

KUNGLIGA TEKNISKA HÖGSKOLAN

EIT InnoEnergy Master in Nuclear Energy

Reactor Physics Division

Master Thesis

Synthesis of uranium nitride fuel from UF_4 stock

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Supervisor: Dr. Mikael Jolkkonen



Stockholm, Sweden, Spring 2022

EIT InnoEnergy Master's Programme in Nuclear Energy (120 ECTS)

Master Thesis (30 ECTS)

Synthesis of uranium nitride fuel from UF_4 stock

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Place: KTH Royal Institute of Technology, Reactor Physics Division
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Spring 2022

*Αρχάς είναι των όλων ατόμους και κενόν,
τα δ' άλλα πάντα νενομίσθαι.*

The beginning of everything is atoms and void,
and everything else is perception.

Democritus, 460-370 BC

Acknowledgments

With this opportunity, I would like to thank everyone who helped me making this thesis possible. Firstly, I would like to thank my family, particularly my parents and my sister, for their immeasurable support during these academic years.

Also, I'd like to thank my supervisor, Dr. Mikael Jolkkonen, for his assistance during the experimental work, guidance throughout the nuclear fuel research field, and of course, for all the interesting discussions. Furthermore, I thank Prof. Torbjörn Bäck for his guidance and advises on the electronic controllers and motors. Additionally, my friends and colleagues deserve many thanks for their support, especially Richard Härlin for his assistance in the CAD design.

Finally, I would also like to express my gratitude to all the professors in KTH and INP Phelma who helped me carry out my master's thesis in the best possible conditions.

Abstract

This thesis focuses on the research of producing high purity UN fuel with the method of fluoride ammonolysis. A UF_4 powder was heated up to 800 °C under NH_3 gas to produce UN_2 . Then the UN_2 was heated up to 1100 °C under Ar, producing the final product of UN. During the experiments a variety of equipment was designed for addressing the main constraints, the oxidation and the uncompleted reactions. Furthermore, a closed type rotated powder drum was designed from scratch, that was intended to crash and mix the powder during the synthesis. Additionally, through a set of interrupted syntheses, the reaction's stages were investigated and the fabrication procedure redesigned with an improved efficiency. Lastly, the reaction of UF_6 with NH_3 was tested and UN synthesis was achieved with UF_6 .

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Chapter 1

Introduction

From the day that the first nuclear reactor started operating until today, scientists from all around the globe have been searching for new ways and methods to improve the operation of such a complex technology. Especially nowadays, as nuclear energy moves towards a more sustainable future by introducing the Gen-IV and the Small Modular reactors, the need for innovative materials, technology and methods are more significant than ever. Reactors of the future should be much safer, environmentally friendly, and sustainable.

One significant part of the current research is devoted to the fabrication of advanced nuclear fuel that will replace the traditional oxide type (UO_2) used today. Except for the oxide fuels, there is a broad spectrum of other options with advantages and disadvantages regarding safety, sustainability, and efficiency. One possible candidate is the use of ceramic fuels such as the uranium nitride fuel.

Nitride fuels are well known for their high thermal conductivity, and high melting point so they can be used in a more efficient reactor design. Additionally, uranium nitride has a higher fissile density as it contains 40% more uranium than UO_2 . This characteristic leads to a higher conversion ratio and burn-up. A higher burn-up means that the need for fuel replacement in the reactor comes later than when using UO_2 , affecting the economic benefits of UN use positively. Furthermore, the UN has adequate chemical behavior with many metal alloys, so different types of cladding could be used. Lastly, uranium nitride can be dissolved in HNO_3 , so the PUREX technique can be used for the spent fuel dissolution [1] [2].

Of course, nitride fuels are not perfect, as some drawbacks exist. One disadvantage is the high fabrication cost that arises from using ^{15}N instead of the standard ^{14}N . In case that ^{14}N would be used, then radiotoxic ^{14}C formats increasing the quantity of the radioactive waste [3]. But as the required fuel rods per assembly is smaller, and the requirement of uranium enrichment is lesser, the high cost can be balanced.

Secondly, and more importantly, the sensitivity of nitride fuels to oxidation is an important issue. The fuel could get seriously damaged when it gets in contact with the coolant or steam in case of a cladding failure. Also, the UN can be oxidized even from getting in contact with the atmospheric oxygen, so special procedures during loading of the fuel pellets in the cladding should be performed, increasing the cost of the fuel's use even more [4].

This thesis addresses the fabrication of high purity UN fuel with the ammonolysis method from fluorides. In the second chapter, the methodology and the equipment that were used for all the experiments are presented. Continuing with Chapter 3, the procedures and the results of the fuel synthesis from UF_4 are explained. This chapter contains several attempts to produce UN fuel in large quantities (15-20 g) per run and analytical research that tried to identify the different stages during the synthesis reaction.

Another topic of the thesis described in Chapter 4 is the fabrication of UN from UF_6 . The chapter is not as extensive as the previous one because the research on UF_6 was mostly a side-project rather than an official topic of the thesis. Nevertheless, the synthesis of this fluoride was successful and meaningful results were obtained. It is worth noting that no other project at this University has tried to address the synthesis from UF_6 in the past due to its high volatile character and handling complexity. So except for the experience gained, a new initial point was set for further research in this orientation in the upcoming years.

Lastly, in the fifth chapter, the conclusions of all the experiments are collected. In general, this research's overall success exceeded the initial planning.

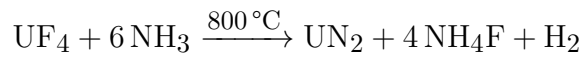
Chapter 2

Methodology and Equipment

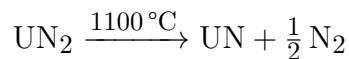
2.1 Ammonolysis of UF₄

The production of UN powder from UF₄ can be summarized into two reaction steps [5]:

1. The UF₄ is heated up to 800 °C under a stream of NH₃ stream, producing UN₂ and NH₄F as a by-product.



2. The UN₂ is then heated up to 1100 °C under Ar stream producing the final UN product.

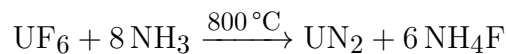


As the UN is very sensitive to oxidation, it is essential to be transferred and handed under argon atmosphere during all the steps of the experiment.

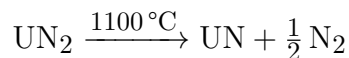
2.2 Ammonolysis of UF₆

The production of UN powder from UF₆ can also be summarized into two reaction steps [5]:

1. The UF₆ is heated up to 800 °C under a stream of NH₃ gas, producing UN₂ and NH₄F as a by-product.



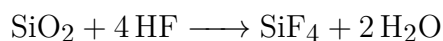
2. The UN₂ is then heated up to 1100 °C under Ar stream producing the final UN product.



2.3 Constraints of the experiment

2.3.1 Oxidation

Oxidation of the UN samples is one of the most critical issues on these experiments, so many measures to reduce oxide formation were taken. Except for oxidation from atmospheric air, the primary source of oxygen was the quartz tube used during all experiments. The quartz tube can release oxygen according to the following reaction.



Avoiding oxidation was one of the main aims of the research, so all the powder transfers and examinations were performed under an Ar atmosphere through air-tight transfer equipment. Also, the unloading of the samples from the synthesis reaction vessels to the XRD analysis sample holder was performed in an argon atmosphere glove box. Although UN₂ powder is less sensitive to oxidation, the same procedure was performed to examine UN₂ samples to achieve the highest possible purity of the final product.

Special measures were also taken to reduce the interaction of the powder with the water vapors occurring from the quartz tube during the synthesis procedure. New reaction vessels and filters were designed from scratch to reduce the oxide impurities as much as possible.

2.3.2 Catalytic decomposition of NH₃

The second problem that was addressed, was the catalytic decomposition of ammonia gas by the alloys that are placed inside the synthesis quartz tube. Metals like Fe, Ni, and Cr were identified to decompose the NH₃ molecules, leading to an insufficient reaction.

An extensive research that was carried out in the previous years from the same research facilities tested multiple alloys and evaluated their catalytic behavior under high temperatures up to 800 °C. Only two materials were proven to be suitable for this kind of experiments copper or tantalum. Except for the un-catalytic behavior, these alloys were confirmed not to form oxides, hydrides, and fluorides during all synthesis phases.

Based on this research, only equipment made of copper or tantalum was used inside the quartz tube during the experiments.

2.3.3 Caking effect

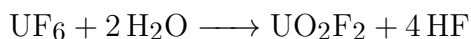
An additional significant problem was the incomplete reaction of UF_4 under certain conditions. The powder when it was placed in a small open boat, and its mass was exceeding the 1 g threshold, was only reacting on the outer surface but not in the inside core. The result was a solid cake product with a formation of a thin UN film on the surface of the unreacted UF_4 core [6] [7].

One of the main motivations for designing a new synthesis setup was to avoid this effect. A mechanism that could mix the powder properly should be invented as the aim was to be able to produce UN powder in quantities of 15-20 g per batch.

2.3.4 Handling of UF_6

Expect the fabrication of UN with UF_4 , a limited number of runs were performed with the use of UF_6 as the starting raw material. UF_6 is identified to be much more difficult to handle than the UF_4 due to its physical and chemical properties.

Firstly, UF_6 has a relatively low evaporating point of 57 °C. That means that any effort to handle it at room temperature will lead to the release of fumes as UF_6 gets hydrolysed by the atmospheric humidity. Second and more important problem is the reaction of UF_6 with H_2O , such as the water vapors in the atmosphere. The reaction releases hydrogen fluoride (HF) that it is known for its corrosive properties and the health risks in case of inhalation. Another product of this reaction is UO_2F_2 . The complete reaction is presented below [8] [9].



For all the above reasons, the UF_6 canister was cooled down to -190 °C by submersion in liquid nitrogen before use, as shown in Figure 2.1. Additionally every used tool, the reaction vessel and one part of the quartz tube were cooled with liquid nitrogen.



Figure 2.1: The UF_6 canister in a tube submerged in a liquid nitrogen bath.

2.4 Analysis equipment

2.4.1 XRD Analysis

The primary evaluation method of the produced sample quality was the X-ray diffraction analysis. The analysis was performed using the SIEMENS D5000 XRD analysis that exists in the Hultgren laboratory in KTH.

The analysis was performed in a range of angles between 10° - 90° , sampling time of 0.02 s/step and time per step of 2 s/step. The output files were produced in RAW or TXT form. Then the data analysis was performed with the use of the PROFEX software. As the samples were radioactive and oxygen sensitive, a closed type dome-shaped sample holder was used. The loading of the sample holder was always done in the glove box under Ar atmosphere. Then the plastic cap of the holder was screwed tightly, making an airtight seal. Due to the characteristics of the holder, no sample rotation during the analysis could be used.

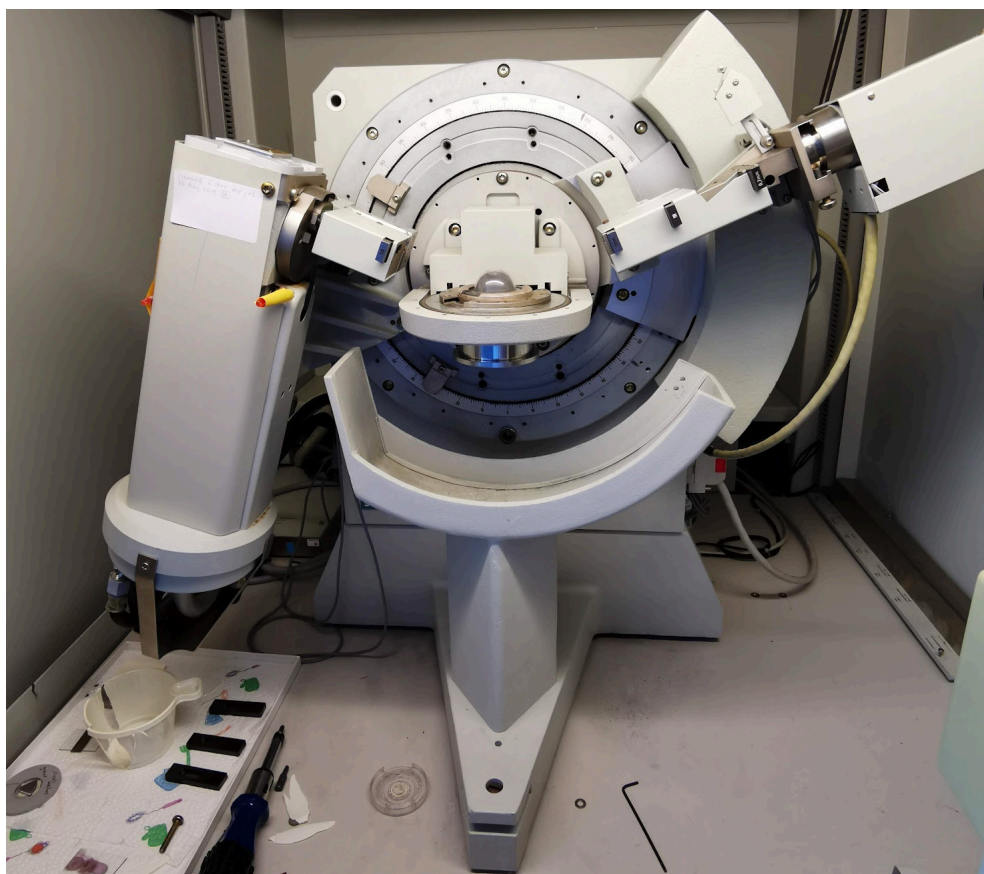


Figure 2.2: The SIEMENS D5000 XRD analyzer loaded with a sample.



Figure 2.3: The BRUKER airtight sample holder with the assembly tool.

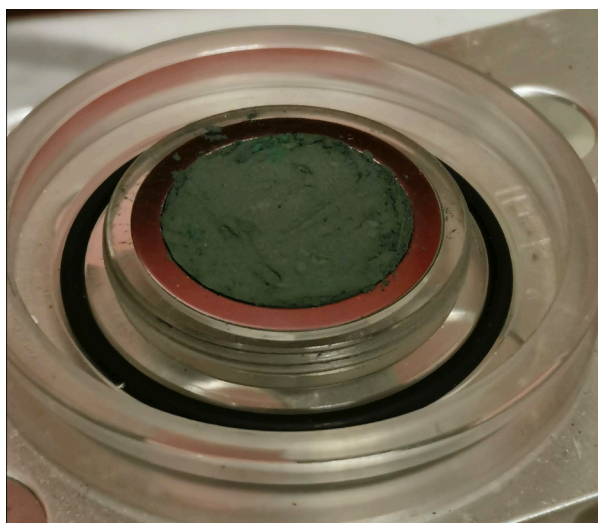


Figure 2.4: UN₂ powder loaded on the sample holder.

