

Characterization of Uranium Residue from Solid Mo-99 Manufacturing Waste and Development of a Recovery Process using Carbonate Solution – 14399

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ABSTRACT

The alkaline dissolution process routinely used in the production of Mo-99 at NTP Radioisotopes SOC Ltd, a subsidiary company of Necsa South Africa, generates an inhomogeneous solid residue that contains enriched uranium, a highly valuable material. This residue (containing fission products and small quantities of transuranium products) is currently stored in stainless steel canisters, while treatment and disposal options are being evaluated. One option under consideration is recovery of the uranium for re-manufacture of uranium/aluminium alloy target plates and immobilization and disposal of the small quantity of radioactive waste that will be generated with this option. Necsa is investigating the feasibility of an alkaline process to recover and purify the uranium to a predetermined standard. Characterization of the residue showed a U(IV) to U(VI) ratio of 15 to 85, with the uranium likely present as a mixture of the compounds UO_2 , UO_3 and $\text{Na}_2\text{U}_2\text{O}_7$. The dominant radionuclide impurity in the residue is Sr-90, followed by Pu-239, Ce-144, Cs-137, Ru-106, Sb-125 and Eu-155. Parameters for a carbonate-based dissolution process have been optimized using simulated unirradiated residue. The optimized dissolution parameters were confirmed on small samples of irradiated residue with decay ages between 5 and 11 years, inside a small experimental hot cell. Complete recovery of uranium from the solid residue was obtained within three successive carbonate/peroxide leaches.

INTRODUCTION

During the early 1990s the South African Nuclear Energy Corporation (Necsa) initiated the production of Mo-99, the mother nuclide of Tc-99m which is one of the most widely used isotopes in nuclear medicine today [1]. Over the last few years NTP Radioisotopes SOC Ltd, a subsidiary company of Necsa, has become one of the largest suppliers of Mo-99 to the world market. During each production run irradiated uranium/aluminium (U/Al) alloy target plates containing enriched uranium are subjected to an alkaline dissolution process followed by the extraction of Mo-99. Historically medium-enriched uranium (46 % U-235) has been used in the target plates, but conversion to LEU-based Mo-99 production started in 2010. During the dissolution process, the precipitated residue still contains enriched uranium which is a valuable asset that should be recovered for re-use. This residue is currently being stored in stainless steel canisters and is considered to be a waste liability.

In 2010, Necsa embarked on a program that focused on the development of a process to recover and purify the commercially valuable enriched uranium contained in the Mo-99 process solid residue. A carbonate dissolution process was selected since it offers significant advantages when compared to the classical acid dissolution route, with its associated problems such as metal corrosion, NO_x gas emissions and release of volatile fission products. An added advantage is that the low solubility of most of the contaminants in the uranium residue in a carbonate medium will ensure that good initial purification can be achieved during the dissolution step.

Mixtures of sodium carbonate and sodium bicarbonate were previously used as a dissolution medium for the recovery of uranium from residue generated in an alkaline based Mo-99 process [2-4]. The influence of different oxidation reagents like Ce^{4+} /ozone and H_2O_2 were tested [3]. The effect of varying the counter cation (NH_4^+ , Na^+ , K^+ , and Rb^+) in carbonate solutions on the dissolution of UO_2 , U_3O_8 , and UO_3 has been investigated [5]. Results indicated that the most rapid dissolution occurs in $(NH_4)_2CO_3$ solutions with H_2O_2 as the oxidant and the dissolution rates decreased in the order: $UO_3 \gg U_3O_8 > UO_2$. This is to be expected since uranium dioxide is insoluble in a carbonate medium; to create a soluble form, UO_2 must be oxidized from U(IV) to the U(VI) oxidation state. Results also indicated that the dissolution rate of UO_2 in 1.0 mol.dm^{-3} $(NH_4)_2CO_3$ increases linearly with H_2O_2 concentrations in the range of 0.05 to 2.0 mol.dm^{-3} . The dissolution rate of UO_2 in 1.0 mol.dm^{-3} $(NH_4)_2CO_3$ / 0.1 mol.dm^{-3} H_2O_2 was also found to increase linearly from 15-60 °C [6].

The effectiveness of ammonium carbonate and hydrogen peroxide as a dissolution medium has been demonstrated in the recovery and decontamination of uranium in irradiated fuel [7]. These studies have indicated that on a 13 g scale more than 98% of the irradiated fuel dissolved, and subsequent expulsion of carbonate from the dissolver solution precipitates more than 95% of plutonium, americium, and curium as well as substantial amounts of fission products thus effectively partitioning the fuel at the dissolution step.

Kim and co-workers [8, 9] have also recently reported on the carbonate leaching of simulated spent fuel containing uranium and sixteen possible contaminants, namely Ce, Gd, La, Nd, Pr, Sm, Eu, Y, Mo, Pd, Ru, Zr, Ba, Sr, Re (as simulant for Tc), and Te. It was shown that only Cs, Tc, Te, and Mo dissolved to any appreciable extent, along with the uranium. The dissolved elements were considered to exist in the forms of Cs^+ , TcO_4^- , $TeO_2(OH)_2^{2-}$, and MoO_4^{2-} in the carbonate solution. The other elements remained undissolved thus affording a good decontamination that can be achieved simultaneously with dissolution. The uranium residue generated in the Mo-99 production process has a different composition to that of spent fuel and is unlikely to contain Cs, Tc, Te, and Mo since these elements would be soluble in the alkaline solution that was used to dissolve the target plates.

The promising literature results reported on the use of ammonium carbonate and hydrogen peroxide as a dissolution medium, have led to the decision to pursue an ammonium carbonate recovery route through further development work. It is important to note that although there is significant literature available on the use of ammonium carbonate and hydrogen peroxide as a leaching solution from spent UO_2 nuclear fuel and uranium ores (especially in-situ leaching of carbonate-containing ores [10]), none of these methods have been applied to the uranium residue that is generated from an alkaline based Mo-99 production process, which is unique in terms of its composition. Both the SIMFUEL tested by Kim and co-workers [8, 9] and the irradiated fuel tested by Soderquist et al. [7] consisted of UO_2 only. The use of ammonium carbonate and hydrogen peroxide as a recovery medium for the uranium residue from the Mo-99 process at Necsa, therefore represents a novel application of this dissolution medium.

An important input into the recovery project is a complete understanding of the constitution of the uranium residue in terms of fission products, chemical impurities and also the oxidation state of the uranium, which requires analytical characterization of this residue. The solid uranium residue generated during alkaline dissolution of the U/Al target plates in the Mo-99 production process has been characterized in terms of:

- Uranium and chemical impurity content and also the oxidation state of the uranium, using residue obtained from dissolution of unirradiated depleted uranium target plates.
- Uranium and chemical impurity content as well as levels of fission and activation products and actinide activity content in irradiated residue with a decay age of between 5 and 11 years.

