Purification of uranium from uranium ore concentrates dissolved in ammonium carbonate and hydrogen peroxide to be used as a feed stock material for a new conversion plant

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DECLARATION

This dissertation reports original research carried out in the Nuclear Waste Research Department at the South African Nuclear Energy Corporation (Necsa) in collaboration with the Centre of Applied Radiation Science and Technology (CARST) at the North-West University (Mafikeng campus) between 2010 and 2013. It has not been submitted in part or in whole for a degree at any other university. Data presented here are original and any other sources of data acquired through collaborative activities are fully acknowledged.

Signature 

ROSETH SENOSI

March 2014

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Ke Letlhoromisa la ga thebe tshunyana

Abstract

Enriched Uranium (EU), the primary material used to fabricate fuel for nuclear power plants, is manufactured using uranium oxide as feed material. Currently South African gold mines produce tonnes of uranium as a byproduct during gold extraction and this uranium byproduct ore converted at the Nuclear Fuel Corporation of South Africa (Nufcor) into uranium oxide (UOC) for example triuranium octaoxide (U_3O_8). However other possible sources (gold mines from international suppliers) of uranium oxide for example U_3O_8 or UO_2 could contain impurities that will cause problems in a conversion plant as experienced previously in a conversion plant at Necsa (1976 - 1979). Impurities in the ammonium diuranate (ADU) as feed material resulted in the formation of sintered UO_2F_2 particles during the conversion process (Ponelis et al., 1987). Purification of UOC is therefore, required to ensure a continuous pure UOC feed for conversion plants.

This study deals with the development and optimization of an ammonium carbonate ($(NH_4)_2CO_3$) based dissolution process using hydrogen peroxide (H_2O_2) as an oxidant for UOC and the purification of uranium from the generated solutions. The dissolution experiments were performed in a pressurized autoclave as well as bench experiments. Experimental parameters that were investigated for optimum dissolution efficiency; include addition of H_2O_2, temperature, solid/liquid ratio, H_2O_2 concentration, $(NH_4)_2CO_3$ concentration and stirring rate. The reaction time required for optimum dissolution was also determined.

The results obtained indicated a complete dissolution of UOC at 60 C, after three hours in a 1 M ammonium carbonate solution with 1M hydrogen peroxide. The rate of the reaction and the yield of uranium were found to increase as a function of both the concentration of hydrogen peroxide in the range of 0.5 to 2.5 M and the temperature between 30 and 60°C.

Three purification processes were investigated to purify the generated uranyl solution, namely ion exchange resins, solvent extraction and precipitation. For the ion exchange technique, various resins were tested for the efficiency of absorption of the impurities such as potassium, sodium, tungsten, molybdenum, calcium and aluminium from solutions

containing high concentrations of uranium. Results to be presented indicated that Amberlite RFH 252 and Purolite S957 could be considered for purification purposes.

For the solvent extraction technology, the possibilities of purifying uranium from impurities in an alkaline medium using Aliquat 336 or TBP as extractants in the presence of xylene, dodecane and kerosene as diluents were studied. Results indicated that, although uranium extraction was possible from an alkaline medium using Aliquat 336 in xylene, impurities were also extracted.

Precipitation technology (steam stripping) was also investigated for selective precipitation of uranium. Results indicated possible and feasible recovery of uranium by steam stripping between 70 and 90 C.

Purification of uranium feed stock for a conversion plant from different sources (which might contain impurities) as a three steps approach was recommended. The first step is the dissolution of uranium feed stock by alkaline solution followed by purification by ion exchange using Amberlite RFH 252 or Purolite S 957. In the third step, the eluent must be precipitated and the precipitates need isolation for feed material.

The recommended solution consists of a combination of ion exchange and liquid separation technologies.

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Terminology

ADU	Ammonium diuranate
AUC	Ammonium uranyl carbonate
AUT	Ammonium uranyl tricarbonate
EDTA	Ethylenediaminetetraacetic acid
DTPA	Diethylenetriamine pentaacetate
EU	Enriched uranium
HF	Hydrogen fluoride
H_2O_2	Hydrogen peroxide
HNO_3	Nitric acid
IAEA	International atomic energy agency
MBR	Moving bed reactor
$(NH_4)_2CO_3$	Ammonium carbonate
NH_3	Ammonia
NNP's	Nuclear power plants
Nufcor	Nuclear fuel corporation of South Africa
PAL	Pelindaba analytical laboratory
PUREX	Plutonium-Uranium extraction
TBP	Tributyl-n-phosphate
UOC	Uranium oxide concentrates
UO_2	Uranium dioxide
UO_3	Uranium trioxide
UV-vis	Ultraviolet visible spectroscopy
U_3O_8	Triuranium octaoxide
UF4	Uranium tetrafluoride
UF6	Uranium hexafluoride
UNH	Uranyl nitrate hexahydrate
XRD	X-ray diffraction

Chapter 1

1 Literature review

1.1 Introduction to project

International pressure on industries and governments to decrease their carbon emission as well as growing concern about the limited number of fossil fuel reserves lead to increased attention to alternative energy sources. Although coal, oil and natural gas still fulfill energy needs, the transition to other sources of energy will be inevitable in the long run.

The dependence of South Africa on fossil fuels for electricity supply, the growth in electricity demand as well as global warming have contributed to the recent interest in nuclear energy as one of the alternative technologies to generate electricity. A nuclear energy policy for South Africa, confirmed in June 2008 (WNA, 2009), addresses the growing electricity demand and the country's 87% reliance on coal for the supply of electricity. The current South African nuclear energy policy confirms the need for an increase in electricity production and included in the policy is the possibility of establishing a nuclear fuel cycle to produce reactor fuel for future nuclear reactors such as Koeberg (WNA, 2009).

Enriched Uranium (EU) that is the primary material used to fabricate fuel for nuclear power plants is manufactured using uranium oxide as feed material. Currently South African gold mines produces tonnes of uranium as a byproduct during gold extraction and this uranium byproduct is converted at the Nuclear Fuel Corporation of South Africa (Nufcor) into different uranium oxides (UOC) such as triuranium octaoxide (U_3O_8) and uranium dioxide (UO_2). UOC is currently exported from South Africa to international nuclear fuel manufacturers and with the possible re-establishment of the fuel cycle in South Africa, UOC and other uranium containing materials will be needed for a new conversion plant.

Nufcor certifies the purity of UOC to indicate the presence of impurities. However other possible sources of UOC for example U_3O_8 or UO_2 from international suppliers, could contain impurities causing problems in the conversion plant as experienced previously in a conversion plant at Necsa (1976 - 1979). Impurities in the ammonium diuranate (ADU) as feed material resulted in the formation of sintered UO_2F_2 particles during the conversion

process (Ponelis et al., 1987). Purification of UOC is therefore required to ensure a continuous pure UOC feed material for conversion plants. This will ensure that the operation parameters will remain constant under plant conditions.

Extensive experimental research has been done on the removal and purification of uranium from its ore. Natural uranium, U_3O_8, is treated by a wet process to produce an ammonium uranyl carbonate solution (AUC). The main processes include dissolution, extraction, evaporation and precipitation (Saeidi, 2005). Currently at Necsa the PUREX process that is based on nitric acid dissolution, is used to purify uranium for reactor fuel.

The purpose of this study is to investigate the possibility of purifying uranium oxides (UOC) as feed material for a new conversion plant using alkaline treatment technology. The results of this alkaline route should indicate if an alkaline process could be used at Necsa as well as for the PUREX process. The alkaline method can extend the life time of such a facility since corrosion of equipment will be less than when employing the current acid technologies.

1. Problem Statement

According to Theo Scholtz, through 'personal communication' Necsa and Brazil are currently discussing the possibility of a collaborative effort to establish uranium conversion technology in both countries using uranium oxides. Previous operations at a conversion plant at Necsa (started in 1979) using unpurified uranium feed material have resulted in the formation of sintered UO_2F_2 particles during the conversion process due to the presence of certain impurities. The formation of this sintered UO_2F_2 led to blockages and shutdown of the plant (Ponelis, A., 1989).

1.3 Aim and Objectives

1.3.1 Aim

The aim for this study is to determine the effectiveness of an alkaline process to purify UOC in order to produce pure, homogeneous feed material for the conversion plant.

1.3.2 Objectives of study

Three objectives were identified from the project aim and are:

- To determine the dissolution rate of uranium oxide (U_3O_8) using ammonium carbonate and hydrogen peroxide solutions by optimizing the temperature, ammonium carbonate concentration, time to leach, effect of stirring and solid-liquid volume ratio.
- To purify uranium from impurities such as potassium, sodium, tungsten, calcium, aluminium and molybdenum present in U_3O_8 by investigating solvent extraction, ion exchange and precipitation.
- Recommend possible technologies to purify uranium that meet nuclear specifications.

1.4 Layout of the Research Project

Chapter 1: Introduction

Covers general introduction of the research work done and the aims and objectives are established.

Chapter 2: General Literature review

Consists of a general literature review of the origin of uranium ore concentrates (UOC), oxidation state, production of uranium oxide (mining) and the conversion process.

Chapter 3: Dissolution of UOC using ammonium carbonate oxidized with hydrogen peroxide.

Investigate the efficiency of an alkaline medium to dissolve UOC (literature section), experimental procedure and results for the dissolution of UOC using ammonium carbonate with hydrogen peroxide.

Chapter 4: Use of ion exchange technology to purify UOC

Deals with objective 2 and contains a literature section, the experimental procedure and the results for the purification of U_3O_8 using ion exchange technology.

Chapter 5: Use of solvent extraction technology to purify UOC

Also deals with objective 2 and contains a literature review section, the experimental procedure and the results for the purification of uranium from U_3O_8 using a solvent extraction technique.

Chapter 6: Precipitation using steam stripping technology

Deals with objective 3 of precipitation of the uranyl salt generated from dissolution of UOC from studies described in Chapter 1. Chapter 6 also consists of a literature section, the experimental procedure and the results for precipitation using steam stripping technology.

Chapter 7: Conclusion and Recommendations

Covers the conclusion and recommendations of the whole project

Chapter 8: Annexure A, B, C, D and E.

Covers raw data results from chapters 3, 4, 5 and 6

1.5 References

WNA (World Nuclear Association), 2009. Nuclear Power in South Africa. http://www.world-nuclear.org/info/inf88.html, [Accessed on 06 September 2010]

Ponelis, A.A., Slabber, M.N., Zimmer C.H.E. 1987. Conversion of non–nuclear grade feed stock to UF_4. In Advances in uranium refining and conversion, IAEA – TECDOC – 420:pp. 11-140.

Saeidi, M. 2005. Nuclear fuel cycle activities in Iran. Proceedings of the World Nuclear Association Annual Symposium. Available at http://www.iranwatch.org/sites/default/files/iran-aeoi-worldnuclearassociation-saeidi-090705.pdf
[Accessed on 28 October 2011]

Chapter 2

2 General literature review of uranium production

To keep the current fleet of world nuclear reactors operational, huge amounts of uranium from mines and secondary sources are needed for the production of reactor fuel. The uranium is converted in a conversion plant to produce UF_6; this is then enriched in order to be able to produce fuel. A description of the uranium mining process and the South African experience regarding the conversion of UOC to UF_6 in a conversion plant is as follows:

2.1 Uranium mining

The use of nuclear reactors to generate electricity in the early 1950s resulted in the commencement of uranium exploration for the manufacture of nuclear fuel (OECD, 2005). In nature, uranium consists primarily of two isotopes, namely uranium 238 (^{238}U) and uranium 235 (^{235}U) that occur approximately as 99.28 % and 0.71% respectively. Worldwide various uranium deposits (Table 2.1) are evaluated to determine the extractable amount of uranium as well as the technical methodology for uranium extraction.

Table 2.1: Various forms of uranium found in nature (Merritt, 1971).

Material	U_3O_8 content (ppm)
High grade veins	30.000 to 70, 000*
Vein ores	2000 to 10, 000
Sandstone ores	500 t0 4, 000
Pegmatite ores	50 to 1,000
Uraniferous hydrocarbons	10 to 1, 000
Uniferous granites	15 to 100
Uranium mines	5 to 15

***10,000 ppm = 1%**

The extraction of uranium is dependent upon the type of ore, location of ore body, size and the grade of uranium. The different mining techniques for uranium are as follows:

2.1.1 Open pit mining

Open pit mining techniques are employed to exploit ore deposits that are relatively close to the surface of the earth. Topsoil is typically removed separately and stockpiled. Overburden, the material overlying the deposit is then removed using scrapers or trucks with mechanical shovels (EPA, 1995). In Figure 2.2, an open pit process used at Navachab gold mine (located 170 km North West of Windhoek) is shown. A significant quantity of open pit mining is also done in the Congo and Gabon (WNA, 2011). The uranium used for the Manhattan project was for instance mined at Shinkolobwe mine in Katanga.

Figure 2.1: Navachab Gold open pit mine (Mining Background, 2011).

2.1.2 Underground mining

Underground mining involves sinking a shaft near the ore body to be mined and extending levels from the main shaft at various depths. As underground mining techniques are able to leave much of the non-ore bearing material in place, the ratio of waste (development) rock to ore is much lower than stripping ratios in open pit mines. Ratios of waste rock to ore range from 1:1.5 to 1:16 (EPA, 1995). Figure 2.3 illustrates the Ezulwini mine found in South Africa in which the underground mining technique is used. The same operation is also found at the Olympic Dam mine in South Australia.

Figure 2.2: Ezulwini underground mine, South Africa (Scheele, 2011)

Underground mining technology used at the Rossing mine in Namibia produced 3519 tonnes of uranium in 2009, making it the 3rd largest underground uranium mine in the world (OECD, 2005).

2.1.3 In situ leaching

In situ leaching involves dissolving uranium from unconsolidated sandstone with liquids without removing the host rock. The method uses leaching liquids, for example sulphuric acid (H_2SO_4), being pumped into the uranium ore through boreholes. Uranium dissolves in the acid, and the solution is pumped from a lower level in the rock. A requirement is that the uranium must be located below the water table in a confined aquifer range (Zavodska et al., 2012). This process is used in Kazakhstan (Scheele, 2011) and is also in operation at Honeymoon mine in South Australia (Hardy, 1972). Figure 2.4 illustrates the in situ leaching mining.

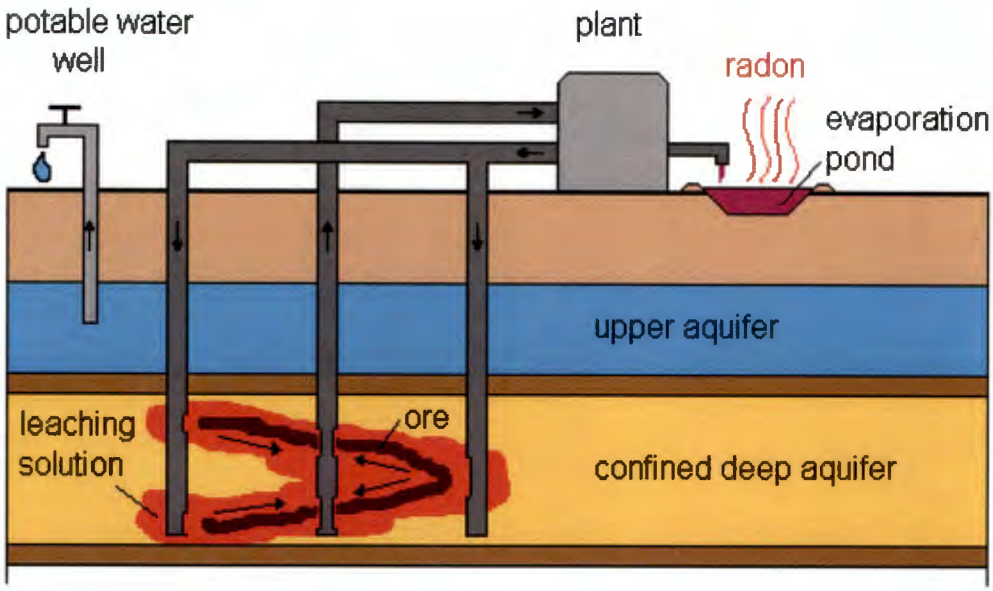

Figure 2.3: In situ leaching (Scheele, 2011)

2.2 Recovery of uranium in South Africa

Uranium exploration in South Africa (SA) started in 1944 whereby much attention was initially focused on the occurrence of uranium in the gold bearing Witwatersrand quartz-pebble conglomerates. South African uranium production started in late 1952 at two gold mines with the generation of 40 tonnes of U_3O_8 from gold plant residues. This can be considered the first commercial plant for recovery of uranium in SA and was carried out at West Rand Consolidated mines (Young, 1980).

Currently uranium is recovered as a byproduct from gold production for economic benefits to minimize the environmental impact and often uranium bearing ore contains potentially economic concentrations of rare earths metals (Edwards and Oliver, 2000). The production of uranium ore concentrates (as a byproduct from gold mining) are currently produced as follows: i) Milling of ore, ii) Production of leach liquor from the ore by alkaline or acid leaching process. iii) Purification of the leach liquor solution by solvent extraction or ion exchange processes and. iv) Precipitation of the yellow cake with ammonia, magnesia or other reagents (Hardy, 1972). A short description of each of these steps is as follows.

2.2.1 Milling

In the milling operation the ore is mechanically processed in order to optimize the surface area for chemical extraction of uranium. The first step in the milling process involves crushing and grinding the ore into smaller, uniform particles. Uranium present in these particles is usually around 0.1 % from the total ore being processed.

Often water or lixiviant (i.e. a liquid medium used in hydrometallurgy to selectively extract the desired metal from the mineral or ore) is added during the milling stage to control dust and to facilitate the milling process. Screens separate fine particles from coarse particles and the coarse particles are recirculated back to the milling circuit. Dust that is not sufficiently suppressed by the addition of the lixiviant is generally collected by air pollution control mechanisms and the dust returns as fugitive particles to the milling process. The material produced from the milling process is usually sent to the refineries for further processing. Figure 2.5 illustrates the ore before milling.