2.4.2 Oxygen/nitrogen analyzer

A LECO EF-500 oxygen/nitrogen analyzer was partially used in the experiments to determine the amount of the oxide impurities in the samples. As the equipment remained out of service for many years, some time was required for minor repairs and calibration. The results were used as an additional evaluation of the results from the XRD analysis.



Figure 2.5: The LECO EF-500 oxygen/nitrogen analyzer.

2.5 Heating equipment

A Nabertherm RT 50-250/13 tube furnace was used for all these experiments. It measures a 50 mm tube diameter opening, and the maximum temperature is 1300 °C. It can also be used in an upright position, but this function was not used during this project. The furnace is able to keep heating programs in its memory, and it is equipped with a precise thermocouple.



Figure 2.6: Nabertherm RT 50-250/13 tube furnace.

2.6 Synthesis powder reaction vessels

During this research in fuel synthesis, a variety of powder reaction vessels was used. When the experiment was aiming the production of UN, the vessel's material was tantalum as it can withstand the high temperature of the synthesis. On the other hand, if only the first step of UN₂ producing was tested, the material was chosen to be copper, as it is cheaper and much easier to handle.

All the reaction vessels were fabricated either by hand or by a qualified technician in the University's workshop. The raw materials were always as oxygen free as possible to avoid any production of impurities during the synthesis. Before and after every run, the mass of each vessel was measured, and the changes in each property were reported. In the following subsections, all the different vessels used are presented.

2.6.1 Open-end Ta boat

For the first full synthesis tests of the equipment, a 105 mm long boat with open ends was used. It was made out of 1 mm thick tantalum sheet, and it could hold up to 4 g of powder. As the ends were open, the handling of the boat during the insertion or the extraction was difficult and extra care should be taken to avoid powder spilling from the ends. Also, a Ta sheet was used to cover the inside surface of the quartz tube, reducing the oxygen absorption in the powder. In Figure 2.7 and Figure 2.8 the Ta boat and the lining are shown.



Figure 2.7: The Ta open-ended boat.



Figure 2.8: The Ta lining.

2.6.2 Provisional Cu drum

For testing the rotation idea, which would prevent the caking effect, a provisional Cu drum was manufactured. As the caking effect is identified to happen in the first step of the synthesis, the material was chosen to be copper.

The shape of the drum was cylindrical with lightly crimped edges to avoid spillage upon turning. It measured 80 mm in length and 22 mm in outer diameter. The crimped edges also made the retraction after the synthesis easier. A large hook was used for this purpose.

The shaping of the copper is often made with a blowtorch and hammering, a technique that imports amounts of oxygen into the material. So in this case, the drum was manufactured with as little hot hammering as possible. Lastly, the provisional drum could be loaded with Cu balls that would help mix the powder better during the rotation, but this function was not tested in practice. Lastly, the drum was used during the partial synthesis from UF_6 experiment. In the following Figure 2.9 this drum is displayed.



Figure 2.9: The provisional Cu drum.

2.6.3 Retractable Cu boats

During this project, a series of interrupted syntheses was performed. For these runs, the boats should be rapidly extracted from the furnace's hot zone and without disturbing the atmosphere inside the quartz tube. As these experiments were limited to the first part of the synthesis, up to 800 °C, the material of use was Cu.

As the main idea was that the retraction to be possible without opening the tube's end seal, a method using magnets was designed. The boats were hand-made from a copper sheet of 0.2 mm thickness. On one of the ends, a hole was made where a Cu wire was attached. On the other end of the wire, a metallic washer was placed. The length of the wire was an important factor, as the metallic washer should be sufficiently away from the hot zone, so that the metal would not lose its magnetic properties.

Then, using a strong magnet outside of the tube, the boat could be retracted as planned. Since copper gets soft at these high temperatures, the boats tend to deform due to the pulling forces, so in each run, a new boat was fabricated from the same material and similar dimensions. Each boat was designed to hold up to 2 g of powder. In the following Figure 2.10 such a Cu boat, loaded with UF_4 powder, is presented.



Figure 2.10: The magnetic retractable loaded Cu boat

2.6.4 Upscaled rotating drum

As the main purpose of this project was to produce high purity UN, on a large scale of 15-20 g per run, a larger, more advanced drum was fabricated. The design started from scratch, using the experience and the results of all the previous runs. It should be closed and cylindrical-shaped to avoid oxygen absorption from the surroundings and be able to rotate to avoid the caking effect. The design should also be such to allow the insertion of metal balls for better powder mixing and crushing without spilling it outside.

Starting from the material choice, Cu was selected. The new drum would be intended to address the caking effect on the first part of the synthesis, then the produced UN₂ could be de-nitrated in a simple Ta boat at a higher temperature. Also, as Cu is cheaper and more easily modified than Ta, the new drum would act as a prototype. If its operation would be proven to be satisfactory after possible modifications, a new final version of the large scale drum made from Ta could be proposed in a future project. The construction of the whole setup was assigned to the University's machine shop, with the duration of the work exceeding one month due to the complexity of the design.

The new setup consisted of four parts, and it is able to rotate in a larger quartz tube of 48 mm outer diameter. The main part is a cylindrical drum that would contain the powder during the synthesis. Also, nine Cu balls could be inserted inside. The drum's ends are removable, allowing easier powder transfer. The outer diameter is 40 mm, and the length is 140 mm. In the Figure 2.11 and Figure 2.12, the opened main drum and the Cu balls are presented.

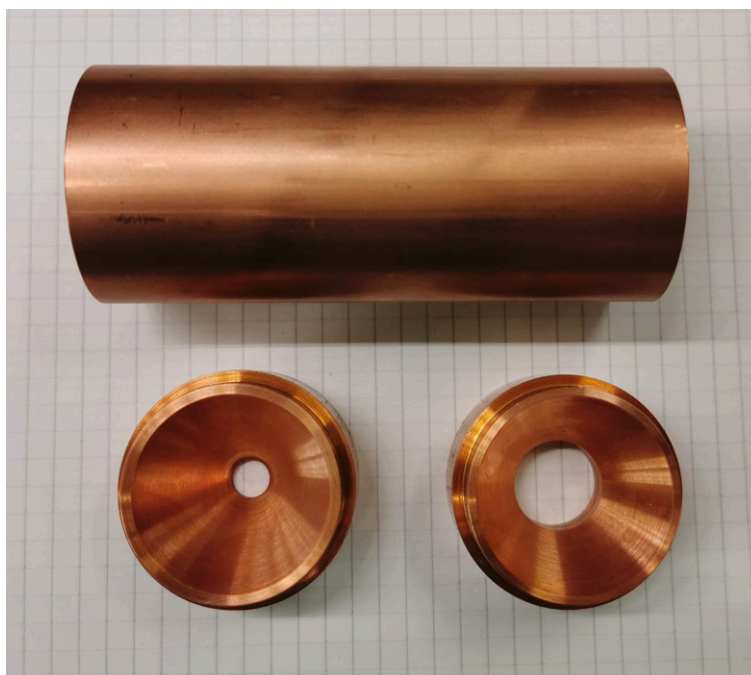


Figure 2.11: The opened drum of the new setup.



Figure 2.12: The nine copper balls used for mixing and crushing.

The second part was a 6 mm diameter Cu tube that acted as the gas inlet, transferring the Ar or the ammonia straight in the drum. The main difference from the previous vessels is that the gas did not pass through the quartz tube, but it was transferred in the drum, increasing the efficiency. Additionally, this tube acted as a stationary point for the rotation function. A copper sleeve attached to the left side of the tube permitted the rotation of the drum.

The third part was a 10 mm diameter Cu tube that acted as a gas outlet but also as a shaft for the rotation. Contrariwise to the inlet, this part was fixed on the right side of the drum for transferring the rotation's motion. A section of it was also perforated so the ammonium fluoride gas could escape easily to the outer quartz tube. These three parts are presented in the Figure 2.13 and Figure 2.14 as assembled and as disassembled .

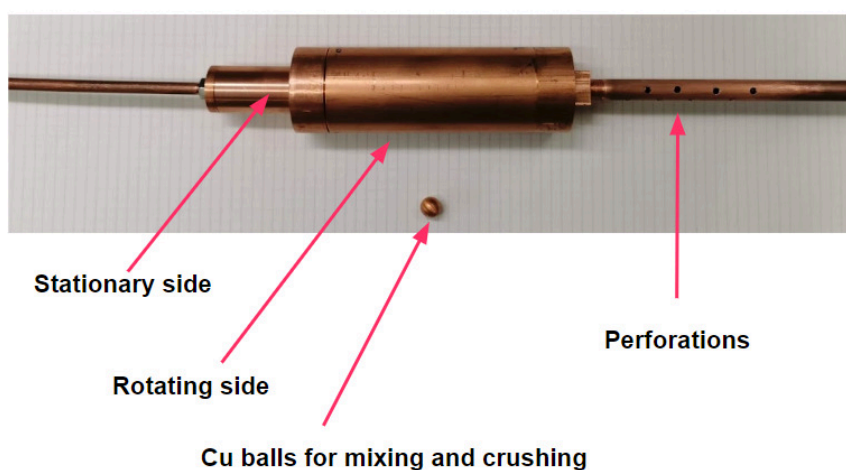


Figure 2.13: The assembled rotating setup.

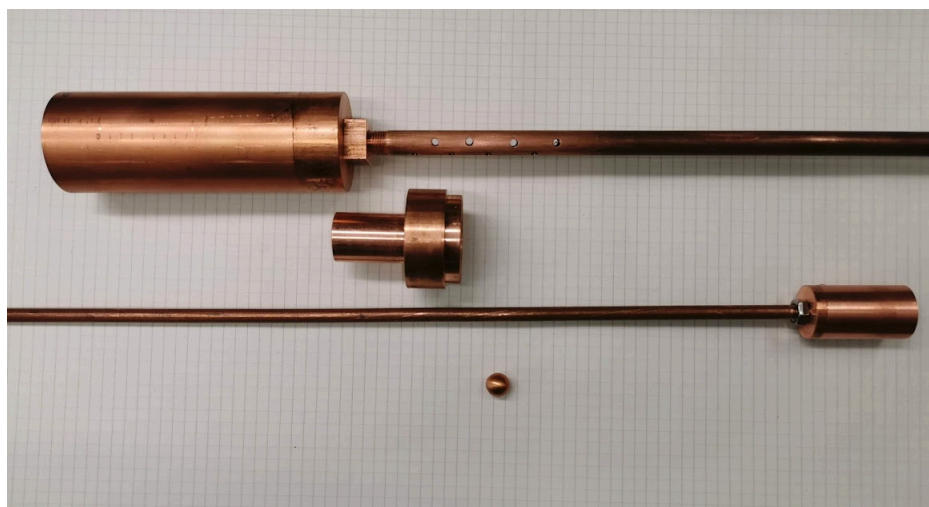


Figure 2.14: The rotating setup with the inlet tube disassembled.

The whole setup should be able to rotate inside the large quartz tube, and at the same time, the inside atmosphere should stay undisturbed. A step motor would be the perfect fit for this idea, but it could not be placed inside the quartz tube as it would gradually be destroyed by the high temperature and the ammonium fluoride. So the motor was placed externally, and the rotation was contactlessly transferred to the shaft by the use of magnets.

The fourth part, namely the magnetic component, was placed on the shaft and consists of two magnets placed on a base on the far right end of the exhaust tube. The base could rotate in the tube without the magnets touching and possibly breaking the tube. This was achieved with the help of two small ball-bearings that roll on the tube's inner surface, keeping the magnets at a safe distance from the tube. If the magnets overheat, they would permanently lose their magnetic properties, so special care for their thermal insulation should be taken. As Cu conducts heat easily, the exhaust tube was made long enough to avoid the overheating of the two magnets. The magnets' base is presented in Figure 2.15 and in Figure 2.16.

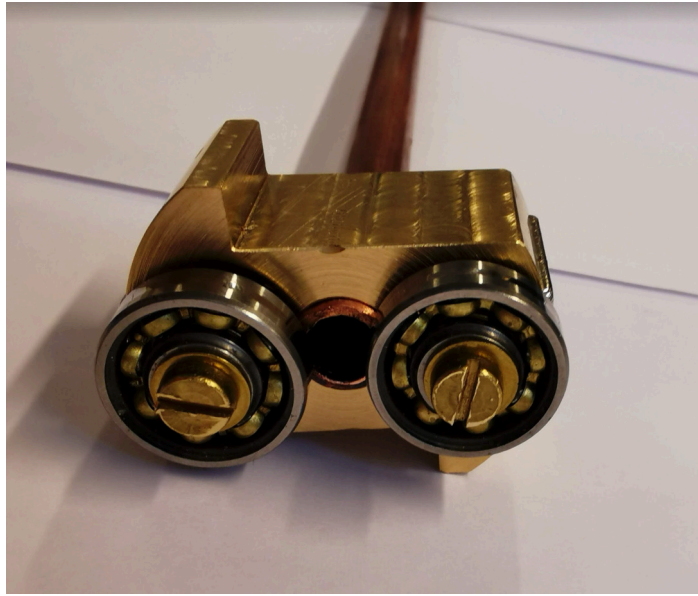


Figure 2.15: Close-up view of the shaft's magnets' base.

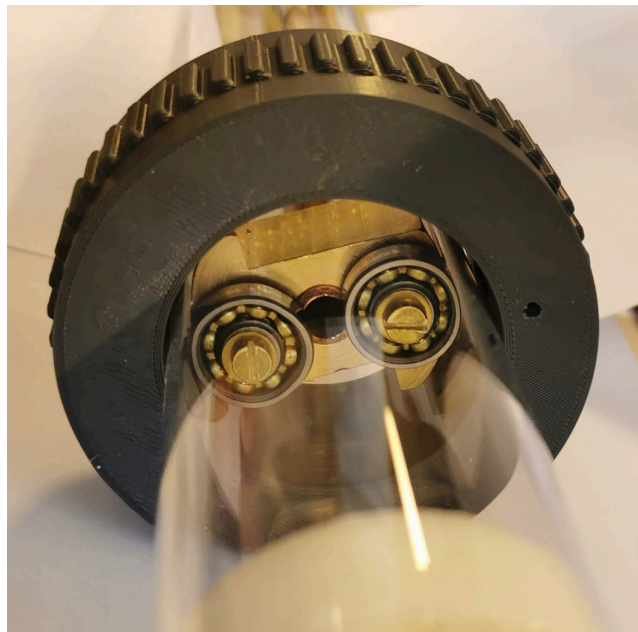


Figure 2.16: The magnets' base during testing.