The dissolution parameters in ammonium carbonate using hydrogen peroxide as an oxidant were optimized using simulated depleted uranium residue and the optimized dissolution parameters were tested on approximately one gram samples of real irradiated residue with decay ages between 5 and 11 years, in a small experimental hot cell facility.

DESCRIPTION OF METHODS, RESULTS AND DISCUSSION

Preparation of Unirradiated Residue

Most of the characterization work and dissolution parameter optimization work was performed using unirradiated uranium residue, since more extensive characterization techniques can be applied using this material as it poses a low radiation hazard. No shielding is required, and all the characterization work could be performed in so-called “blue” radiologically classified laboratories at Ncsa, where a dose limit of 0.025 mSv/h applies. This residue was obtained through dissolution of unirradiated U/Al target plates with the same configuration and dimensions as the irradiated target plates being used in the Mo-99 production process, except that they contain depleted uranium (0.5% U-235) as opposed to enriched uranium. The depleted uranium target plates were dissolved using the same alkaline dissolution procedure that is followed in the Mo-99 production process. The dark grey residue that formed contained most of the uranium in the form of hydrated oxides. Once the residue was dried completely, it was homogenized into a very fine powder for further use.

Characterization of Unirradiated Residue using XRD

An attempt has been made to characterize the uranium compound in the residue using powder X-ray diffraction (XRD) analysis. A Bruker D8 Advance diffractometer with a copper target tube was used, and the 2007 PDF-2 database from the International Centre for Diffraction Data (ICDD) was used for compound identification. Due to the amorphous nature of the residue yielding very low peak intensities, a definitive identification of the uranium compound present in the residue could not be obtained from X-ray diffraction. The XRD pattern was compared with the following compounds from the ICDD database:

$\text{Na}_2\text{U}_2\text{O}_7$, UO, UO_2 , UO_3 , U_3O_8 , Al_4U , Al_3U .

The closest comparison was obtained for the compound $\text{Na}_2\text{U}_2\text{O}_7$, as indicated in Figure 1.

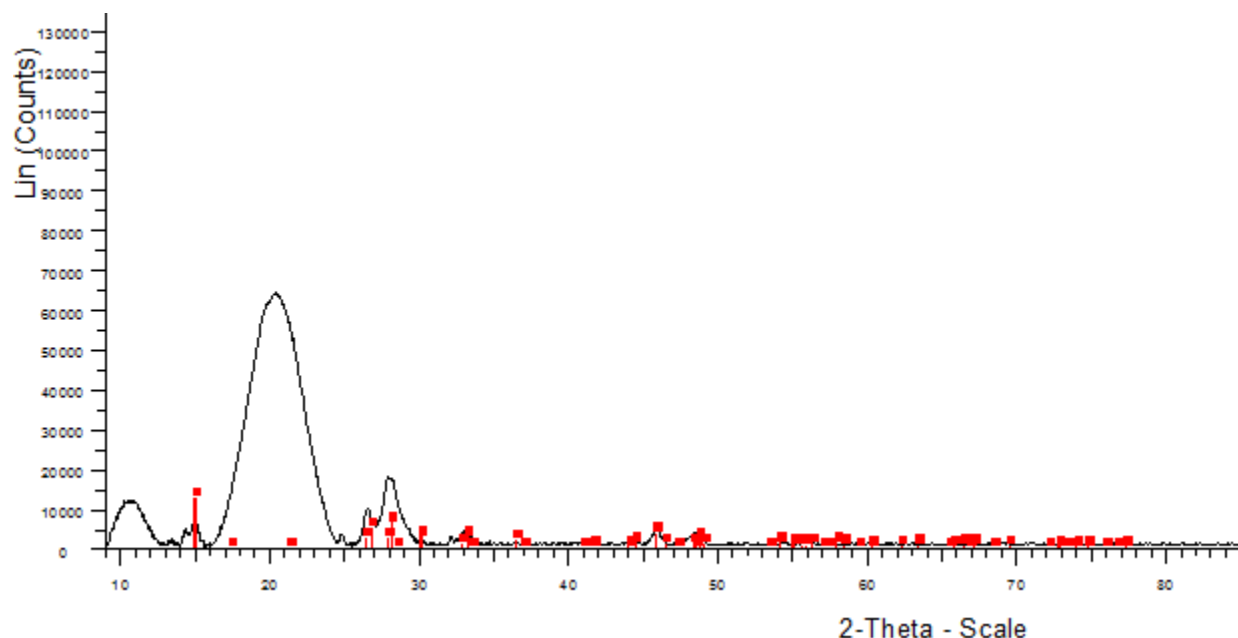


Fig.1. XRD pattern of U residue (—) overlaid with a stick pattern of Na₂U₂O₇ (■)

Characterization of Unirradiated Residue using Spectroscopy Techniques

Characterization of the uranium compound(s) in the residue was also attempted with ultraviolet/visible/near infrared (UV/Vis/NIR), Fourier-transform infrared (FT-IR) spectroscopy and Raman spectroscopy using 1064 nm excitation. On the Raman spectrometer laser burning of the darkly-coloured UO₂, U₃O₈ and U residue occurred, and even after dilution of these samples with KBr their spectra showed a lot of background fluorescence, and were therefore not very suitable to be used for identification of the uranium residue compound(s).

For UV/Vis/NIR analysis a Perkin-Elmer High-Performance Lambda 1050 UV/Vis/NIR spectrometer, fitted with an integrating sphere for diffuse reflectance measurement of solid samples was used, and for FT-IR spectroscopy a Bruker FT-IR spectrometer was used. The spectra of the solid uranium residue sample obtained were compared with the spectra of a few known uranium compounds, including

- UO₂ (obtained from a crushed UO₂ fuel pellet),
- U₃O₈ (prepared from uranium oxide composite (UOC), through heating at 800 °C for 3 h in an induction radio-frequency oven),
- Na₂U₂O₇ (precipitated from a nitric acid solution of uranium through addition of NaOH),
- UO₃ (precipitated from an ammonium carbonate solution of uranium through heating at 100 °C, whereby ammonia and CO₂ are volatilized).

The UV/Vis/NIR spectra of the uranium compounds obtained with the solids in a quartz cuvette placed in front of the reflectance beam are presented in Figure 2.

