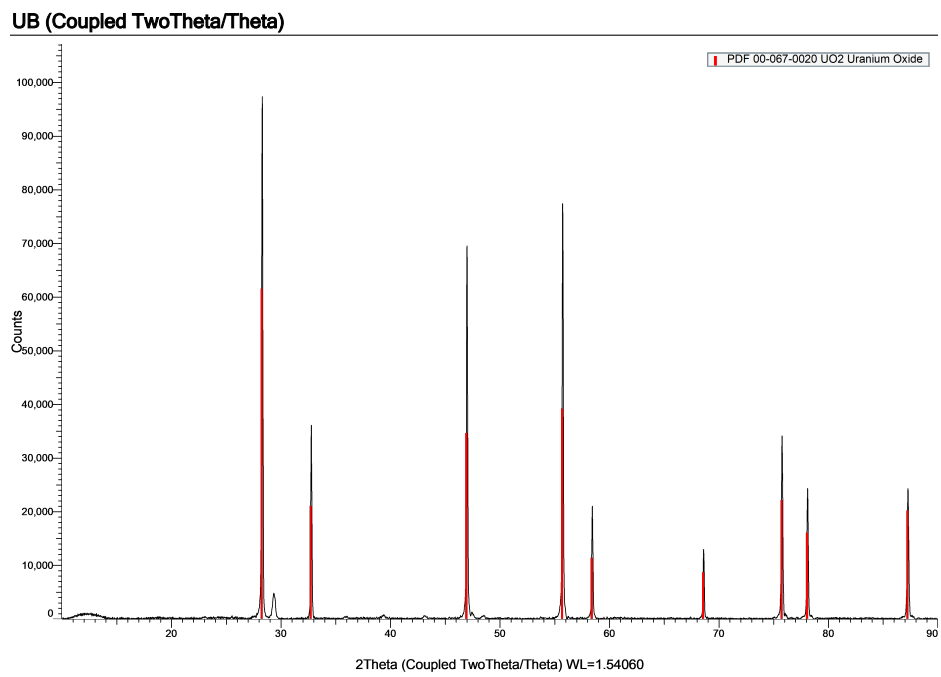


Figure A.9: XRD on sample UB

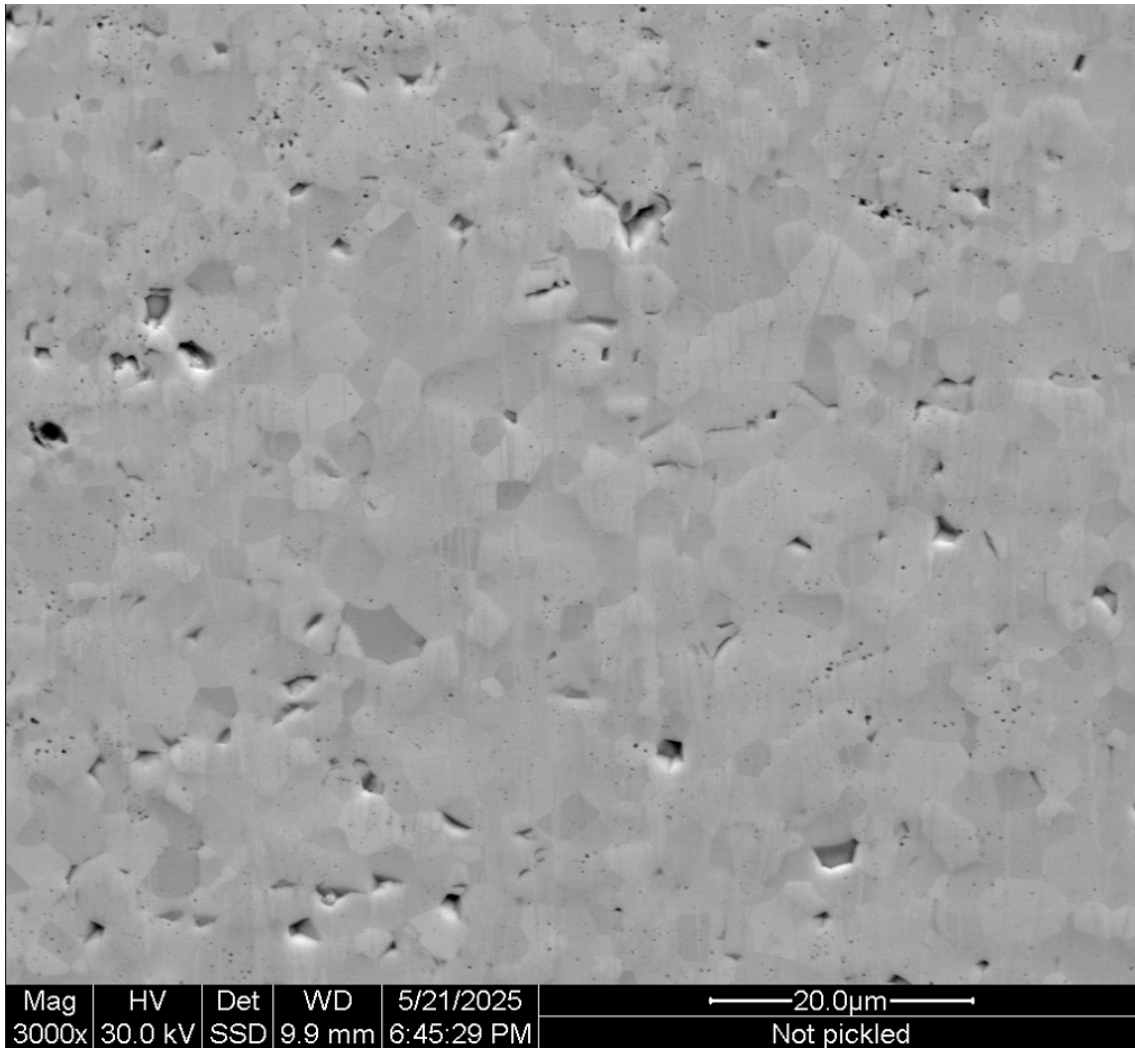


