



Recycling of thorium dioxide scrap from nuclear fuel pellets fabrication



Anton Schneider

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Supervisors: Prof. Dr. Thomas Cardinaels & Dr. Marc Verwerft

Mentors: Dr. Karen Van Hecke & Dr. Simone Cagno

School supervisor: Alexandre Legris

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Table of contents

Introduction	4
The company	4
The context	4
The internship	5
Work preparation.....	6
Bibliographic study.....	6
Analysis methods.....	7
Powder purity analysis.....	8
Safety Trainings.....	9
Dissolution experiments	10
Overview.....	10
Experiments without HF	10
Experiments with HF	15
Conclusion	18
Bibliography.....	19
Annexes.....	20

Glossary

SCK-CEN	Belgian nuclear research center
ORNL	Oak Ridge National Laboratory
BARC	Bhabha Atomic Research Center
NIMS	National Institute for Material Science
NMS	Nuclear Material Science
FMA	Fuel material Group
RCA	Radiochemistry Group
GS	Gamma Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
HF	Hydrofluoric acid
HNO₃	Nitric acid
Th(NO₃)₄	Thorium nitrate
Thoria, ThO₂	Thorium dioxide

Introduction

The company

My internship took place from May to August at SCK-CEN, the Belgian Nuclear Research Center (near the city of Mol) in the north east of Flanders (fig. 1). The center was founded in 1952 by Pierre Ryckmans in order to develop the nuclear science in Belgium. About 700 people work on the development of peaceful industrial and medical applications of ionizing radiation and study the impact on man and the environment. Priority is given to research on the safety and efficiency of nuclear installations, solutions for the disposal of radioactive waste, radiation protection, sustainable development, education and training.

Over the decades many technical, administrative, medical and residential buildings were constructed all around the center. Four experimental nuclear reactors were built, including the BR1 in 1956 which was the first nuclear reactor built outside of the USA. Three of them (including the BR2, fig. 2) are still in use for the research on nuclear fuels, materials science and also for medical radioisotopes production.



Fig 1: Localisation of Mol



Fig 2: Belgian Reactor 2

More precisely, I was in the Nuclear Materials Science (NMS) department inside which I worked with both Radiochemistry (RCA) and Fuel Material (FMA) groups. The main fields investigated by this department are the behavior of materials under radiations and new nuclear fuels.

The context

Thorium dioxide as an alternative nuclear fuel to uranium dioxide is gaining more and more interest. Thorium dioxide is indeed very suitable as fuel matrix due to its chemical inertness, high crystal lattice stability and extremely high melting temperature (ca. 3300 °C). During its irradiation in a nuclear reactor, lower amounts of minor actinides are formed compared to uranium dioxide. However, because ^{232}Th (the isotopic composition of natural thorium is almost exclusively ^{232}Th) is not a fissile but a fertile isotope, a fissile component such as ^{235}U or Pu (containing fissile ^{239}Pu and ^{241}Pu) needs to be added.

An important aspect in fuel production is the recycling of scrap produced throughout the total production process. Origins of scrap are fuel pellets (fig. 3) discarded during quality control and powder dust from the grinding step. A viable manufacturing route has to optimize the recycling of these losses back into the fuel fabrication process. For uranium dioxide fuel fabrication, this is easily done by converting UO_2 into U_3O_8 , which can be reinserted in the UO_2 feed powders. For thorium dioxide, this is much more complicated due to the physicochemical inertness of thorium dioxide. Thermal redox reactions are not possible due to the fixed 4+ valence state of thorium so that other conversion processes are to be considered.



Fig 3: Thorium dioxide pellets

The internship

Besides the scrap recycling, thoria needs to be dissolved correctly for analysis purposes. Previous dissolution attempts performed at SCK-CEN before this internship showed an important deviation between the thorium quantity before and after the dissolution.

The purpose of my internship was to find a better method to dissolve the thorium dioxide, both from the yield and the safety points of view.

It consisted in three distinct tasks. The first one was the bibliographic study, in order to learn what had already been tried in the past around the world. The best procedures were selected, adjusted and experimentally tested. Finally the results were analyzed by gamma spectrometry and ICP-MS in order to better adjust the parameters and optimize the dissolution process.

1. Work preparation

Bibliographic study

The first weeks of the internship were dedicated to the bibliographic study in order to have an overview of the work which has already been done on that topic. Many books and scientific papers were found on the internet, by using some online tools like "Web of Science" or "Google Scholar", other documents were also available directly in the research center. The most important bibliographic source concerning the thorium dissolution is the Oak Ridge National Laboratory, USA (ORNL) which conducted a lot of research between the 1950's and the 1970's on thoria based fuels. A lot of papers were also written by the Bhabha Atomic Research Center, India (BARC) and the National Institute for Materials Science, Japan (NIMS). Lots of practical advices were also given by some colleagues here in SCK-CEN who have worked on (Pu-Th)O₂ based nuclear fuels dissolution.

According to the report on ORNL THOREX process development of R. H. Rainey & J. G. Moore, the most efficient thorium oxide dissolution experiments were conducted using a solution of nitric acid and hydrofluoric acid. Many experiments were indeed conducted with various acid solutions (for instance hydrochloric acid and sulfuric acid) but those had a really low yield. Moreover the use of nitric acid without adding HF doesn't give good results, although quantitative results are quite different from one lab to another. [2]

It was decided to investigate in that way in order to find the best parameters but it was also chosen to try to find an alternative to the use of HF in order to lower the chemical waste burden and increase the safety of the experiments and also avoiding interferences in ICP-MS due to fluorine.