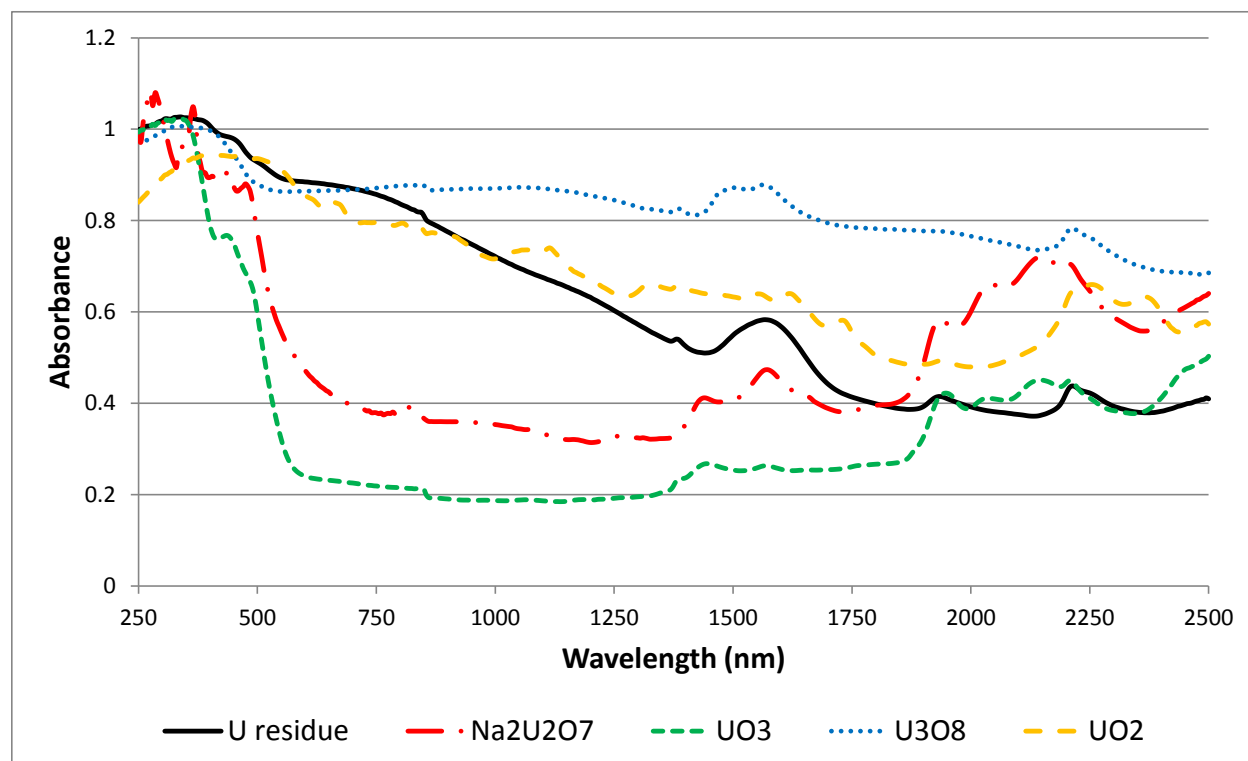


Fig.2. UV/Vis/NIR spectra of U residue compared with known U compounds

The results indicate that the closest correspondence between the spectrum of the uranium residue and that of the tested uranium compounds is with U_3O_8 . This could just be an indication that the residue consists of a mixture of U(IV) and U(VI) compounds similar to U_3O_8 (2:1 ratio of UO_3 and UO_2), since U_3O_8 is normally prepared by oxidizing other uranium oxides at temperatures above 500 °C, which would not be applicable to the uranium residue.

Clearly defined FT-IR spectra were obtained for the uranium residue and $Na_2U_2O_7$. The spectra of UO_2 , U_3O_8 and to a lesser extent UO_3 show a low signal to noise ratio, but can at least be used to identify the possible composition of the U residue. The spectra are shown in Figure 3 (note that due to large differences in reflectance the different spectra obtained had to be normalized in order to fit on the same graph - the U residue and $Na_2U_2O_7$ are on the same scale and the range of this scale is 1.25 times larger than the range of the scale on which UO_3 , UO_2 and U_3O_8 are plotted).

Closest correspondence is obtained with UO_3 (corresponding peaks at 1557, 1064, 828, 736 and 720 cm^{-1}), with some similarities also seen with $Na_2U_2O_7$ (corresponding peaks at 1354, 1064, and 828 cm^{-1}) and UO_2 (corresponding sloping line from 600 to 400 cm^{-1}).