Figure 2.4: Ore before milling and leaching of uranium (Uranium ore, 2011)

2.2.2 Dissolution of milled ore

In the uranium ore processing the mineralogy of the ore affects the leaching step as the characteristics of the gangue mineral and the concentration of the uranium mineral present dictate the conditions to be used in the dissolution process (Gow, 1985). Uranium can be leached by acid or by alkaline solutions. However, the oxidation of uranium is the first step in any uranium dissolution operation as a high percentage of uranium is found mostly in nature in the (+4) oxidation state. This is mainly insoluble and must be converted into soluble U

(VI). For instance UO_2 present in Uraninite requires oxidizing to the hexavalent form for extraction:

$$UO_2 + 2e^- \rightarrow UO_2^{2+} \quad (1)$$

The oxidation reaction of uranium can be quite complex (Hardy, 1972). In acid dissolution medium oxidation is sometimes achieved by the addition of ferric ions:

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+} \quad (2)$$

For the dissolution with a carbonate medium, ferric ions will not be successful due to precipitation under alkaline conditions. For oxidation of these solutions copper (II) ammonium can be used (Hardy, 1972).

The second step in a dissolution process is the stabilization of the uranyl ions in solution (International mining, 2008). Uranyl ions form stable, soluble complexes with sulphate (SO_4^{2-}) or carbonate (CO_3^{2-}) (International mining, 2008). For example in a sulphuric acid solution the complexes $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ are formed while in carbonate solutions, depending on the pH, the complexes $UO_2(CO_3)$, $UO_2(CO_3)^{2-}$ and $UO_2(CO_3)_3^{4-}$ are formed (Hardy, 1972).

The dissolution can be described by the following equations (Hardy, 1972):

Oxidation reaction: $UO_3 + 2H^+ \rightarrow UO_2^{2+} + H_2O.$ (3)

In acid leachate: $UO_2^{2+} + 3SO_4^{2-} \rightarrow UO_2(SO_4)_3^{4-}$ (4)

In alkaline leachate: $UO_2^{2+} + 3CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-}$ (5)

Alkaline leaching is preferred when the initial raw ore contains a significant portion of limestone (greater than 12%), as the acid leaching process requires uneconomically large amounts of acid to neutralize the limestone before leaching. Alkaline leaching, however, requires much finer ground ore in comparison to those used for acid leaching. At the Langer Heinrich uranium mine in Namibia, the uranium is liberated from the ore body using a tank based alkaline leach process followed by ion exchange and roasting to produce the final product, U_3O_8 (Mining background, 2011).

2.2.3 Uranium recovery in South African gold mine operations

In South African gold mines, crushed ore is dissolved in sulphuric acid to recover gold. Gold is removed from the solution through filtration and then uranium remains as a uranyl sulphate $UO_2(SO_4)_2^{2-}$ in solution. The uranyl sulphate solution can be processed by different methods depending on the goal production method used (Colborn et al., 1980). A general method is as follows:

An ion exchange plant which consists of three to four columns packed with a strong base anion-exchange resin is used. Uranium is adsorbed onto the resin as a uranium sulphate complex $UO_2(SO_4)_2^{2-}$. After leaching the uranium from the resins, the pH of the generated solution is adjusted by the addition of calcium oxide. This results in the precipitation of iron and other impurities still present, thereby purifying the uranium solution (Colborn et al., 1980). Once the uranium has been concentrated by evaporation of the solution, precipitation to produce yellow cake is initiated (Figure 2.6). The precipitate is then washed, filtered and drummed for further uranium processing processes (International mining, 2008).

The yellow cake is then transported for further purification and treatment at Nufcor. The final product from such refineries is usually of nuclear purity but the specification differs from country to country (Hardy, 1972).

Figure 2.5: The final product of uranium recovery process called yellow cake.

2.3 Conversion of ammonium diuranate (ADU) to UOC at Nufcor.

The South African gold mining industry produces ammonium diuranate slurry which is converted to uranium oxide concentrates in a plant operated by (Nufcor) since 1953 (Figure 2.7). Currently Nufcor produces about 500 tonnes of uranium per year from material trucked in from various gold mines and Phalaborwa copper mines. The procedure at Nufcor is first to blend the product received from different mines to ensure a constant homogeneous grade of product. This is done as follows:

Materials collected from mines are transported in a sealed container unit to be weighed and sampled by Nufcor. During the process of weighing and sampling, the material is loaded into one of two rubber lined sample tanks and mixed with agitator paddles on a vertical shaft. Primary samples are then drawn by suction into a flask through stainless steel tubes passed down through the depth of the liquid during agitation (Young, 1980).
After sampling, the slurry is pumped to one of a bank of larger interconnected storage tanks which are also rubber lined and fitted with agitation paddles. Where required it can be mixed with ADU from other mines before further treatment. The second step at Nufcor is to remove the excess water to minimize the weight of the material. This is done by filtration.

There are three similar production lines and these can be operated simultaneously in parallel. Each consists of a pair of rotary drum filters, an extruder, a belt dryer and rotary calcining kiln. Each of these lines was originally designed to have a capacity of almost 2000 tons of U_3O_8 per year giving a total installed capacity of just under 6000 tons per year (Young, 1980).

The filters are mounted on a platform above a perforated plate on which filter cakes fall. The cake is pressed by a cake pair roller through 6 mm diameter holes in the plate to form spaghetti like extrusions on the dryer belt below (Young, 1980). During the drying process the extrusion of ADU filter cake cracks into 6 mm pellets which although abraded and shrunk, are used in a subsequent part of the process to determine the characteristics and texture of concentrates from the plant (Young, 1980).

The ADU is dried in an air stream in a totally enclosed container under slight negative pressure and air is drawn back into the dryer by fans. The air used is heated by steam and electrically to 130° C before circulating over the belt. The moist air is then released outside the building through the dryer. ADU chips are recovered by a screw conveyor into three calcining furnaces which are horizontal cylinders of stainless steel of 1 mm diameter and 6 mm long supported and turned by electrically driven rollers (Young, 1980).

In the final step the oxidation of ADU to UOC is as follows:

The calcined ADU is heated externally by the Calrod elements surrounded by heavy thermal insulation. The calcining temperature reaches more than 500° C. The chips are transformed successively from yellow ADU at the inlet through orange UO_3 to grey- green concentrates made up of UOC. The total energy used for the calcination operation is above 300 kW.h per tonne of U_3O_8 produced (Young, 1980).

The UOC from Nufcor is hygroscopic and re-calcination of the material has to be prolonged at 800° C to stabilize the product before it can be sealed in sample bottles for further processing (Young, 1980).

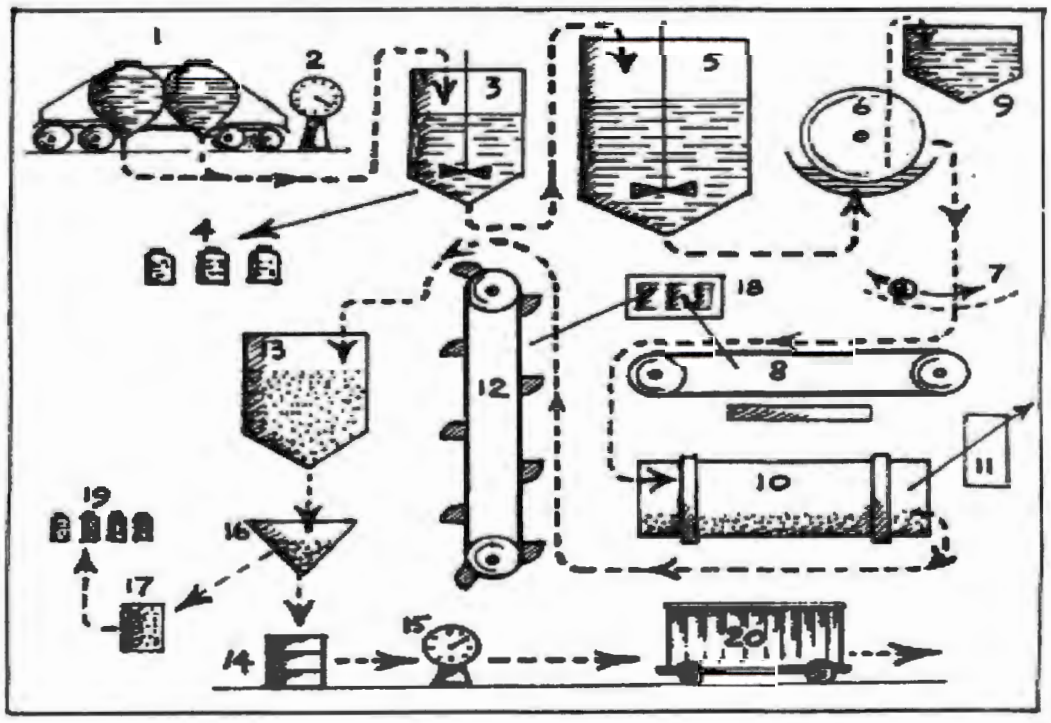

Figure 2.6: Illustrates the process for the Nufcor plant

The Nufcor plant process: 1 road tanker; 2 weighbridges; 3 ADU sampling tank; 4 ADU samples; 5 ADU storage tank; 6 ADU filter; 7 ADU extruder; 8 ADU dryer; 9 filtrate settling tank; 10 calcining furnace; 11 wet scrubber; 12 bucket elevator; 13 dry storage hopper; 14 steel drum; 15 platform scale; 16 falling stream sampler; 17 primary sample; 18 dust filters; 19 secondary samples; 20 shipping container (Young, 1980).

2.4 Conversion of UOC into UF_6 for the nuclear industry

The conversion process is the process that involves fluorination of a solid uranium oxide into gaseous uranium hexafluoride as UF_6 used in the isotope enrichment process. The conversion process can be described as follows:

$$UO_3(s) + H_2(g) \rightarrow UO_2(s) + H_2O(g) \quad (6)$$

Uranium dioxide is then reacted with hydrogen fluoride to form uranium tetrafluoride:

$$UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 4H_2O(g) \quad (7)$$

The tetrafluoride is then fed into a fluidized bed reactor and reacted with gaseous fluorine to obtain the hexafluoride:

$$UF_4(s) + F_2(g)) \rightarrow UF_6(g) \quad (8)$$

The $UF_6(g)$ is then liquefied and this UF_6 liquid is fed into a distillation column that removes low boiling impurities at the top. The high boiling impurities together with UF_6 are withdrawn from the bottom of the first column and introduced into the center section of a second higher boiling distillation column. The UF_6 is then collected as the top of this second column as a distillate (Edwards and Oliver, 2000).

Alfredson (1972) reviewed the different methods and technologies for the production of UF_6 and reported that for UOC, three processes were developed for the production of UF_6 (Figure 2.8).

A description of the three processes is as follows:

Process A: UOC is dissolved in nitric acid to form uranyl nitrate solution. From the solution uranium can be purified using a solvent extraction process. Ammonia is injected into the

purified uranyl nitrate solution in order to precipitate the uranium as ADU. This process was used at the first uranium plant in the United Kingdom and by COMURHEX at its Malvesi plant in France. The process has also been studied by the Australian Atomic Energy Commission and improvements were made to the plant (Alfredson, 1972).

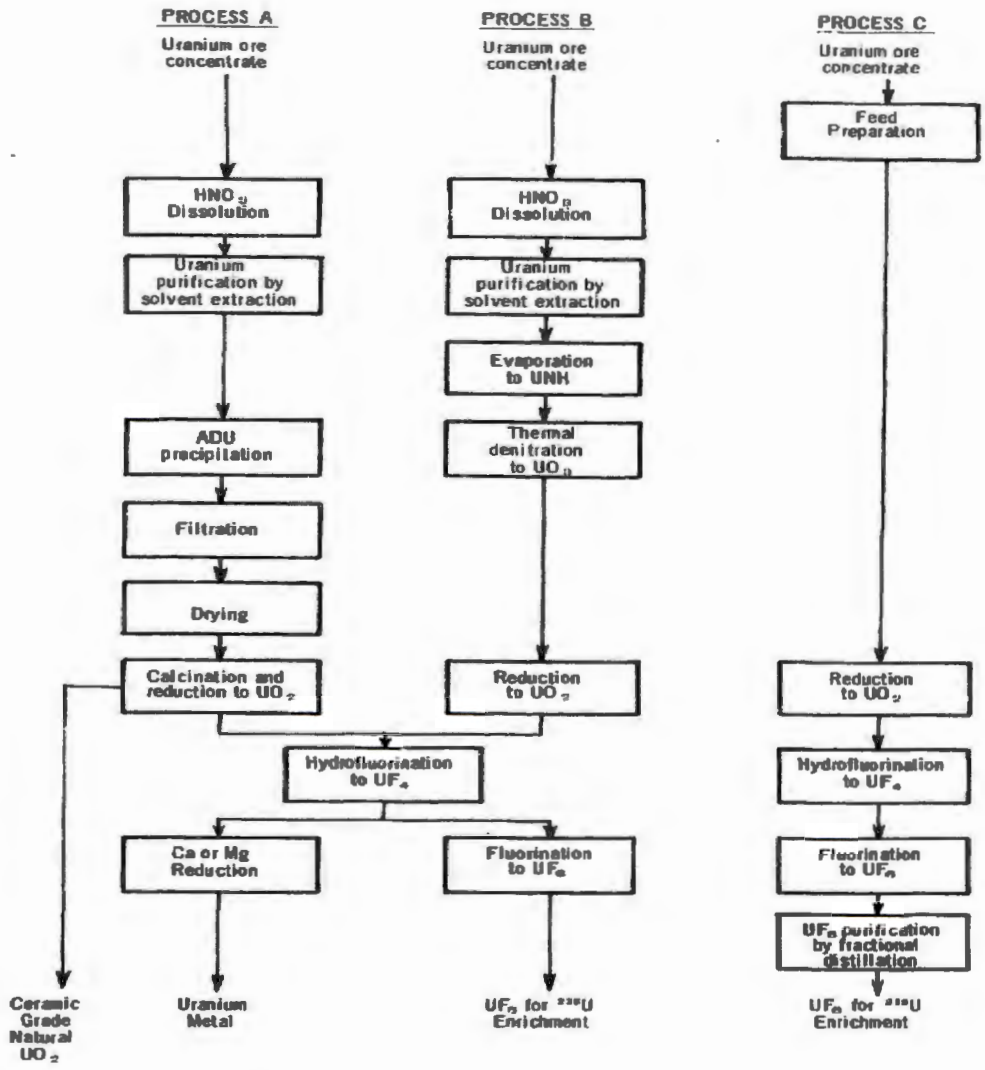

Figure 2.7: Illustrates process for the production of nuclear grade UF_6 for UOC.

Process B: The purified uranyl nitrate solution from solvent extraction is evaporated to form uranyl nitrate hexahydrate (UNH) and then thermally decomposed into UO_3. The UO_3 is reduced to UO_2, and the same process as in process C is followed. This process was used by British Nuclear Fuels Limited at Springfields and also in the United States by Eldorado Nuclear Limited at its refinery in Canada (Alfredson, 1972).

Process C:

Yellow cake material is modified in order to make it suitable for the fluidized bed operation. During this method some of the sodium and potassium impurities are removed. The formed UO_3 is then converted to UF_6 as described in process A. This process was used by the Allied Chemical Corporation in its plants at Metropolis and Illinois (Alfredson, 1972).

In South Africa a uranium conversion facility was built in the early 1980s and originally used for the conversion of ammonium diuranate (ADU) $(NH_4)_2U_2O_7$ (received from an outside supplier) to UO_3, the UO_3 converted to UF_4 and finally the UF_4 into UF_6, as the latter was required for the enrichment process. In some cases U_3O_8 was obtained from the outside suppliers as feed material to produce UO_3.

The SA process utilizes a moving bed reactor (MBR) for the conversion of triuranium oxide (UO_3) to uranium tetrafluoride (UF_4) with a countercurrent flow of the reacting gas phase. In the first section of the reactor UO_3 is reduced to UO_2 by means of ammonia (NH_3) and not by hydrogen and in the second the UO_3 is hydrofluorinated to UF_4 by means of hydrogen fluoride (HF). The gases and the solid counter currently flow in the reactor (Ponelis, 1982) (Figure 2.10).

After grinding, the formed materials of the fine UF_4 particles are fed into a flame reactor by means of a dosing screw to control the ratio between UF_4 and fluorine. In order to obtain a maximum efficiency, excess fluorine is necessary but the efficiency was not hundred percent due to the formation of small quantities of unburnt material such as UO_2F_2, U_2F_9, U_4F_{17} and UF_5 that were removed and drummed. Then UF_6 is filtered by means of sintered "Monel filters''. Unburned materials are recycled at the top of the flame reactor until the accumulated dust reaches a radiation level of 500Remμ. After filtering, the purified UF_6 passes through two cold traps assembled in line and liquified at -40° C (Ponelis, 1982) (Figure 2.10).

The alternative reactor used at Honeywell and BNFL is a high temperature fluid bed with a bed of solid calcium fluoride. The inert bed improves heat transfer and maintains a more even temperature, thus prevent sintering of UF_4 feed. UF_4 and F_2 are added to maintain a temperature in the range of 450 – 475 ^{0}C (Edwards and Oliver, 2000).