Concerning the first of those ways, the hydrofluoric acid concentration has to be extremely low. HF only has here a catalyst role and its concentration should not exceed 0.035mol/L according to Takeji Takeuchi. [3]

The reaction which occurs is: $\text{ThO}_2 + 4 \text{HNO}_3 = \text{Th}(\text{NO}_3)_4 + 2 \text{H}_2\text{O}$ [6]

The nitric acid concentration used in those experiments was always 13mol/L, we will see later in the reaction mechanisms that thorium dioxide first needs to react with water to begin the reaction, so pure nitric acid isn't the best solution.

It is important to mention that thorium nitrate has a high solubility in nitric acid solutions. It goes from around 200 g/L in 8 mol/L nitric acid up to 400 g/L in 13 mol/L nitric acid.[6]

Concerning the impact of temperature on the reaction, the report on ORNL THOREX process development, indicate that the more you approach the boiling point, the more effective is the dissolution. That's why during the experiment, heating will always be set over the boiling point in order to ensure the boiling (the solution itself can't overpass this point as a liquid).[2]

According to the ORNL report 2519 written by W. D. Bond, one last kinetic parameter is the state of the thorium dioxide before the experiment. Powders are indeed the easiest to dissolve, due to their very high contact surface. It's a bit more difficult to dissolve a non-sintered pellet (it has less contact surface than the powder but there is a lot of porosities), and even more to dissolve a sintered pellet because most of the pores are closed due to the sintering process. [4]

One can notice that there are a lot of sources in the literature where aluminum nitrate is added to the solution. According to M. Akabori, the purpose is to avoid the corrosion of the cladding and the stainless steel vessels (usually used in the fuel reprocessing plants) caused by HF. Aluminum nitrate is also used as salting-out agent. Glassware was used in this work, that's why this aluminum nitrate wasn't required. [5]

Analysis methods

In order to measure the yield of the dissolution, two methods were used: Gamma Spectrometry (GS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The principle of GS (fig. 4) is the following: Some radioactive nuclides emit gamma-rays with a certain energy and intensity. When the sample is placed in the spectrometer, those gamma-rays are absorbed by a crystal (here: high purity germanium), converted to pulses and analyzed by electronics in order to distribute them depending on their energy to create the gamma-spectrum of the sample. The peaks on the spectrum show the presence of some particular nuclides in the sample, more particularly daughter nuclides of the nuclide we are interested in. By knowing the equilibrium state of the isotope with its daughters, we can determine its own activity. Finally, by comparing the determined activity to the specific activity of the nuclide we are able to find out the mass of thorium in the sample.



Fig 4: Gamma Spectrometer



Fig 5: ICP Mass Spectrometer

Concerning the ICP-MS (fig. 5), the sample is atomized and ionized by being injected in argon plasma. The application of an electromagnetic field by means of a quadrupole allows to filter and detect separately the various ions, depending on their mass/charge ratio. One particularity of this method is that the sample needs to be highly diluted, in order to reach a concentration around some parts per billion (ppb).

One can notice that ICP-MS has the advantage of being highly reliable (provided that dilution and tuning are correctly done), whereas measurement uncertainty of GS depends on the count rate, which can be a problem, as we'll see later. ICP-MS also has the advantage of an extremely low detection limit, it can indeed detect up to some ppb of the element. Contrary to it, GS need a certain level of emissions to work properly (especially the detector used for this work which isn't a low count rate detector). On the other hand, GS can support high levels of emissions and analysis of the sample as such, whereas ICP-MS which requires high dilutions of the sample.

The two methods were adapted for this work but GS was preferred due to its particular ease of use. ICP-MS indeed requires high dilution rates which generate a lot of waste.

Powder purity analysis

In order for the results to be relevant, one has to know the purity level of the powder which is used in the dissolution tests. An ICP-MS analysis was conducted in order to determine the mass percentage of impurities. It revealed the existence of some impurities in the powder like zirconium, sulfur or silicon). What we need to know is the speciation of these impurities (which bounds does they have with other species) in order to evaluate their actual mass percentage.

In order to investigate this, a powder sample from the same batch was submitted to a X-ray diffraction (XRD) test. The sample first needed to be prepared by putting the powder into the sample holder and flattening its surface. Then the holder was placed in the diffractometer (fig. 6) which works like this: The X-ray is focused on the sample at some angle θ , while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. The incident angle is then increased over time while the detector angle always remains 2θ above the source path. X-rays are partially scattered by atoms when they strike the surface. The part of the X-ray that is not scattered goes through to the next layer of atoms, where it is again partially scattered. It leads to a diffraction pattern, depending on the phase differences between the scattered beams.



Fig 6: X-Ray Diffractometer

The XRD analysis revealed some impurities in the powder among these some seem to correspond to thorium sulfate and thorium silicate. Yet the diffractometer is not enough sensitive to identify and quantify with certitude those diffraction peaks. Silicon elemental analysis should be made on the basis of XRD results.

As far as we can't determine those impurity levels for now, the conclusions of the experiments will have to take this into account. The dissolution efficiency may be underestimated since the powder may not be pure from the beginning.

Safety trainings

As can be imagined, the safety rules in a nuclear center are very strict. Actually, safety trainings took a major part of my time during the first weeks. In the first place I had to watch some explicative movies and I had to pass a test concerning those movies before even entering into the center. Once this was done, I received again some trainings in order to gain access to the labs (for instance about the procedures in case of contamination, the nuclear material accountancy...etc, see the extract of the guidance plan in annex 1) including a complete medical examination and an anthropogammametry in order to know the natural radiation background of my body.

Otherwise, it is mandatory to wear a passive dosimeter (fig. 7) that you change every month in order to record the integrated radiation dose you were exposed to during that month. When you enter the controlled area, you have to add to this an active electronic dosimeter which alerts you if the dose rate is higher than a certain threshold level.