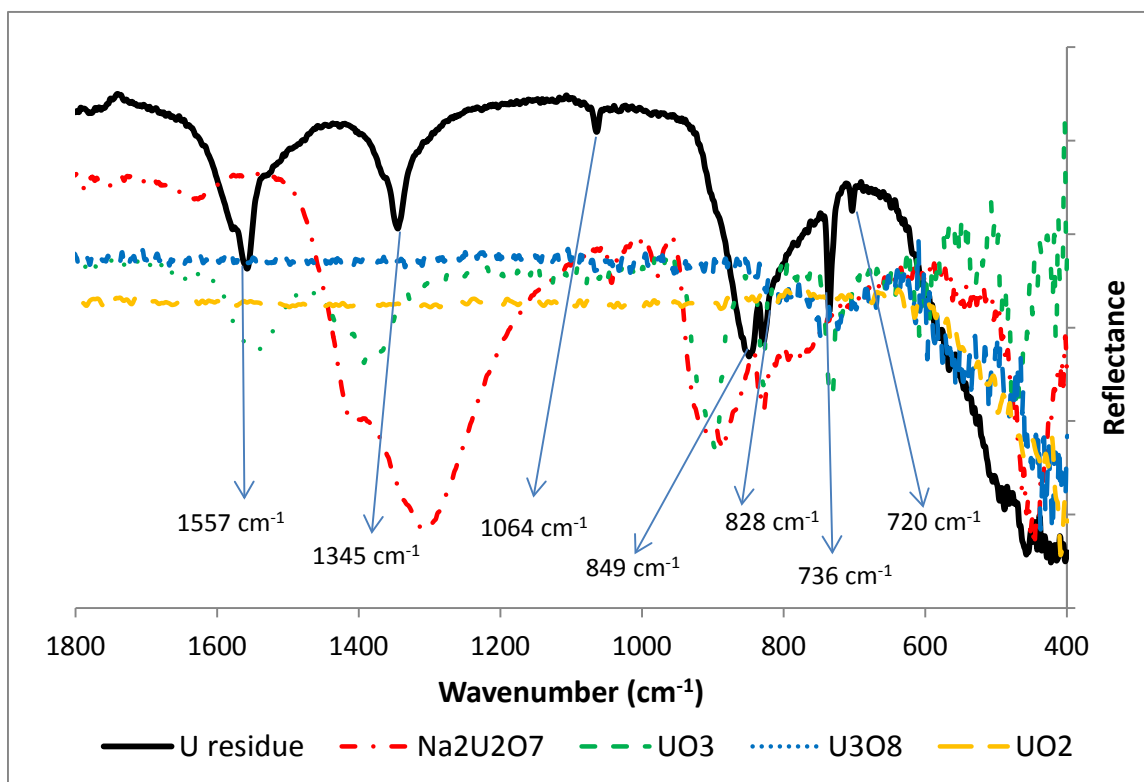


Fig.3. FT-IR spectra of U residue compared with known U compounds

Determination of Uranium Oxidation State in Unirradiated Residue

Sinkov et al. [11] give a detailed account of a method to determine the uranium oxidation state distribution in uraninite slurries using a 0.141 mol.dm⁻³ Na₂SO₄ solution in concentrated (85 wt.%) H₃PO₄. Oxidation of U(IV) by atmospheric oxygen is minimized through complexation in this mixture. They verified the applicability of the Beer-Lambert Law by acquiring optical absorption spectra and determining molar absorptivities for solutions of a known uranium oxidation state and concentration prepared from well characterized uranium materials. The wavelengths 406.2 and 642.6 nm were used for determination of U(VI) and U(IV) in these mixtures respectively. The molar extinction coefficients of U(VI) and U(IV) at these two wavelengths were determined through plotting the measured absorbance values against the U(VI) or U(IV) concentrations. Since the path length of the spectrophotometric cell used was 1 cm, the calculated slopes of these plots are equal to the molar extinction coefficients at the relevant wavelengths.

The concentration of U(IV) in Na₂SO₄/H₃PO₄ solutions also containing U(VI) can be determined by measuring the absorbance at 642.6 nm and then calculating the U(IV) concentration by rearranging the Beer-Lambert Law equation to $c = A/(b \times \epsilon)$, where the light absorbance A measured by the spectrophotometer is a linear function of the molar extinction coefficient ϵ , the path length of light through the solution b , and the solution concentration c .

The contribution of U(VI) to the spectrum at 642.6 nm is negligible and can be ignored. However, the contribution of U(IV) to the absorbance at the U(VI) peak maximum at 406.2 nm is appreciable. To account for the U(IV) contribution, its absorbance at 406.2 nm must be deducted from the total absorbance measured at 406.2 nm. The absorbance of U(IV) at 406.2 nm is proportional to the absorbance of U(IV) at 642.6 nm with the proportionality given by the ratios of the U(IV) molar extinction coefficient at 406.2 and 642.6 nm respectively:

$$A_{U(IV) \text{ at } 406,2 \text{ nm}} = A_{U(IV) \text{ at } 642,6 \text{ nm}} \times \frac{\epsilon_{U(IV) \text{ at } 406,2 \text{ nm}}}{\epsilon_{U(IV) \text{ at } 642,6 \text{ nm}}} = A_{U(IV) \text{ at } 642,6 \text{ nm}} \times R \quad (\text{Eq.1})$$

R is defined as the ratio of the molar extinction coefficient of U(IV) at 406.2 nm to the molar extinction coefficient of U(IV) at 642.6 nm. Therefore:

$$A_{U(VI) \text{ at } 406,2 \text{ nm}} = A_{\text{total at } 406,2 \text{ nm}} - (R \times A_{U(IV) \text{ at } 642,6 \text{ nm}}) \quad (\text{Eq.2})$$

From this result, the concentration of U(VI) in a mixture of U(IV) and U(VI) can be determined:

$$c = \frac{A_{U(VI) \text{ at } 406,2 \text{ nm}}}{b\epsilon_{U(VI) \text{ at } 406,2 \text{ nm}}} \quad (\text{Eq.3})$$

This method was used for determination of the U(IV)/U(VI) ratio in the uranium residue prepared from depleted uranium target plates. U(IV) and U(VI) standard solutions were prepared as described below, as well as U₃O₈ solutions of known concentrations, whereby the accuracy of the method could be tested. A solution of the uranium residue in Na₂SO₄/H₃PO₄ was also prepared.

Preparation of U(IV) standard:

UO₂ was dissolved in a solution of 0.141 mol.dm⁻³ Na₂SO₄ in 85 wt.% H₃PO₄, by heating the slurry overnight at 130 °C in an oven. After cooling, the solution was diluted with a Na₂SO₄/H₃PO₄ solution to produce a stock U(IV) standard solution with U concentration 0.0259 mol.dm⁻³.

Preparation of U(VI) standard:

U₃O₈ was dissolved in 10 ml concentrated HNO₃ (65 wt.%) and evaporated under a heat lamp to oxidize the uranium to U(VI). Another 5 ml of concentrated HNO₃ was added to re-dissolve the dried U(VI) nitrate solids and the resulting solution was evaporated again to dryness to ensure full conversion to U(VI). The solution was heated overnight at 250 °C to remove water and to accomplish denitration and conversion to UO₃. The dried UO₃ was dissolved in Na₂SO₄/H₃PO₄ solution to produce a stock U(VI) standard solution with U concentration 0.0718 mol.dm⁻³.

Preparation of U₃O₈ solutions:

U₃O₈ was dissolved in a solution of 0.141 mol.dm⁻³ Na₂SO₄ in 85 wt.% H₃PO₄ through heating the slurry overnight at 130 °C in an oven. After cooling the solution was diluted with Na₂SO₄/H₃PO₄ solution to produce a stock U₃O₈ solution with U concentration 0.0738 mol.dm⁻³.

Preparation of U residue solution:

A mass of 0.215 g of U residue was dissolved in a solution of 0.141 mol.dm⁻³ Na₂SO₄ in 85 wt.% H₃PO₄. This residue dissolved easily with no heating required.

The vividly coloured solutions obtained are shown in Figure 4. From the colours it can already be seen that U_3O_8 and the U residue solution is a mixture of U(IV) and U(VI).



Fig. 4. U solutions in Na_2SO_4 -bearing H_3PO_4
Left-to-right: $0.0259 \text{ mol.dm}^{-3}$ U(IV)
 $0.0718 \text{ mol.dm}^{-3}$ U(VI)
 $0.0738 \text{ mol.dm}^{-3}$ U in U_3O_8
U residue solution

UV/Vis spectra were obtained for the U residue solution and the U(IV), U(VI) and U_3O_8 stock solutions, on the Perkin-Elmer High-Performance Lambda 1050 UV/Vis/NIR spectrometer, using 1 cm quartz cuvettes. The results in Figure 5 indicated the presence of a mixture of U(IV) and U(VI) in the U_3O_8 and U residue solutions.