Figure A.10: SEM image on sample UCEB1

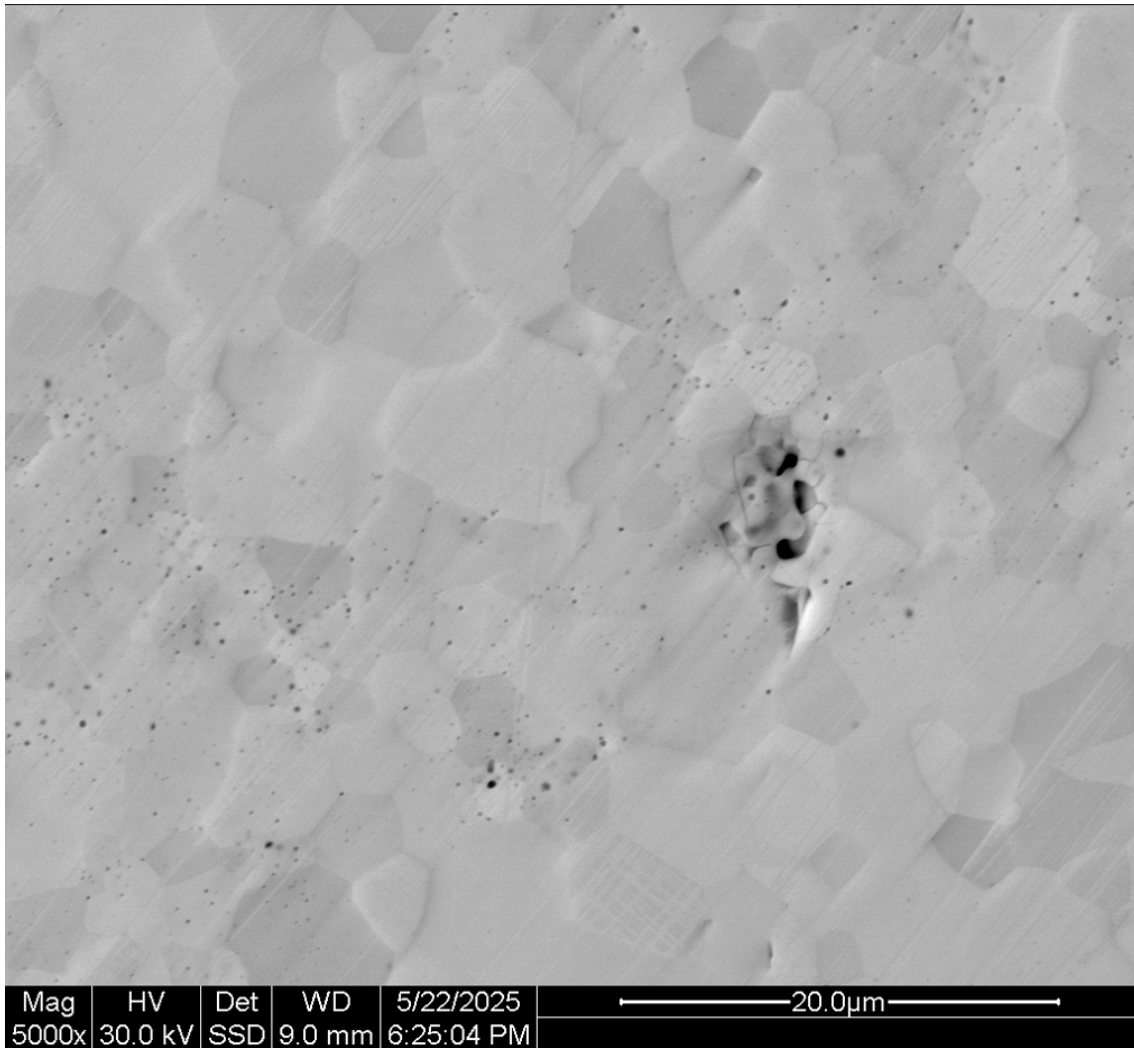


Figure A.11: SEM image on sample P1

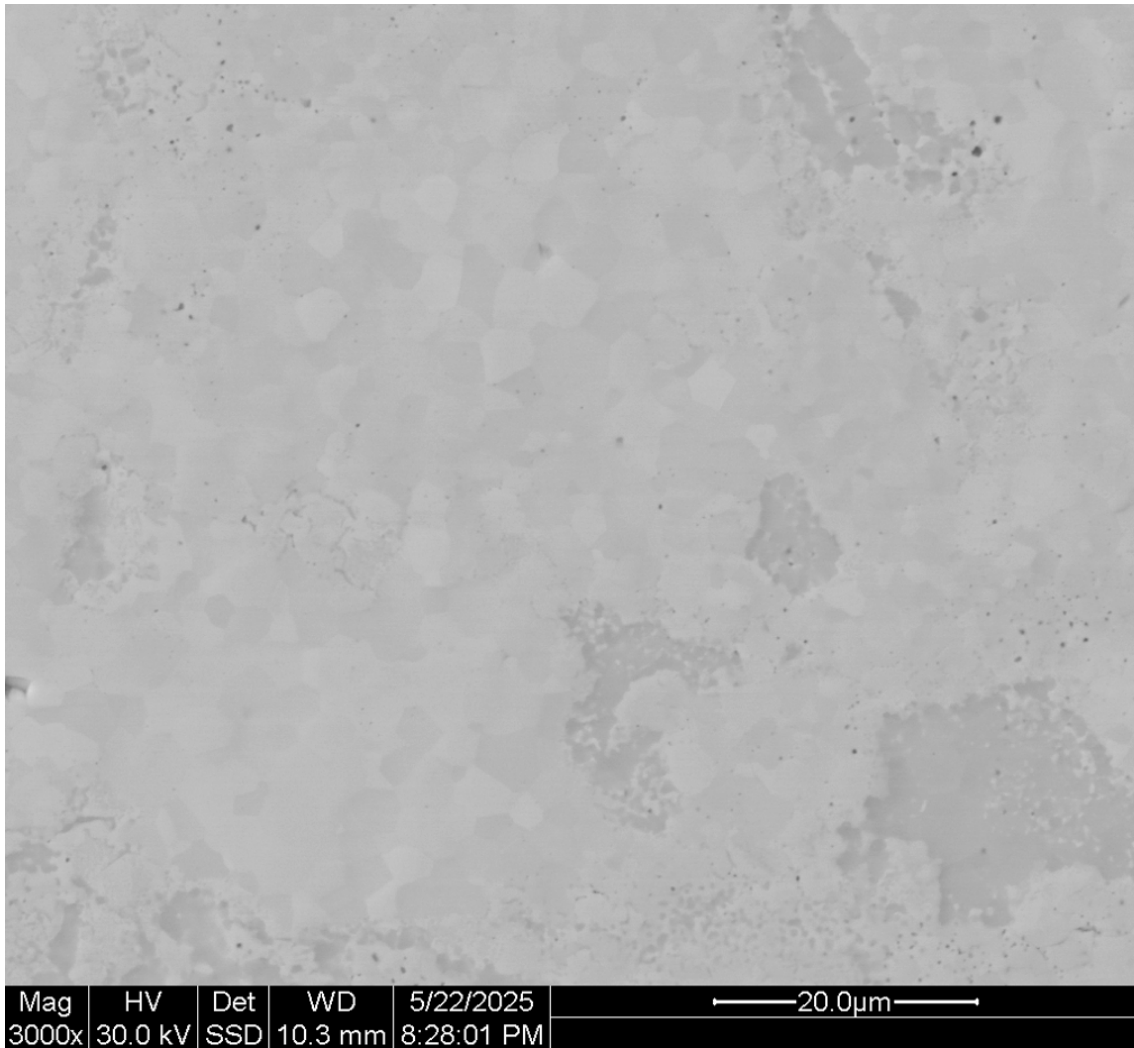