Fig 7: Passive dosimeters

I also received some training about the use of hazardous substances such as concentrated acids and especially hydrofluoric acid which requires some particular precautions.

All of this was necessary to be able to begin the experiments.

2. Dissolution experiments

2.1 Overview

After the bibliographic study, two ways of investigation were selected. On the one hand, it was tried to find an alternative to the use of hydrofluoric acid in order to lower the chemical waste, and some corrosion issues. On the other hand, it was tried to dissolve the thorium dioxide powder with a solution of nitric acid and hydrofluoric acid in order to have the highest possible dissolution yield. For each experiment, a gamma-spectrometry sample was made in order to measure the amount of thorium dissolved in the solution, and deduce the dissolution yield.

All of the thorium dioxide samples come from the same batch, a list of the used equipment can be found in annex 3.

2.2 Experiments without HF

2.2.1 Dissolution in nitric acid

As a first try, nitric acid without hydrofluoric acid was preferred in order to have a benchmark of the dissolution efficiency. A reflux setup was built in order to allow the solution to boil without losing any volume. The acid was diluted instead of using pure acid for the reason explained in the first part of this report.

The first step of the experiment was to fill a risk assessment sheet (annex 2) where the whole experiment had to be described, including the chemical species and their risks, the equipment which was going to be used, and also the risks related to radionuclides. Once it was finished, it needed to be reviewed by my mentor, the laboratory responsible and the head of the expert group. The first execution was followed up by a health physics agent, later repetitions were performed autonomously.

Then a new batch of thorium oxide had to be created from the existing reserves. It included two steps: The powder weighing and the accountancy update. First the existing batch has been taken in the storage and put in a fume hood, once the contamination had been checked, the container was opened and the powder was weighed on an analytical balance and transferred into a small glass container. After that, the accountancy file needed to be updated with the creation of the new batch.

Finally, a transfer bon was needed to move the powder sample from the weighing lab to the experiment lab. When the transfer was allowed, the glass container has been placed in an aluminum container (fig. 8) which needed to be checked by a health physics agent.

Now that the thorium oxide powder was in the fume hood, the first experiment could begin.

The nitric acid solution was prepared by diluting 25.2 mL of 65% nitric acid in 2.5 mL of milliQ water, which gave 27.7 mL of a 13.09 mol/L nitric acid solution.

0.5 g of the $^{232}\text{ThO}_2$ powder (0.44 g of Th-232) was put in 25 mL of the previous nitric acid solution in a round-bottom flask which was heated under reflux (fig. 9) at 121°C for 32 h (as it's unsafe to heat unsupervised over night, it was heated during 4 consecutive working days). Some pH paper was placed at the output of the condenser in order to control its outcome.



Fig 8: Transport Container



Fig 9: Dissolution setup

One unexpected problem was that the solution wasn't boiling at all even with the heating mantle set to the maximum temperature (450°C). The other issue was the escape of nitrogen oxides (orange fumes) from the condenser, even with the minimum cooling temperature. From this point, other equipment such as a longer condenser to improve condensation and also a new heating mantle with a better fitting round-bottom flask were asked for.

Despite those problems, it was chosen to perform a gamma spectrometry analysis, so the sample had to be prepared. By visual inspection it was found that the dissolution efficiency was clearly very bad, since there was still a lot of powder in suspension in the solution. Therefore the mixture was filtered with a Büchner funnel. The gamma spectrometry can't indeed differentiate the thorium from the solution and the thorium from the powder in suspension, it would invalidate the measurements. Once the filtration was complete, 20 mL of the solution was transferred into a GS tube (fig. 10) and the measurement was done over a whole week-end.



Fig 10: 20mL Gamma-spectrometry tube

The GS analysis gave the following results:

Table 1: GS results of experiment 1 (54000 s)

Nuclide	Activity (Bq/mL)	Uncertainty (2s)
Bi 212	10.3	30%
Ti 208	3.3	15%

Bi 212 and Ti 208 are both daughter nuclides of thorium 232. By using the databases on nucleonica.com, it was possible to determine the activity of thorium 232, with which they were in equilibrium, which was 10.8 Bq/mL. The activity of thorium in the whole solution was calculated by multiplying by its total volume. Knowing that the specific activity of Th-232 is 4050 Bq/g, the activity concentration had to be divided by this value to find that there was 0,066 g (+/- 0,02 g) of Th-232 dissolved in the solution.

Knowing that 0.44 g of Th-232 was introduced into the solution, we concluded that **the dissolution yield was here 15% with 3% of absolute (2 sigma) uncertainty.**

This is a low yield but it's within the reported yield range for dissolution in only nitric acid. Moreover, one can notice that some sources in the literature consider the thorium as insoluble at all in nitric acid.

2.2.2 Dissolution in nitric acid in a teflon beaker

On the advice of a colleague with experience in dissolution experiments, the second experiment that was performed was still without hydrofluoric acid but this time the dissolution took place in a teflon beaker instead of in glass equipment. Since the purpose of adding HF in the solution is to use the fluor ions as a catalyst, it was thought that it may be possible to obtain this effect by taking benefit from the surface fluorine on the beaker walls since teflon is actually Polytetrafluorethylene (PTFE).

For this experiment, it was planned to re-use the thorium powder left from the first experiment. All that was needed was indeed a qualitative result (just to see if it works), and it allows to lower the amounts of nuclear waste, which are expensive.

Approximately 0.4 g of thoria powder (0.35 g of Th-232) left from the previous experiment were dissolved in 20 mL of 65% nitric acid in a PTFE beaker. It was heated with a hot plate with magnetic stirring (fig. 11). The beaker was covered to avoid projections.

Since there was no reflux, the nitric acid was evaporating little by little so 10 mL of 65% nitric acid had to be added every day into the beaker in order to compensate this evaporation (it's not a problem since the thorium does not evaporate).