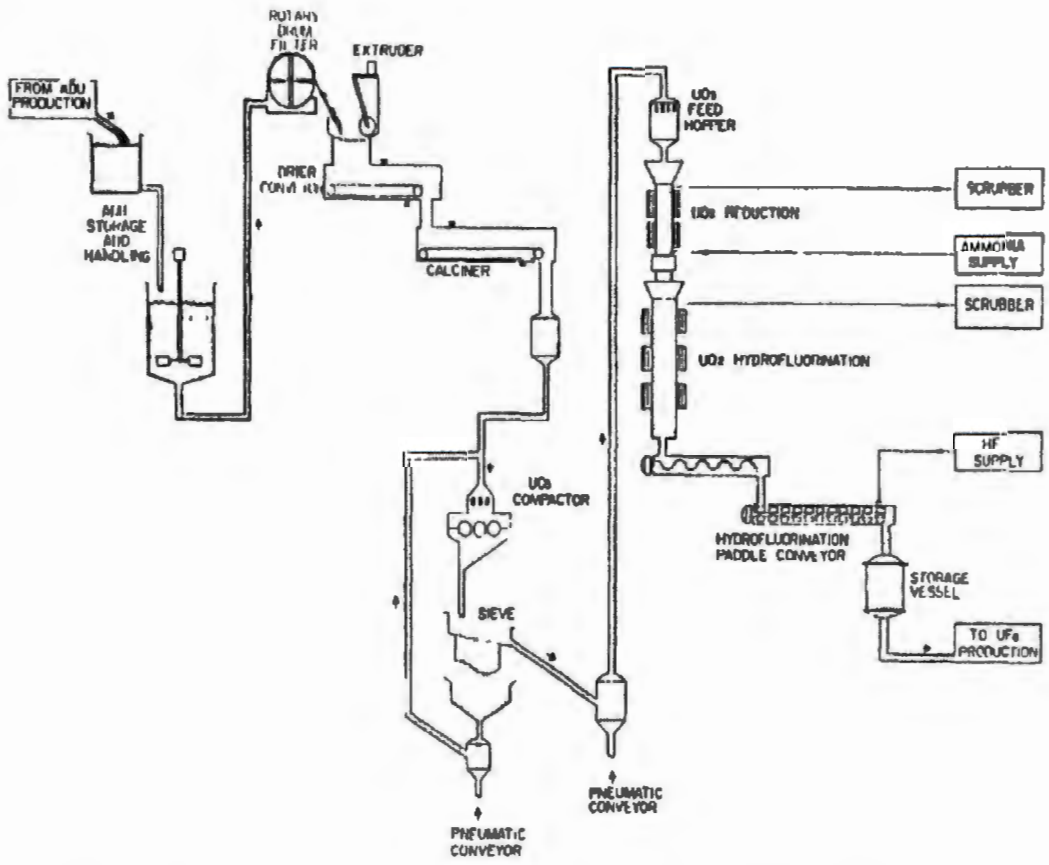

Figure 2.8: Schematic presentation of ADU to UF_4 production at Necsa

In the SA process the hydrofluorination has been affected by the reaction of the gaseous HF with solid UO_2 at elevated temperatures, often resulting in significant excesses of HF in the off gas and additional contaminated waste from off gas treatment processes. Fluorination is carried out by the concurrent flow of solid UF_4 and F_2 gas in shaft reactors called flame towers because of the extremely exothermic reaction, typically operating near 500 ^{0}C (Edwards and Oliver, 2000).

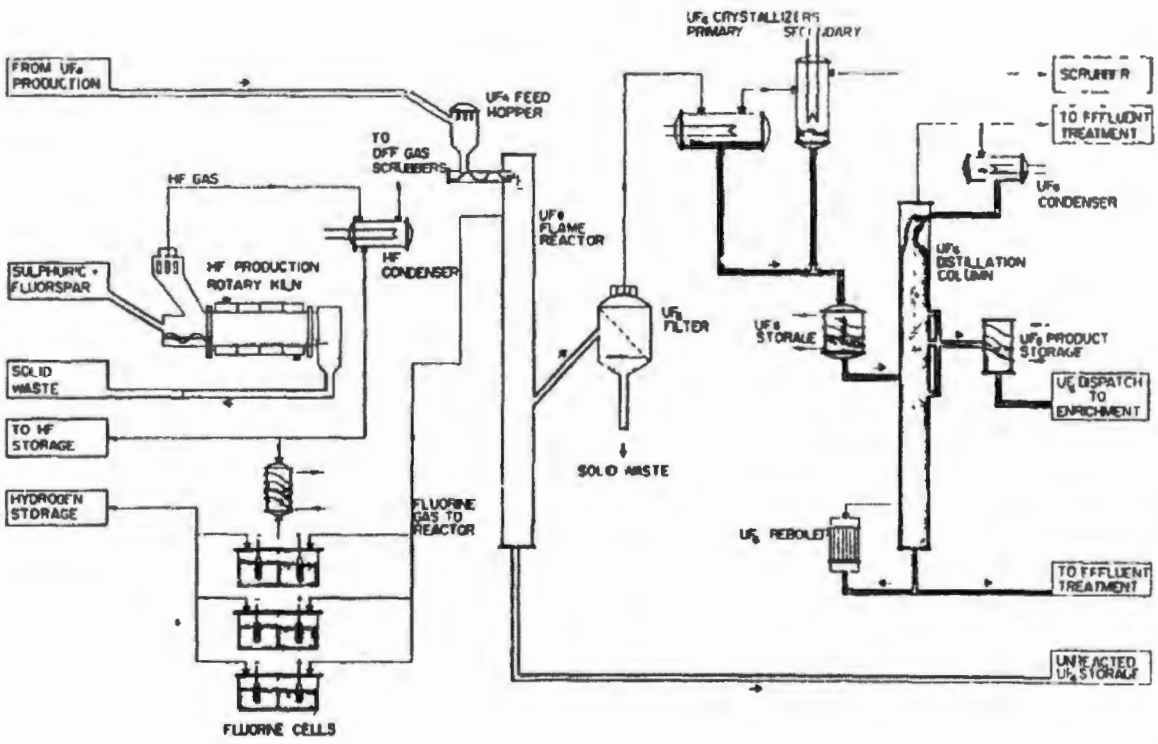

Figure 2.9: Schematic presentation of UF_4 to UF_6 production

During the conversion of UOC to UF_6 at Necsa, results indicated that the formation of sintered solids during the UF_4 phase has resulted in huge amount of stockpiles in the plant due to pipe blockages. Research by Ponelis (1982) indicated that this sintering process is directly related to impurities in the feed material. His research confirmed the following:

- The HF interacts with the Na and K salts (impurities) resulting in a lower conversion rate.
- The presence of Na and K changes the redox condition in that the reverse reaction become more prominent thus giving a decrease in conversion.
- On the surface a NaF – UF_4 compounds forms and prevents the diffusion of HF required to convert particles to UF_4 as indicated in Figures 2.10 and 2.11.

Although problems did arise, the South African conversion plant was able to accept ammonium diuranate slurries which differ considerably (impurities), depending on the producing mine, and to process these slurries directly to uranium trioxide as a suitable intermediate feed stock. This approach, however, has the

disadvantage that the uranium hexafluoride produced does not immediately comply with nuclear grade requirements and has to be purified by distillation.

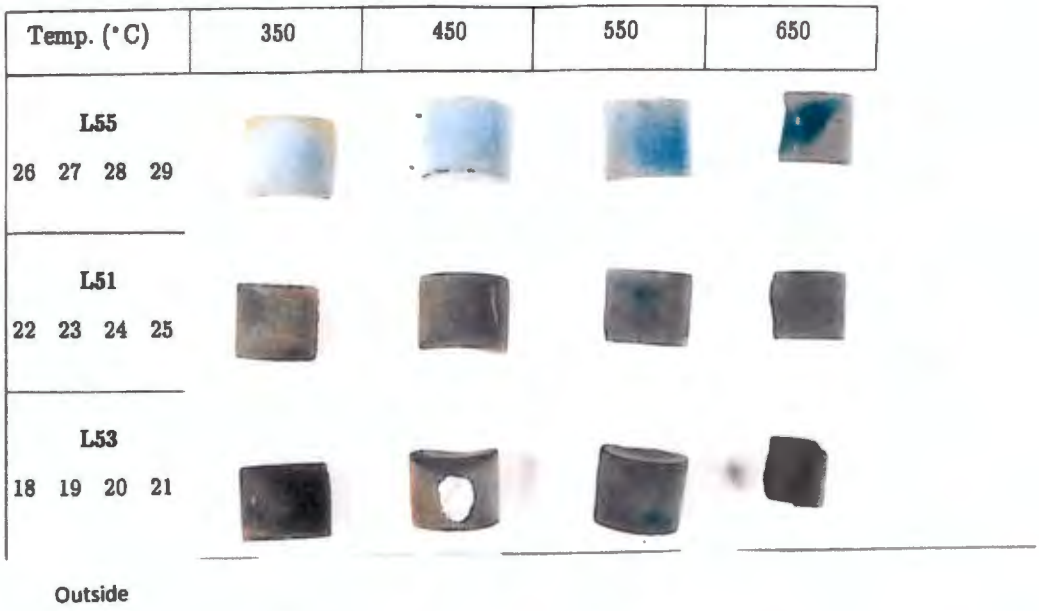

Figure 2.10: Shows the effects on the outside of the sintered material from the conversion process (Ponelis, A., 1989).

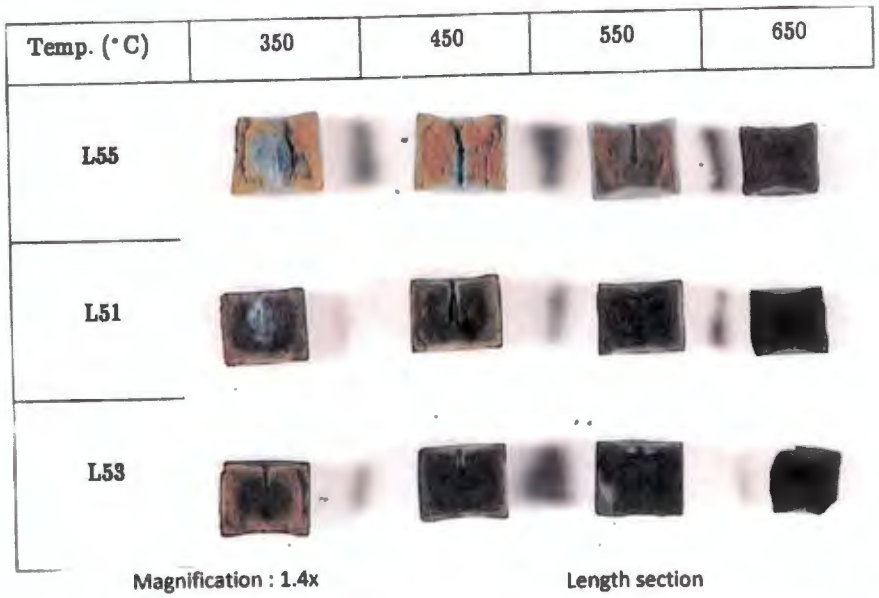

Figure 2.11: Shows the effects on the length side of the sintered material from the conversion process (Ponelis, A., 1989).

This type of purification step was followed in the past at Necsa, but the presence of Mo as impurity renders it not a worthwhile process.

The goal of this study is to study the use of the carbonate route to purify the UOC from the different mines in order to create a homogeneous clean feed material. The carbonate route and not an acid route was selected due to the low solubility of the impurities in a carbonate medium during initial dissolution can contribute to an in situ purification step. Research is then expected to include the purification of the generated alkaline solution.

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Chapter 3

3 Dissolution of UOC using ammonium carbonate with hydrogen peroxide as an oxidant

3.1 Introduction to dissolution of uranium ores

Different solvents can be used to extract uranium from ores and dissolutions are normally based on the characteristics of the uranium in ore; type of uranium mineralization and the nature of the other minerals in the ore (Venter and Boylett, 2009). Acid is generally used in the industry to dissolve uranium powders and uranium can be purified by using liquid-liquid extraction processes or ion exchange technology (Ashbrook, 1986). Necsa uses nitric acid to dissolve uranium powders to form Uranyl Nitrate ($UO_2(NO_3)_2$) that is purified further using liquid – liquid extraction (Stassen & Suthiram, 2011).

Alternatively, the use of alkaline dissolution methodology was first demonstrated on irradiated uranium dioxide powder (UO_2), whereby a mixture of sodium carbonate and hydrogen peroxide was used as leaching reagents (El-Nadi, 2003). This procedure was also investigated at Necsa using simulated post reactor material with different combinations of sodium carbonate/bicarbonate mixture and hydrogen peroxide as an oxidant. However, due to inconsistent results this research was terminated (Stassen & Suthiram, 2011).

The aim of this chapter focuses on the dissolution of UOC using a combination of ammonium carbonate and hydrogen peroxide as leachants. As literature information is very limited on the application of UOC with alkaline leaching agents, UO_2 and UO_3 (composition of UOC) will therefore be included in literature search.

3.2 Literature Review

3.2.1 General Literature

Alkaline dissolution is being considered as an alternative for acid leaching in order to reduce corrosion in a hot cell. In the presence of carbonate solutions at pH > 6, species such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are formed and these soluble species enhance the mobility of uranium under oxidizing conditions (Steward & Mones, 1996).

Uranium has two main oxidation states; an insoluble U (IV) and a soluble U (VI) state. The oxidation of the insoluble U (IV) to soluble U (VI) is important during any leaching operation. The first step in alkaline dissolution / leaching operation is therefore the oxidation of the uranium oxides that are in tetravalent state (U^{4+}) to the soluble hexavalent state (U^{6+}).

The oxidation mechanism of uranium (UO_2) from the tetravalent to the hexavalent oxidation state proceeds in three steps. In step one the gaseous oxygen dissolved in solution adsorbs onto the active sites of the uranium oxide surface. This reaction is relatively fast. The next rate determining step in the oxidation process is the surface reaction between UO_2 and the adsorbed O_2, to form UO_3. Data (Merritt, 1971) has shown that the overall rate of the reaction is directly proportional to the UO_2 surface area and to the square root of the oxygen partial pressure in H_2O. The mechanism on the surface of uranium can therefore be described as follows:

O_2 (gas) $\rightarrow$ O_2 (solution) (fast) (1)

$2UO_2$ (surface) + O_2 (solution) = $2UO_2.O$ (fast) (2)

$UO_2.O$ (surface) = UO_3 (surface) (slow) (3)

The removal of UO_3 from the surface of UO_2 by reacting with carbonate to form $UO_2(CO_3)_2^{2-}$ and the uranyl tricarbonate ion is very slow Merritt, (1971). A suggested mechanism is as follows:

$2HCO_3^{2}$ + H_2O_2 $\leftrightarrow$ CO_3^{2-} + H_2CO_3 + 2OH (4)

$$UO_3 + 2CO_3^{2-} + H_2O_2 \leftrightarrow H_2O + UO_2(CO_3)_2^{2-} + \uparrow O_2 \quad \text{(slow)} \quad (5)$$

$$UO_2(CO_3)_2^{2-} + HCO_3^- \leftrightarrow UO_2(CO_3)_3^{4-} + H^+ \quad \text{(fast)} \quad (6)$$

$$UO_2(CO_3)_2^{2-} + CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-} \quad \text{(fast)} \quad (7)$$

De Pablo et al. (1999) presented evidence of alternative bicarbonate promoted oxidative dissolution mechanism in the hydrogen carbonate solution and interpreted it as a three step process:

1. Initial oxidation on the U(VI) oxide surface
2. Reaction of HCO_3^- with U(VI) at the oxidized layer,
3. Detachment of the U (VI) – carbonato surface complex.

When UO_2 is dissolved in a carbonate solution containing H_2O_2, the dissolution mechanism becomes more complicated and the uranium ions exist in the form of mixed uranyl peroxy – carbonato complexes as shown in the following equation (8) (Kim et al 2009):

$$UO_2 + yCO_3^{2-} + xH_2O_2 + 2xOH^- = [UO_2(O_2)_x(CO_3)_y]^{2-2x-2y} + 2xH_2O + 2e^- \quad (8)$$

Where x/y has three cases of ½, 2, and 3.

The possible different uranium-carbonate complexes that can form during the alkaline leaching are illustrated in Figure 3.1.

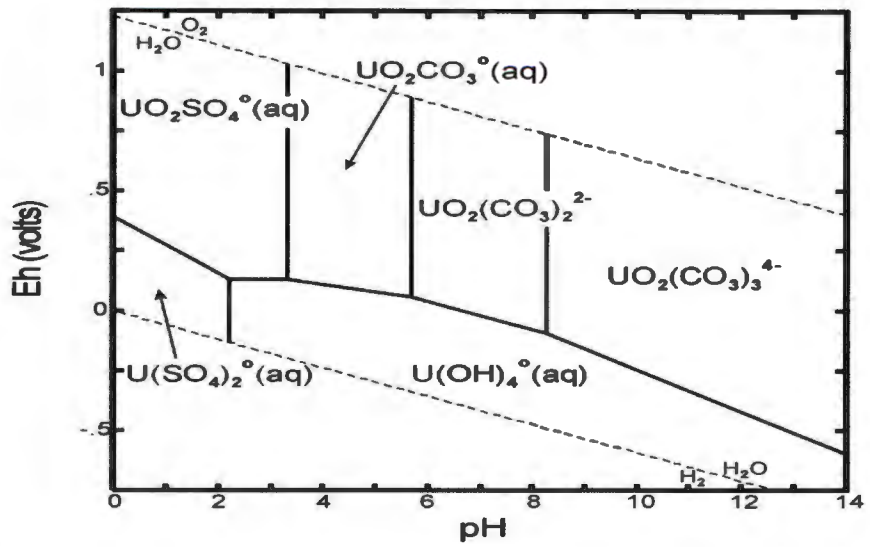

Figure 3.1: EH – pH diagram showing the dominant complexes of uranium in carbonate and sulphate solutions (Krupka and Serne, 2002)

Many studies have been done regarding uranium dissolution using bicarbonate solution but not with ammonium carbonate. Thus an overview on the alkaline leaching of uranium using bicarbonate medium will be presented giving only the main results, in the following section.

3.2.2 Alkaline leaching based on a carbonate medium

Hartley (1972) who studied conventional processes to produce yellow cake indicated that during the alkaline dissolution of uranium (davidite) with bicarbonate solution, the reaction rate almost doubles for every 10 °C increase in temperature (between 60 °C and 100°C).

Results by Hartley, (1972) also indicated that the extraction of uranium present in interstitial cementing material is influenced by particle size as uranium with small particle size extracted faster when compared to coarse uranium material embedded into cement.