Figure A.12: SEM image on sample I1

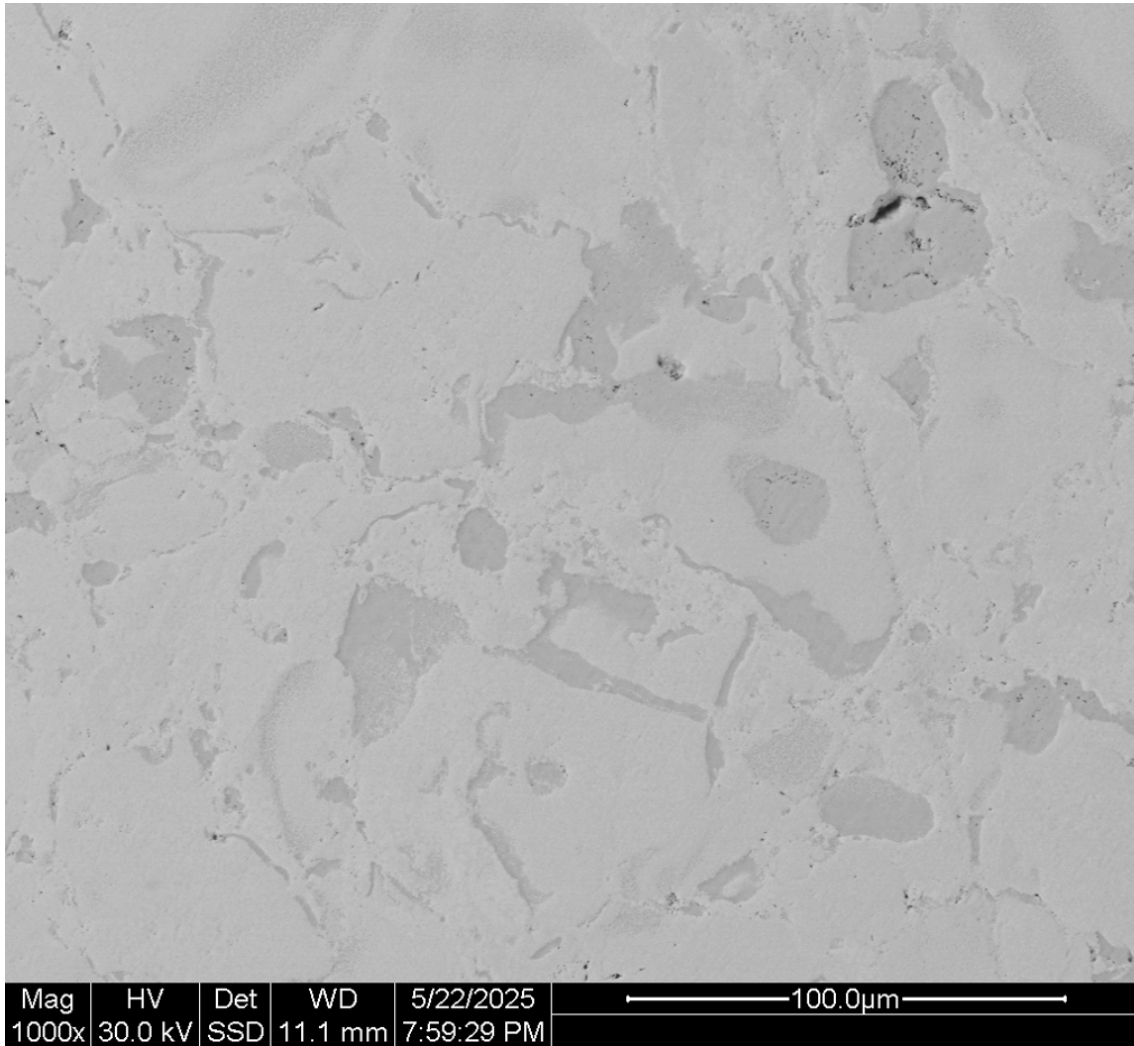


Figure A.13: SEM image on sample 9,1