2.7 Synthesis filters

A variety of different filters were used during the syntheses to avoid the back-flow of gas into the powder, minimizing the oxygen transportation and absorption. These filters were made out of copper for the partial syntheses and from tantalum for the full syntheses. Additionally, special care was taken for thermal expansion calculations, so the expanded materials would not damage the tube. The positions of the filters were usually at ends of the powder boats and were made out of Ta or Cu shavings and sheets. In Figure 2.17 and in Figure 2.18, the Ta funnel-shaped filter and the Cu shavings filter are presented.



Figure 2.17: Ta funnel made from metal sheet.

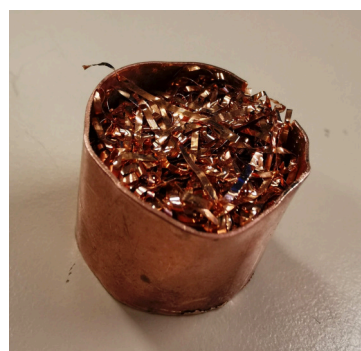


Figure 2.18: Cu filter made from shavings.

2.8 Mechanical and electronic parts

2.8.1 Step motor and controller

The rotation of the whole setup was provided by a step motor equipped with an electronic controller. The motor type was NEMA-17, operating at 12 V, rotating by 1.8° per step, and having a maximum torque of 0.22 Nm. The controller of the motor was based on a L298N H-Bridge drive unit, which could handle up to 2 A of current. The main board of the circuit was an Arduino UNO R3 which was used for providing the operating signals to the controller. There was also a rotation speed switch based on a potentiometer, allowing different rotation settings. Lastly, the whole circuit was built on a temporary breadboard base for easier modification. If it would be decided to use the entire circuit in a future project, a soldered circuit board may be built. The code loaded in the Arduino is described in the following list.

- Read of the analog input from the potentiometer
- Adjust the motor speed according to the reading
- Rotate the motor clockwise for 1.5 full rotations
- Pause for 1 s.
- Rotate the motor anti-clockwise for one complete rotation
- Pause for 1 s.
- Repeat all the above steps.

The rotation pattern was chosen with regard to the better mixing and crushing of the powder. By using a not symmetric movement, with one and a half rotations forward and one backward, it was planned that the balls would move along all of the inner surface, without leaving any trace of uncrushed powder. The setup with the motor, the controller, and the Arduino board is presented in the following Figure 2.19.

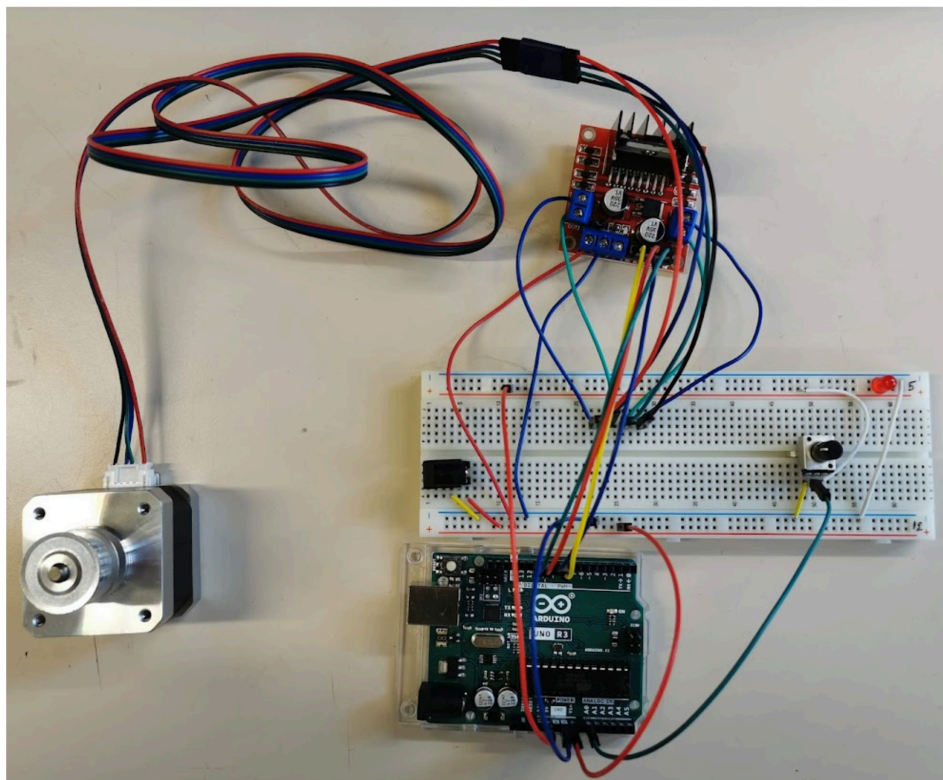


Figure 2.19: The complete motor setup.

2.8.2 Transmission of rotation

A pulley for the contactless transmission of rotation from the outer to the inner space of the quartz tube was manufactured. This pulley was designed using AutoCAD and Solidedge software, and was 3D-printed. This procedure allowed the test of few different designs keeping the cost and the construction time to a minimum. Regarding the 3D-printing, a common 1.75 PLA wire was used with standard printing quality settings. The infill of the pulley was set at 20%, and a honeycomb structure was selected, as shown in the following Figure 2.20.

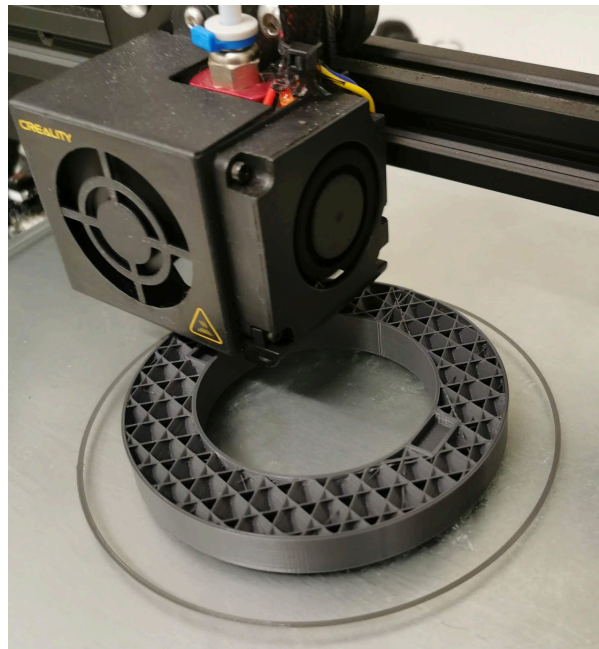


Figure 2.20: The honeycomb structure during a test 3D-printing.

As the external surface of the quartz tube tends to conduct heat, a design that would avoid the contact of the PLA with the surface and provides sufficient ventilation for the magnets should be used. So the pulley was designed with a number of holes that permit the air to circulate and also two holes for the magnets placement.

Additionally, any friction should be avoided, so two ball-bearings were placed inside the plastic pulley, providing near frictionless rotation on the tube. The ball-bearings measure an inner diameter of 50 mm that would give a good fit on the 48 mm outer diameter quartz tube. The pulley and motor were connected with a 3/8" 508 mm timing belt. One extra function of the pulley, except for the rotation, was to apply an axial force on the large powder drum, keeping all parts in place. In the following Figure 2.21 and Figure 2.22, the 3D-printed pulley with a ball-bearing and the whole mechanical setup, are presented.



Figure 2.21: The 3D-printed pulley with a ball-bearing and the magnets attached.

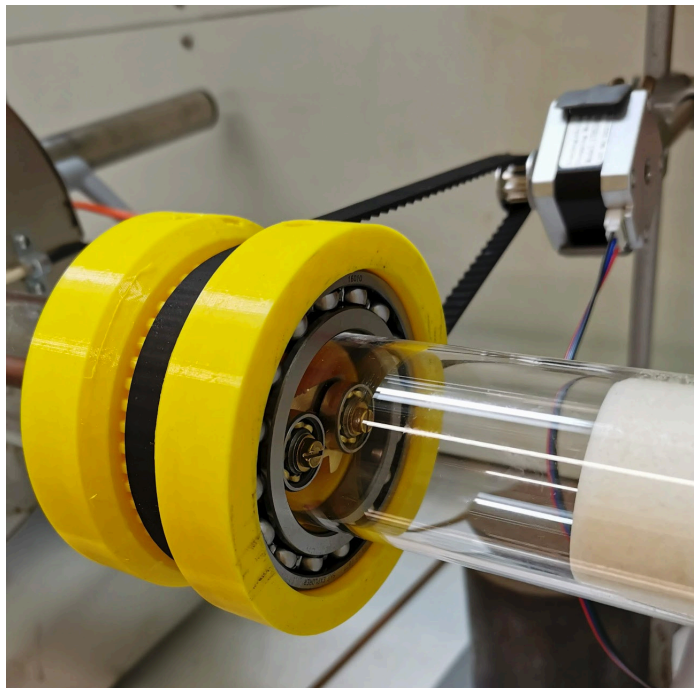


Figure 2.22: All the parts of the rotation attached in place.

Chapter 3

Procedures and Results using UF_4

3.1 Full synthesis using the existing equipment

A good starting point for every new experiment is the last point of the previous experimental work. So for this new research, the equipment that had been used before should be tested in a full-scale experiment. Also, the previous results should be re-evaluated and provide a solid base for modifications and further research. Based on the existing notes and experience, the equipment was set up using the same materials and methods from the last time a successful synthesis was performed.

3.1.1 The setup

For this experiment, a quartz tube (1000 mm length, $\varnothing 25\text{mm}$ in, $\varnothing 28\text{mm}$ out) was used, with brass fittings at the ends. The sample was loaded in an open-ended Ta boat with a length of 105 mm and a width of 0.1 mm. The inside surface of the quartz tube was lined with a 105 mm tantalum sheet to prevent the reaction of the quartz with the produced HF, as it is described in the Subsection 2.3.1. The mass of the UF_4 sample was 0.844 g.

Then the quartz tube containing the tantalum boat was placed precisely in the center of the furnace heat zone. A gas inlet tube was attached to the left tube seal, and the right exhaust seal was connected to the pair of ammonia absorption filters.

3.1.2 Procedure

- Furnace turn on
- N_2 gas flow set to 0.2 ℓ/min
- Heating from 20 $^\circ\text{C}$ to 500 $^\circ\text{C}$ in 48 min (10 $^\circ\text{C}/\text{min}$)
- Temperature plateau at 500 $^\circ\text{C}$ for 40 min, Gas change to NH_3 (0.2 ℓ/min)

- Heating from 500 °C to 600 °C in 20 min (5 °C /min)
- Heating from 600 °C to 800 °C in 100 min (2 °C /min)
- Temperature plateau at 800 °C for 110 min
- Gas change to Ar (0.2 ℓ/min)
- Heating from 800 °C to 1100 °C in 30 min (10 °C /min)
- Temperature plateau at 1100 °C for 300 min
- Cooling from 1100 °C to 20 °C in 108 min (10 °C /min)
- Extraction of the sample under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.1.3 Results

The first observation of this experiment is the formation of an ammonium fluoride layer close to the tube exit side. The NH₄F started to deposit at 520 °C, and it became very opaque at 650 °C. Furthermore, during the 800 °C temperature plateau, it started to form cracks and be looser from the quartz inner surface, as shown in the following Figure 3.1.



Figure 3.1: The slightly deformed NH₄F layer at the end of the run.

During the extraction of the sample in the glovebox, the weight loss was measured to be 0.174 g; the color was black, and the sample was made from fine powder.

The powder was easy to crush with a spatula, and no visual UF₄ impurities were observed. The XRD analysis showed a successful result as there were no traces of UF₄, 92.93% of UN, and 7.07% of UO₂. The XRD graph is presented in Figure 3.2 below.

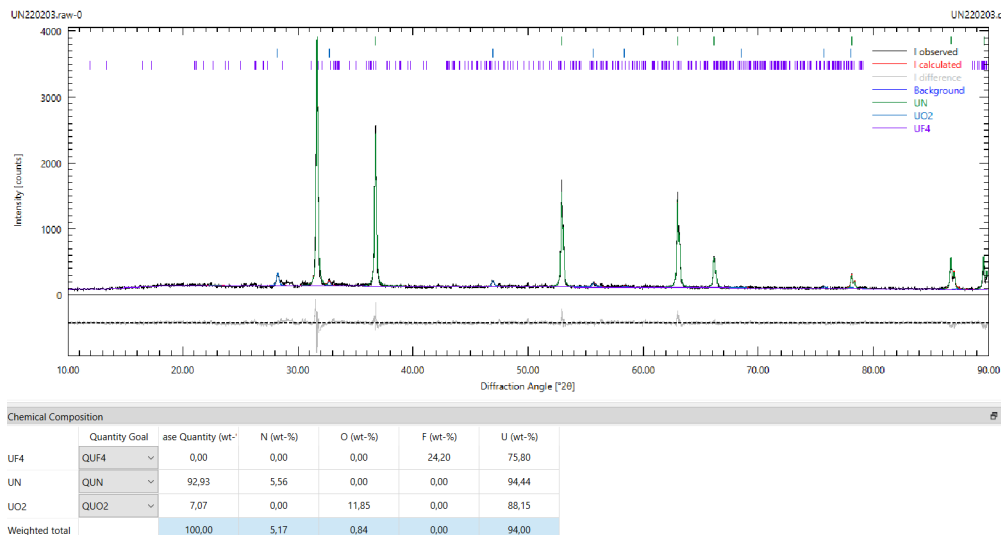


Figure 3.2: XRD result of the full synthesis test.

Table 3.1: Experiment measurements of the full synthesis test.

Powder mass before synthesis	0.844 g
Powder mass after synthesis	0.670 g
Boat mass before synthesis	5.223 g
Boat mass after synthesis	5.237 g
Extracted powder color	Evenly black
Extracted powder characteristics	Lightly sintered fine

3.2 Partial synthesis using the provisional drum

In this experiment, the first try of the up-scaling method was tested. A provisional closed-type copper drum was used; as the shape of the drum is cylindrical, the result of the sample rotation in it could be tested. A drum of this type would also decrease the amount of oxygen absorption as the upper part of the sample would not be exposed anymore. The partial synthesis during this experiment produced only UN₂, as the caking effect was observed to be present only at the first step of the reaction. On the other hand, if the experiment had been done as a full synthesis, the provisional drum should have been made out of tantalum, as the copper would melt at a higher temperature. The use of tantalum was avoided to decrease the manufacturing costs and construction time.