Hartley (1972) also reported that the rate of U_3O_8 dissolution increased with increasing leachant (mixture of sodium carbonate and bicarbonate) concentration. Bicarbonate was

necessary to prevent precipitation of dissolved uranium however excess bicarbonate will precipitate if NaOH is present.

Grandstaff (1976) found that at low carbonate concentration (1 mmol/dm^3); the rate of uraninite dissolution was directly proportional to the carbonate concentration. However the same author found no dependence when working at higher carbonate concentrations (0.5 mol / dm^3).

Sharma and co – workers (1996) conducted studies on the kinetics of UO_2 dissolution in carbonate medium using sodium hypochlorite as alternative oxidant. Results indicated that in the temperature range between 303 and 318 K, the leaching increased linearly. The activation energy was calculated to be 57 kJ / mol. This relatively high activation energy value indicates a chemically controlled behaviour of UO_2 dissolution.

Torrero and co workers (1997) determined the dissolution rate of uranium dioxide under oxidizing conditions as a function of pH (between 3 and 12). They postulated that the rate order is influenced by the oxygen concentration, the oxidant adsorption, electron transfer (slow step) and product release from the surface in the form of U (VI). From the data the following rate equation was postulated:

$$r\ (mol.s^{-1}.m^{-2}) = (3.5 \pm 0.8).10^{-8}.\ [H^+]^{0.37\pm0.01}.\ [O_2]^{0.31\pm0.02}\ (3<pH<6.7) \qquad (9)$$

Nguyen and co - workers (1999) studied the dissolution kinetics of UO_2 in a simple pass flow through method in oxygenated carbonate / bicarbonate buffer solution at 25^0C. They reported that the dissolution rate of UO_2 was independent of the oxygen fugacity and was correlated to the carbonate or bicarbonate concentration in the leaching solution. This is in contrast with Torrero (1997) findings. The HO_2^- is a precursor of radicals that can produce stronger oxidizing environments than that of the hydrogen peroxide itself (Andreozzie et al. 1999).

Edwards and Oliver (2000) reviewed technology for the uranium processing and indicated that alkaline carbonate leaching has an additional advantage of being selective for uranium in the presence of other impurities. This has been attributed to solubility values.

Peper et al. (2004) studied the dissolution kinetics of UO_2 in alkaline solutions with various oxidants such as NaOCl, H_2O_2 and $K_2S_2O_8$ at room temperature. Results from this study indicated that with the presence of hydrogen peroxide (H_2O_2), the dissolution rate increased. This was attributed to the fact that H_2O_2 acts as an oxidant as well as ligand under alkaline conditions.

Investigating the dissolution of unirradiated UO_2 by hydrogen peroxide between pH 7 and 9, Clarens et al. (2004) confirmed a linear increase of the dissolution rate with increasing pH. This was attributed to the formation of perhydroxy anions under high pH conditions.

Furthermore, Pierce et al. (2005) studied the dissolution of UO_2, both monolithic and powder using carbonate solution oxidized with oxygen in a single pass flow through system. Results reported that the rate of UO_2 dissolution increased by an order of magnitude with a 30°C increase in temperature. Pierce et al. (2005) also indicated that the rate of UO_2 dissolution in carbonate solution increased with pH and decreased as the dissolved U concentration approached saturation.

In another study Casas et al. (2009) investigated the combined effect of HCO_3^- and H_2O_2 on UO_2 dissolution rates in the absence oxygen. The author reported an increase in the dissolution rate as the concentration of the hydrogen peroxide increased from 10^{-6} to 5×10^{-4} mol dm^{-3} using a fixed bicarbonate concentration of 2×10^{-3} mol dm^{-3}. The study also found that the rate of H_2O_2 consumption increased with increasing HCO_3^- and UO_2 concentrations.

In addition, a dissolution increase with the increase in pH can be related to the increase in the decomposition of the hydrogen peroxide in the alkaline media, as indicated in Equation 10.

$$H_2O_2 \rightarrow HO_2^- + H^+ \qquad pKa = 11.65 \qquad (10)$$

In another study by Kim et al. (2009) with H_2O_2, the results indicated that H_2O_2 can control the redox potential in a solution as it is a salt free oxidant with a redox potential that will only oxidize uranium in the presence of actinide and other fission products.

Results by Smith et al. (2009a) concluded that within the pH range from 8.8 to 10.8, the dissolution rate of uranium is independent of the HCO_3^- / CO_3^{2-} ratio and that high concentrations of HCO_3^- and CO_3^{2-} prevent the precipitation of uranium in solution.

Kim et al. (2009) recently reported this during the oxidative leaching of simulated spent fuel in 0.5 M Na_2CO_3 using H_2O_2 as an oxidant. Using SIMFUEL powders containing uranium and 15 possible contaminants, such as Ce, Gd, La, Nd, Pr, Sm, Eu, Y, Mo, Pd, Ru, Zr, Ba, Sr, Re (as simulant for Tc), and Te, results indicated that only Cs, Tc, Te, and Mo leached together with the uranium. The dissolved impurities were considered to exist in the forms of CsOH, TcO_4^-, $TeO_2(OH)_2^{2-}$ and MoO_4^{2-} in the carbonate solution. As the other elements remained undissolved, good decontamination was achieved during this dissolution step.

3.2.3 Alkaline leaching with ammonium carbonate

Ammonium carbonate is not much used in industry for the leaching of uranium, although it has the benefits of selectivity and the fact that it decomposes to ammonia and carbon dioxide during steam stripping to recover uranium. De Pablo et al. (1999) studied the oxidative

dissolution mechanism of uranium dioxide (with H_2O_2) in ammonium carbonate and reported that the dissolution process increased by increasing the temperature from 10 to 60°C.

Smith et al. (2009b) studied the dissolution of UO_2, U_3O_8 and UO_3 in ammonium carbonate solutions with counter cations NH_4^+, Na^+, K^+, and Rb^+ as impurities. Results indicated that in the presence of 0.1 M H_2O_2 and $(NH_4)_2CO_3$ as leachates, dissolution rates of different uranium oxides decrease in the order: $UO_3 >> U_3O_8 > UO_2$. This could be attributed to the presence of unextractable U^{4+}. The dissolution of UO_2 increases linearly with the addition of hydrogen peroxide from 0.05 to 2 M to form the U^{6+} species that could be extracted.

When studying the dissolution kinetics of UO_2, Pierce et al. (2005) reported that the rate of UO_2 dissolution increased by an order of magnitude with a 30°C increase in temperature. This was also confirmed by the results of Smith et al (2009b) that indicated that the dissolution rate of UOC increased linearly with the increase in temperature (15 to 60°C).

A recent publication by Soderquist et al. (2011) demonstrated the effective recovery and decontamination of uranium during the dissolution of irradiated fuel using an ammonium carbonate and hydrogen peroxide solution. These researchers indicated that although more than 98 % of the irradiated fuel dissolved, 95 % of plutonium, americium, and curium as well as substantial amounts of fission products remains as precipitates thus effectively partitioning the uranium during the dissolution step.

3.2.4 Experimental Approach

The literature review shows that the dissolution of uranium oxides with ammonium carbonate and hydrogen peroxide was done mostly on UO_2, U_3O_8 and UO_3 samples. The current study aimed to investigate the dissolution of Uranium ore concentrate (UOC) which is the mixture

of UO_3 and U_3O_8 using ammonium carbonate and hydrogen peroxide as leachants. Various parameters will be studied and optimized for UOC dissolution.

- Influence of Temperature
- Influence of H_2O_2 concentration
- Influence of $(NH_4)_2CO_3$ concentration
- Dissolution rate

The following section will elaborate upon the equipment and reagents used to achieve the objective of this study.

3.3 Experimental

3.3.1 Equipment used

Pressurized autoclave 100 ml (Parr 4848 reactor controller instrument containing a glass liner capacity of 50 ml) equipped with a thermocouple for accurate temperature control and a high speed overhead stirrer (Figure 2).

A four necked round bottom flask (500 ml) coupled to a reflux condenser (closed system), a thermocouple for accurate temperature control and a magnetic stirrer.

pH meter with a glass electrode and pH measurement papers for the determination of pH. The pH meter was calibrated with commercial buffers at 4.0, 7.0 and 10.0.

Mass balance was used for weighing the UOC mass to be dissolved and all other solid reagents used for the experiments.

Ultra violet spectroscopy (UV VIS) was used to measure the uranium concentration at the absorbance at 450 nm

3.3.2 Reagents

Ammonium carbonate and Hydrogen peroxide were purchased from Merck. Various concentrations of ammonium carbonate solution were prepared using Necsa demineralized water. The UOC powders used in all experiments was obtained from Nufcor.

3.3.3 Experimental procedure

The dissolution of UOC in alkaline medium was investigated using a pressure vessel and round bottom flask apparatus.

3.3.3.1 Leaching of UOC using pressure vessel

The pressure vessel used for the dissolution of UOC was a Parr 4597 Micro Reactor with a 100 ml fixed head, 50 ml glass liner and a 4848 reactor controller (Figure 3.2). Due to a volume limitation of the pressure vessel, the total volume used was maintained at 30 ml throughout all the tests. The UOC (1-3 grams) was dissolved in variable concentrations of ammonium carbonate $(NH_4)_2CO_3$ (1.0, 1.5 and 2.0 M). Hydrogen peroxide (H_2O_2) was added ranging from 0 to 2.5 M to investigate the effect of this oxidant. The effect of temperature on the dissolution rate of UOC in 1.0 M $(NH_4)_2CO_3$ and 1.0 M H_2O_2 was evaluated ranging from 30 – 70 °C using the pressurized autoclave connected to a temperature controlled water circulating pump.

The whole experiment was performed as follows: 30ml of 1M leachant (27 ml of $(NH_4)_2CO_3$, 3 ml of H_2O_2) was mixed at the bench and poured into the autoclave glass liner. Then followed the addition of a minimum amount of 3 grams of UOC into the solution. After adding the UOC, CO_2 formation was observed as an indication of the initial reaction between UOC and leachates. Immediately after adding the UOC, the reactor was closed. The temperature was set on the control panel to the required value and the system was pressurized to 4 Bar with oxygen. The pressure of the solution increased with the increase in temperature during the dissolution process ranging from 4 to 6 bars.

After the dissolution, the generated solution was filtered with Whatman 150mm filter paper and the undissolved residue was washed, dried and weighed to determine the amount of the undissolved uranium.

Figure 3.2: Pressurized autoclave that was used to investigate dissolution of UOC

In the case of the oxygen experiments, initial reactants were 30 ml of 1.0 M $(NH_4)_2CO_3$ and 3g of UOC. No H_2O_2 was used. As oxidant, oxygen at 4 or 6 bars pressure was used to pressurize the reactor vessel through the gas inlet valves. After the oxygen was supplied to the required amount, the temperature was set to the required level and the experiment was left to run for three hours.

3.3.3.2 Bench experiments

Dissolution rates were determined by bench experiments. The setup used involves a round bottom flask (500 ml), Heidolph hot plate with flask coupled to a reflux condenser (closed system), a thermocouple for accurate temperature control and a magnetic stirrer in order to agitate the reaction mixture at a speed between 0 and 500 rpm (Figure 3.3). For bench

experiments a mass of 17g UOC was used with 166.7 ml of leachants made up of 150 ml of 1M $(NH_4)_2CO_3$ and 16.7 ml of 1M H_2O_2 solutions. The procedure for adding the mixture was similar to that for the pressure vessel experiments.

The pH of the solution was monitored throughout the leaching process by means of a pH meter using a combined glass electrode. The dissolution reaction rate was determined for different completion times (1 hour, 2 hours and 3 hours) for every 10 minutes from the onset.

Aliquots (5 ml) were periodically removed from the flask using a pipette to a vial. Accurate measurements of uranium were performed as follows: The solution in a vial was centrifuged at 6000 rpm speed for 5 minutes to separate undissolved UOC and liquid. After separating the solids from the liquid, the liquid solution was left for 24 hours to cool down before analysis.

The uranium concentration in the liquid was determined by ultra violet visible spectroscopy using the carbonate / peroxide method.

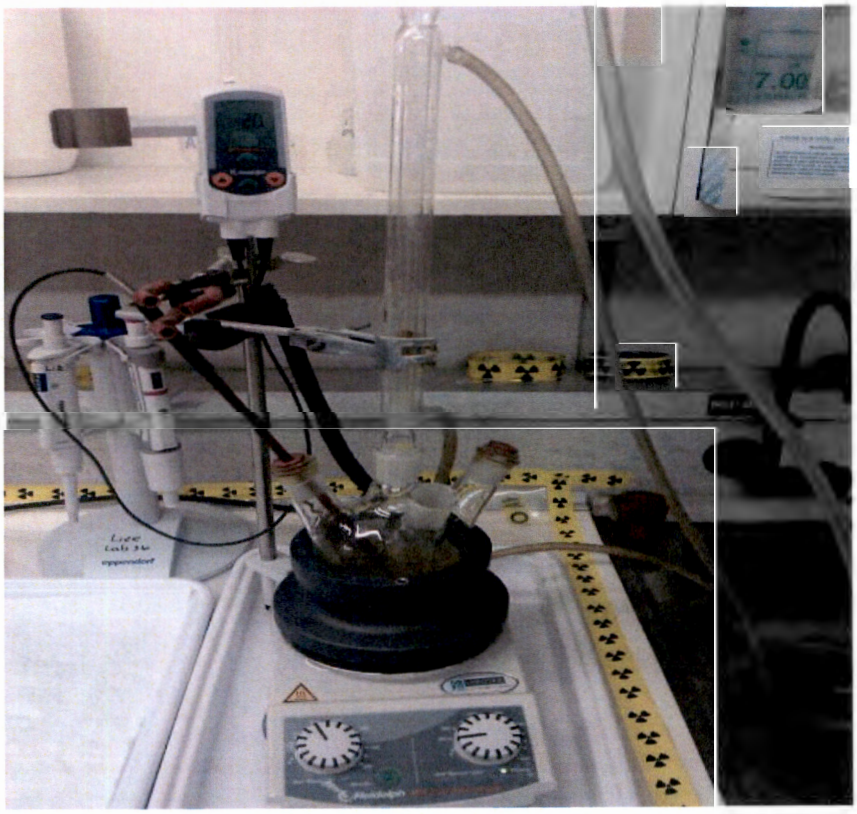

Figure 3.3: Experimental closed system set-up used to investigate the dissolution of the unirradiated U residue (bench runs).

3.3.4 Analytical techniques

As mentioned in Section 3.3.3.2 the leach solutions were analyzed for uranium concentration using the standard hydrogen peroxide-carbonate spectrophotometric analytical method.

This hydrogen peroxide-carbonate spectrophotometric method is suitable to analyse uranium concentrations in the 20-200 ppm range. It is based on the intense yellow colour of the $[UO_2(CO_3)_2OOH]^{3-}$ - complex which can be measured at 450 nm. A very short description of this Ultra violet visible spectroscopy method is as follows:

The term spectrophotometer analysis is a technique whereby the interaction of chemical species with electromagnetic radiation is determined and documented by means of a spectrum. In a UV- Spectrophotometer instrument, an input device is used to convert chemical information of a sample into information in the form of electromagnetic radiation. Therefore the device is a transducer that encodes the chemical information into another form, i.e. electromagnetic radiation. To extract the chemical information encoded in the radiation, a second transducer, called the detector is required.

Ultraviolet – visible spectroscopy is a useful and reliable technique to carry out qualitative and quantitative analysis of liquid samples with low and high concentration of uranium.

Peroxide / Carbonate method

This method was first developed during the Manhattan project (Rodden, 1950) and has since been used worldwide. This method was used is as follows:

Four standard solutions (50; 100; 150 and 200 ppm), using a 1000 parts per million (ppm) U standard solution, was made by diluting 1.25; 2.5; 3.75 and 5.0 ml into respective 25 ml volumetric flasks.

The $[UO_2(CO_3)_2OOH]^{3-}$ complex was developed as follows:

3 ml of 2M Na_2CO_3 was added to each flask followed by the addition of 1 ml of 30% H_2O_2. The flasks with a mixture of standard solutions, 2M Na_2CO_3 and 30% H_2O_2 were filled with de-mineralized water to a known volume and shaken to assume a homogeneous mixture. The absorbance at the 450 nm wavelength was measured by the spectrometer.

A calibration curve can be obtained by plotting the absorbance value versus the uranium standard's concentration as illustrated in Figure 3.4. An equation for the best line fitting the plot can be obtained by using a linear regression with the method of least squares. This equation was then used by interpolation to calculate the uranium concentration of samples.

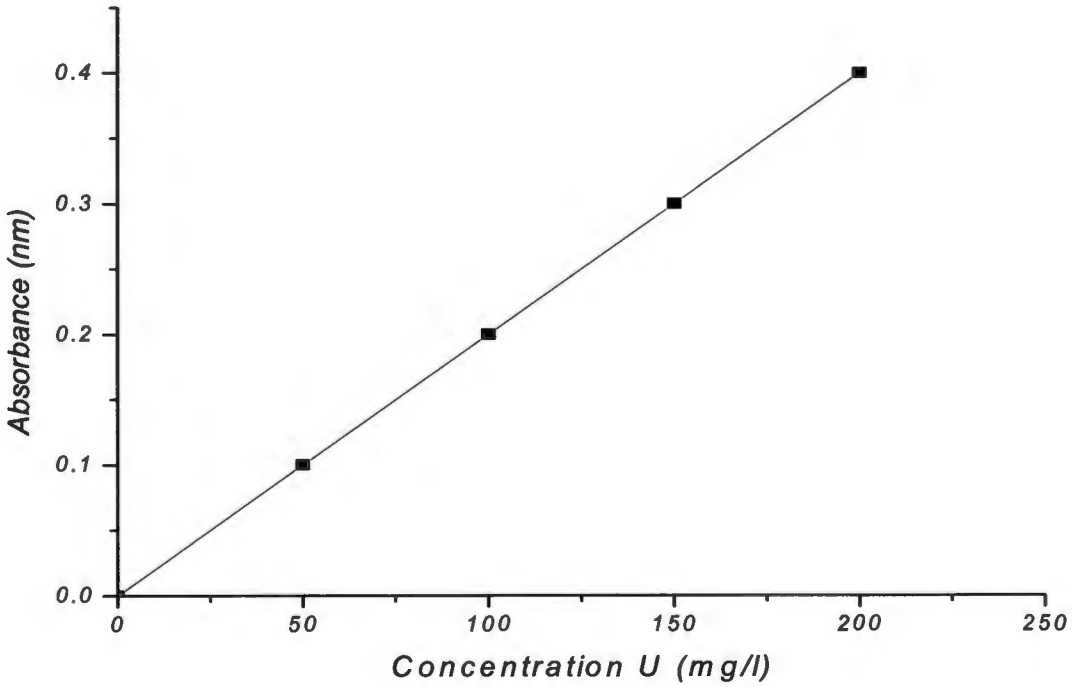

Figure 3.4: Carbonate calibration curve of uranium standard solutions.