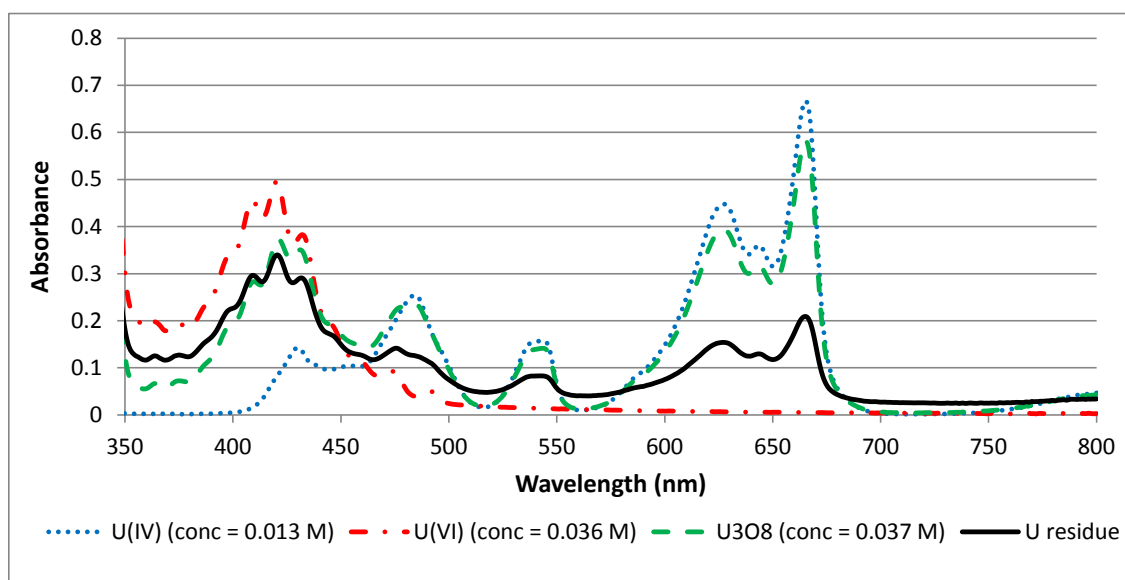


Fig. 5. UV/Vis spectra of U solutions in Na_2SO_4/H_3PO_4 , showing peaks for U(IV) and U(VI)

Using the molar extinction coefficients reported by Sinkov et al. [11], the U(IV) and U(VI) concentrations calculated for U₃O₈ and the U residue solution are presented in Table I and Table II respectively.

TABLE I: Calculation of U(IV) and U(VI) concentration in U₃O₈ standard solutions, using molar extinction coefficients from Sinkov *et al.* [11]

Vol. of U ₃ O ₈ std.	A _{642 nm}	A _{406 nm}	Prepared [U(IV)] /M	Measured [U(IV)] /M	% rec.	Prepared [U(VI)] /M	Measured [U(VI)] /M	% rec.
10 ml	0.6407	0.5135	0.0246	0.0229	93.0	0.0492	0.0488	99.1
5 ml	0.3153	0.2541	0.0123	0.0113	91.6	0.0246	0.0242	98.1
2 ml	0.1213	0.0974	0.0049	0.0043	88.1	0.0098	0.0093	94.0
1 ml	0.0563	0.0441	0.0025	0.0020	81.7	0.0049	0.0042	85.0
0.5 ml	0.0315	0.0264	0.0012	0.0011	91.5	0.0025	0.0025	102.3
Average recovery:					89.2	Average recovery:		95.7

TABLE II: Calculation of U(IV) and U(VI) concentration in U residue solution using molar extinction coefficients from Sinkov *et al.* [11]

A _{642 nm}	A _{406 nm}	Calculated A _{U(VI) at 406 nm}	Measured [U(IV)] /M	Measured [U(VI)] /M	U(VI)/U(IV)
0.1299	0.2770	0.2700	0.0046	0.0275	5.9

The calculated ratio of 5.9 translates to a percentage of U(VI) of 85.6% and U(IV) of 14.4%.

Characterization of Unirradiated Residue using Elemental Analysis

Elemental analysis was performed on samples of the unirradiated residue to determine uranium and chemical impurity content. The results are given in Table III.

TABLE III: Chemical analysis results of uranium residue

Element	Analytical result (% by mass in residue)	Analysis method
U	70.1 ± 1.7	X-ray fluorescence (XRF) – average of 5 batches
Al	0.92 ± 0.44	Inductively coupled plasma optical emission spectrometry (ICP-OES) – average of 4 batches
Na	5.5 ± 0.9	Neutron activation analysis with delayed neutron counting – average of 4 batches
O	5.5	Combustion analysis on ELTRA elemental analyzer
H	0.69	Combustion analysis on ELTRA elemental analyzer

Sodium and aluminium are expected to be the main chemical impurities in the uranium residue, based on the dissolution medium of the U/Al target plates in the Mo-99 production process

(NaOH), and the Al content of the target plates. The Al concentration per kg U exceeds the re-use specification value by a factor 60, and the purification process to be implemented for the uranium residue will therefore have to provide a decontamination factor of this magnitude for aluminium.

An attempt has been made to reconcile the elemental analysis results and the determined U(IV)/U(VI) ratio of 15:85, with the expected uranium compounds in the residue from the XRD, diffuse reflectance UV/Vis and FT-IR results, through calculation. It is assumed that the U(IV) content must be due to either UO_2 or as part of U_3O_8 . U(VI) could be present as $Na_2U_2O_7$, UO_3 , $UO_3 \cdot 2H_2O$ or as part of U_3O_8 . The closest correspondence with the measured values is obtained with U(IV) present as UO_2 and U(VI) being due to either $Na_2U_2O_7$ or UO_3 as outlined in Table IV.

TABLE IV: Calculated scenario's for possible U compound in residue

U compound:	% of total U	Molar mass (g/mol)	% U	% O	% H	% Al	% Na
Measured in residue:			70	5.5	0.68	0.81	5.5
<i>Scenario 1: U(VI) present as $Na_2U_2O_7$</i>							
$Na_2U_2O_7$	85	634	75.1	17.7	0.0	0.0	7.3
UO_2	15	270	88.2	11.9	0.0	0.0	0.0
Combined:		579	77.0	16.8	0.0	0.0	6.2
Normalized to measured U %:			70.0	15.3	0.0	0.0	5.6
<i>Scenario 2: U(VI) present as UO_3</i>							
UO_3	85	286	83.2	16.8	0.0	0.0	0.0
UO_2	15	270	88.2	11.9	0.0	0.0	0.0
Combined:		284	84.0	16.0	0.0	0.0	0.0
Normalized to measured U %:			70.0	13.4	0.0	0.0	0.0

The oxygen content in these scenarios is still considerably higher than what was measured. The low oxygen content can only be explained if an appreciable quantity of a uranium oxide in a lower oxidation state is also present, but this cannot be confirmed with the current results. Furthermore, the percentage uranium in these scenarios is higher than the measured value in the residue, which suggests a “missing” component in these scenarios. Since a percentage of between 0.5 and 1 % Al and O was also measured in the residue, other compounds containing these elements should also be present, but not at levels high enough to completely account for the discrepancy between measured uranium and the levels in these scenarios. Further investigation is required.