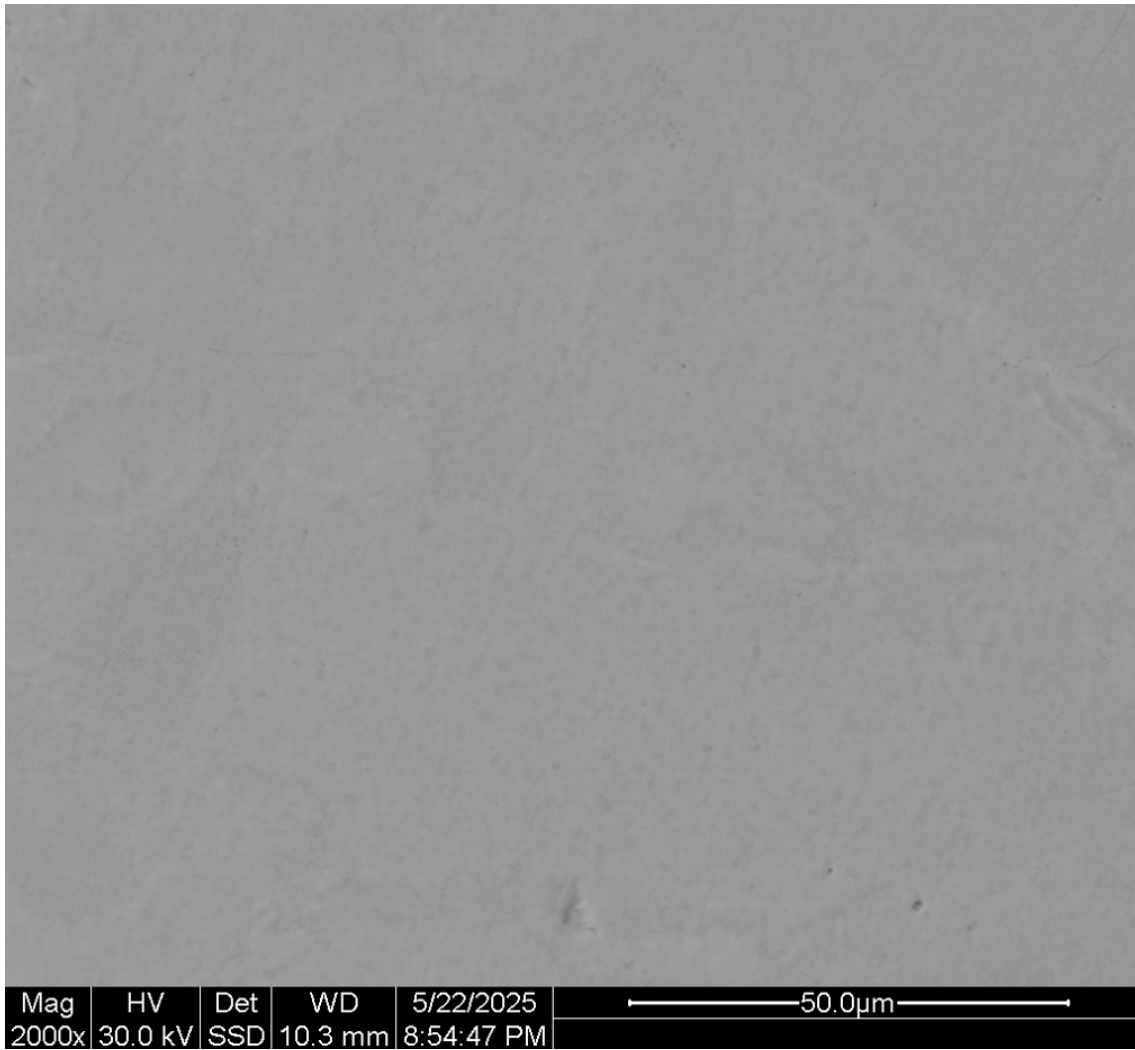


Figure A.14: SEM image on sample 7,1

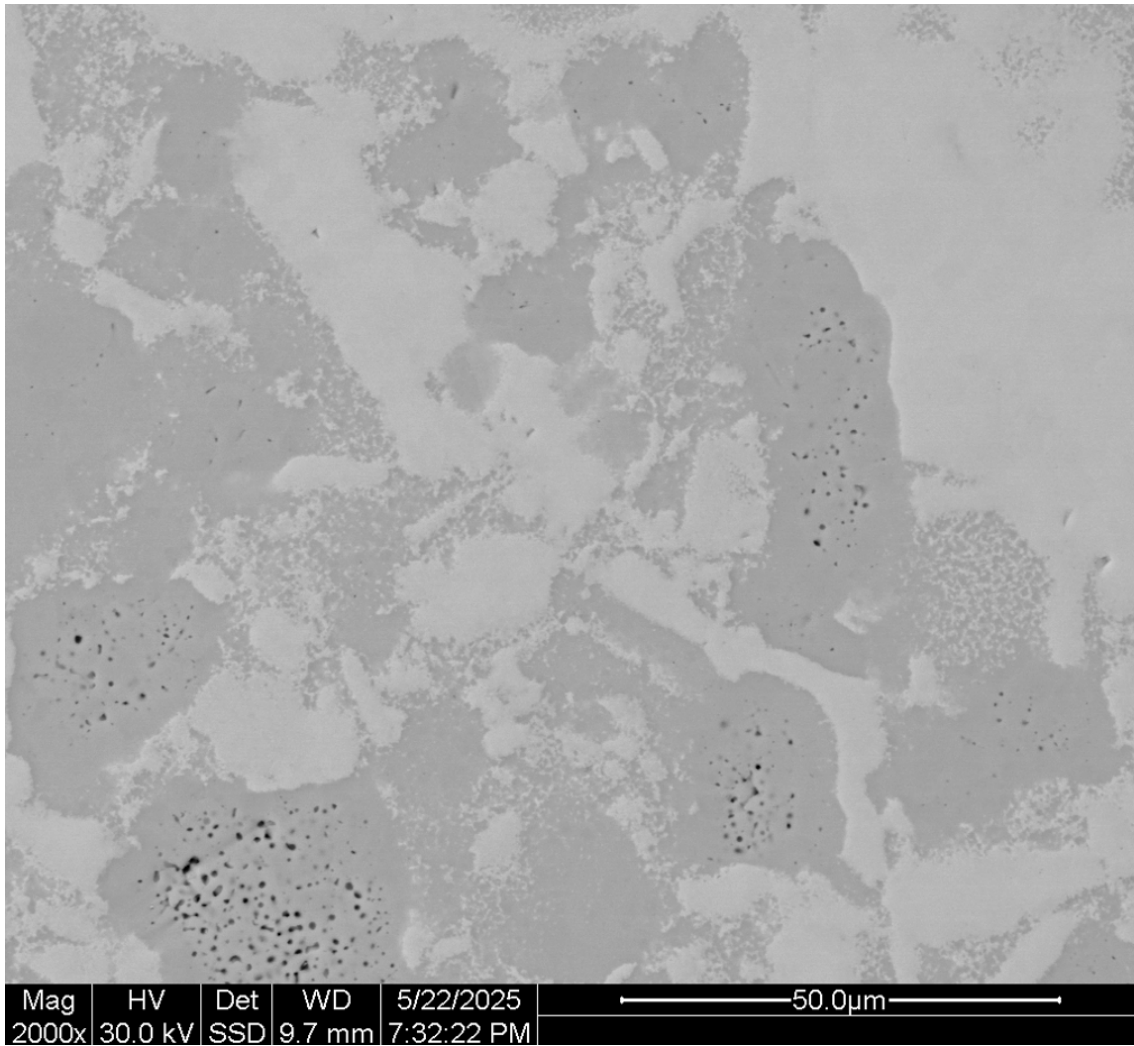