Since the solution had a milky aspect, it had to be filtered with a Büchner funnel similar to the first experiment. The filtered solution was then diluted in 50 mL of 2 mol/L nitric acid.

A GS analysis was then made on a 20 mL sample which was analyzed for 54000 s.



Fig 11: PTFE beaker on a hot plate

Here are the results of the gamma-spectrometry:

Table 2: GS results of experiment 2 (54000 s)

Nuclide	Activity (Bq/mL)	Uncertainty (2s)
Ac 228	0.64	20%
Bi 212	6.0	6%
Tl 208	2.3	15%
Pb 212	2.1	15%

At first sight, the activity values may seem low compared to the previous experiment but one has to take the dilution of the sample into account.

Activities of the different nuclides lead to a Th-232 activity of 6.3 Bq/mL. Knowing that the solution was containing 70mL and that the Th-232 specific activity is 4050 Bq/g, there was 0.1 g of Th-232 among the 0.31 g inserted which means **a dissolution yield of 32% with 2% absolute uncertainty**. It was slightly better than the first experiment, so the teflon seemed to have an impact on the dissolution.

2.2.3 Further investigations

Since PTFE is not the only fluoropolymer, the same experiment was tried with this time PFA instead of a PTFE beaker (PFA beaker are often used for ultrasonic digestion).

The nitric acid solution was prepared by diluting 10 mL of 65% nitric acid in 10 mL of MilliQ water, which gave 20 mL of a 7.2 mol/L nitric acid solution.

0.25 g of thoria powder (0.22 g of Th-232) was brought into the 20 mL nitric acid solution and the solution was heated during 14 h on a hot place.

Since the dissolution was visually not complete, the solution was filtered with a Büchner funnel. The 10.58 mL remaining (determined by weighing) were put into a gamma-spectrometry vial, and completed up to 20 mL with 9.42mL of MilliQ water. It was measured for 54000 s.

Here are the results of the gamma-spectrometry:

Table 3: GS results of experiment 2-B (54000 s)

Nuclide	Activity (Bq/ml)	Uncertainty (2s)
Bi-212	5.1	10%
Tl-208	1.6	15%
Pb-212	4.6	8%
Ra-224	4.0	10%

Activities of the different nuclides lead to a Th-232 activity of 4.8 Bq/mL. Knowing that the solution was containing 70mL and that the Th-232 specific activity is 4050 Bq/g, there was 0.024 g of Th-232 among the 0.22 g inserted which means **a dissolution yield of 11% with 1% absolute uncertainty**.

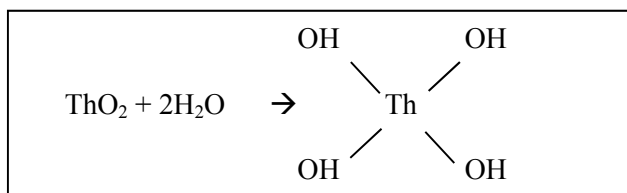
The dissolution yield is clearly better with PTFE than with PFA beaker. It may come from the higher chemical inertness of PFA (it has indeed a higher chain entanglement than PTFE). It would be interesting to further investigate on this path, for instance by trying the same experiment with other fluoropolymers to find an alternative to the use of HF. It would be relevant to make some dissolution experiments with fluoropolymer beads in a glass beaker instead of changing the beaker.

2.3 Experiments with HF

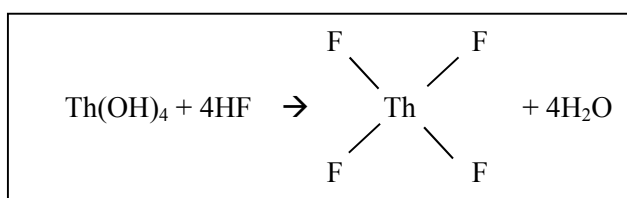
2.3.1 Dissolution in nitric acid with HF

The point here was to reproduce the first experiment with the heating under reflux, with adding some drops of HF into the solution in order to catalyze the dissolution of thoria. According to T. Takeuchi, here is the mechanism of the expected reaction:[3]

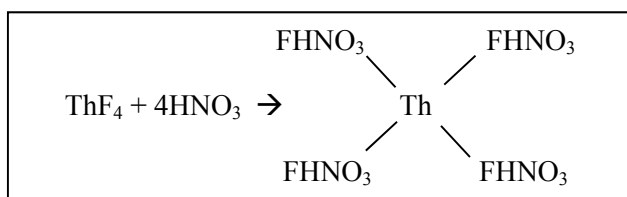
In the first place, thorium dioxide reacts with water to form hydroxyl complexes.



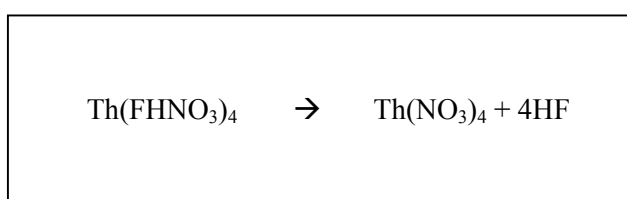
That complex then adsorbs the fluorine from HF to form a fluoride.



That fluoride adsorbs a nitric acid molecule.



Thorium nitrate ion is finally formed by rejecting the HF molecule.



As we can notice, HF is here only a catalyst, it's not consumed during the reaction, that's why a very little quantity is enough to completely change the reaction efficiency. According to the work of Takeji Takeuchi on dissolution kinetics, its optimal concentration is around 0,035mol/L.[3]

After the problems encountered during the first experiment, new equipment was received, especially a longer condenser and a new heating mantle better fitted to the round-bottom flask. To be sure, the equipment was tested with cold acid (without radioactive material) and it boiled easily.