3.2.1 Setup

For this experiment, the usual quartz tube was used with brass fitting on the ends. A sample of UF₄ measuring a mass of 4.395 g was placed inside the provisional drum. The inside surface of the quartz tube was lined with the 105 mm tantalum sheet. Inside the sheet, the drum was placed with a not very tight fit taking into account the thermal expansion of the copper but at the same time having the ability to rotate along with the manual rotation of the quartz tube.

3.2.2 Procedure

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 300 °C in 28 min (10 °C /min)
- Heating from 300 °C to 500 °C in 40 min (5 °C /min)
- Temperature plateau at 500 °C for 70 min
- Gas change to NH₃ (0.2 ℓ/min) after 40 min in the plateau
- Heating from 500 °C to 600 °C in 10 min (10 °C /min)
- Heating from 600 °C to 800 °C in 70 min (2.8 °C /min)
- Gas change to Ar (0.2 ℓ/min) at 650 °C
- Temperature plateau at 800 °C for 110 min
- Cooling from 800 °C to 20 °C in 78 min (10 °C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

The tube was turned at an angle of 180° every 5 min from the temperature of 355 °C until the change of gas to ammonia. The rotation continued with the same angle up to 600 °C every 1 min and finally up to 800 °C every 5 min.

3.2.3 Results

The first observation was that all parts made from Ta were completely degraded, including the Ta funnel. On the other hand, the Cu drum did not show any signs of damage. The degradation of the Ta parts was so extensive that both broke into fragments during the extraction of the sample. In the next Figure 3.3, the degraded sheet and funnel are visible.

One possible explanation for this result could be oxygen absorption in the Cu during the fabrication process. But after measuring the weight of the drum, an increase of 0.041 g was noticed. This result could not provide any notion that the Cu drum could have released significant quantities of oxygen. An XRD analysis identified the brittle residue as metallic Ta.

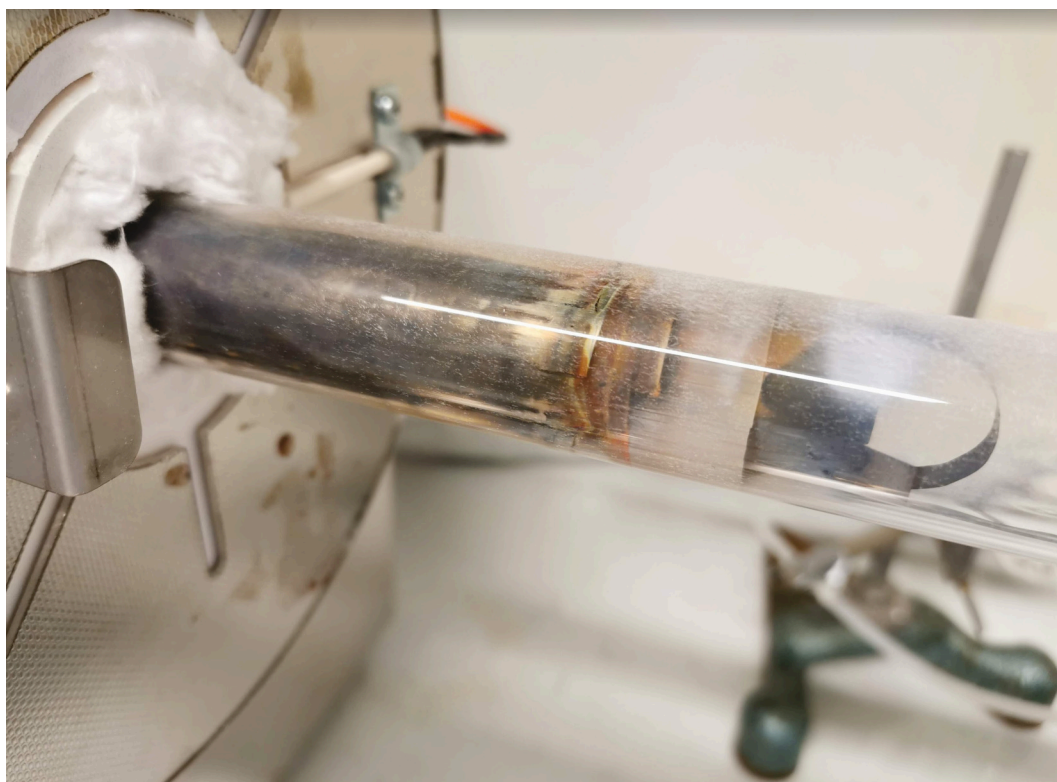


Figure 3.3: The degraded Ta parts.

The extracted powder was gray colored with some green streaks and tiny lumps. The XRD analysis also revealed a not so optimal composition. Indeed the oxygen contamination kept low, producing only 1.56% UO₂, but 48.18% of UF₄ remained underacted. The rest 50.26% reacted successfully to UN₂ as shown in the next Figure 3.4. Lastly, the final powder was examined by a small optical USB microscope; in Figure 3.5 the green area indicates the presence of unreacted UF₄.

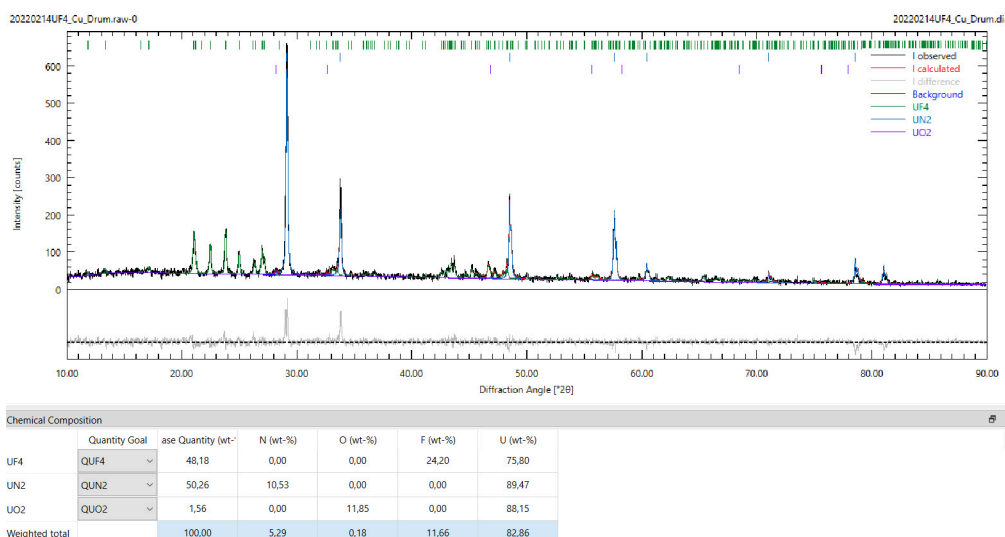


Figure 3.4: XRD result from provisional drum's first run.



Figure 3.5: Microscope image of the unreacted UF₄ in the sample.

Table 3.2: Experiment measurements from the provisional drum's first run.

Powder mass before synthesis	4.395 g
Powder mass after synthesis	3.611 g
Drum mass before	44.443 g
Drum mass after	44.505 g
Extracted powder color	Graphite gray with green streaks
Extracted powder characteristics	Non-sticky, easy pouring

3.2.4 Second run using the same powder.

As the results from the first test using the provisional drum were not satisfactory, a second run using the same powder was decided. The sample was loaded again in the drum after being crushed. The Ta lining was replaced by a Cu sheet of 0.2 mm thickness. This time, no conical filter was used as the previous one was damaged beyond repair. For this run, no rotation was applied as the remaining UF₄ lumps were crashed, and the probability of forming a cake pattern was minimal. Lastly, the same heating program was used, and the exposure to ammonia lasted longer, up to 780 °C.

Regarding the observations during synthesis, at 650 °C, a substantial white ring of NH₂F bank appeared; at 700 °C, three separate rings were visible. Finally, at 750 °C, all three rings merged into an opaque, dense ammonium fluoride formation.

After the run was completed, the powder was graphite colored with tiny bits of green grains due to some remaining UF₄, but flowability was good without any sticky grains.

The XRD analysis confirmed the improved result as after the second run, only 10.64% UF₄ left with a tiny impurity of 1.61% UO₂. The remaining 87.85% was identified as UN₂. It is noteworthy that only during this analysis an open rotating XRD container was used. The rotation produced a more accurate result as the powder composition was not uniform. In the following Figure 3.6, the XRD result as it was calculated from PROFEX software is presented.

The main conclusions of these two runs are that firstly the drum's rotation idea has a positive impact on reducing the caking effect and a closed-type drum helps reduce oxygen absorption. Of course, this design was not sufficient because a fair amount of UF₄ was left even after two runs, but the general idea seems to work, and more improvements should be made. For this reason, the design of the new larger closed cylindrical rotated drum started after that experiment.

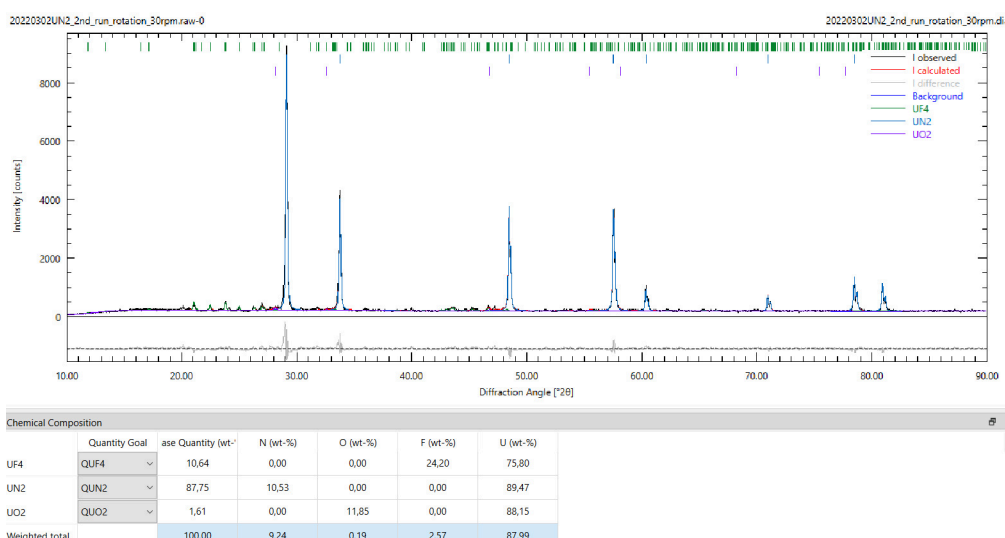


Figure 3.6: Second XRD result from provisional drum.

Table 3.3: Experiment measurements from provisional drum's 2nd run.

Powder mass before synthesis	3.611 g
Powder mass after synthesis	Omitted
Drum mass before synthesis	44.484 g
Drum mass after synthesis	44.492 g
Extracted powder color	Graphite gray with tiny green spots
Extracted powder characteristics	Non-sticky, lumpy, easy pouring

3.3 Partial synthesis intermediate reactions

As has been described, the synthesis of UN₂ from UF₄ requires heating of the powder up to 800 °C under ammonia gas. Although this final temperature is known, there was no information on the reactions during the lower temperatures. So, a part of this project was devoted to study the possible emergence and conversions of intermediate compounds during the reaction. The results would shed light on the mechanism of UN₂ production and lead to a better, more efficient heating ramp for the following experiments.

3.3.1 Setup

Again, the usual quartz tube (1000 mm length, Ø25mm in, Ø28mm out) was used, with the usual brass fittings on the ends. The main difference in comparison with previous experiments is that now a magnetically retractable boat, as shown in Figure 2.6.3 was used. This type of boat would allow the rapid retraction of the sample out of the furnace hot zone without opening the quartz tube; in this way, the result at a specific temperature would be examined. Lastly, a 0.2 mm Cu foil was placed around the sample on the inner surface of the tube, but no filters were used for easier sample retraction.

These experiments aimed to slowly reach up to four different target temperatures, rapidly retract the sample and continue with an XRD analysis as usual. The studied temperatures were 500 °C, 600 °C, 700 °C, and 800 °C. Similar steps were followed for each of the four individual runs as presented on the following lists.

3.3.2 Procedure at 500 °C

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 300 °C in 28 min (10 °C /min)
- Heating from 300 °C to 500 °C in 40 min (5 °C /min)
- Temperature plateau for 70 min, gas change to NH₃ (0.2 ℓ/min) after 10 min
- Sample magnetically retracted out of the hot zone
- Quick cool-down of sample to 35 °C under NH₃ gas
- Gas change to Ar (0.2 ℓ/min)
- Furnace cooling to 20 °C (10°C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.3.3 Results at 500 °C

The first visible result during the temperature plateau at 500 °C was a slight bank of NH₄F. During the extraction of the powder in the glove box, it was noted that the color was green with some gray little areas, giving the first indication that most of the UF₄ remained unreacted. The XRD analysis confirmed this hypothesis as the percentage of UF₄ was significantly high at 97.70%, followed by a 2.14% of UO₂ impurity and finally only 0.16% of UN₂. This result revealed that the temperature of 500 °C is not enough for almost any reaction toward the synthesis of UN₂. The XRD graph is presented in Figure 3.7 and the experiment's data in the following Table 3.4.