3.4 Results and Discussion

3.4.1 Experiments with autoclave

As shown in the literature section, the dissolution rate of UOC should depend on the pH, the concentration of leachate, temperature, oxidant, impurities in the mineral and uranium solubility in the leachate solution.

For this study, the influence of several parameters on the dissolution process of UOC using alkaline leachants under the autoclave conditions was investigated. These include for instance the influence of ammonium carbonate concentration, H_2O_2 concentration, Oxygen as oxidant, influence of temperature and influence of agitation.

3.4.1.1 Influence of Agitation

By stirring a solution, the dissolution rate will increase due to the replacement of new leachate at the dissolution surface. To determine if this phenomenon is also applicable to UOC, two experiments were performed as described in Section 3.3.5. The uranium analysis were done as mentioned in section 3.3.5 (Experimental) with the exception that for one dissolution experiment the solution was stirred by a magnetic stirrer and the other not. The results from this experiment (analysis of uranium dissolved) are presented in Figure 3.5 and the raw data is in Table 8.1 in Annexure A.

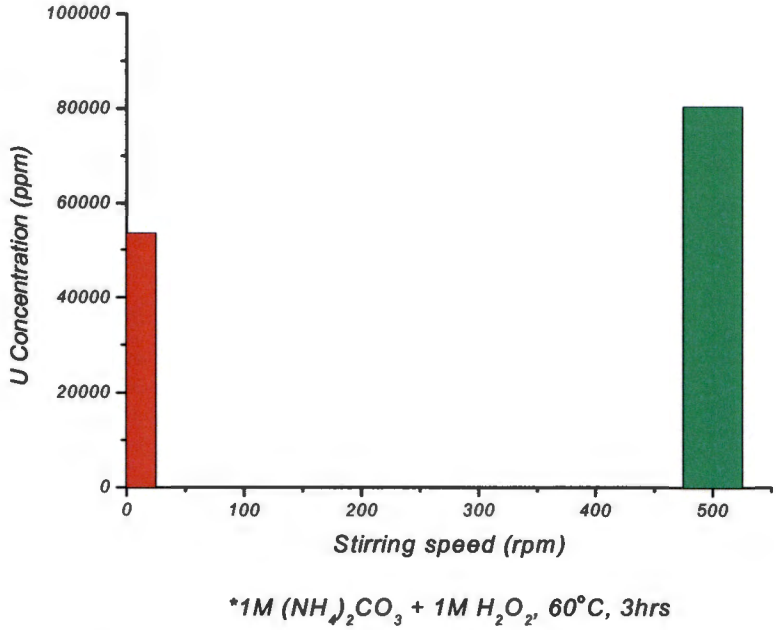

Figure 3.5: The effect of stirring on the dissolution of UOC.

The results in Figure 3.5 clearly indicated that with additional stirring the amount of UOC that was dissolved during the same period increased from 53314 ppm to 80201 ppm for the same amount of UOC and volume of reagents. Therefore all the following experiments will be done with the stirring option of 500 rpm by means of magnetic stirring.

3.4.1.2 Influence of H_2O_2

The literature indicated in section 3.2.2, that for maximum extraction of uranium, the uranium must be in VI oxidation state. It is therefore important to maintain this oxidation state. As the material of this study is UOC (U_3O_8 and UO_3) the influence of oxidants on the dissolution rate must be determined. The experiment was done as described in Section 3.4.1 and the results are shown in Figure 3.6. The raw data used to construct Figure 3.6 are in Table 8.2 and Tables 8.7 to 8.10 in Annexure A. Percentage error is less than 3% and this was based on three successive experiment performed.

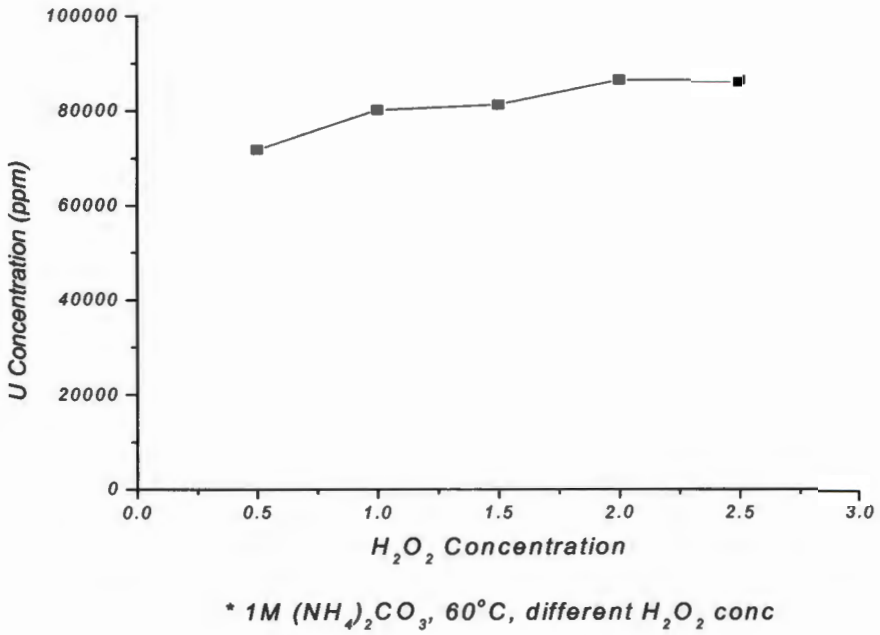

Figure 3.6: The effect of Hydrogen peroxide concentration on the dissolution of UOC.

The results in Figure 3.6 indicated that the dissolution of UOC increases with an increase in H_2O_2 concentration. This observation is consistent with that reported by Smith et al. 2009. The amount of Uranium dissolved increased from about 70 000 ppm to 90 000 ppm with the addition from 0.5 to 2.5 M H_2O_2. The results indicated that an optimum is reached at 2 M H_2O_2 where after the dissolution remain the same. This increase in dissolution can be attributed to the oxidation of the U (IV) to U (VI) in UOC powder.

The possible reaction is as follows:

In the absence of H_2O_2 in the dissolution of UOC the predominant chemical reactions are:

$$U_3O_8(s) + 6(NH_4)_2CO_{3(aq)} \rightarrow 3UO_2(CO_3)_2^{2+} + 3(NH_4)_4^{+} + O_2^{-} \quad (11)$$

$$UO_3(s) + 3(NH_4)_2(CO_3)(aq) \rightarrow UO_3(CO_3)_3^{4-}(aq) + 6\,NH_4^{+}(aq) \quad (12)$$

When H_2O_2 is present in the solution, the formation of carbonate peroxo complex is as follows:

$$U_3O_8(s) + 6(NH_3)_2\,CO_3(aq) + H_2O_{2(aq)} \rightarrow 3UO_2(O)(CO_3)_2^{2-} + 6\,NH_4^+ + H_2O \quad (13)$$

$$UO_3(s) + 3(NH_4)_2\,CO_3 + H_2O_2 \rightarrow (UO_2)(O_2)(CO_3)_3 + 6\,NH_4 + H_2O \quad (14)$$

The experimental results affirm that H_2O_2 is needed to optimize the dissolution of UOC with ammonium carbonate solution.

3.4.1.3 Influence of Oxygen as oxidant

The results in Section 3.4.1.2 indicated that for maximum dissolution of UOC using ammonium carbonate solutions, the uranium (IV) present must be oxidized to the extractable U (VI) in order to form a carbonate complex. The replacement of H_2O_2 by oxygen as oxidant (and used as pressure gas for the autoclave) was investigated to evaluate the efficiency of oxygen to oxidize the uranium from +4 to +6 state. The investigation was limited to two experiments as described in Section 3.3.3.1. The data summarized in Table 8.3 in Annexure A was used to plot Figure 3.7.

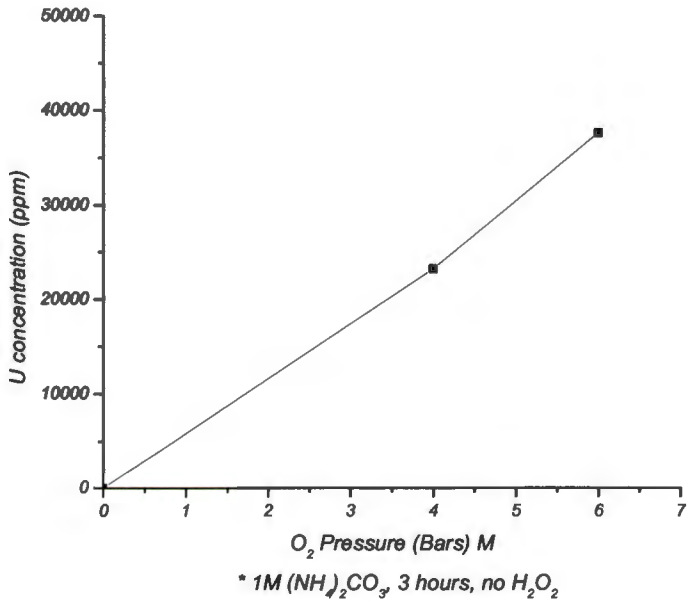

Figure 3.7: Effect of oxygen on the dissolution of UOC

The results in Figure 3.7 indicated that at 4 bar O_2, 22000 ppm concentration of uranium was obtained and at 6 bar O_2, 37000 pm concentration was obtained under the same experimental conditions. This lower dissolution than with H_2O_2 could be attributed to the following possible scenarios:

Oxygen of (6 bars) did not facilitate the conversion of U(IV) to U (VI) as found in the UOC powder and the mass transfer of oxygen from the gas phase to solution phase is slow.

$UO_2(CO_3)_2$ complex formation is very slow in the presence of oxygen (Merritt, 1971) compared to the complex formation of $UO_2(O_2)(CO_3)_3^{4-}$ complex where H_2O_2 is present.

The rate of the oxidation of U(IV) to U(VI) is slower with Oxygen than with H_2O_2 .This was similar to that reported by (Merritt, 1971 and Torrero et al. 1997).

When comparing with the previous experiment done with H_2O_2, it is clear that oxygen is not an effective oxidant to oxidize UOC. As H_2O_2 is kinetically a faster oxidant than oxygen, all the remaining experiments were done using H_2O_2.

3.4.1.4 Influence of $(NH_4)_2CO_3$ concentration

Hartley (1972) in the literature Section 3.2.2 indicated that with sodium carbonate leaching the rate of dissolution increases with increasing leachant concentration. Since the leachate for this study is ammonium carbonate, the influence of ammonium carbonate concentration on the dissolution rate of UOC was determined. The experiment was done as described in Section 3.3.3.1. The results in Figure 3.8 (raw data in Tables 8.4 and Table 8.11 to 8.13 in Annexure A) illustrate the influence of various $(NH_4)_2CO_3$ concentrations on the dissolution of 3.0 g UOC with 1.0 M H_2O_2.

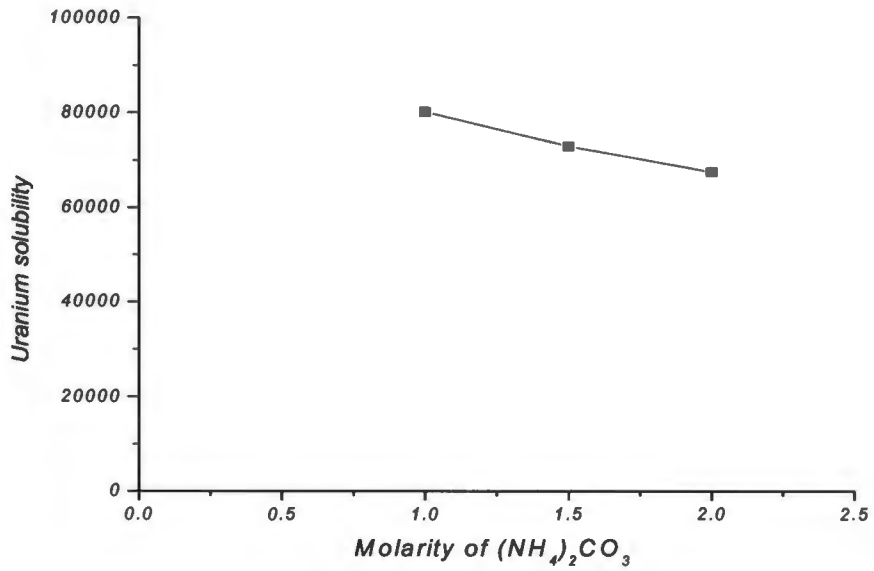

Figure 3.8: Effect of Ammonium carbonate on dissolution of UOC

The results in Figure 3.8 indicated that a decrease in $(NH_4)_2CO_3$ concentration results in an increase in uranium present in solution. (2M: 67448 ppm compared to 1.5 M: 72899 ppm and 1 M: 80201 ppm). This could be explained in terms of the solubility of uranium in the leachate ($(NH_4)_2CO_3$ + H_2O_2) as previously reported by Hurst and Crouse, (1961) for the solubility of ammonium uranyl tricarbonate in ammonium carbonate solution. The results they give indicated that the solubility decreases with increasing concentration of $(NH_4)_2CO_3$ (Figure 3.9).

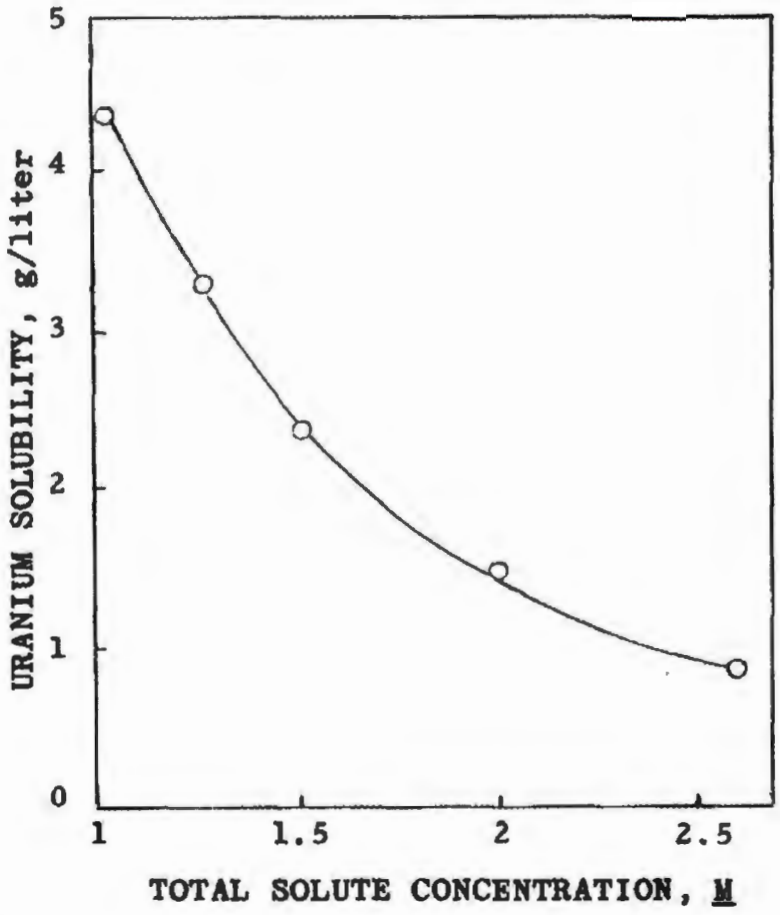

Figure 3.9: Solubility of ammonium uranyl tricarbonate (AUT) in $(NH_4)_2CO_3$ solution at 25°C (Hurst & Crouse, 1961).

This is confirmed by the presence of a dark green precipitate that formed during the dissolution of UOC with a mixture of 1 M $(NH_4)_2CO_3$ and 1M H_2O_2 (Figure 3.10). Upon heating this mixture at 60°C for 3 hours the dark green solution turned into a yellow solution (Figure 3.11) as AUC decomposes into a more soluble uranyl carbonate species.