The nitric acid solution was prepared by diluting 55.6 mL of 65% nitric acid into 44.4 mL of MilliQ water, which gave 100 mL of a 8.01 mol/L nitric acid solution.

The same experiment as the first one was performed but just after putting the thorium dioxide powder in 45 mL of the previous nitric acid, 60 μ L of HF were added into it (HF is at so low concentration that using it in normal borosilicate glassware isn't a problem) (fig. 12).

It was planned to heat it under reflux for 32 h like in the first experiment, but after 1h the powder was visually already completely dissolved. So it cooled down and the gamma sample was made after 3 h. In order to be sure, it was re-heated and a second sample was made after 10 h.

Once again unexpected experimental outcome appeared: there was a re-precipitation during the night. However, the solubility limit of thorium nitrate in 8 mol/L nitric acid is much higher than what was used here (around 250 g/L) [6], the nature of these precipitates is consequently unknown. One hypothesis could be that those precipitates are based on impurities. A possibility to figure it out would be to remake this experiment, filter the solution to have the precipitate, and then dissolve it in a known solution to analyse it via ICP-MS.

In order to avoid this phenomenon, the solution was diluted with more nitric acid to obtain a higher volume, which succeeded. Nevertheless, the precipitate had already stucked on the glass and it was really complicated to re-dissolve. It took a lot of efforts to clean the glass but it succeeded by eroding the white marks (fig. 13) with a magnetic stirrer.



Fig 12: Reflux setup of experiment 3



Fig 13: Re-precipitation marks on the glass

Two gamma-spectrometry samples were prepared, one after 1 h (sample A) of heating and the other after 7 h (sample B). For both samples, 5 mL of the solution was transferred into a gamma-spectrometry vial which was completed up to 20 mL with 15 mL of 2% nitric acid which was analyzed for 54000 s.

Here are the results of those two sample measurements:

Table 3: GS results of experiment 3 (54000 s)

A	Bq/ml	2s
Ac-228	4.5	20%
Bi-212	4.2	6%
Tl-208	1.7	15%
Pb-212	4.2	15%
Ra-224	4.6	15%

B	Bq/ml	2s
Ac-228	4.7	12%
Bi-212	4.1	30%
Tl-208	1.6	15%
Pb-212	4.4	15%
Ra-224	4.3	15%

Sample A showed a Th-232 activity of 4.6 Bq/mL, but since the sample was diluted, the activity was actually 18.4 Bq/mL, which gave 828 Bq for the whole solution. **A dissolution yield of 93% with a 6% absolute uncertainty was found.**

Sample B showed a Th-232 activity of 4.8 Bq/mL, but since the sample was diluted, the activity was actually 19.2 Bq/mL, which gave 864 Bq for the whole solution. **A dissolution yield of 97% with a 12% absolute uncertainty was found.**

The uncertainties are really high because the dilution rate was so high. One can also notice that the re-precipitation may have already begun when the GS samples were made.

The problem here is that we had to dilute a lot to avoid the re-precipitation. As a consequence, an increase of uncertainty was caused by the dilution, which caused a lower count rate.

In order to get more results about this dissolution, an ICP-MS measurement was performed. It first needed to dilute the sample further down, in order to reach the optimal detection range of the spectrometer. For the detector to be efficient, the mass of the element we are looking to analyze has to be in the ppb range. That's why the initial sample had to be diluted in 2% HNO₃ by a factor of 10⁵ before the analysis. The dilution was made in two steps to avoid creating too much liquid wastes.

A blank solution sample was also made in order to calibrate at best the spectrometer, it consisted in the same protocol, only with cold nitric acid without thorium).

Table 4: Different dilution steps for ICP-MS analysis

Mother Solution	
Thorium mass (g)	0.22
Liquid volume (mL)	80
Thorium concentration (ppb)	2750000

Intermediate Solution	
Mother sample mass (g)	1.31
Total mass (g)	927.05
Thorium concentration (ppb)	3886

Sample	
Intermediate sample mass (g)	0.1
Total mass (g)	10.29
Thorium concentration (ppb)	37.76

Here are the results of the measurement: In the mother solution (before any dilution) there was 2610 (+/-260) $\mu\text{g/g}$ of Th-232.

Since 0.22 g of Th-232 was introduced in 80mL of solution, Th-232 was at a concentration of 2750 ppm. By dividing 2610 by 2750, we obtain 95% which is the fraction of the initial thorium dissolved in the solution. **The dissolution yield of 95% (+/-10%) was found.**

Another solution had to be found in order to lower this uncertainty. That's why the sample B was also measured by low activity gamma-spectrometry. It gave the following results:

Table 5: Low activity gamma-spectrometry results

Nuclide	Activity	Uncert.	Unit	Nuclide	Activity	Uncert.	Unit
²⁰⁸ Tl	1.77	0.14	Bq/mL	²¹² Bi	4.91	0.35	Bq/mL
²¹² Pb	5.0	0.7	Bq/mL	²²⁴ Ra	5.1	0.8	Bq/mL
²²⁸ Ac	5.01	0.32	Bq/mL				

The sample showed a Th-232 activity of 5.1 Bq/mL, but since the sample was diluted, the activity was actually 20.4 Bq/mL, which gave 918 Bq for the whole solution. **A dissolution yield of 103% with a 6% absolute uncertainty was found.**

2.3.2 Dissolution in low concentration nitric acid with HF

In order to investigate on the effects of nitric acid concentration, it was then tried to repeat the dissolution with a much lower nitric acid concentration. It actually could affect the kinetics of the dissolution reaction, but it could solve the re-precipitation issue if this precipitate is more soluble in water

A 0.3 mol/L nitric acid solution was prepared by diluting 0.9 mL of the 65% nitric acid in 39.1 mL of MilliQ water.