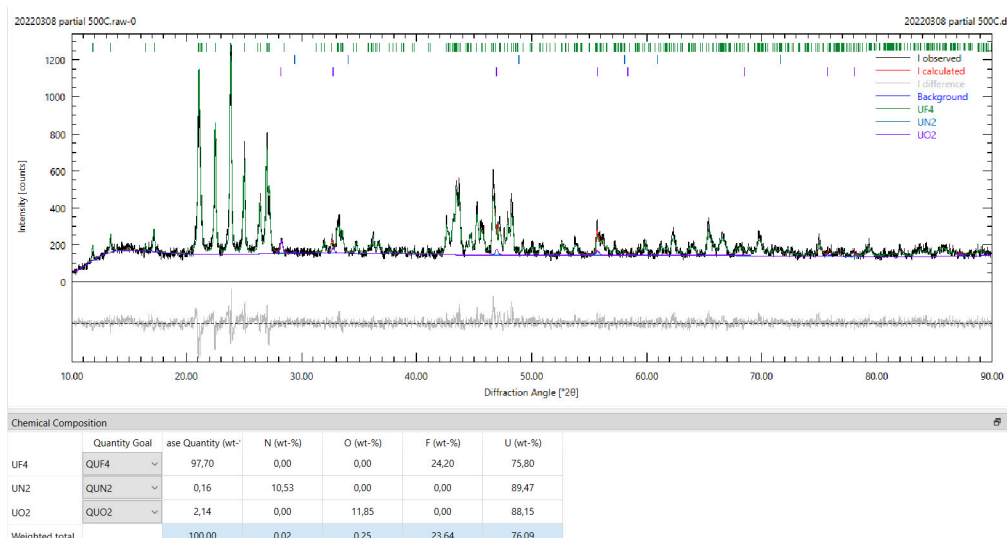


Figure 3.7: XRD result of the intermediate reaction to 500 °C.

Table 3.4: Experiment data of the intermediate reaction to 500 °C.

Powder mass before synthesis	1.159 g
Powder mass after synthesis	Omitted
Boat mass before synthesis	1.396 g
Boat mass after synthesis	1.398 g
Extracted powder color	Evenly green with gray spots
Extracted powder characteristics	Not crunchy, no caking

3.3.4 Procedure at 600 °C

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 300 °C in 28 min (10 °C /min)
- Heating from 300 °C to 500 °C/ in 40 min (5 °C /min)
- Temperature plateau for 70 min, gas change to NH₃ (0.2 ℓ/min) after 10 min
- Heating from 500 °C to 600 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Sample magnetically retracted out of the hot zone
- Quick cool-down of sample to 35 °C under NH₃ gas
- Gas change to Ar (0.2 ℓ/min)
- Furnace cooling to 20 °C (10°C /min)

- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.3.5 Results at 600 °C

During the experimental procedure, the first indication of ammonium fluoride production started to appear at 600 °C. From that temperature until the end of the heating program, an opaque ring of NH₄F was created on the inner surface of the quartz tube.

The retrieved sample composed of a green core with a thin brown crusty surface indicated the large presence of UF₄. Once again, the caking effect took place, permitting only the outer surface of the powder to be involved in a reaction and leaving the inner core mostly without any change. The XRD analysis proved that the composition of this sample was only 2.66% UN₂, with 2.25% of UO₂ and leaving the rest 95.09% unreacted as UF₄. The data and the XRD result are presented below in the Figure 3.8 and in the Table 3.5.

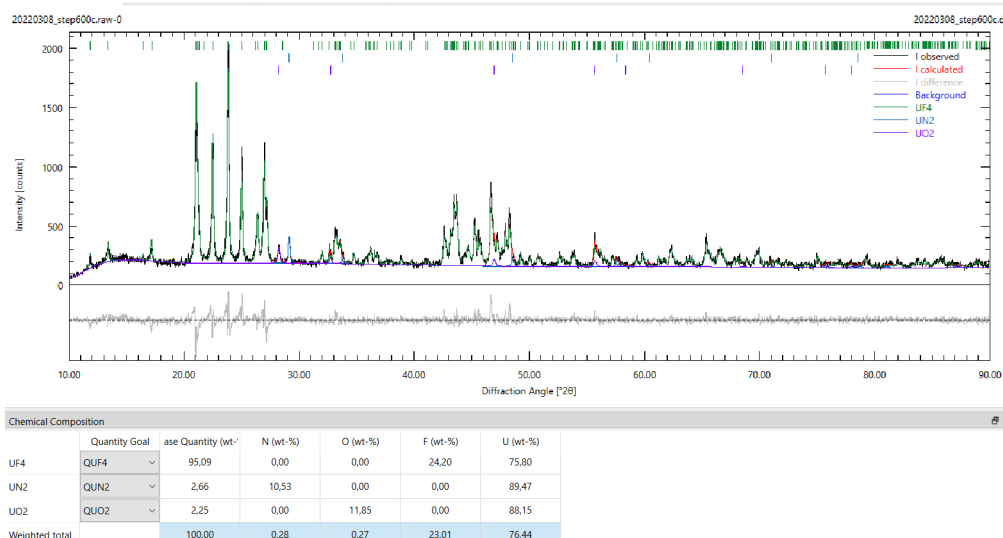


Figure 3.8: XRD result of intermediate reaction until 600 °C.

Table 3.5: Experiment data of the intermediate reaction to 600 °C.

Powder mass before synthesis	1.284 g
Powder mass after synthesis	Omitted
Boat mass before synthesis	1.398 g
Boat mass after synthesis	1.399 g
Extracted powder color	Green with a gray crust
Extracted powder characteristics	Easy crumbled, little caking

3.3.6 Procedure at 700 °C

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 300 °C in 28 min (10 °C /min)
- Heating from 300 °C to 500 °C/ in 40 min (5 °C /min)
- Temperature plateau for 30 min, gas change to NH₃ (0.2 ℓ/min) after 10 min
- Heating from 500 °C to 600 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Heating from 600 °C to 700 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Sample magnetically retracted out of the hot zone
- Quick cool-down of sample to 35 °C under NH₃ gas
- Gas change to Ar (0.2 ℓ/min)
- Furnace cooling to 20 °C (10°C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.3.7 Results at 700 °C

Starting with observations during the synthesis, an opaque bank of NH₄F began to appear at 700 °C and continued to get denser and wider until the end of the run. It is noted that during the temperature plateau at 700 °C, the ammonia gas flow was observed to have decreased; the flow was set back to normal, but maybe the results have been affected by this incident.

During the extraction with the magnet, the powder boat turned upside-down, resulting in a small spill of powder; hence, no powder weighting was performed after the synthesis. The remaining material had a dark green color, and it appeared in the form of caked flakes with a light green core. As the color was darker than before, a higher percentage of UN₂ was anticipated. Indeed the XRD-analysis presented in Figure 3.9 showed that the UN₂ was increased to 14.95% with 83.61% of UF₄ remaining unreacted; the UO₂ impurity was 1.43%. The weight measurements of the run are presented in the Table below 3.6. Lastly, also in this run, no other intermediate product was detected.

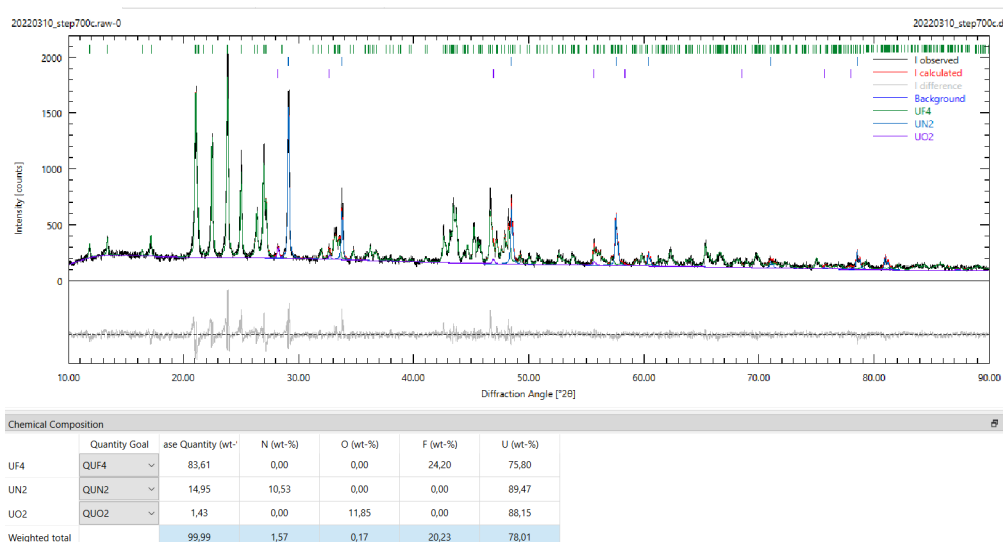


Figure 3.9: XRD result of intermediate reaction until 700 °C.

Table 3.6: Experiment data of the intermediate reaction to 700 °C.

Powder mass before synthesis	1.231 g
Powder mass after synthesis	Omitted
Boat mass before synthesis	1.399 g
Boat mass after synthesis	1.400 g
Extracted powder color	Dark green
Extracted powder characteristics	Easily crumbled, caked

3.3.8 Procedure at 800 °C

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 300 °C in 28 min (10 °C /min)
- Heating from 300 °C to 500 °C/ in 40 min (5 °C /min)
- Temperature plateau for 30 min, gas change to NH₃ (0.2 ℓ/min) after 10 min
- Heating from 500 °C to 600 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Heating from 600 °C to 700 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Heating from 700 °C to 800 °C in 10 min (10 °C /min)
- Temperature plateau for 60 min
- Sample magnetically retracted out of the hot zone
- Quick cool-down of sample to 35 °C under NH₃ gas
- Gas change to Ar (0.2 ℓ/min)
- Furnace cooling to 20 °C (10°C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.3.9 Results at 800 °C

During the synthesis, a very opaque bank of NH₄F started to get visible during the 800 °C plateau and continued getting denser until the end of the run. At the end of synthesis, the extracted material was dark green - light gray colored and heavily caked in large and small flakes.

The composition was proven to be the best achieved as the amount of UN₂ was measured to be 56.4%. The XRD analysis in the Figure 3.10 also showed a relatively high amount of UO₂ at 5.3%, leaving 35.52% of unreacted UF₄. The remaining 2.77% was identified as U₂N₃, indicating an early sign of high temperature de-nitriding. Finally, no intermediate product appeared in the results.

In the following Table 3.7 the experimental data of the run are presented; the weight measurement of the boat was omitted again as it was discarded after the run due to the extensive deformation.

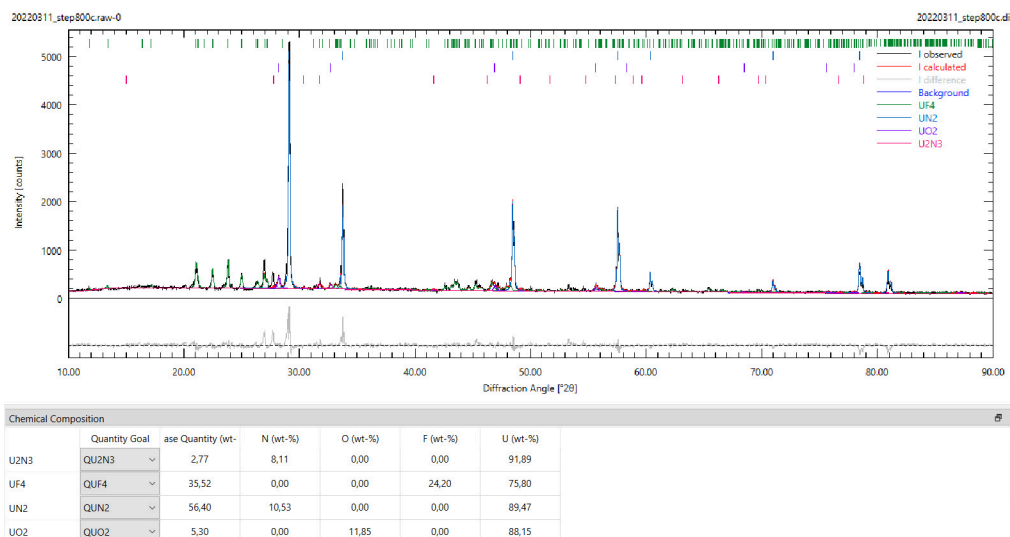


Figure 3.10: XRD result of intermediate reaction until 800 °C.

Table 3.7: Experiment data of the intermediate reaction to 800 °C.

Powder mass before synthesis	1.247 g
Powder mass after synthesis	Omitted
Boat mass before synthesis	1.400 g
Boat mass after synthesis	Omitted
Extracted powder color	Dark green
Extracted powder characteristics	Easily crumbled, very caked

3.3.10 Conclusions

From the above experiments at four different temperatures, it is mainly concluded that the efficient production of UN₂ starts at 700 °C. For this reason, there is no need for a slow heating ramp until this temperature; however, slow heating and extended temperature plateaus seem to be very important for the UN₂ production. According to these results, the heating ramps of the following experiments were optimized, leading to a much more time-efficient experimental procedure. Additionally, it is noted that no intermediate product, was observed during the runs. Furthermore, a small quantity of U₂N₃ was found at the 800°C, indicating the start of the UN₂ to UN process. Finally, the caking effect being noted in all the runs, suggests that the problem appears from the beginning of the partial synthesis.

3.4 Optimized partial synthesis

In the light of the earlier series of experiments, which indicated that no intermediaries are involved in the reaction and that nothing much except the production of UN₂ occurs at temperatures up to 600 °C; the purpose of the present experiment was to see if the early lower-temperature steps can be omitted with impunity. In particular, if the entire reaction can just as well be performed in the range of 700 °C to 800 °C. This information would speed up the procedure and conserve ammonia while spending more time at temperatures that appear to be effective.

3.4.1 Setup

The usual quartz tube (1000 mm length, Ø25mm in, Ø28mm out) was used, with brass fittings at the ends. About 1.5 g of UF₄ was loaded in an open-ended simple boat made from Cu sheet of 0.3 mm thickness. A part of the same sheet was used to cover the inside surface of the tube. For even better shielding from oxygen transfer, two filters made of Cu shavings were placed at the ends of the boat inside the furnace. In this run, no proper weighting of the sample took place.

3.4.2 Experimental procedure

In this experiment the heating ramp was optimized according to the observations of the previous experiment. The procedure is described in the following list.

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 700 °C in 68 min (10 °C /min)
- Temperature plateau for 15 min, gas change to NH₃ (0.2 ℓ/min) after 10 min
- Heating from 700 °C to 800 °C in 100 min (1 °C /min)
- Temperature plateau for 100 min
- Gas change to Ar (0.2 ℓ/min)
- Furnace cooling to 20 °C (10°/min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.4.3 Results

The first observation during the synthesis was noted at 700 °C when the first traces of NH₄F were observed. At 740 °C, the produced NH₄F was much denser, measuring 4 cm in length. Lastly, at the end of the 800 °C temperature plateau, the formation was completely opaque, covering most of the surface of the right part of the tube.

Continuing with the XRD analysis in Figure 3.11, the results were surprisingly good. The produced UN₂ was measured to be 98.05%, followed by only 0.30% of UF₄. The oxygen impurity was also very low at 1.65%, characterizing this experiment as one of the most successful.