Figure A.15: SEM image on sample 1,1

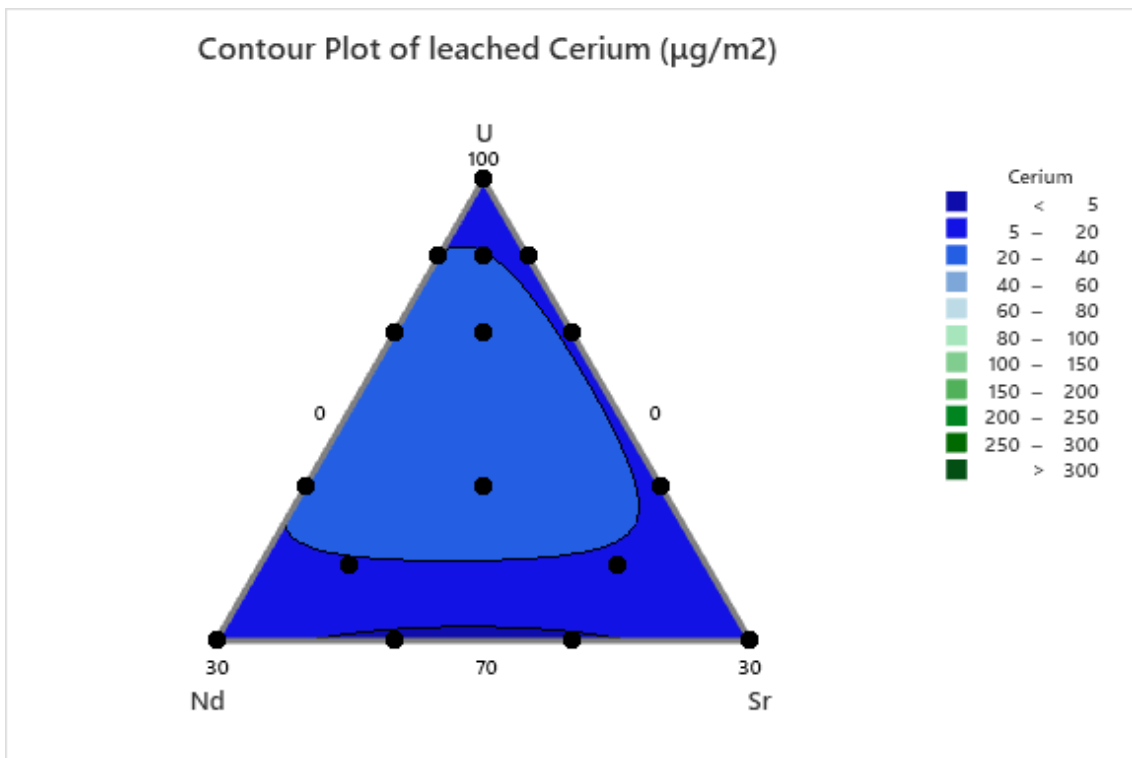


Figure A.16: Contour plot of leached cerium in samples without added cerium.