The same as the previous experiment was tried with this time only 35 mL of the 0.3 mol/L nitric acid solution and 30 μ L of HF. 0.25 g of thoria powder (0.22 g of Th-232) was brought into the solution. The solution was heated under reflux for 8 h. As expected, the reaction rate was clearly lower (in the previous experiment, all the powder had visually disappeared after 1h, it took five times longer here) but we got absolutely no re-precipitation. The gamma-spectrometry sample was prepared after 8h of heating at boiling point, it was analyzed for 54000 s.

Here are the results of the gamma-spectrometry measurement:

Table 6: GS results of experiment 4 (54000s)

Nuclide	Activity (Bq/ml)	Uncertainty (2s)
Ac-228	23.9	10%
Bi-212	22.6	15%
Tl-208	7.5	16%
Pb-212	22.1	8%
Ra-224	22.5	10%

This sample showed a Th-232 activity of 23,7 Bq/mL, which gave 828 Bq for the whole solution. **A dissolution yield of 93% with a 9% absolute uncertainty was found.**

The uncertainty was still quite high but it showed that this dissolution is very effective even at low HNO₃ concentrations.

Conclusion

The purpose of the internship was to find a better method to dissolve the thorium dioxide, both from the yield and the waste points of view.

Concerning the dissolution yield, the uncertainties are too high to confirm or not the deviation from quantitative dissolution which was already experienced by researchers of the RCA group before this internship. However, the low activity gamma-spectrometry measurement gave some really good results (between 97% and 100% dissolution yield) and further measurements should be done in the future in order to confirm this yield. I would also recommend to perform a gravimetric ICP-MS instead of a volumetric one in order to reduce by half the uncertainty on the measurement. Some silicon elemental analysis should be made on the basis of XRD results to finally determine at what level is the thoria powder pure.

Otherwise, some interesting discoveries were made concerning the safety improvement and the waste (and costs) lowering. It was indeed shown that really low concentrations of acid are quite enough to dissolve properly the thoria powder, even if the kinetics aren't adapted to sintered pellets. Low nitric acid concentration is also important to avoid corrosion issues in hot cells. It remains to be investigated if we can find a compromise at medium concentrations to have the benefits from both kinetics and low nitric acid concentration. Moreover, it was also shown that a teflon beaker can be used as a catalyst for the reaction instead of HF: The results are not as good but there is a certain impact. It was shown that PFA is less efficient than PTFE, that's why it could be interesting to further investigate on this way by testing other fluoropolymers and comparing old and new beakers.

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Annex 1 – Extract of the guidance plan



GUIDANCE PLAN (I)

Naam betrokkene : Anton Schneider Expertisegroep: RCA	Functie: internship Naam mentor: Karen Van Hecke/Simone Cagno
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Training needs	When: Periode van – tot –	Who: New collaborator + mentor, member of guidance team or others ...	Date: Finished or adapted:
<ul style="list-style-type: none"> • Initiation ⇒ Safety quiz 	Start internship (T0)	Toegangscontrole	
<ul style="list-style-type: none"> • Training for independent access to the controlled area in the SCH building ⇒ training alarms Pu-wing (incl. guided tour in the controlled area) ⇒ reading of safety procedures SCH (PV.SCH.030, PV.SCH.031, PV.SCH.0040) 	T0 + 2 weeks	E. Aegten/S. Cuyvers Self study Anton	
<ul style="list-style-type: none"> • General training for safe working with radioactive substances ⇒ Self study course on radiation protection ⇒ Course on working with open radioactive sources ⇒ introduction bookkeeping of fissile/fertile materials & waste procedures ⇒ practical training in the lab 	T0 + 3 weeks T0 + 6 weeks	Anton Karen / Simone Els Verheyen/ Wendy Mentens Karen/ Simone/ Vanaken	
<ul style="list-style-type: none"> • General training for safe working with chemical hazards ⇒ Course on working with hazardous substances like acids (incl. HF) ⇒ Practical training in the lab 	T0 + 3 weeks T0 + 6 weeks	Liliane Vos Karen/ Simone Karen/ Simone/ Vanaken	

Annex 2 – Extracts of a risk assessment

Risk assessment for experiments as part of an FMA research project

Reference number: ThO2-dissolution_method 1/RA/2015-XXXX/1.0

Date: 11-05-2015

1. Identification of the user

Name: Anton SCHNEIDER

Phone number: 014 33 32 61

Project leader: K. Van Hecke and S. Cagno

Project WBS: NRCA00000-03

Expert Group: RCA

Head of Expert Group: Thomas Cardinaels

Institute: NMS

2. Identification of the experiment

Title: Thoria powder dissolution in nitric acid

Start date: 28/05/2015

End date: 02/06/2015

- (N) New experiment
 (E) Existing experiment without prior RA
 (M) Modification/expansion of an existing experiment with prior RA: (enter reference number)

This modification concerns:

- Persons
 Rooms of the experiment
 Chemicals
 Radioactive materials
 Prolongation
 Other: (describe)

(C) Experiment in the context of existing activity: (enter reference number)

(T) Continuous tests (unattended activity within or outside working hours)

Table 1. Description of the chemicals used (or formed).*

Product name	Cas number	Chemical formula	Physical state	Quantity used	Concentration used	Chemical hazard class**
1. nitric acid	7697-37-2	HNO ₃	liquid	25mL	concentrated	E3
2. thorium dioxide	1314-20-1	ThO ₂	solid	0,50g	pure	E4
3. thorium nitrate	13823-29-5	Th(NO ₃) ₄	aqueous	0,91g	7,5e-2 M	E4
4.						

*If possible, replace highly hazardous products or processes by less hazardous ones!