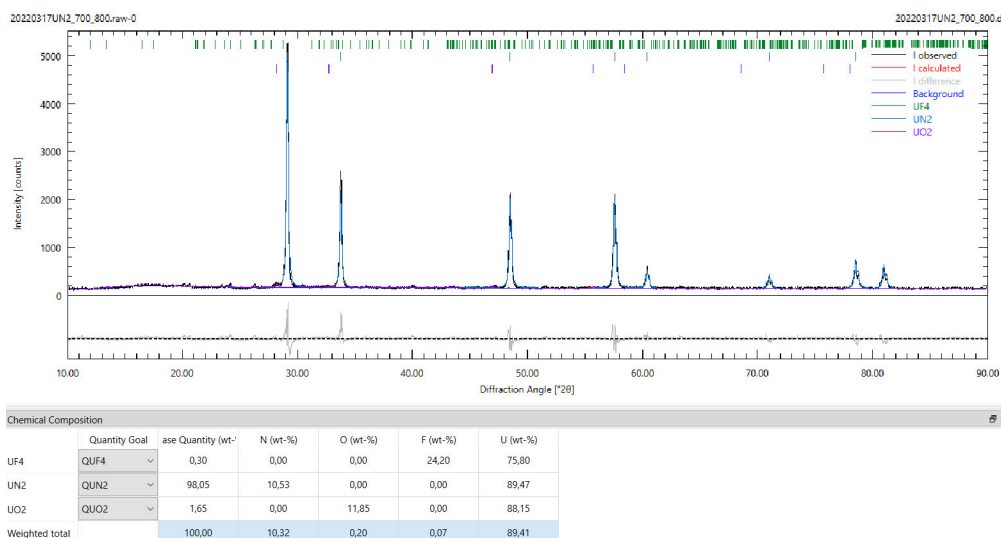


Figure 3.11: XRD result of the optimized partial synthesis.

During this experiment, the oxygen/nitrogen analyzer was tested. After the proper calibration of the equipment, the measurement of the sample showed the presence of 0.434% of oxygen and 9.091% of nitrogen.

To be able to compare the results from the two analysis method, the percentage of UO₂ should be calculated from the percentage of oxygen. In 100 g of sample, there is 0.434 g of oxygen, 9.091 g of nitrogen, and the rest of 90.475 g is uranium. The oxygen combines with $238 \cdot 0.43415 / (2 \cdot 16) = 3.229$ g uranium to form 3.663 g of UO₂. So it is concluded that the two different techniques agree precisely on the percentage of UO₂, confirming the success of this experiment.

3.5 Optimized full synthesis

Following the successful, optimized partial synthesis of the previous Section 3.4, a full synthesis was now tested. The aim of the current experiment was to try if the UN could be fabricated in one step using a rapid heating ramp.

3.5.1 Setup

As Cu can not be used in full synthesis, since the temperature exceeds its melting point (1085 °C), equipment made from tantalum was used. So the 110 mm long tantalum boat manufactured from a 0.1 mm thick sheet was used. A tantalum sheet measuring 140 mm length was lined on the inner surface of the usual quartz tube (1000 mm length, Ø25mm in, Ø28mm out). Some Ta shavings were packed on both sides of the boat to prevent air convection that leads to oxygen transfer.

3.5.2 Experimental procedure

On the following list, the optimized heat ramp is presented, this time leading to a full synthesis of UN.

- Furnace turn on
- N₂ gas flow set to 0.2 ℓ/min
- Heating from 20 °C to 700 °C in 68 min (10 °C /min)
- Temperature plateau for 15 min, Gas change to NH₃ (0.2 ℓ/min) after 10 min
- Heating from 700 °C to 80 °C in 100 min (1 °C /min)
- Temperature plateau for 100 min
- Gas change to Ar (0.1 ℓ/min)
- Heating from 800 °C to 1100 °C in 30 min (10 °C /min)
- Temperature plateau for 300 min
- Furnace cooling to 20 °C (10°/min)
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.5.3 Results

Once again, the NH₄F production started to form at 700 °C, followed by a very opaque formation at the end of the 800 °C temperature plateau.

The XRD analysis in Figure 3.12, showed again a successful experiment, resulting to production of 97.47% UN and 2.53% of UO₂. The amount of UO₂ is double than the partial synthesis, probably due to the longer experiment's duration, but still, it

was considered acceptable. The weight measurements are presented in the following Table 3.8.

Lastly, the oxygen/nitrogen analyzer was used one more time. The results were 0.31% of oxygen and 5.51% of nitrogen. The conversion from oxygen percentage to UO₂ was made, resulting in: An amount of 100 g containing 0.310 g of oxygen, 5.507 g of nitrogen, and the rest of 94.183 g is uranium. Then $238 \times 0.3104 / (2 \times 16) = 2.309$ g U formed 2.619 g of UO₂.

The values from the two analysis techniques are surprisingly similar, proving another very successful run. Finally, it is concluded that the optimized heating ramps during partial and full synthesis lead to very high purity nitride powders in a time-efficient way.

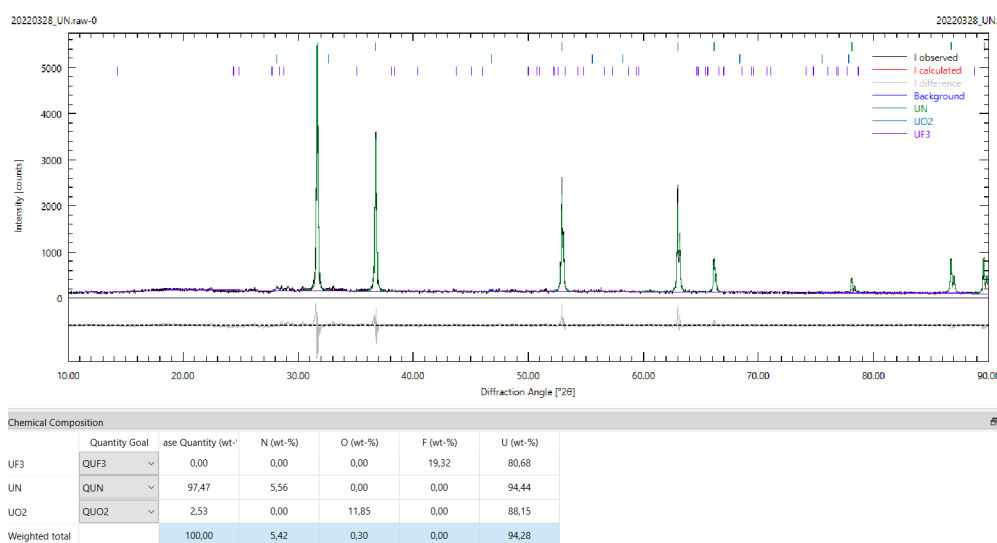


Figure 3.12: XRD result of the optimized full synthesis.

Table 3.8: Experiment data of the intermediate reaction to 800 °C.

Powder mass before synthesis	1.267 g
Powder mass after synthesis	0.996 g
Boat mass before synthesis	5.235 g
Boat mass after synthesis	5.236 g
Extracted powder color	Evenly black
Extracted powder characteristics	Sticky, easily flattened

3.6 Upscaled synthesis

The final experiment on the UF₄ research was performed using the large-scale drum described in the Subsection 2.6.4. The procedure included all the steps known for a partial synthesis and some high-temperature tests of the equipment.

These tests were mandatory as the whole setup was altogether new and its behavior in synthesis conditions unknown. Additionally, several modifications were performed to improve the drum's reliability.

3.6.1 Setup

A larger quartz tube (1000 mm length, Ø44mm in, Ø48mm out) was used this time to accommodate the upscaled drum. As the gas inlet and outlet pipes of the drum were directly connected to the gas feed tube and filters, there was no use of brass fittings; instead, a couple of silicon fittings were used.

Due to the high thermal conductivity of Cu, the new setup with extended pipes on both sides, was conducting much more heat than the previous smaller reaction vessels. For this reason, temperature measurements during furnace operation without any sample loaded was performed. A thermocouple measured the temperature in the center of the drum when the furnace was set to 800 °C and at the far end of the exhaust tube where the magnets' base was placed.

As it was expected, the temperature in the center could not reach the wanted value as Cu conducted heat out of the furnace's hot zone. For this reason, the desired temperature was reset to 910 °C, resulting in an acceptable value of 750 °C actual temperature inside the drum. The measurement at the end of the exhaust tube showed 110 °C, a temperature that should not affect the functionality of the magnets.

The drum was filled with 22.745 g of UF₄, and the nine Cu balls were placed inside, as shown in Figure 3.13 and in Figure 3.14. The next step was to place the drum inside the quartz tube but not in a fully attached position. Firstly, a flow of 0.1 ℓ/min of Ar was started in order to flush the atmosphere on the left side of the quartz tube. After 30 min, the drum was set in an attached position between the stationary and the rotating part. The flow of Ar was continued for another 30 min to reduce the oxygen quantity in the system.



Figure 3.13: The upscaled drum loaded with UF_4 .

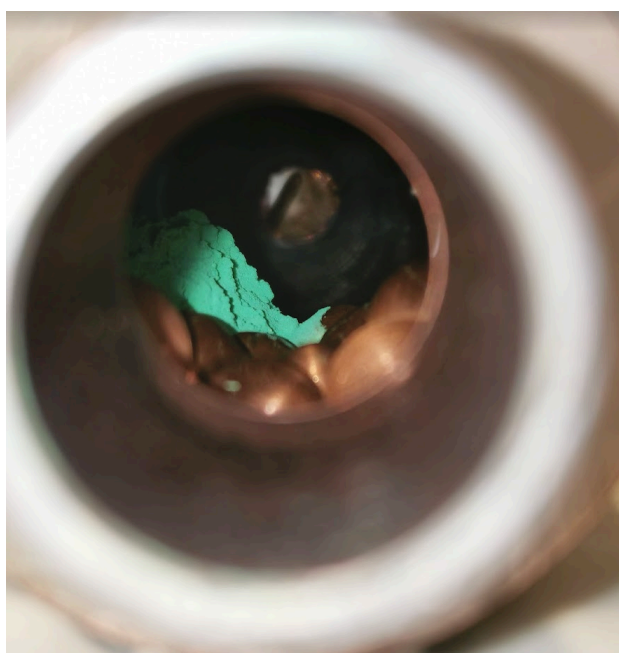


Figure 3.14: Close-up view of the Cu balls and the powder inside the drum.

Finally, the rubber belt was attached to the pulley and to the step-motor, and the electronic parts were turned on. The rotation pattern was set to one and a half rotations forward, followed by one full rotation backward, endlessly repeating. This scheme would involve better mixing without any zones of the drum being unmixed. The period of a full rotation was measured to be 156 sec. The complete experimental setup is presented in the following Figure 3.15.



Figure 3.15: The complete setup of the experiment during the synthesis.

3.6.2 Experimental procedure

- Furnace turn on
- Ar gas flow set to 0.2 ℓ /min
- Heating from 20 °C to 600 °C in 58 min (10 °C /min)
- Rotation started at 200 °C
- Temperature plateau for 10 min, Gas change to NH₃ (0.2 ℓ /min)
- Heating from 600 °C to 700 °C in 10 min (10 °C /min)
- Heating from 700 °C to 910 °C in 210 min (1 °C /min)
- Temperature plateau for 60 min
- Furnace cooling to 20 °C (10°/min)
- Gas change to Ar (0.2 ℓ /min) at 700 °C
- Sample extraction under Ar flow
- Ar gas turn off
- Deposition of sample on XRD sample holder in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

3.6.3 Results

The first visible proof that the reaction had started was a slight deposition of NH₄F at 600 °C on the right-side inner surface of the tube. The deposition continued to grow more and more until the temperature of 750 °C, when it was observed to be very opaque. At 850 °C, the deposition length was measured to be 18 cm, retaining the opaque light gray color.

After the synthesis, the drum was opened inside the glove box, revealing a somewhat disappointing result. A large part of the sample had formed a cake on one side of the drum. The other part was in powder form, and its gray color suggested that the reaction probably was completed. The two kinds of material were separated in different plastic tubes, their mass was measured, and two XRD analyses were performed. In Figure 3.16, the caked powder is presented alongside the used Cu balls.

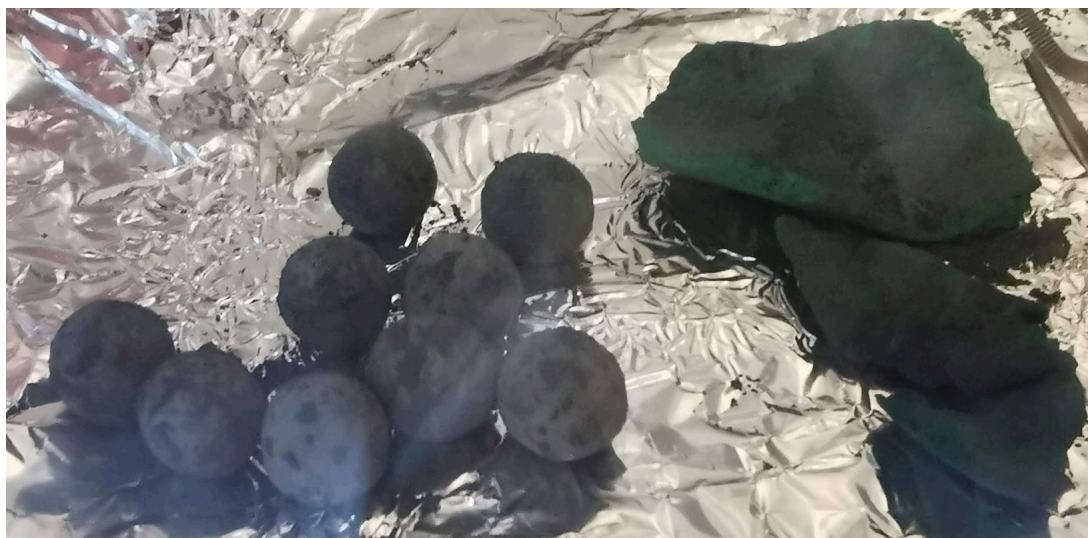


Figure 3.16: The caked powder next to the used Cu balls.

CHAPTER 3. PROCEDURES AND RESULTS USING UF₄

The first XRD analysis, as shown in Figure 3.17, for the loose powder revealed the successful production of low purity UN₂. The UN₂ phase was measured as 70.58%, with 26.53% of UF₄ remaining unreacted. The oxygen impurity was kept low, amounting to 2.89% of UO₂.