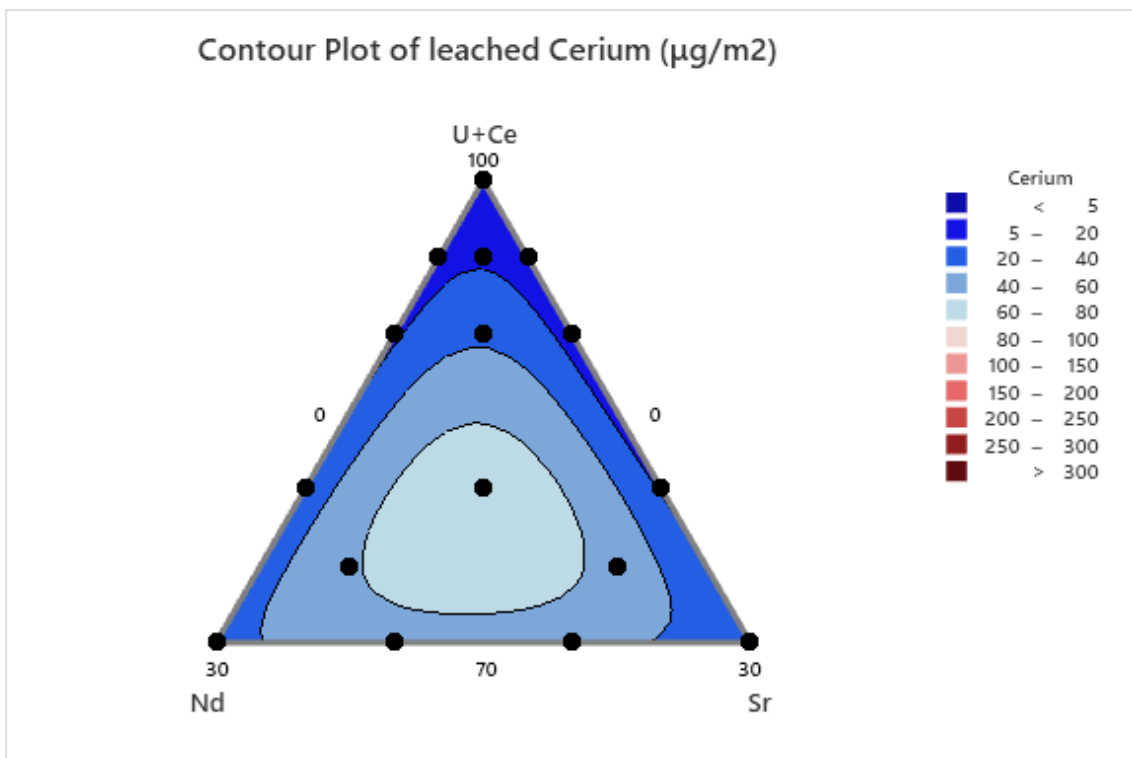


Figure A.17: Contour plot of leached cerium in samples with added cerium.