** E4: very hazardous, E3: hazardous, E2: mildly hazardous, E1: barely hazardous; if the chemical hazard class is unknown, state why you choose a certain class for a certain compound.

3. Description of experiment and risk assessment

Table 2. Description of handling and techniques

Number* of sub-experiment	Description of handling and techniques	Equipment used	Numbers** of chemicals used/formed	Supervision required
1.	Dilution of 25mL of concentrated nitric acid in 2,50mL of water in a 100mL beaker in order to prepare 27,50mL of a 13M nitric acid solution	100mL beaker, 25mL pipette, propipette, digital micropipette	1	<input checked="" type="checkbox"/>
2.	Transfer of 25mL of the 13M nitric acid solution with a 25mL volumetric pipette in a 250mL round-bottom flask	25mL pipette, propipette, 250mL round-bottom flask	1	<input checked="" type="checkbox"/>
3.	Transfer of the thorium oxide powder from the sample container to the funnel with a spatula	Spatula, glass funnel, analytical balance	2	<input checked="" type="checkbox"/>
4.	Addition of the weighed ThO ₂ powder to the round-bottom flask	Spatula, 250mL round-bottom flask	1 2	<input checked="" type="checkbox"/>
5.	Heating under reflux of the mixture during 4x8 hours at 121°C (heating during the work hours, cooling during the night)	250mL round-bottom flask, flask heater, condenser, water chiller	1 2 3	<input checked="" type="checkbox"/>
6.	Transfer of 20mL of the solution in a gamma-spectrometry tube with a 10mL volumetric pipette	Gamma-spec tube, 10mL volumetric pipette, propipette	1 3	<input checked="" type="checkbox"/>
7.	Analysis by Gamma-spectrometry	gamma-spec tube	1 3	<input checked="" type="checkbox"/>
8.	A 2% nitric acid solution is prepared with 5mL of pure nitric acid and 245mL of MilliQ water in a volumetric flask.	Digital micropipette, 250mL volumetric flask	1	<input checked="" type="checkbox"/>
9.	The sample is diluted by 2000 times by adding 100µg of it into 200mg of the 2% nitric acid solution with a digital micropipette	Digital micropipette, 250mL beaker	1 3	<input checked="" type="checkbox"/>
10.	Transfer of 10mL of the solution in a ICP-MS tube with a digital micropipette	Digital micropipette, ICP-MS tube	1 3	<input checked="" type="checkbox"/>
11.	Analysis by ICP-MS	ICP-MS tube	1 3	<input checked="" type="checkbox"/>

* Number of the subactivity as indicated under "Location of experiment".

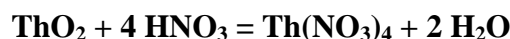
** Number of the chemicals as indicated in "Description of the chemicals used (or formed)".

Frequency of the experiment:

Daily Weekly Monthly Less than monthly Unique

Table 3. Detailed information about the experiment (e.g. reaction schemes, literature data,...).

This experiment takes inspiration in the Thorex process: The purpose is the dissolution of the thorium dioxide by the nitric acid. The thorium is dissolved as thorium nitrate as shown in the following equation:



Here is an overview of the experimental work:

-Lab116 We dilute the concentrated nitric acid to a 13M solution by mixing 25mL of the concentrated nitric acid with 2,50mL of water in a 100mL beaker, using volumetric pipettes and a digital micropipette.

-Lab116 The dissolution will take place in a 250mL round-bottom flask (in order to heat the mixture) so we put 25mL of the 13M nitric acid solution from the beaker to the round-bottom flask with a 25mL volumetric pipette.

-Lab45 The Thorium dioxide powder must be transferred from the sample container to a weighing funnel which is on a balance. We have to transfer 0,50g of it.

Transfert of the powder from lab 45 to lab 116

-Lab116In order to begin the dissolution, we add the weighted thorium dioxide powder in the round-bottom flask.

-Lab116As soon as the mixture is in the flask, we heat it under reflux with a flask heater and a column condenser (with a water chiller) for 4 times 8 hours (4 working days, cooling during the nights) at 121°C.

-Lab116After that, we transfer 20mL of the solution in a gamma-spectrometry tube with a 10mL volumetric pipette (then we close the tube and write the information on it).

Transfert of the solution from lab 116 to lab 73

-Lab73 The sample is ready for gamma-spectrometry analysis, it will be brought and stored in the gamma-spectroscopy laboratory.

Transfert of the solution from lab 73 to lab 116

-Lab116 Preparation of a 2% nitric acid solution by adding 5mL of pure nitric acid in 245mL of MilliQ water in a 250mL volumetric flask with a micropipette.

-Lab116 The sample is diluted by adding 100µg (73µL) of it in 200mg (200mL) of the 2% nitric acid solution in a beaker, in order to prepare it for the ICP-MS analysis.

-Lab116 10mL of the sample is transferred in a ICP-MS tube with a 10mL volumetric pipette and the tube is closed and identified.

Transfert of the solution from lab 116 to lab 56

-Lab56 The sample is ready for ICP-MS analysis. It is stored in the laboratory 56.

Transfert of the solution from lab 56 to lab 116

-Lab116 After the ICP-MS analysis, the sample goes in a 10L container of BelgoProcess as a liquid inorganic nuclear waste.

-Lab116 The 5mL left of the solution are liquid inorganic nuclear wastes, they must be stored in the BelgoProcess container.

-Lab 116 About 5,77mL left of the 13M nitric acid are chemical wastes.

-Lab 116 About 33mL left of the 0,28M nitric acid are chemical wastes.

Before handling chemicals, identify the associated risks (R or H and S or P phrases). These can be found in the Materials Safety Data Sheet supplied by the manufacturer. Indicate the hazards of the products in table 6.