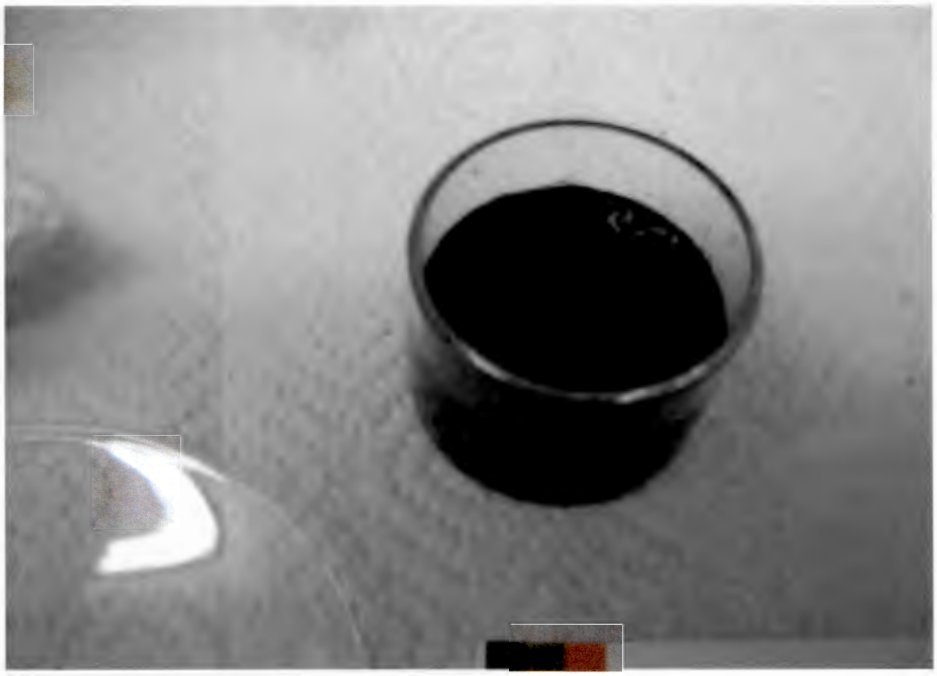

Figure 3.10: Initial uranyl solution during dissolution of UOC

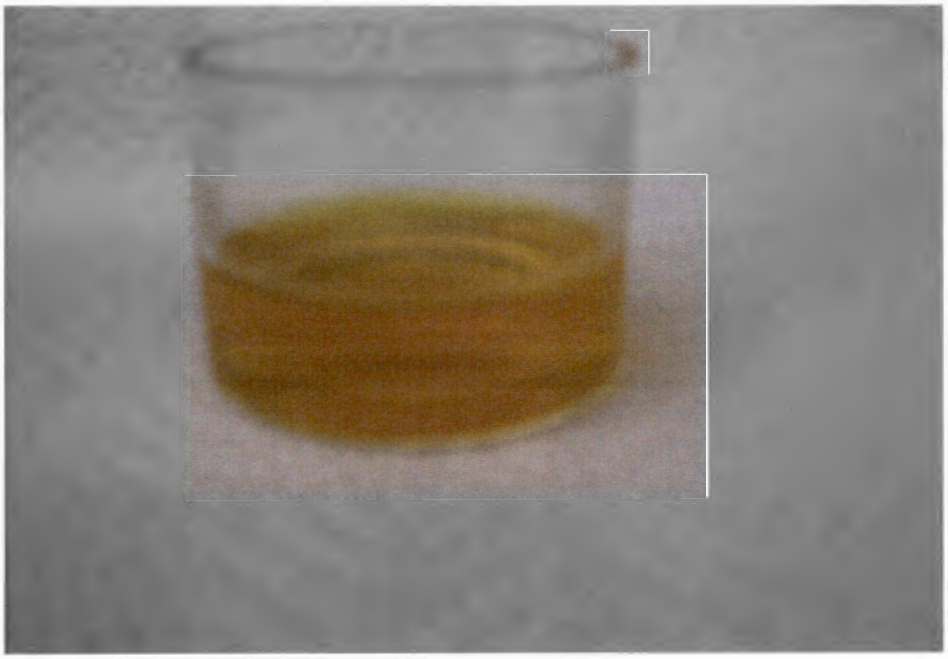

Figure 3.11: Formation of ammonium uranyl carbonate after heating the mixture.

The results shown in Figure 3.12 and 3.13 also indicated the formation of a precipitate after cooling the resulting leachate.

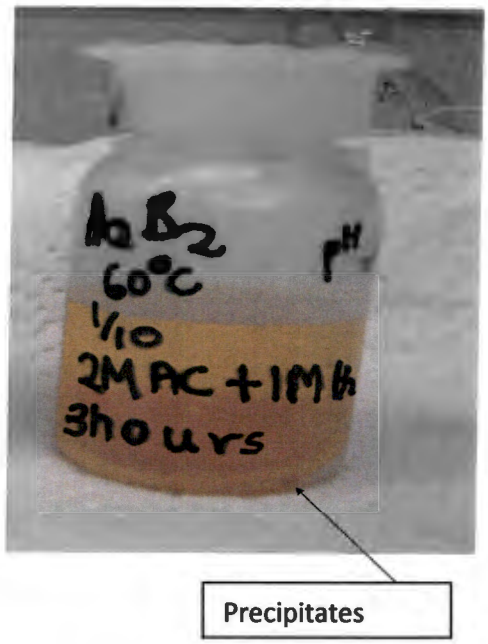

Figure 3.12: UO_3 precipitate formed

This implies using 2M $(NH_4)_2CO_3$ caused the solubility of the uranium to be exceeded that led to the formation of precipitates.

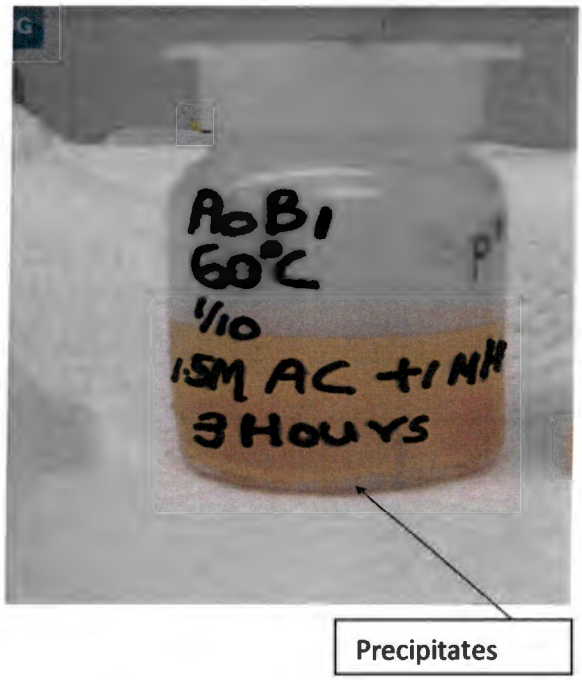

Figure 3.13: UO_3 precipitate formed

The results indicated with concentrations of $(NH_4)_2CO_3$ between 1.5 M and 2.0M that the solubility of uranium decreases upon cooling and therefore 1M $(NH_4)_2CO_3$ is recommended for the dissolution of UOC to prevent precipitation formation.

3.4.1.5 Influence of Temperature

From the literature it was indicated in Section 3.2.3 that increasing temperature enhances the dissolution rate of UO_2. The use of $(NH_4)_2CO_3$ implies that the research cannot be performed at high temperature as $(NH_4)_2CO_3$ decomposes above 60°C. To test the influence of temperature, it was decided to study the dissolution of UOC between the temperatures of 30 to 70°C in an autoclave. The experimental procedure was performed as described in Section 3.3.3.1. The summation of the raw data in Table 8.5 and Tables from 8.14 to 8.18 in Annexure A is presented in Figure 3.14.

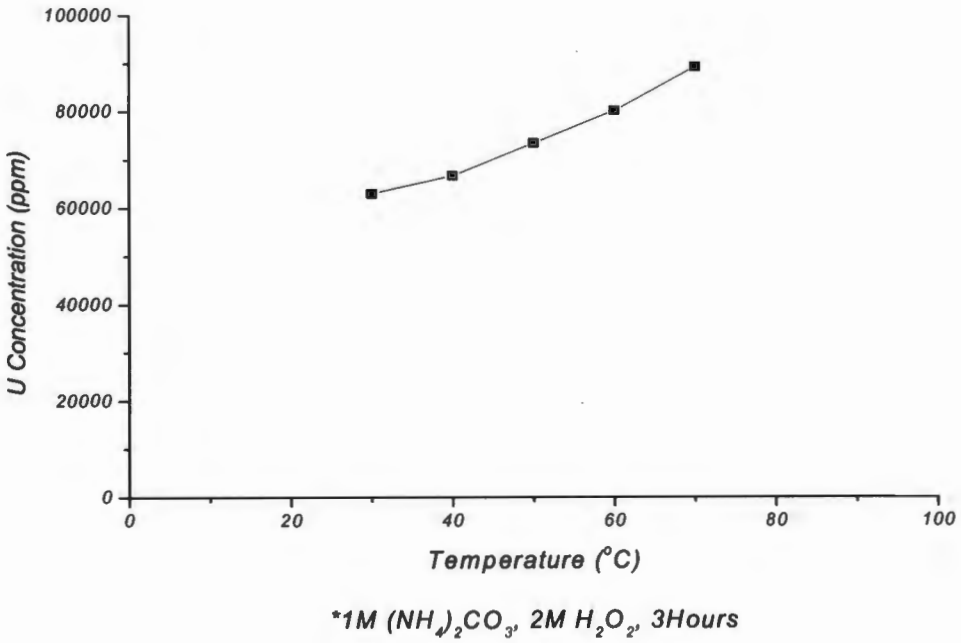

Figure 3.14: Effect of temperature on the dissolution of UOC

The results in Figure 3.14 indicated that the dissolution of UOC is influenced by temperature. At 30°C the uranium in solution that dissolves after 3 hours was 62944 ppm while at 70°C nearly 89325 ppm uranium concentration was observed after 3 hours. The amount of the undissolved mass of uranium at 30°C was 0.568g and at 70°C it was 0.0241g. These results are in line with the results obtained by Smith et al, 2009 that shows that the dissolution rate of UO_2 increased linearly with the increase in temperature. As the temperature of 70°C cannot be exceeded due to possible reagent breakdown, it was decided to continue the research at a temperature of 60°C to ensure that no breakdown of the leachate occurs.

3.4.1.6 Possible rate determinants

Current experiments have been performed for 3 hours per experiment. As it is impossible with the current autoclave to do in situ rate studies, it was decided to reduce the experimental time in order to indirectly determine the dissolution rate. Experiments were done as described in Section 3.3.3 with the exception that experiments were stopped after 1, 2, and 3 hours. The composition, volume and amount of UOC and leachate were kept exactly the same at the onset of all the experiments.

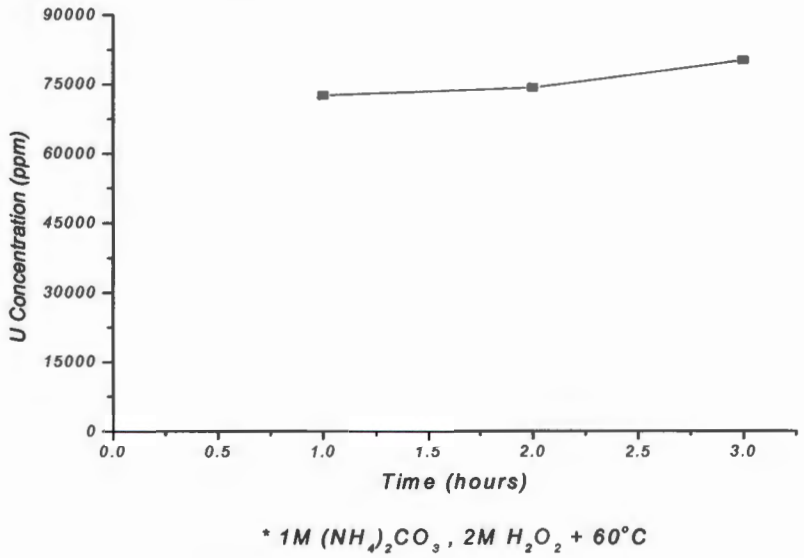

Figure 3.15: Effect of time on the dissolution of UOC.

The results in Figure 3.15 and raw data in Table 8.6 (Annexure A) indicated that after one hour 73 000 ppm of uranium was present in solution compared to 75 000 ppm after 2 hours

and 81 000 ppm after 3 hours. The results clearly affirm that the dissolution of UOC in ammonium carbonate solution slightly increases with time.

3.4.2 Conclusion on experiments with autoclave

The results in Section 3.4.1.6 demonstrated that optimum UOC dissolution can be obtained (80201 ppm uranium) when using a mixture of 1M $(NH_4)_2CO_3$ solution in the presence of 2M H_2O_2 as oxidant in the pressurized reactor at 60oC. The dissolution results with the current experiment configuration indicated that the uranium concentration increases when the concentration of H_2O_2 increases, the temperature increases and with continuous stirring. However for industrialization it is difficult to use autoclave technology, so the results were used as guidance for the following bench experiments.

3.5 Bench experimental results

As indicated in Section 3.4.2 for the autoclave experiment, the dissolution of UOC depends on for instance the concentration of leachate, the pH, oxidants present and temperature. Due to safety precautions (pressure) and volume limitations for an autoclave, bench experiments were proposed for the rate determinations. The same process of optimizing and analyzing of parameters was to be done at the bench. The parameters that were investigated to determine rate of dissolution were the influence of ammonium carbonate concentration, the influence of agitation of the solution, influence of H_2O_2 concentration and temperature.

3.5.1 Influence of agitation

From the results of the autoclave experiments it was very clear that by stirring a solution, the dissolution rate increases due to the replacement of leachate at the dissolution surface. In order to obtain rate values, the experiment and uranium analysis were performed as mentioned in Section 3.3.3.2 (Experimental procedure). Three agitation experiment methods

were done: mechanical stirring, air stirring and no stirring. The results from these experiments (by analysis of uranium dissolved with time) are presented in Figure 3.16 and the raw data is in Table 8.1 in Annexure B.

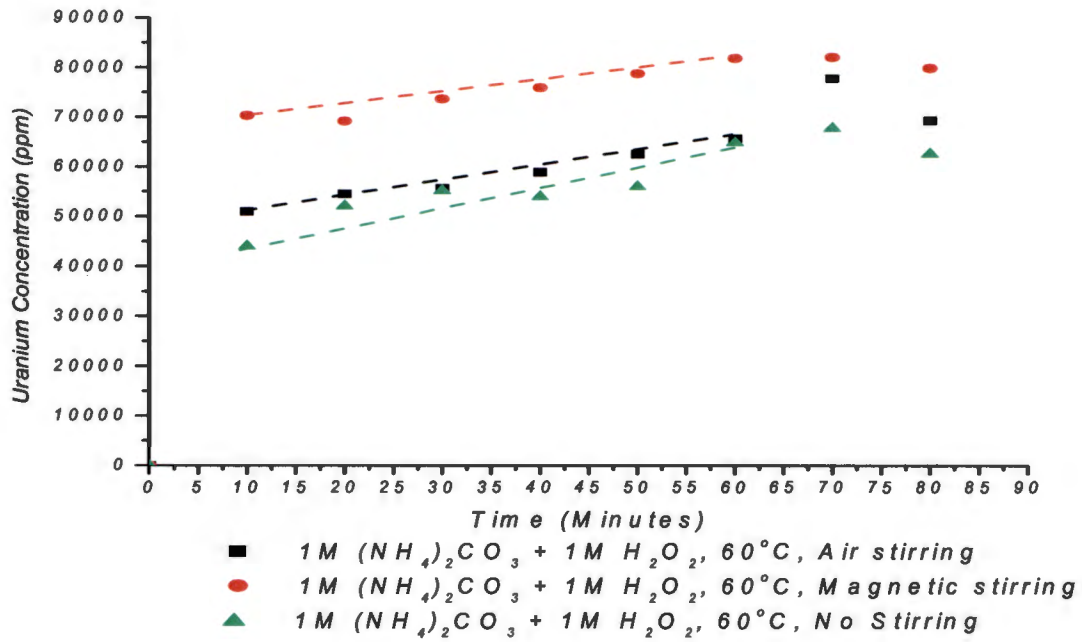

Figure 3.16: Effect of stirring methods on dissolution rate of UOC using 1M ammonium carbonate and 1M hydrogen peroxide.

The results in Figure 3.16 indicated that after 20 minutes for no stirring and air stirring methods, the uranium concentrations were 52142.45 ppm and 54517.71 ppm respectively while with magnetic stirring the uranium concentration increased to 69137.84 ppm. The results affirm that the movement of both liquids and solids increases the initial dissolution rate of UOC. Therefore, stirring is essential during the leaching process in order to increase the rate of the reaction. Moreover, it is clear that magnetic stirring is a definite requirement for optimal dissolution as compared to air stirring and no stirring methods.

3.5.2 Influence of Ammonium carbonate concentration

The influence of ammonium carbonate concentration on the leaching rate of UOC was investigated. Three different ammonium carbonate concentrations (1.0, 1.5, and 2.0 M) were tested. Although the autoclave results indicated that precipitation formed at 1.5 and 2.0 M, it was decided to repeat the experiment. The experimental procedure was performed as described in Section 3.3.3.2. A UOC mass of 16.7 g was weighed and added to $(NH_4)_2CO_3$ and 1M H_2O_2 solution and the reaction temperature were set to 60°C with continuous stirring using a magnetic stirrer. The raw data in Table 8.2 in Annexure B was used to construct Figure 3.17 showing the final results.

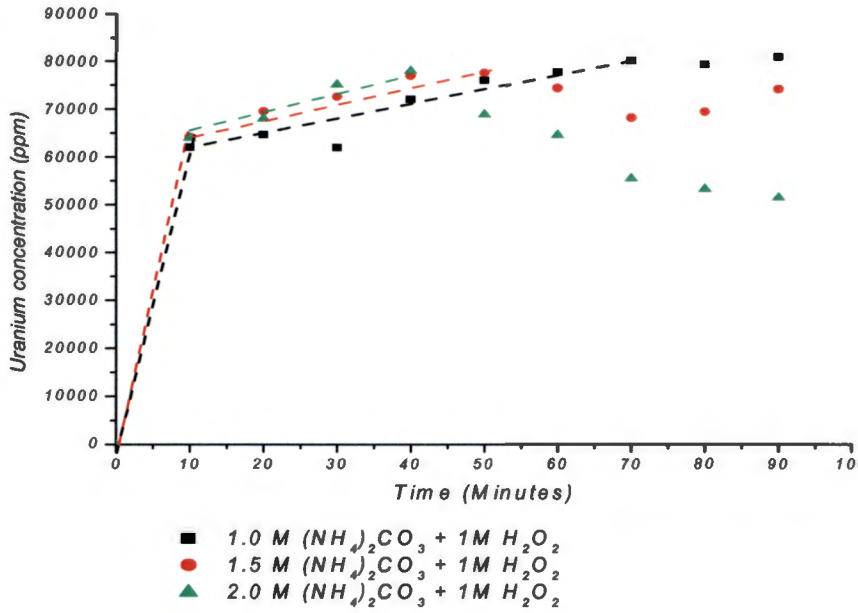

Figure 3.17: The effect of $(NH_4)_2CO_3$ concentration on the dissolution of UOC at 60° C with magnetic stirring

The rate of dissolution of UOC with 2M and 1.5 $(NH_4)_2CO_3$ and 1M H_2O_2 after 40 minutes resulted with 78032.32 ppm, 76996.79 ppm and 72052.89 ppm uranium dissolved respectively. Precipitates occurred at 2 M ammonium carbonate concentration resulting in a decrease in uranium concentration in solution as observed in Figure 3.18. No precipitate formation was observed using 1M ammonium carbonate.