A definitive identification of the uranium compound(s) is currently not possible, but based on the results from XRD, diffuse reflectance UV/Vis, FT-IR spectroscopy and the elemental analysis results the most likely scenario is where U is present as a mixture of UO_2 , UO_3 and $Na_2U_2O_7$.

Optimization of Dissolution Parameters using Unirradiated Residue

A number of parameters were investigated in order to achieve a set of optimal conditions for dissolution of the residue in ammonium carbonate with hydrogen peroxide as oxidant. An experimental set-up with a 500 ml round-bottom flask coupled to a reflux condenser (closed

system), a thermocouple for accurate temperature control and magnetic stirring for agitation of the reaction mixture was used. The experiments were conducted on a 10 g residue scale and the parameters which were varied to achieve a set of optimal conditions for dissolution, included timing of H₂O₂ addition, solid/liquid ratio, temperature, H₂O₂ concentration, (NH₃)₂CO₃ concentration, stirring rate and reaction time. The uranium recovery rate was determined through analysis of the uranium content of the undissolved residue using X-ray Fluorescence (XRF).

A dissolution yield of at least 99% could be obtained with a solid/liquid ratio of 1:12, using 1 mol.dm⁻³ ammonium carbonate with hydrogen peroxide added as oxidation agent at a temperature of 60 °C. Several days after the experiments it was observed that the solution containing the dissolved uranium residue showed a gradual change in colour from orange to yellow and that the dissolved uranium had started to re-precipitate out of solution. This phenomenon was further investigated by analyzing the solution from which the uranium precipitated (solution A) using UV/Vis spectroscopy (Figure 6).

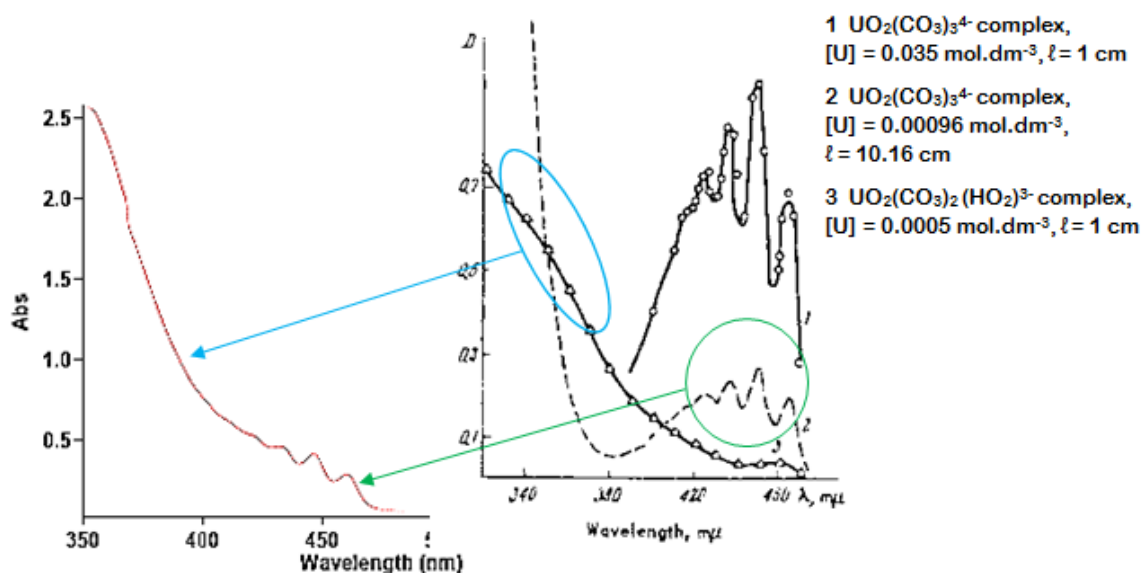
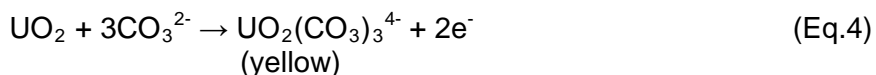


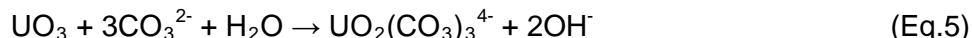
Fig. 6. UV/Vis spectrum of Solution A (left) and UV/Vis spectrum of known uranium carbonate complexes from literature [12]

The UV/Vis spectrum of Solution A (left) exhibits the presence of both the UO₂(CO₃)₃⁴⁻-complex (three peaks at about 450 nm) and the UO₂(CO₃)₂(HO₂)₃³⁻-complex (long sloping line to 350 nm), when compared to spectra from literature [12] (right).

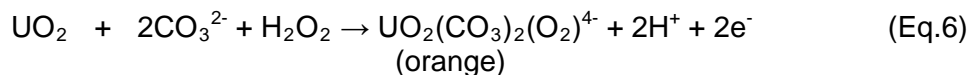
Due to the fact that the exact complexes of uranium present in the residue from the Mo-99 process are unknown, a complete reaction cannot be proposed for the dissolution process. It is however known that UO₂ dissolves in carbonate medium to form the yellow species UO₂(CO₃)₃⁴⁻ according to the reaction [13]:



UO₃ dissolves according to the reaction [14]:



However more recent literature indicates that in the presence of carbonate and H₂O₂ the dissolution and complexation of UO₂ occurs according to the following reaction [9]:



The presence of the peroxo-uranium compound (either UO₂(CO₃)₂(HO₂)³⁻ or UO₂(CO₃)₂(O₂)⁴⁻) in solution is easily identified by its characteristic orange-red colour compared to the yellow colour of UO₂(CO₃)₃⁴⁻. It is likely that originally the dissolution of the uranium residue results in the formation of mostly the orange UO₂(CO₃)₂(O₂)⁴⁻ complex. With time this complex reverts to the yellow UO₂(CO₃)₃⁴⁻ complex which could be less soluble and subsequently precipitates out of solution as (NH₄)₄UO₂(CO₃)₃.

The sodium salt of the UO₂(CO₃)₃⁴⁻ complex has a solubility limit of 66 g U/l in water [15], which decreases with increasing sodium carbonate concentration to about 14 g U/l at 1.0 mol.dm⁻³ Na₂CO₃. If similar values are valid for (NH₄)₂CO₃ then this implies that a solid/liquid ratio of at least 1:50 for this specific residue (70% U content) would be necessary to ensure that in a 1.0 mol.dm⁻³ (NH₄)₂CO₃ solution, the uranium remains solubilized, if present completely in the form of the UO₂(CO₃)₃⁴⁻ complex.