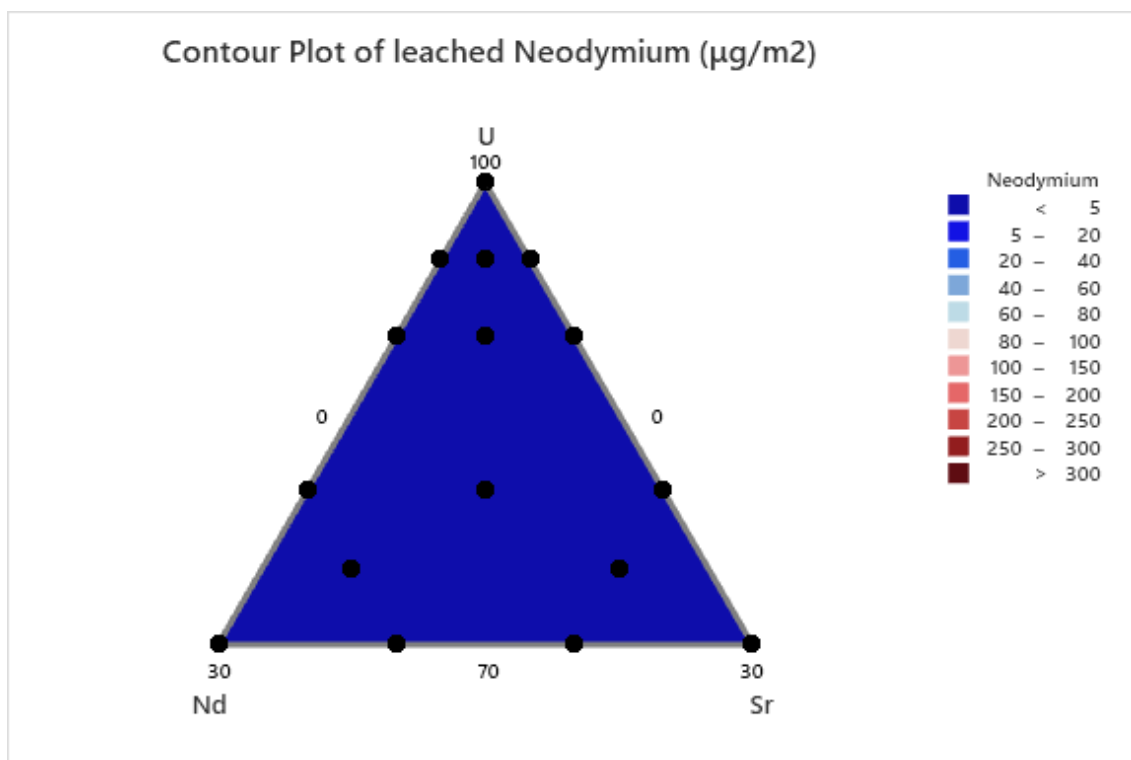


Figure A.18: Contour plot of leached neodymium in samples without added cerium.

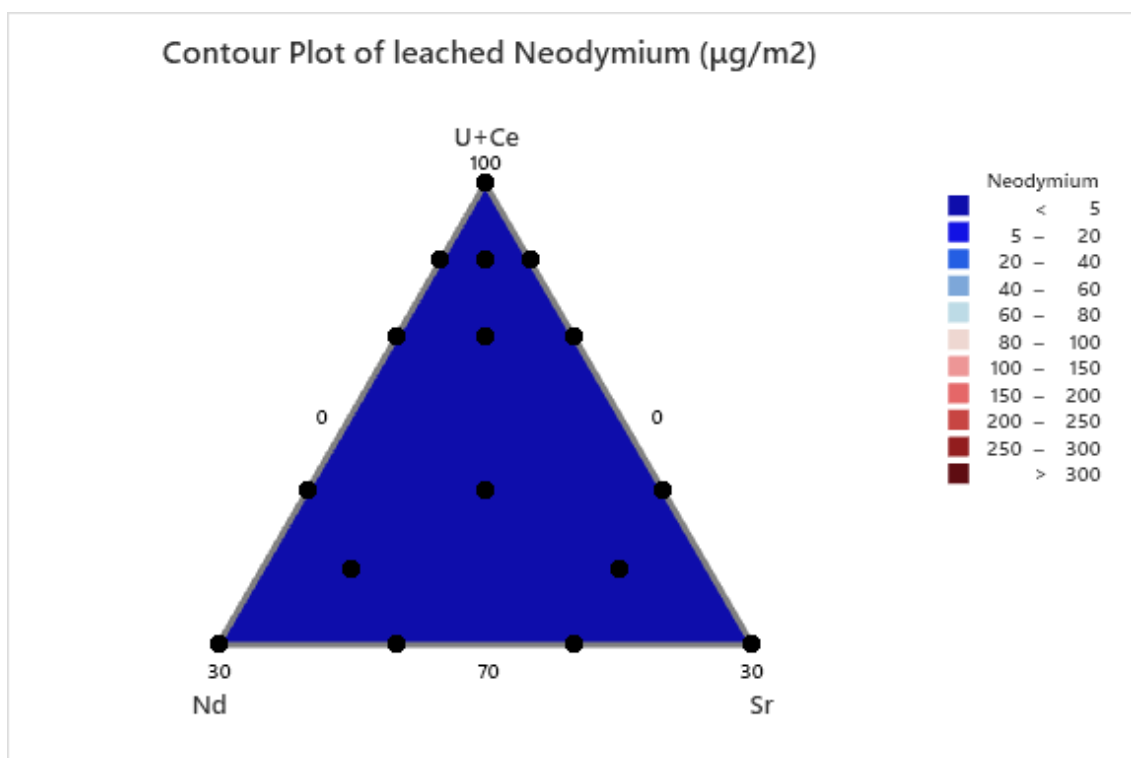


Figure A.19: Contour plot of leached neodymium in samples with added cerium.