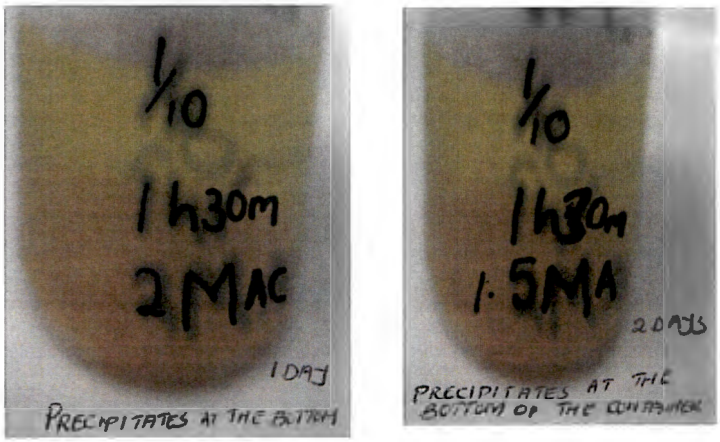

Figure 3.18: Precipitate formed for 1.5 and 2.0 M $(NH_4)_2CO_3$

This implies that the solubility decreases with the increase in the ammonium carbonate concentration as described in the solubility graph in Figure 9 (Hurst & Hurst, 1961).

The mass of the precipitates after filtering the filtrates was 4.574 g for 2M $(NH_4)_2CO_3$ and 2.748 g for 1.5 M $(NH_4)_2CO_3$. The precipitate formed is assumed to be peroxo-oxide which can be explained by the following chemical reaction:

$$U_3O_8 + 6(NH_4)_2\,CO_3 + 2H_2O_2 \rightarrow 3(NH_4)_4\,UO_4(CO_3)_2^{2+} + 2H_2\uparrow \qquad (15)$$

1M ammonium carbonate with 1M H_2O_2 will be essential for the industry, especially on a large scale, to dissolve UOC without the formation of precipitates.

3.5.3 Effect of Temperature

The influence of reaction temperature on the dissolution rate was investigated. Three different temperatures namely 40, 50 and 60°C were tested. All the experiments were performed as indicated in the procedure in Section 3.3.3.2 whereby all other parameters were

kept constant and only temperature was changed. The results presented in Figure 3.19 (based on raw data in Table 3 in Annexure B) shows the effect of temperature on the kinetic runs of uranium dissolution with 1.0 M $(NH_4)_2CO_3$ and 1M H_2O_2 at various time intervals.

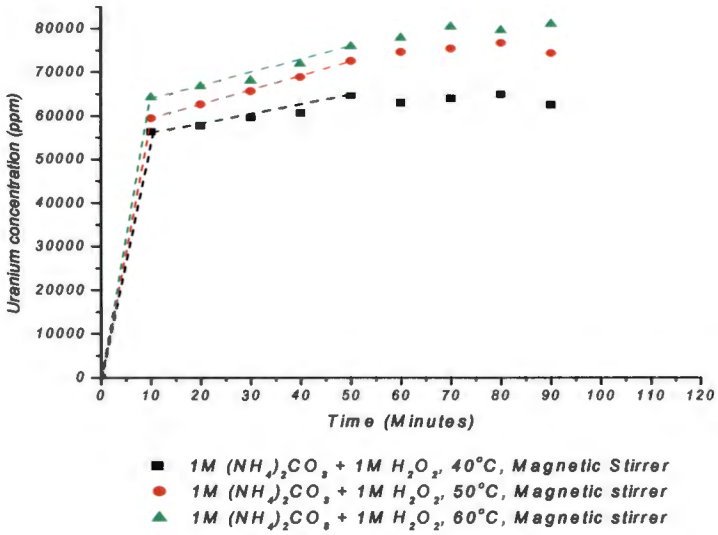

Figure 3.19: Effect of temperature on dissolution of UOC using ammonium carbonate with hydrogen peroxide.

The results in Figure 3.19 indicated that an increase in temperature resulted in a considerable increase in the reaction rate. At 60°C after 30 minutes, a uranium concentration of 68011.14 ppm was recorded. At 50°C, 65625.99 ppm of uranium concentration was recorded and at 40°C, 59571.68 ppm uranium concentration was recorded.

3.5.4 Effect of H_2O_2

The influence of hydrogen peroxide on the dissolution of UOC was investigated to determine if it can be used to oxidize possible U^{4+}present in the sample to U^{6+}. The experimental procedure was performed as described in section 3.3.3.2 with the exception of different amounts of H_2O_2 being used. The results obtained are presented in Figure 3.20. (Raw data in Table 8.4 in Annexure B).

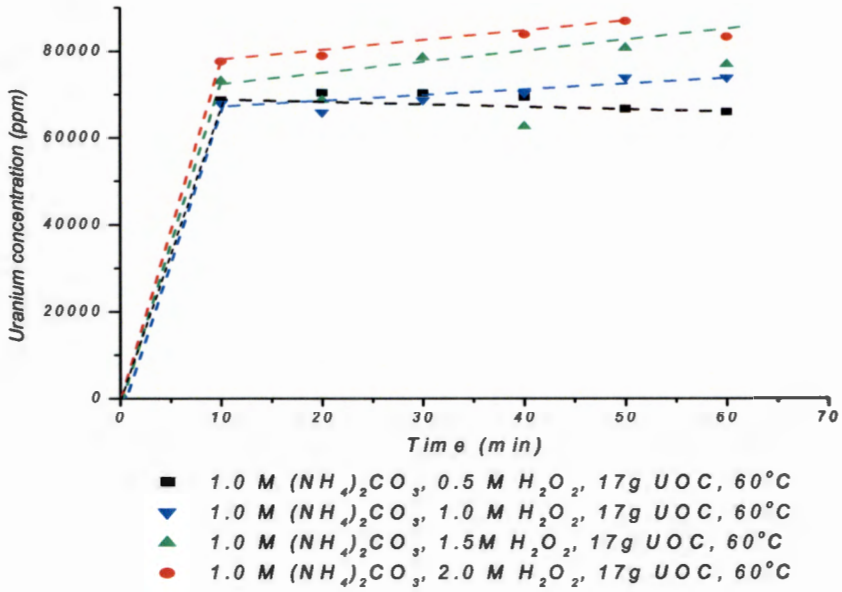

Figure 3.20: Effect of H_2O_2 on the dissolution of UOC using 1M $(NH_4)_2CO_3$ at 60°C with magnetic stirring

The results in Figure 3.20 indicated that an increase in hydrogen peroxide concentration resulted in a considerable increase in the initial reaction rate. The results clearly show that in the first 10 minutes of leaching the initial concentration of uranium obtained with a concentration of H_2O_2 of 0.5 M H_2O_2 was 6869.62, at 1.0 M it was 67990.23, at 1.5 M it was 73169.88 and at 2M it was 77939.38. Therefore, the increase in the concentration of H_2O_2 increases the dissolution rate of UOC.

3.6 Conclusion

Dissolution of UOC has been successful by using 1M ammonium carbonate, 1M hydrogen peroxide, at 60°C for 3 hours. Using 1.5 and 2.0 M ammonium carbonate leachate, results in precipitates during cooling of the solution (Figure 3.12 and 3.13). The next step in the study is to purify uranyl solution obtained from the dissolution step using different technologies.

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Chapter 4

4 Use of ion exchange technology to purify UOC

4.1 Introduction

This chapter describes the research that was performed with various resins to determine the possible removal of impurities from an alkaline uranium waste stream solution generated by the dissolution of UOC from mines and Nufcor.

Ion exchange is one of the most common and effective treatment method used for the purification of liquids. It is a well developed technique that has been employed for many years in both the nuclear and other industries (such as mining) (IAEA, 2002). Ion exchange technology (IX) is a process in which mobile ions from an external solution are exchanged with ions that were electrostatically bound onto the functional groups that are contained within a solid matrix.

By taking advantage of the fact that under certain conditions, ion exchange media have a greater affinity for certain ionic species than for others; a separation of these species can be made (IAEA, 2002).

4.2 History of ion exchangers.

The history of ion exchangers (Koivula, 2003) is remarkably long. One of the oldest applications of inorganic ion exchangers was the purification of seawater with a layer of sand, something that was known to Aristotle in the fourth century BC. The first scientific experiments with inorganic ion exchangers were performed on Chabazite (a type of zeolite). Clinoptilolite, a material isomorphous to Chabazite, is presently in use for Cs and Sr separation at Sellafield nuclear fuel reprocessing plant (Koivula, 2003).

The weak chemical stability of the early inorganic ion exchangers led to the development and synthesis of organic ion exchangers (organic resins) in the 1930s. With few exceptions,

organic resins, based on a chemically very stable polystyrenedivinylbenzene (SDVB) backbone, were used to replace the inorganic ion exchangers.

The needs of the nuclear industry - high selectivity, tolerance for ionizing radiation and possibly high temperatures - were the basis for the further development of inorganic ion exchangers. Since the mid 1960s, after the appropriate analytical techniques and knowledge of ion exchange processes became available, new inorganic materials were synthesized and studied with particular attention to the relation of structure to the ion exchange properties of the material (Clearfield, 2000). Hundreds of inorganic materials have been synthesized, studied and tested for use in radioactive waste environments. Currently, materials with better chemical stability than zeolites are still being sought among natural minerals.

4.3 The use of ion exchangers in the nuclear power industry to purify water solutions (Koivula, 2003).

At present, organic resins are used in almost every section of the nuclear fuel cycle. For example, ion exchange resins are used at NPPs (depending on the reactor type) for purification and chemical control of primary coolant water, polishing of steam condensate, production of make-up water, purification of spent fuel storage pond water and treatment of waste solution. The treatment of waste solutions is to remove radioactive ionic contaminants, mainly cesium, and other radioactive contaminants, such as cobalt and nickel to prevent radiation build up in the reactor system. Typically two different kinds of ion exchange process are employed:

- Conventional deep bed columns and pre-coat filters. In these processes the ion exchange resins function as ion exchangers for the ionic contaminants and as mechanical filters for particulate contaminants. Ion exchange resins that are used are strong acidic (sulfonic - SO_3^-) or strong basic (quaternary - $N(CH_3)_3^+$) types with a macro porous structure to form a type of additional filter system after packing of a column bed
- Gel type for pre-coat filter applications.

Ion exchange processing can also be accomplished by either a batch method or a column method. In the first method, the resin and solution are mixed in a batch tank and the exchange is allowed to proceed until equilibrium is reached. The resin is then separated from the solution. The degree to which the exchange takes place (K_d value) is limited by the preference the resin exhibits for the ion in solution. Consequently, the use of the resins exchange capacity will be limited unless the selectivity for the ion in solution is far greater than for the exchangeable ion attached to the resin. As batch regeneration of the resin is a chemically inefficient process, batch processing (by ion exchange) has limited potential for industrial applications.

The ion exchangers used in NPPs are almost, without exception, of nuclear grade which means organic resins of high quality, low in metallic impurities and coherent in particle size. Annual consumption of organic resins in an operating water cooled reactor may be as high as 10 tonnes, and for the final disposal the resins can be incinerated or mixed directly with cement.

For their part, inorganic ion exchangers in NPPs have primarily been used in the decontamination of radioactive waste solutions originating from drain waters, decontamination operations and leaks. A common approach to remove contaminants from these waste streams is to reduce the volume with the aid of evaporators, precipitation by adding chemicals and resins to concentrate contaminants before final disposal. Dozens of different materials and combinations of materials have been tested with varied success, but only a few groups of materials (resins) have shown constant and good performance in radionuclide separation (Tusa, 2001). The use of inorganic exchangers to reduce the volume of the concerned wastes has generated substantial economic savings.

4.4 Resins that are used to remove impurities from alkaline solutions

The presence of the impurities such as Na, Al, K, Ca, Mo and W in the uranium feed material for conversion plant has a great concern because of their interaction with UF_4 to form sintered precipitates that cannot be fluorinated to UF_6. Therefore there is a need to study the

removal of the combination of these impurities from alkaline solution containing high concentration of uranium.

In this study both organic and inorganic resins were to be investigated for the removal of ionic impurities from ammonium uranyl carbonate solution. The focus will be on the ion exchange resins and the processes that are currently used on an industrial scale or are in an advanced stage of development. Literature about the following resins will be discussed in summary to outline their potential to remove impurities from alkaline solutions:

- Zeolite (Chabazite) resins
- Amberlite resins
- Purolite resins
- Activated carbon resin

4.4.1 Chabazite resins

Chabazite resin is a natural zeolite which was the first material that was used in an ion exchange process for the separation of impurities from the effluent waste waters. Zeolite resins are microporous, aluminosilicate minerals widely used in water purification, petrochemical and nuclear reprocessing industries as catalysts for the preparation of advanced materials. The zeolites are used for agricultural and medical purposes to extract nitrogen from air in order to increase oxygen content. They have a porous structure that can accommodate a wide variety of cations such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Mo^{4+} and W (Figure 4.5). These positive ions are rather loosely held and can readily be exchanged for others in a contact solution (Bostick et al, 1997).

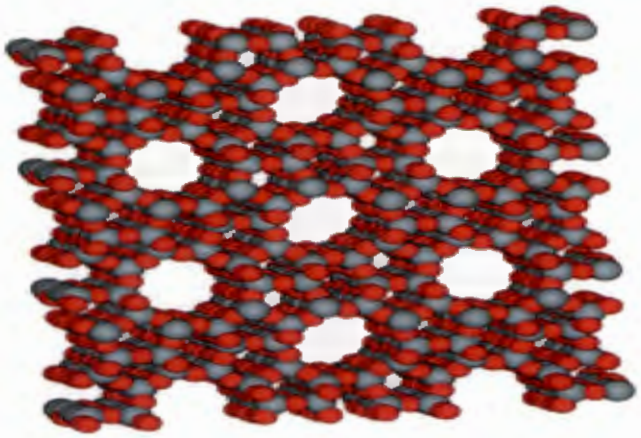

Figure 4.1: Structure of the Zeolite resin (www.lenntech.pl)

The cation exchange behaviour of zeolites is a function of:

- the nature, size (both hydrated and anhydrous) and charge of the cation species;
- the temperature;
- the concentration of the cation species in solution;
- the anion species associated with the cation in solution;
- the solvent (most exchange has been performed in aqueous solutions, although some work has been done in organic solvents and molten salts);
- the structural characteristics of the particular zeolite.

Zeolites have been used in advanced reprocessing methods as their micro-porous ability can capture selective ions while other elements are not absorbed. This has resulted in the efficient removal of fission products from nuclear waste. Zeolites with absorbed fission products can be hot pressed into an extremely durable ceramic form, therefore closing the pores and trapping the waste in a solid block. This generated waste form greatly reduces the hazard compared to conventional reprocessing systems. In the aftermath of the Fukushima Daiichi nuclear disaster, sandbags of zeolite resins were dropped into the seawater near the power plant to adsorb radioactive cesium which was present in elevated levels (Bostick et al, 1997).

Dyer and Zubair, (1998) investigated the separation of Sr and Cs from mixed metal contaminated effluent onto Chabazite. The results from this study show that the potential for the treatment of aqueous nuclear waste streams on the adsorption of Sr and Cs was found to

be a function of the concentration ratios of other metals such as K, Rb, and Na which compete for sites within the Chabazite framework.

High sorption capability of Clinoptilolite on the following radionuclides: ^{137}Cs, ^{90}Sr, ^{60}Co, ^{110m}Ag, ^{226}Ra, and ^{133}Ba (Table 1) has been reported by Stefanova (1999). Data from the report also indicated that the Clinoptilolite has high selectivity for Cs, Rb, Ag, Pb, Sr and Ba as compared to Na, Ca, and Mg. Results further indicated that the radiation stability of Clinoptilolite is very high as no structural changes or changes in sorption properties were observed when Clinoptilolite was irradiated up to 10^7 Gy. Results also showed that the thermal stability of the Clinoptilolite depends on the type of exchangeable cations absorbed on the resin.

Table 4.1: Sorption properties of natural Clinoptilolite (Stefanova, 1999)

1. Ion exchange capacity	>1.0 meq.g^{-1}: Cs^+, Rb^+, K^+, NH_4^+, Sr^{2+}, Ba^{2+}, Ag^+, Tl^+, Pb^{2+}, Hg^{2+}; 0.5–1.0 meq.g^{-1}: Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; <0.5 meq.g^{-1}: Fe^{3+}, Cr^{3+}, Ce^{3+}, Ru^{3+}, Zr^{4+}, Nb^{4+}, Co^{2+}
2. Distribution coefficient	10^3–10^4 ml.g^{-1}: ^{137}Cs, ^{110m}Ag, ^{204}Tl, ^{226}Ra, ^{133}Ba 10^2–10^3 ml.g^{-1}: ^{90}Sr, ^{60}Co, ^{54}Mn, ^{56}Fe, ^{65}Zn, ^{115m}Cd; <10^2 ml.g^{-1}: ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{95}Nb
3. Selectivity - in presence of Na, Mg and Ca	high: ^{137}Cs, ^{110m}Ag, ^{204}Tl, ^{210}Pb, ^{90}Sr, ^{226}Ra, ^{133}Ba satisfactory: ^{60}Co, ^{54}Mn, ^{56}Fe, ^{65}Zn, ^{115m}Cd; low: ^{144}Ce, ^{106}Ru, ^{95}Zr
- in presence of K and NH_4	low selectivity for all ions studied
- in presence of citric and tartaric acids	high: ^{137}Cs, ^{204}Tl, ^{90}Sr, ^{110m}Ag,
- in presence of oxalic acid	high: ^{137}Cs, satisfactory: ^{204}Tl
- in presence of EDTA	high: ^{137}Cs, ^{204}Tl, satisfactory: ^{90}Sr
4. Optimum pH	from 5 to 9
5. Thermal and radiation stability	sufficient for liquid radioactive waste treatment and long term stability in disposal environment

Based on the available information, it was decided to investigate Chabazite (also used in Oak Ridge National Laboratories), Clinoptilolite (a zeolite used in other countries [Robinson 1991, Banarjee, 2004]), RF resin (used by Savannah River) and Cs treat to study the decontamination of the possible waste streams.