The yellow crystalline re-precipitated uranium compound (P1) was dried and qualitatively analyzed using X-ray diffraction to determine the uranium species present. The best correspondence between the measured diffractogram and the one contained in the ICDD database was for the compound ammonium uranyl carbonate, (NH₄)₄UO₂(CO₃)₃ (Figure 7). This is consistent with the results of the UV/Vis analysis of Solution A.

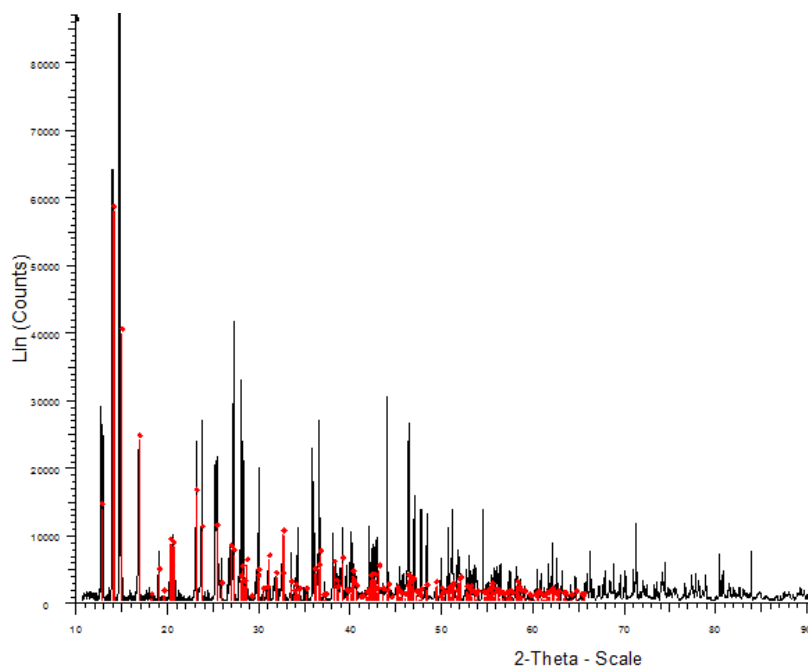


Fig. 7: X-ray diffractogram of precipitated U (U) overlaid with a stick pattern of ammonium uranyl carbonate (U)

Characterization and Testing Optimized Dissolution Parameters using Irradiated Residue

A small experimental hot cell facility was available for performing dissolution experiments on irradiated uranium residue samples. Figure 8 gives a front view of the hot cell, which consists of a removable box manufactured from stainless steel with a Perspex window, fitted inside a lead enclosure with a lead glass window. Two manual tongs were fitted to the hot cell for manipulating equipment and samples inside the box. The box was fitted with all equipment required to do the dissolution runs on irradiated samples.



Fig. 8. Experimental hot cell for processing of irradiated U residue sample

A total of six runs were performed using approximately one gram samples of real irradiated residue. The samples of residue were taken from batches of residue with decay ages varying from 5 to 11 years.

The dissolution experiments in the hot cell were performed using normal laboratory glassware and a hotplate, in some instances modified for easier manipulation with the tongs inside the hot cell. Reagents were added from outside the hot cell using syringes attached to silicone tubing threaded through a cork-screw lead plug which ensures shielding integrity. Sampling of solutions for analytical purposes was done using an electronic syringe, and weighing of all samples and solutions on an analytical balance with 0.001 g readability.

Characterization of the total uranium and radionuclide impurity content in the residue was achieved through dissolution of the residue in an ammonium carbonate solution with the optimized dissolution parameters, and dissolution of any remaining undissolved residue in a nitric acid/hydrochloric acid mixture. Small samples of all the solutions were taken and after dilution were analyzed using alpha, beta and gamma spectrometry for radionuclide content, and ICP-OES for uranium content and the impurities aluminium and iron.

The average U content in the irradiated residue is $47.7 \pm 1.0\%$ by mass (average of 4 batches). This is at least 20% lower than the U content measured during the characterization of U residue from unirradiated depleted U target plates. This large difference could be partly attributed to the presence of iron - up to 7% iron content per mass of residue present in the irradiated residue - which is thought to be caused by corrosion of the Type 304 stainless steel canisters in which the uranium residue is being stored. Since this steel also has a large chromium content of up to 20%, a significant amount of chromium should also be present in the residue, although an analysis for this element in the irradiated residue has not yet been done. It is estimated that up to 10% of the residue mass could therefore consist of corrosion products from the stainless steel canisters.

The results for the measured chemical and radionuclide impurities for residue batches with different decay ages from 5 to 11 years, as well as the decontamination factor (DF) which would be required from carbonate leaching plus subsequent purification processes to purify the uranium to within specification levels for subsequent target plate manufacture, are given in Table V and VI respectively.

TABLE V: Chemical impurities in residue samples with decay ages from 5 to 11 years

Element	Spec. (mg/kg U)	11-year old residue		10-year old residue		5-year old residue	
		Measured (mg/kg U)	DF required	Measured (mg/kg U)	DF required	Measured (mg/kg U)	DF required
Fe	300	8.83×10^4	2.9×10^2	3.30×10^4	1.1×10^2	7.40×10^3	2.5×10^1
Al	150	2.33×10^4	1.6×10^2	2.89×10^4	1.9×10^2	3.45×10^4	2.3×10^2

TABLE VI: Radioactive impurities in residue samples with decay ages from 5 to 11 years

Nuclide	Half-life	Spec. (Bq/g U)	11-year old residue		10-year old residue		5-year old residue	
			Measured (Bq/g U)	DF required	Measured (Bq/g U)	DF required	Measured (Bq/g U)	DF required
Co-60	5.3 yr.	1.0×10^2	3.03×10^4	3.0×10^2	6.26×10^4	6.3×10^2	7.90×10^4	7.9×10^2
Nb-95	35 days	1.2×10^4	5.17×10^4	4.3×10^0	2.49×10^4	2.1×10^0	6.64×10^4	5.5×10^0
Zr-95	64 days	1.2×10^4	3.83×10^4	3.2×10^0	3.00×10^4	2.5×10^0	5.41×10^4	4.5×10^0
Ru-106	1.0 yr.	1.2×10^4	7.23×10^5	6.0×10^1	1.13×10^6	9.4×10^1	4.22×10^7	3.5×10^3
Sb-125	2.7 yr.	1.2×10^4	2.39×10^6	2.0×10^2	4.14×10^6	3.5×10^2	1.35×10^7	1.1×10^3
Cs-137	30 yr.	1.2×10^4	5.50×10^6	4.6×10^2	1.01×10^7	8.4×10^2	2.37×10^7	2.0×10^3
Ce-144	285 days	1.2×10^4	1.49×10^6	1.3×10^2	2.51×10^6	2.1×10^2	2.79×10^8	2.3×10^4
Eu-154	8.6 yr.	1.2×10^4	1.07×10^5	9.0×10^0	1.94×10^5	1.6×10^1	2.93×10^5	2.4×10^1
Eu-155	5.0 yr.	1.2×10^4	4.06×10^6	3.4×10^2	6.22×10^6	5.2×10^2	1.26×10^7	1.0×10^3
Sr-90	29 yr.	5.0×10^3	7.01×10^8	1.4×10^5	1.01×10^9	2.0×10^5	9.99×10^8	2.0×10^5
Pu-239	2×10^4 yr.	5.0×10^2	6.51×10^5	1.3×10^3	8.02×10^5	1.6×10^3	8.59×10^5	1.7×10^3