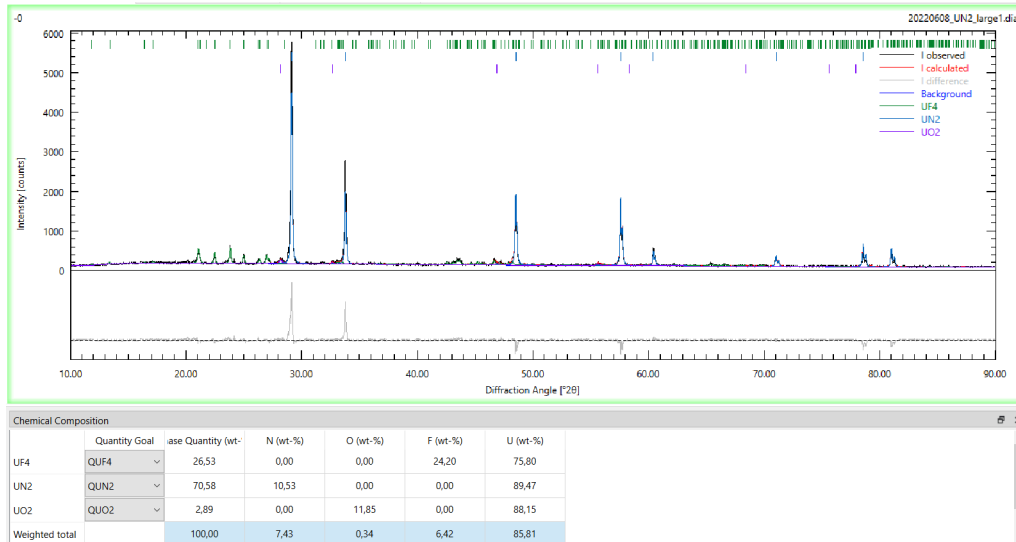


Figure 3.17: XRD results from the loose powder.

Regarding the XRD results from the caked powder, as shown in the following Figure 3.18, most of the UF₄ remained unreacted. Indeed the UF₄ percentage was measured to be 93.87%, with only 5.88% of UN₂ produced. The oxide impurity was only 0.25%.

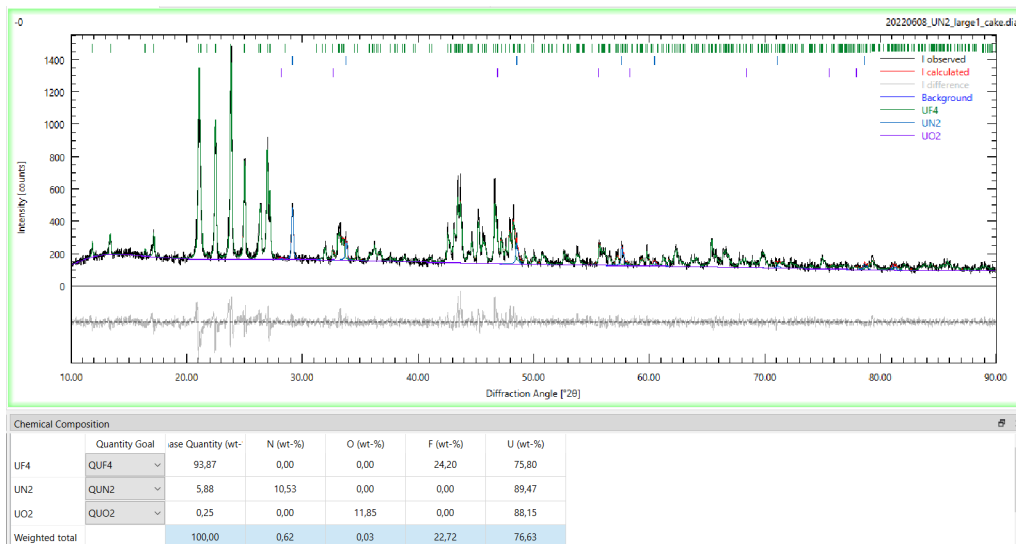


Figure 3.18: XRD results from the caked powder.

The experimental measurements of this run are gathered in the following Table 3.9. The unsatisfying results of this experiment indicate that many parameters should be redefined. Although the idea of the rotating drum may be promising, there is space for improvement in the design of the setup parts and also in the experiment's procedure.

Table 3.9: Experiment data of the upscaled experiment.

Powder mass before synthesis	22.745 g
Loose powder mass after synthesis	7.808 g
Caked powder mass after synthesis	11.528 g
Percentage of loose powder	34.3%
Percentage of caked powder	65.7%
Loose powder color	Light gray
Caked powder color	Dark green
Loose powder characteristics	Soft, not crunchy
Caked powder characteristics	Very hard, difficult to break

Chapter 4

Procedures and Results using UF_6

The main objective of the current project was the fabrication of UN fuel from UF_4 , but during the experimental procedure, there was sufficient time, and some tests using UF_6 were performed. UF_6 is commonly used in the industry for nuclear fuel production, but on the other hand, its handling is complicated and sometimes challenging. Most likely, the best fuel production method with UF_6 is the direct injection in gaseous form into the ammonia stream. But such a method would require complicated and costly equipment [10]. For this reason, it was decided to research its properties and potential uses through a similar process to the UF_4 synthesis. In the first part, the reaction of solid UF_6 with ammonia gas was tested. Then the syntheses of UN_2 and UN from UF_6 was demonstrated.

4.1 Testing the UF_6 reaction with NH_3

This test aimed to determine the result of the reaction between UF_6 and NH_3 . The option to apply external heat to the reaction was included, in case the reaction was very slow or some traces of UF_6 were left unreacted.

4.1.1 Setup

A simple Pyrex U-shaped tube and a heating mantle were used for this experiment. One end of the U-Tube was connected to a gas inlet tube and the other to the gas exhaust tube. As UF_6 is highly volatile in room temperature conditions, the chemical canister, the tube, and all the equipment were cooled down with dry ice. A bubble tube, filled with kerosene, was placed in line with the exhaust. This component acted as a gas flow indicator, as a barrier between the reaction and the atmosphere, and also as a trap of possible UF_6 escaping particles.

Further down the exhaust line, the gas flow passes through a pair of filters containing CaCl_2 solution that absorbs the excess ammonia gas. The following Figure 4.1 presents the U-Tube setup.

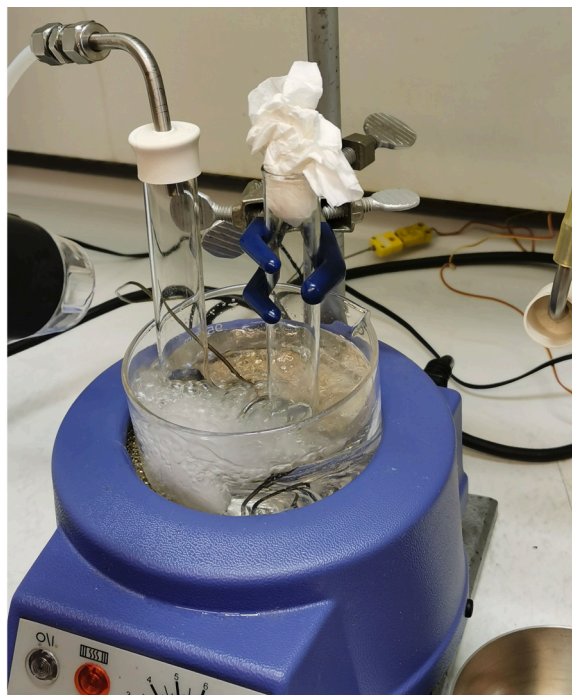


Figure 4.1: The U-Tube in a dry ice bath before the experiment.

4.1.2 Experimental procedure

Firstly, the cooled-down powder was transferred from the canister to the bottom of the U-Tube. The UF_6 mass was approximately 0.3 g, and no proper sample weighting was able under these conditions. The next step was to switch the gas from Ar to ammonia. At that moment, a camera was focused on the bottom of the tube, allowing the creation of a short time-lapse video of the reaction.

Immediately after the gas change, the UF_6 reacted with the NH_3 gas producing a light green colored product. The flow continued for 10 min without any changes being observed. Then with the mantle, the sample was heated slowly to $75\text{ }^\circ\text{C}$ and then rapidly to $300\text{ }^\circ\text{C}$ still under ammonia flow. This procedure aid the reaction of any UF_6 traces that may have remained. It also helped with the separation of NH_3 molecules from the powder. Lastly, the whole setup was set to cool down, the U-Tube was transferred with both ends sealed in the glovebox, and an XRD sample was prepared. In the following Figure 4.2, the produced green substance immediately after the exposure to ammonia gas is shown.



Figure 4.2: The green reaction product after exposure of UF₆ to NH₃ gas.

4.1.3 Results

The XRD analysis showed no traces of unreacted UF₆ or any formation of UF₄. On the contrary, some intermediate phases were formed. The main one was (UF₄)₃(NH₄F) followed by smaller quantities of (UF₄)(NH₄F)₄ and (UF₄)₆(NH₄F)₇. The XRD analysis results are presented in Figure 4.3 below. One peak remained unidentified at 2 θ = 12.65°.

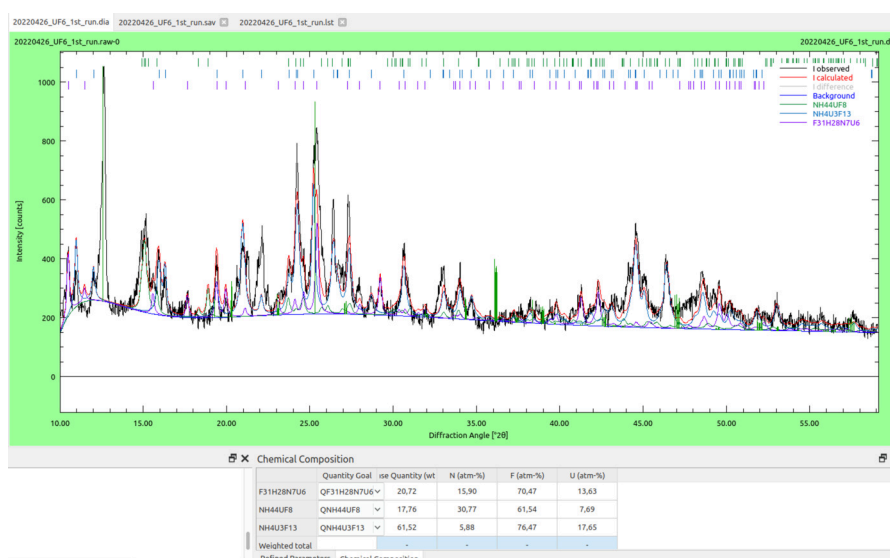


Figure 4.3: XRD results from the first UF₆ test.

4.2 Partial synthesis from UF₆

The previous experiment confirmed that UF₆ is able to be transferred safely and react with ammonia. So at that point, the next step would be to synthesize UN fuel out of UF₆. As in the case of UF₄, the two-step reaction was also tested, and the same procedure was applied. The first fuel production attempt was a partial synthesis, meaning the production of UN₂ only. At this step, the temperature does not exceed 800 °C, so a reaction vessel made out of Cu could be used.

4.2.1 Setup

Again the usual quartz tube (1000 mm length, Ø25mm in, Ø28mm out) was used, with brass fittings at the ends. The chosen reaction vessel was the provisional Cu drum from the previous UF₄ experiments, which is described in Subsection 2.6.2. The idea of the preparation was the same as before. The canister and the provisional drum were cooled with liquid nitrogen. But in this case, any ice formation should be avoided on the drum as it would introduce oxygen to the reaction.

For this reason, the provisional drum was placed in the quartz tube close to the edge without any lining, and small amounts of liquid nitrogen were poured inside. To minimize ice formation and to produce an oxygen-free atmosphere in the tube, Ar gas was flowing in the tube during all the preparation steps. When the temperature of the provisional drum dropped low enough, seven micro-spoonfuls of UF₆ powder were placed inside it. Then the drum was pushed into the middle of the tube, and filters of Cu shavings were placed on each end, the quartz tube's end was sealed, and the gas was changed to ammonia immediately.

4.2.2 Experimental procedure

After 10 min exposure to ammonia gas, the following heating steps were applied using the furnace. The gas flow was estimated at approximately 0.2ℓ/min.

- Heating from 20 °C to 700 °C in 68 min (10 °C /min)
- Temperature plateau at 700 °C for 15 min
- Heating from 700 °C to 800 °C in 100 min (1 °C /min)
- Temperature plateau at 800 °C for 100 min
- Cooling from 800 °C to 20 °C in 78 min (10 °C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Preparation of the XRD sample in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

4.2.3 Results

The first visible result, even before the heating, was the production of NH₄F along the bottom of the tube, due to the rapid reaction of UF₆ with NH₃. Then at 450 °C, the usual NH₄F ring was formed and continued to grow till the 750 °C. Finally, at 800 °C, NH₄F had formed an opaque layer on the tube's inner surface. The extracted powder was black with good flowability and not crunchy. The XRD analysis revealed a successful result as the amount of UN₂ was 94.95% and the UO₂ only 5.05%. No traces of unreacted UF₆ were detected.

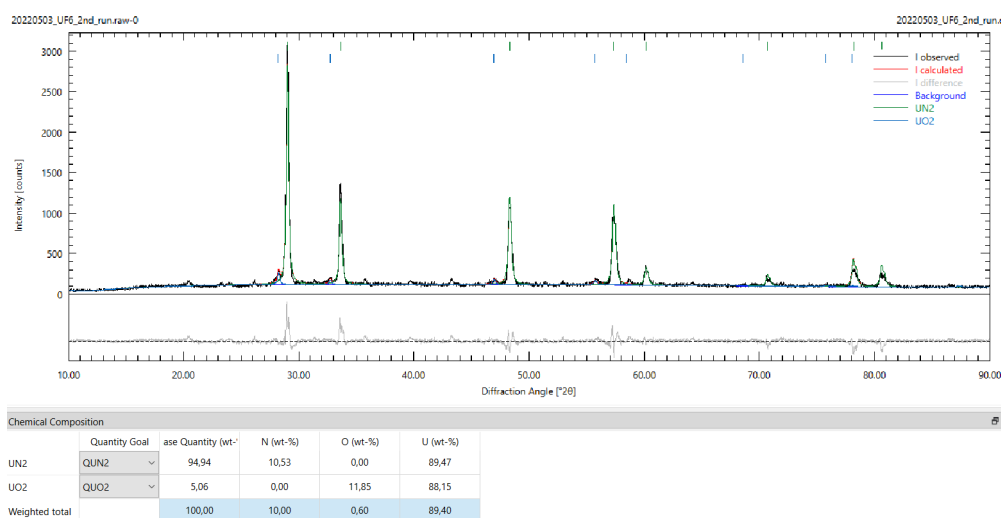


Figure 4.4: XRD results from the UF₆ partial synthesis.