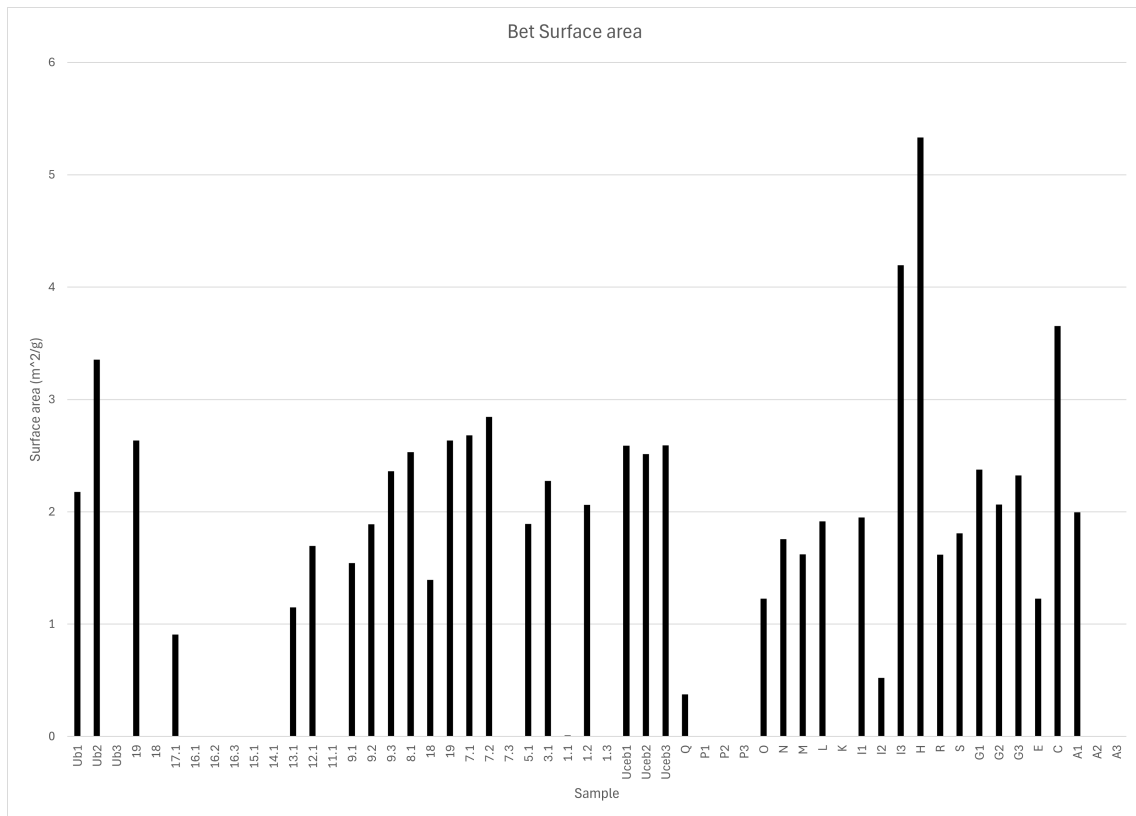


Figure A.26: Surface area of the different samples.

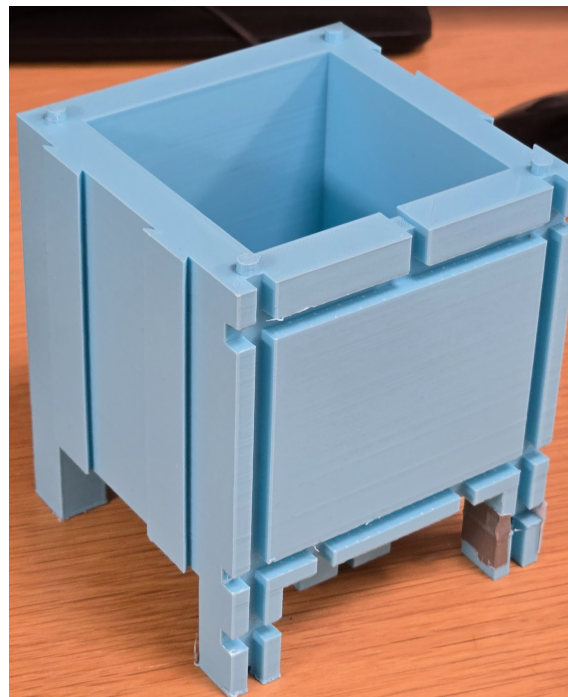


Figure A.27: Leaching apparatus. One leg broke in the process.

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