The average activity per gram U in the residue measured for each nuclide was also compared against theoretically calculated values using the computer code ORIGEN-S, which is part of the SCALE 4.4 system. The average measured to calculated ratio is 0.39, which seems quite plausible taking into account the uncertainties in the parameters used in the calculation, and also considering the fact that a U isotopic analysis showed less U-235 burning than theoretically calculated by ORIGEN-S.

The carbonate dissolution process with parameters optimized in the development work using unirradiated residue was tested in all six runs with the irradiated residue. In the first run a low recovery yield was obtained, which was thought to be caused by the unexpectedly large amount of iron in the residue which co-precipitates some of the uranium during the dissolution process.

The recovery could be increased to 100% by performing successive carbonate leaches. Table VII shows a summary of the results.

TABLE VII: Summary of Uranium Recovery in hot runs

Sample (age)	No of carbonate leaches	Total %U recovery in carbonate	Comments
1 (11 yr.)	1	78	Probable cause of low U recovery yield: presence of large amount of Fe in the U residue which co-precipitates some of the U through its precipitation in CO_3^{2-} solution
2 (11 yr.)	3	100	U recovery improved through consecutive CO_3^{2-} leaching: 1 st leach 75%, 2 nd leach 25%
3 (11 yr.)	3	90	Lower U recovery due to clump of undissolved residue which was not contacted with CO_3^{2-} during 2 nd and 3 rd leaches, and was only dissolved during acid rinsing of the dissolution flask at the end. 1 st leach: 64%, 2 nd leach: 21%, 3 rd leach: 5%
4 (11 yr.)	4	100	U recovery improved because all undissolved residue was transferred from the dissolution flask onto the glass frit before the 2 nd , 3 rd and 4 th leaches, so that no residue remained behind when acid leaching commenced. 1 st leach: 60%, 2 nd leach: 27%, 3 rd leach: 12%, 4 th leach: 1%
5 (10 yr.)	3	100	1 st leach: 63%, 2 nd leach: 30%, 3 rd leach: 7%
6 (5 yr.)	3	100	1 st leach: 79%, 2 nd leach: 17%, 3 rd leach: 4%

CONCLUSIONS

Characterization of the solid uranium residue obtained from unirradiated depleted uranium target plates as simulant of the real irradiated residue from NTP's Mo-99 production process indicated a possible 70% uranium content by mass. The main chemical impurity in the residue is sodium, at a level of 5% of the residue by mass. Another significant chemical impurity is aluminium at around 1% of the residue by mass, but less than 0.5% of the aluminium originally present in the target plates remains in the residue.

The uranium is present in the residue at a U(IV)/U(VI) ratio of about 15:85. This low ratio implies that a large quantity of oxidizing agent would not be needed during dissolution of the residue in ammonium carbonate. The efficiency with which H_2O_2 has been observed to dissolve the residue in ammonium carbonate, may therefore have more to do with its properties as a ligand in the formation of the $[\text{UO}_2(\text{CO}_3)_2(\text{O}_2)]^{4-}$ -complex during dissolution. A definitive characterization of the uranium compounds present in the residue was not possible, but based on XRD, diffuse reflectance UV/Vis and FT-IR spectroscopy, together with elemental analysis results; it seems that the most likely scenario is where uranium is present as a mixture of the compounds UO_2 , UO_3 and $\text{Na}_2\text{U}_2\text{O}_7$.

The measured uranium content of actual irradiated residue from different batches with decay ages varying between 5 and 11 years is about 47% by mass. The presence of corrosion products from the Type 304 stainless steel canisters in which the radioactive residue is stored could be responsible for the discrepancy when compared to the analysis results of the unirradiated

residue. If further investigations on more batches of stored residue reveal the presence of these corrosion products in all of the canisters, consideration will be given to changing the type of stainless steel used for construction of the canisters.

By far the dominant nuclide in the irradiated residue, for which the highest decontamination factor would be required, is Sr-90, followed by Pu-239, Ce-144, Cs-137, Ru-106, Sb-125 and Eu-155.

Simulated Mo-99 residue obtained from unirradiated depleted uranium target plates was successfully dissolved in the order of 99% reproducibly within a closed experimental set-up, using optimized conditions at a temperature of 60 °C with a solid/liquid ratio of 1:12 and 1 mol.dm⁻³ ammonium carbonate with hydrogen peroxide added as oxidant. Stirring of the reaction mixture is necessary to ensure high recovery yields.

Dissolved uranium residue in the ammonium carbonate medium at low solid/liquid ratios exhibits slow re-precipitation of the uranium over time, with the initial orange-red colour of the dissolved uranium in solution transforming into the yellow $\text{UO}_2(\text{CO}_3)_3^{4-}$ compound. The yellow compound that precipitated was characterized as $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$. This precipitation could be ascribed to a lower solubility of the $\text{UO}_2(\text{CO}_3)_3^{4-}$ compound compared to $\text{UO}_2(\text{CO}_3)_2(\text{O}_2)^{4-}$. To avoid this precipitation problem in process lines it is recommended that further processing (purification) should take place without delay or alternatively H_2O_2 should be added periodically to re-form the $\text{UO}_2(\text{CO}_3)_2(\text{O}_2)^{4-}$ compound.

The optimized dissolution parameters were tested on approximately 1 g samples of real irradiated residue with decay ages between 5 and 11 years. With only one carbonate/peroxide leach using the optimized dissolution parameters, a U recovery yield below 80% was obtained. The reason for this low recovery yield was thought to be the presence of an unexpectedly large amount of iron in the uranium residue, which was confirmed by analysis. It is likely that the uranium co-precipitates with the iron in the carbonate solution and this could result in the low uranium recovery yield observed in the carbonate solution during the first hot run.

When at least three successive carbonate/peroxide dissolution steps under optimum conditions were performed on the uranium residue, the U recovery yield increased to 100%. Recovery of uranium from the Mo-99 process residue using dissolution in ammonium carbonate with hydrogen peroxide as oxidant and ligand in the carbonate complex of uranium has therefore been proven to be a feasible process. The purification of the generated uranium solution from chemical and radioactive impurities is currently being investigated.

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