Table 4.1: Experiment measurements from the UF₆ partial synthesis.

Powder mass before synthesis	0.478 g
Powder mass after synthesis	0.229 g
Drum mass before synthesis	44.493 g
Drum mass after synthesis	44.513 g
Extracted powder color	Evenly black
Extracted powder characteristics	Fine, not crunchy, no granules

4.3 Full synthesis from UF₆

The research on UF₆ could not be considered complete if UN powder was not produced, so a full synthesis was tested in this part of the experiment. The procedure was similar to the partial synthesis, with the main difference of the higher temperature and the tantalum-made equipment.

4.3.1 Setup

The usual quartz tube was used again, with a Ta lining and two filters made from Ta shavings. The powder reaction vessel was a Ta tube that had not used again in this research. This Ta tube was flat on both ends, so it could not hold any liquid nitrogen inside. So a different cooling method should be used. The whole quartz tube containing the Ta tube was wrapped with tissue, and liquid nitrogen was poured on it, as shown in the following Figure 4.5. By this way, the installed thermocouple showed that the inner surface of the Ta tube was successfully cooled down to $-170\text{ }^{\circ}\text{C}$. Then, ten micro-spoonfuls of UF₆ were placed in the Ta tube, the quartz tube was sealed, and ammonia gas was turned on immediately.



Figure 4.5: The cooling down procedure with liquid nitrogen.

4.3.2 Experimental procedure

After 10 min in ammonia, the furnace was turned on following the heating steps below.

- Heating from $20\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ in 68 min ($10\text{ }^{\circ}\text{C}/\text{min}$)
- Temperature plateau at $700\text{ }^{\circ}\text{C}$ for 15 min
- Heating from $700\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ in 100 min ($1\text{ }^{\circ}\text{C}/\text{min}$)
- Temperature plateau at $800\text{ }^{\circ}\text{C}$ for 100 min
- Gas change from ammonia to Ar ($0.1\ell/\text{min}$)
- Heating from $800\text{ }^{\circ}\text{C}$ to $1100\text{ }^{\circ}\text{C}$ in 30 min ($10\text{ }^{\circ}\text{C}/\text{min}$)

- Temperature plateau at 1100 °C for 300 min
- Cooling from 1100 °C to 20 °C in 108 min (10°C /min)
- Sample extraction under Ar flow
- Ar gas turn off
- Preparation of the XRD sample in glove-box
- XRD analysis (Angle range: 10°- 90°, Sampling time: 0.02 s/step)

4.3.3 Results

Regarding the visual inspection during the synthesis, a reasonably large quantity of NH₄F was formed after the exposure to ammonia, like in the previous run. At 560 °C, the first ring of NH₄F was formed and continued becoming denser till the temperature reached 800 °C. Also, an unusually high amount of NH₄F was observed in the outlet hose. After the run, the deposit was very opaque with a brown colored formation as shown in the following Figure 4.6.

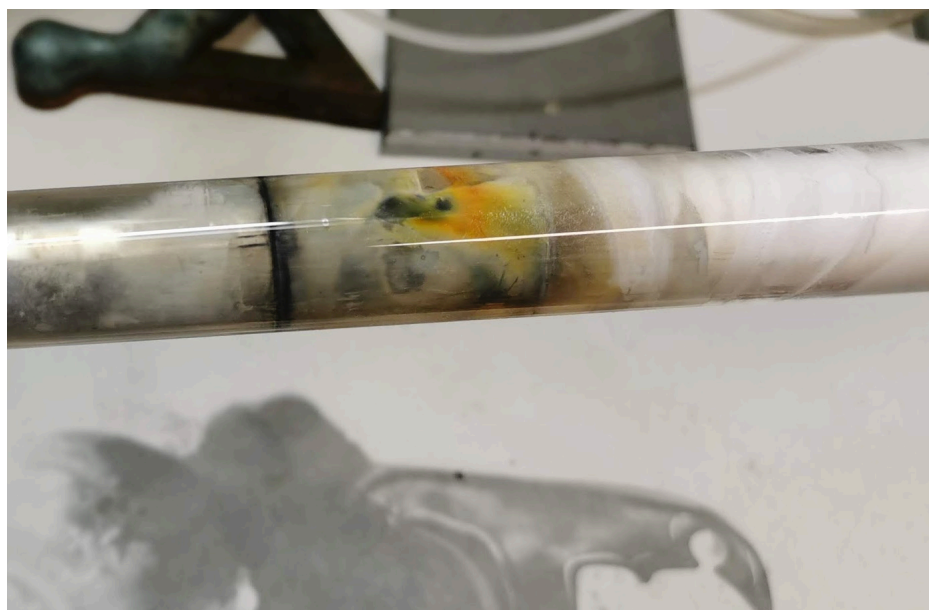


Figure 4.6: The brown colored formation of NH₄F at the end of synthesis.

Following the XRD analysis as it is shown in Figure 4.7 , the experiment was successful since the total amount of UN was 96.89%, and the UO₂ was at 3.11%. This result reveals that synthesis of high purity UN from UF₆ is possible with a simple setup and encourages further research to be continued.

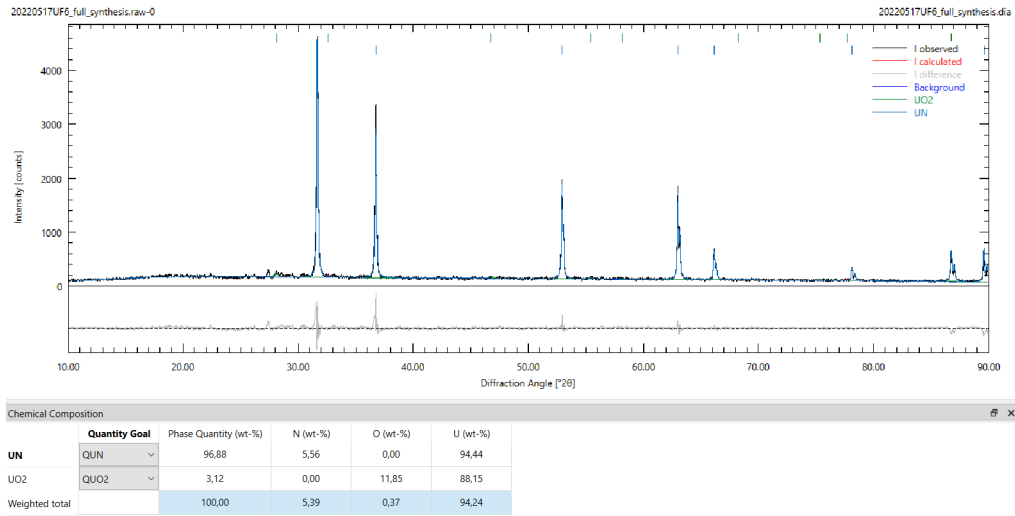


Figure 4.7: The XRD result from the UF₆ full synthesis.

Table 4.2: Experiment measurements from the UF₆ full synthesis.

Powder mass before synthesis	1.583 g
Powder mass after synthesis	0.612 g
Ta tube mass before synthesis	Omitted
Ta tube mass after synthesis	58.569 g
Extracted powder color	Evenly black
Extracted powder characteristics	Fine, soft lumps, not crunchy

Chapter 5

Conclusions

During the course of these experiments, a vast experience in UN fuel synthesis from fluorides with the method of ammonolysis was gained. The results from the simple open boat showed that high purity UN synthesis from UF_4 is achievable, but by this method could not surpass the 1 g threshold. So the design of a more advanced experimental setup was initiated.

From the results of the provisional drum, it is concluded that a closed-type rotating drum has many advantages. Firstly, it is capable of reducing the oxygen absorption, as the powder is less exposed to the water vapors produced by the reaction of the quartz with HF. This positive result was enhanced by using filters on the ends of the drum, that blocked the oxygen carried by the convection through the tube. Secondly, the rotation of the drum was proven to reduce the caking effect, leading to an increase by a factor of four in the fuel quantity that can be produced.

Although the provisional drum showed the way for a new promising design, the experimental procedure should also be optimized. The interrupted synthesis experiments provided a part of the solution to this argument. From these runs, it was proven that between the temperatures of 500 °C to 700 °C, the production of UN_2 is very little. So it is concluded that the heat ramp during these temperatures could be steep, saving valuable time that can be used in the temperature plateau of 800 °C, where the efficiency of the reaction reaches the maximum value. An important observation was also that there were no intermediate phases detected during all the series of the experiments.

The experience gained from the interrupted experiments was evaluated by the optimized synthesis experiments. These runs were performed with quick heating to 700 °C, then slow heating to 800 °C, where the reaction started to produce UN_2 and the runs ended with a long temperature plateau at 800 °C. The partial and the full synthesis using the optimized procedure were very successful, resulting in the production of 98.05% purity UN_2 and 97.47% purity UN respectively. So it is concluded that this optimized procedure is the most time-efficient way of producing UN from UF_4 .

Continuing with the upscaled drum, that was designed for the production of 20 g UN₂ per run, many conclusions have been obtained. Firstly, it was proved that an automatically rotating drum inside a quartz tube is an proven scenario; this result changed the philosophy of the fuel fabrication of this research, that always was based on stationery designs. Secondly, the solid experience of handling mechanisms with moving parts under very high temperatures in a quartz tube will certainly be valuable for future improved setups.

Additionally, the somewhat disappointing behavior of the powder inside the upscaled drum gave the feedback that the experiment's parameters should be redefined. The caking effect was proven to be a much more complicated constraint, leading to the conclusion that a rotating drum with balls inside is not sufficient. This feedback motivated us to search for improvements to the existing drum, like replacing the Cu balls with a Cu roller that could mix and crush the powder in a better way. Other parameters should be also tested, like the heating ramp and the rotation speed. Finally, the complexity of this design gave us the opportunity to gain experience in the previous unfamiliar fields of CAD designing, 3D-printing, metal manufacturing, and Arduino board operation.

Lastly, the research in UF₆ proved that its reaction with ammonia is quite feasible and revealed the interesting reaction products. It also provided valuable experience on the handling of the UF₆ powder canisters and the preparation of the experimental setup. Furthermore, it is concluded that UF₆ is a comparably good material to UF₄ for UN fuel fabrication. The produced 96.89% pure UN from UF₆ documents this conclusion in the best way. Although UF₆ should be used in a gaseous state for upscaled experiments, rather than the solid state used during these experiments, it remains a very promising starting material for future research. The use of UF₆ will allow the production of enriched UN samples for test irradiation, formerly a stumbling block due to the commercial non-availability of enriched uranium metal.

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Summary

This thesis addresses the fabrication of high purity UN fuel with the ammonolysis method from fluorides in large quantities, 15-20 g per run. The main starting material was UF_4 , also a series of experiments was performed using UF_6 . The main constraints addressed during the experiments were the oxidation of the sample, the catalytic decomposition of NH_3 , and the caking effect leading to uncompleted reactions. The sample composition was mainly evaluated with XRD analysis, and several different powder reaction vessels were designed and manufactured from scratch.

To begin with, the equipment used in the previous research was tested, and 0.8 g of UF_4 was successfully converted to 92.9% purity UN. Afterward, a provisional Cu drum was manufactured to test the upscaled production of UN_2 . The new drum was intended to address the caking effect on the first part of the synthesis, then the produced UN_2 could be de-nitrated in a simple Ta boat at a higher temperature. The drum could be rotated manually for better mixing of the powder during the effort to avoid the caking effect. Indeed the provisional drum was able to upscale the UN_2 production by a factor of four and produced 87.9% purity UN_2 .

Furthermore, a series of interrupted synthesis experiments were performed to study the possible emergence and conversions of intermediate compounds during the reaction. The results would shed light on the mechanism of UN_2 production and lead to a better, more efficient heating ramp for the following experiments. For these experiments, a number of magnetically retractable Cu boats were manufactured.

The results showed that the efficient production of UN_2 starts at 700 °C. For this reason, there is no need for a slow heating ramp until this temperature. Additionally, it is noted that no intermediate product was observed during the runs. Furthermore, a small quantity of U_2N_3 was found at 800 °C, indicating the start of the UN_2 to UN process. Finally, the caking effect noted in all the runs suggests that the problem appears from the beginning of the partial synthesis.

In the light of the earlier series of experiments, which indicated that no intermediaries are involved in the reaction and that nothing much toward UN_2 production occurs at temperatures up to 800 °C, two optimized syntheses were performed. The first was a partial synthesis, which produced 98.05% purity UN_2 , and the second was a full synthesis producing 97.47% purity UN. The experiments proved that the optimized heating ramps during partial and full synthesis lead to high purity nitride powders in a time-efficient way.

In the final experiment using UF_4 , an upscaled drum made from Cu was tested. The drum was designed and manufactured at the University and could rotate inside a large quartz tube. The rotation was provided by a step-motor placed externally of the tube. A combination of magnets, a pulley, and ball-bearings transferred the rotation from the motor to the drum contactlessly. Nine copper balls were placed inside the drum for better mixing and crushing the powder.

In this experiment, the upscaled drum was filled with 22.7 g of UF_4 , and a partial synthesis of UN_2 was initiated. Regarding the results after the synthesis, a large part of the sample had formed a cake on one side of the drum. The other part was in powder form, and its gray color suggested that the reaction probably was completed. The XRD analysis of the powder showed the production of 70.58% purity UN_2 . On the other hand, the XRD analysis of the caked part showed that 93.87% of the UF_4 remained unreacted. The unsatisfying results of this experiment indicated that many parameters should be redefined. Although the idea of the rotating drum may be promising, there is space for improvement in the design of the setup parts and also in the experiment's procedure.

Finally, the UN synthesis from UF_6 was tested. In the first experiment, the reaction of UF_6 with NH_3 was demonstrated at room temperature. It was proven that the reaction is possible and some intermediate phases of the UF_6 to UN reaction were identified. Afterward, the syntheses of UN_2 and UN from UF_6 were performed, resulting in the production of 98.05% purity UN_2 and 97.47% purity UN respectively. The successful synthesis of UN from UF_6 proved that UF_6 is an equally good starting material as UF_4 and set the foundations for further research in this field.