Table 4. Hazards associated with the chemicals

Number of chemical as indicated in "Description of the chemicals used (or formed)"	1	2	3				
Explosion and fire hazard							
Extremely or highly flammable (H220, H222, H224, H228, H225) / (R11, R12)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Flammable gas, aerosol, solid (H221, H223, H228)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Self-heating, might catch fire (H251, H252)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Fire, explosive – projection hazard (H204, H202, H203)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Explosive (EUH001, EUH006, H200, H201) / (R1, R2, R3, R5) + combustible materials (H271, H272) / (R9)	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Flammable vapour-air mixture (EUH018)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Explosive peroxides (EUH019)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Incompatible with water (EUH014, H260) / (R14, R15)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Catches fire spontaneously if exposed to air (H250)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Explosive + metals (R4) + O ₂ (R6)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Incompatible with oxidizing materials (R16)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Unstable product (R17, R18, R19)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Acute health hazard							
Highly toxic (H300, H330, H310) / (R26, R27, R28) + acid (EUH032) / (R32)	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Toxic (H311, H331, EUH070) / (R23, R24) + water (EUH029) / (R29) + acid (EUH031) / (R31)	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Severe burns (H314) / (R35)	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Long-term health hazard							
Carcinogenic or possible carcinogenic (H350, H350i, H351) / (R40, R45, R49)	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Teratogenic (H361d, H360d) / (R61, R63) and harmful to fertility (H361f, H360f) / (R60, R62)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Mutagenic (H341, H340) / (R46)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Damage to certain organs (H371, H372, H370) through prolonged or repeated exposure (H373)	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Severe irreversible effects (possible) (R39, R68), health damage after prolonged exposure (R48)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Table 6. Practical information about handling the RA substances.

Nr. of substance	1.	2.	3.
Proximity of user (m)	0,3	0,3	
Duration of exposure (h)	1	0	
Total received dose (μSv)	5e-3	0	
Location for handling*	Fume Hood	Fume Hood	
Additional monitoring required**	<input checked="" type="checkbox"/> AD <input type="checkbox"/> WD <input type="checkbox"/> FD	<input checked="" type="checkbox"/> AD <input type="checkbox"/> WD <input type="checkbox"/> FD	<input type="checkbox"/> AD <input type="checkbox"/> WD <input type="checkbox"/> FD
Additional shielding required	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Transport of source required	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Transferbon required	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

* Possible locations: Fume hood, glove box, hot cell.

** AD: Alarm dosimeter, WD: wrist dosimeter, FD: finger dosimeter

Estimated collective dose

Table 7. Calculation for total received dose

(= sum of total received dose per RA substance) 5e-3 μSv
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Standard operating procedures

1. The radiation control supervisor must give permission that the person carrying out the experiment is competent to do so safely.
2. Anyone working in an environment exposed to ionizing radiation has a responsibility to restrict personal exposure as far as reasonably practicable. (ALARA philosophy)
3. Women that are pregnant or breastfeeding are not allowed in the hot lab facilities.
4. Never eat, drink or apply cosmetics when working in the hot lab facilities.
5. Ask approval of the health physics department to enter the labs with a covered wound or skin damage. Persons with open wounds are not allowed to enter the labs.
6. Keep a sensible distance from the source. Use a tool to handle sealed sources that don't have an integral handle. Keep fingers away from the source by using extra-long forceps.
7. Spend as little time as possible near any radioactive source.
8. Use only one source at a time in any one investigation. If the experiment involves comparing two or more sources, only one should be taken from its container at a time.
9. When carrying sources (even in their containers), the handling time should be minimized. Make sure a clear, uncluttered route to the destination is available. Always use an additional container to transport the source.
10. If a source is dropped or spilled, remain calm and alert the radiation control supervisor and/or any nearby personnel. Await the radiation control supervisor for instructions. Prevent that the contamination spreads.
11. The use of gloves is mandatory when working with RA substances.
12. Measure both hands and feet for contamination before leaving the hot lab facilities. Wash hands, even if only sealed sources were used.

5. Chemical waste

Table 8. Type of chemical waste generated.

13M nitric acid solution : 2,50mL

6. Radioactive waste

Table 9. Type of radioactive waste generated.

Liquid radioactive waste:

Thorium nitrate dissolved in nitric acid

- 25mL 13M nitric acid with 0,91g of thorium nitrate in it
- 250mL 0,28M nitric acid with 2,66mg of thorium nitrate in it

Burnable radioactive waste:

Paper

Waste disposal methodology

- Standard
 Non-standard, specify:

Radioactive wastes will have to be neutralised and volume reduced. If large quantities of liquid waste are generated, they have to be collected in a 10L plastic container from BP (BelgoProcess).

All waste has to be collected in the special waste bins dedicated for thorium contaminated waste. When the waste bags will be disposed, they must have a clear labeling that they are thorium contaminated.

Annex 3 – Experimental equipment

Equipment	Exp 1	Exp 2	Exp 3	Exp 4
250mL borosilicate glass round bottom flask (IKA)	X		X	X
Heating mantle with magnetic stirring (Electro-thermal)	X		X	X
Column glass condenser	X		X	X
Water cooler (Thermo Haake K20/DC50)	X		X	X
Teflon beaker (Savillex)		X		
Hot plate with magnetic stirring (IKA)		X		
1-10mL micropipette (Ependorf Research plus)	X	X	X	X
10-100 μ L micropipette (Thermo Finnpiquette)	X	X	X	X
Büchner funnel (Robu filterporosity 4)	X	X		
Analytical balance (Mettler Toledo AT200)	X	X	X	X
Gamma-Spectrometer (Canberra HPGe)	X	X	X	X
ICP Mass Spectrometer (Thermo Xseries 2)			X	