4.4.2 Amberlite resins

Amberlite resins are generally functionalized acrylic esters or polystyrene with di-vinyl benzene cross-linking. Amberlite is a macroporous cation exchange resin based on sulphonated cross linked polystyrene with SO_3^- sites for exchange (Figure 4.2 and 4.3). It has a moderate degree of cross linking resulting in good regeneration efficiency. It is very resistant to osmotic shock and to mechanical attrition. It is suited for use in a variety of demanding applications, such as condensate polishing or treatment of oxidizing solutions.

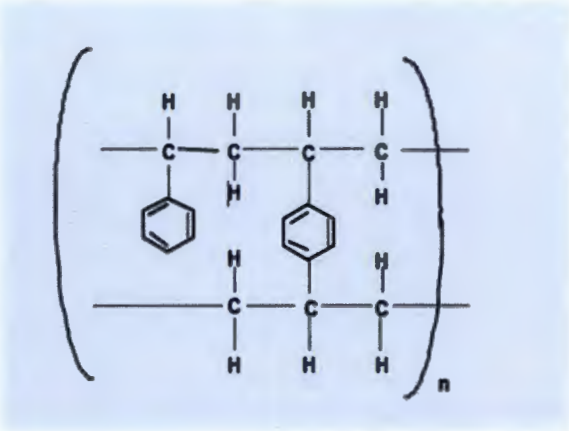

Figure 4.2: Structure of the Amberlite resin

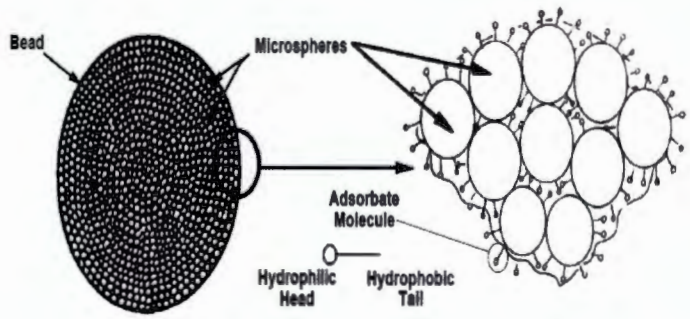

Figure 4.3: Structure of a Hydrophobic, Macroreticular Amberlite XAD-2 Resin Bead

Amberlite 252 RFH has a reduced amount of fines, allowing it to be used at high flow rate or in conventional reverse flow regenerated units. The role of Amberlite resins has increased for the removal of impurities from alkaline effluent in the water, sugar and nuclear industries. De Lucas et al. (1997) studied the removal of potassium from water – methanol – polyol mixtures by ion exchange (Amberlite RFH 252). The results show that the equilibrium for the

uptake of potassium from these mixtures is very favourable and can be considered as irreversible for practical purposes. Breakthrough curves were obtained under a wide range of conditions and being well correlated by the expression for breakthrough curves with a rectangular isotherm. This group also indicated that the effect of the viscosity of the bulk solution and of resin swelling on the diffusion coefficients could be correlated by a simple and accurate empirical equation.

Yalala et al. (2009) used Amberlite 252 RFH resin to investigate the sodium ion Na (I) in brine waste waters as a function of contact time, initial pH of the solution and the concentration of the metal ion. Amberlite resin was shown to have a high metal ion adsorption capacity for Na (I) ion of 25.03 mg/g. This is because Amberlite had proved not to be affected by pH because of it being a strong acid cation exchange resin. The information about the work done previously about Amberlite 252 RFH resin is very limited.

4.4.3 Activated carbon

Activated carbon is a chemically stable material which is known to complex metals from solutions and could be utilised for the purification of waste streams. Commonly activated carbon is used in plating processes for the removal of impurities from plating baths (Leinonen, 1999). Impregnated silver (Ag) activated carbon is used almost exclusively for the removal of gaseous radioiodine at nuclear power plants (Jubin, 1989).

4.4.4 Purolite resins

Purolite resins are macroporous amino-phosphonic acid chelating resin (Table 4.2), designed for the removal of cations of toxic metals such as lead, copper and zinc from industrial effluents at low pH. At somewhat higher pH values, calcium, magnesium and barium, as well as the toxic metals cadmium, nickel, and cobalt are strongly complexed and may be separated from quite high concentrations of univalent cations. The use of Purolite chelation resins for the purification of these waste aqueous streams renders the resulting liquid suitable for disposal through the domestic sewerage system, or direct disposal into suitable aquifers.

Purolite S 950 is more highly selective (under the appropriate conditions) for a range of both heavy metal and common divalent ions. Hence its use may be recommended where it is necessary to remove calcium or magnesium in order to avoid possible precipitation, or where its selectivity for a particular range of metals is highest.

Table 4.2: Purolite resins in industry

Resin Type (Purolite)	Functional group	Matrix	Principal Application
S 920	Thiouronium	Macroporous styrene-divinyl-benzene	Mercury and precious metals removal from aqueous solutions
S930	Iminodiacetic	Macroporous styrene-divinyl-benzene	Effluent treatment, hydrometallurgy (Specific for heavy metal)
S940	Aminophosphonic	Macroporous styrene-divinyl-benzene	Brine purification (removal of calcium)
S 950	Aminophosphonic	Macroporous styrene-divinyl-benzene	Effluent treatment hydrometallurgy

Ladeira and Morais, (2005) studied uranium recovery from ammonium carbonate industrial effluent by ion – exchange column experiments and reported that the use of the ion exchange technique makes the recovery of more than 98% of uranium possible when IRA 910 U was employed for its specific application for extracting uranium.

Ladeira and Morais, (2004) also studied the effect of impurities such as ammonium, carbonate and fluoride on the uranium recovery and concluded that the uranium concentration in solution relative to the impurities was the main factor which interfered in the separation process. From the results obtained by batch experiments with uranium concentrations of 100 mg/l, it was clear that excess of carbonate and fluoride completely inhibit uranium uptake in the pH range from 9.2 to 10.4. Moreover, the results showed that the elevated concentration of fluoride and carbonate completely inhibited the adsorption of uranium on the resin while the presence of ammonia had no deleterious effect on the adsorption process. Although the selectivity of the resin for higher concentrations of $(UO_2 (CO_3)_3)^{4-}$ is very high, the presence of CO_3^{2-} and F^- as impurities influence the process negatively.

4.5 Experimentation

4.5.1 Analytical Equipment used in study

Electronic analytical Weighing Balance (TB-200 from Denver Instrument Company), Orion pH meter (Model 40A), Heidolph Reactor Jacket, Herlme 2200A Centrifuge.

4.5.2 Chemicals used

All chemicals used were of analytical grade and solutions were prepared using Necsa demineralized water. The ammonium uranyl tricarbonate stock solution was prepared by dissolving 16.7 g UOC in 166.67 ml of 1M $(NH_4)_2CO_3$ and 16.7 ml 30% H_2O_2. Additional chemical reagents that were used to simulate impurities were Na_2CO_3, $Al(OH)_3$, Mo(V)Cl, tungsten trioxide , $CaCO_3$ and K_2CO_3. The ion exchange resins selected for this study were from Rohm and Haas and Bio – Rad laboratories as indicated in Table 4.3.

Table 4.3: Resins used in the current study

Full Resin Name	Supplier	Type of resin
Amberlite RFH 252	Rohm and Haas	Aminophophonic chelating resin
Cabsorb ZS 500 RW	Rohm and Hass	Macroreticular Polymeric adsorbent
Purolite S 940	Bio-Rad Laboratories	Aminophophonic chelating resin
Activated Carbon	Rohm and Hass	Macroreticular Polymeric adsorbent
Purolite S 950	Bio-Rad Laboratories	Strong basic type I
Dowex AGI –X4	Bio-Rad Laboratories	Strong anionic resin with trimethylamine
Amberlite XAD - 4	Rohm and Haas	Macroreticular Polymeric adsorbent
Chabazite	Bio-Rad Laboratories	Macroreticular Polymeric adsorbent
Cabsorb ZK 400 MZ	Bio-Rad Laboratories	Macroreticular Polymeric adsorbent

4.5.3 Experimental methods used

4.5.3.1 Batch experiments with unconditioned resins

The batch experiments were performed to determine the ion exchange properties of the resins to produce primary data based on distribution coefficient (K_d values) and percentage of the impurities absorbed.

The initial stock solution of uranyl solution was prepared in a 1000 ml volumetric flask from 84 000 ppm of uranium solution obtained during the dissolution process. The procedure for obtaining uranyl solution with 84 000 ppm concentrations was presented in Chapter 3 Section 3.4.1 and 3.4.3.

The impurities (100 ppm) were added to the uranyl solution. Two experiments were performed which were used to test the uranium adsorption and impurities adsorption by the resins. Firstly a weighed amount of a resin (1g) was added into a 15ml conical centrifuge tube and 10 ml of uranium solution was added into a tube. The tube is immediately capped, shaken and placed in a rotator to be rotated end over end for a period of 24 hours as indicated in Figure 4.4. After 24 hours, the centrifuge tubes were placed in an upright position for five minutes so that the different phases could separate (liquid phase and solid phase). The centrifuge tubes were then centrifuged for 30 minutes at 3500 rpm. In the second experiment the same procedure was repeated using "spiked" uranium containing solution.

After centrifuging, the amount of impurities present in the solution was determined by taking 5ml of the supernatant, transferring it into a 50 ml sample bottle, topping it up with 25 ml demineralized water and sending it to Pelindaba Analytical Laboratory (PAL) for the analysis.

The values of the distribution ratio (K_d) were calculated from the following relationship:

$$K_d = \frac{(C_0 - C_i)}{C_i} * \frac{V}{M}$$

Where: V: Volume of the solution (ml) C_o: Initial concentration

M: Mass of the sample (g) C_i: Final Concentration.

The results obtained will be presented and discussed in the next section.

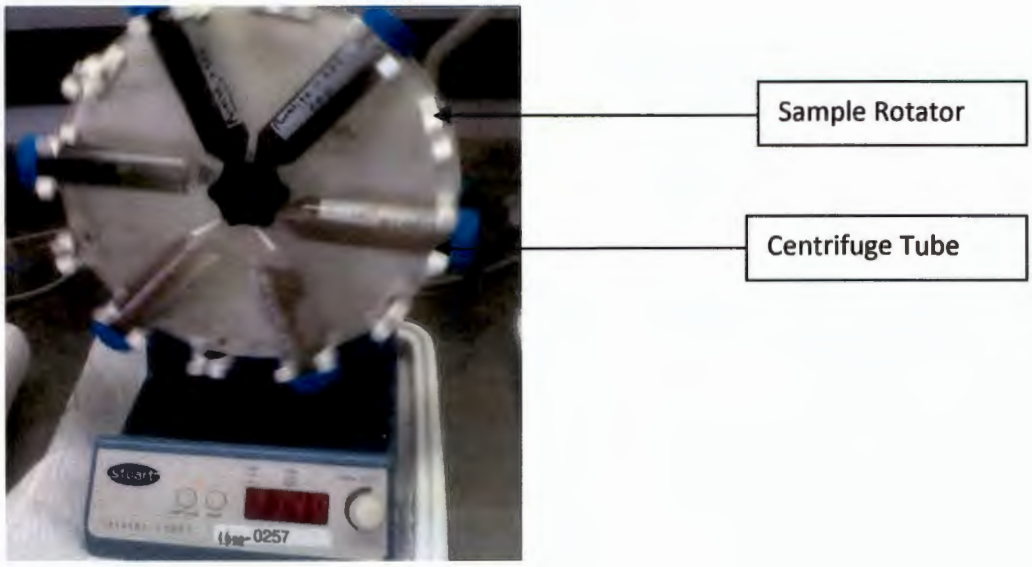

Figure 4.4: Sample rotator

4.6 Results

4.6.1 Initial absorption of uranium on different resins using batch method

The initial tests to determine the partition coefficients (K_d) of uranium on the various resins (listed in Section 4.5.2 in Table 4) were done as described in Section 4.5.3.1. The experiment was repeated three times with each resin. The initial and final uranium concentration as well as the calculated K_d values are recorded in Table 4.4 The raw data used to compile Table 4.4 is in Table 4.7 and 4.8 in Annexure C . This raw data was multiplied by the dilution factor of 5 to obtain final uranium concentration.

Table 4.4: Various resins used in the study, the Uranium concentrations and K_d values

Resin name	Resin mass (g)	Initial [U] (ppm)	Raw data (ppm)	Final [U] (ppm)	K_d values (mg/l)
Amberlite RFH 252	1.0021	200	38.5	192.5	0.3896
AGI-X1	1.0032	200	-1.8	-9	-232.22
Cabsorb ZK 406 MZ	1.0002	200	6.1	30.5	55.563
Cabsorb ZS 500	1.0033	200	4.6	23	79.956
Purolite S 950	1.0041	200	4.8	24	73.33
Purolite S 957	1.0061	200	10.8	54	27.037

Activated Carbon	1.0081	200	5.7	28.5	60.175
Amberlite XAD -4	1.0002	200	6.4	32	52.50

The results obtained from the K_d determinations showed that Purolite S957, Amberlite RFH 252, Amberlite XAD-4 and Purolite S 940 resins are all able to allow more than 80 % of the uranium to pass through. A low K_d values implies that no uranium absorbed onto the resins. The results of the tests of all these resins for their adsorption of the impurities are reported in the next section.

4.6.2 Batch experiments for impurities uptake.

The second process was to investigate the adsorption of the impurities on the resins. The uptake of cationic impurities (K^+, Na^+, Al^{3+}, Ca^{2+}, Mo^{2+} and W) onto different resins was studied in batch experiments under alkaline conditions. A 100 ppm solution of the impurities was prepared by dissolving chemicals specifically selected in Section 4.5.2. The solution was equilibrated with the weighed resins (1g) for 24 hours on a rotary shaker. The K_d values and final concentration of the solution were investigated. The results obtained for these tests are presented in Table 4.4.

The raw data used to calculate the K_d values and the concentration of the solution are presented in Table 8.27 in Annexure C.

Table 4.5: Illustration of the amount of different impurities absorbed onto the resins.

Resin	Impurities	Raw data for impurities	Raw data for adsorption	C_o(mg/L)	Cf_1 (mg/L)	K_d(mg/L)	% Uptake
Amberlite RFH 252 (D)	K	21.5	10.4	52.4	38.7	0.354	26.1
	Na	30.6	14.5	65.4	41.1	0.591	37.2
	Al	37.2	1.7	8.55	3.6	1.375	57.9
	Mo	34.6	18.6	107	56.1	0.907	47.6
	W	59.1	18.3	69.9	51.6	0.355	26.2
Cabsorb ZS 500 RW (H)	K	21.5	24.9	52.4	49.8	0.052	5.0
	Na	30.6	19.9	65.4	59.7	0.095	8.7
	Al	37.2	2.0	8.55	6.0	0.425	29.8
	Mo	34.6	19.4	107	58.2	0.838	45.6
	W	59.1	22.6	69.9	67.8	0.031	3
Purolite S 940 (J)	K	21.5	11.5	52.4	36.9	0.420	29.6
	Na	30.6	18.0	65.4	60.9	0.074	6.9

	Al	37.2	1.8	8.55	4.8	0.781	43.9
	Mo	34.6	17.6	107	54	0.981	49.5
	W	59.1	17.6	69.9	53.1	0.316	24.0
Activated Carbon (K)	K	21.5	13.1	52.4	39.3	0.3333	25
	Na	30.6	15.4	65.4	46.2	0.4156	29
	Al	37.2	1.8	8.55	5.4	0.5833	36.8
	Mo	34.6	19.0	107	57	0.8772	46.7
	W	59.1	16.8	69.9	50.4	0.3869	27.9
Purolite S 950 (B)	K	21.5	13.5	52.4	40.2	0.3035	23.3
	Na	30.6	15.4	65.4	45.6	0.4342	30.3
	Al	37.2	1.0	8.55	3.6	1.375	57.9
	Mo	34.6	17.8	107	55.8	0.9176	47.9
	W	59.1	17.0	69.9	60	0.165	14.2
AG1-X4 (A)	K	21.5	13.5	52.4	40.5	0.2938	22.7
	Na	30.6	15.5	65.4	4.5	3.0074	93.1
	Al	37.2	1.3	8.55	3.9	1.1923	54.4
	Mo	34.6	12.7	107	38.1	1.8084	64.4
	W	59.1	12.5	69.9	37.5	0.864	46.5
XAD (C)	K	21.5	13.5	52.4	41.7	0.2566	20.4
	Na	30.6	15.4	65.4	47.4	0.3797	27.5
	Al	37.2	1.0	8.55	3.6	1.375	57.9
	Mo	34.6	17.8	107	56.7	0.8871	47
	W	59.1	107	56.7	0.8871	47	26.1
S 957 (D)	K	21.5	12.2	52.4	38.7	0.3540	26.1
	Na	30.6	12.9	65.4	41.1	0.5912	37.2
	Al	37.2	1.1	8.55	3.6	1.375	57.9
	Mo	34.6	17.2	107	56.1	0.907	47.6
	W	59.1	17.2	69.9	51.6	0.3547	26.2
Chabazite (E)	K	21.5	27.3	52.4	81.9	<0	<0
	Na	30.6	18.0	65.4	54	0.2111	17.4
	Al	37.2	1.5	8.55	4.5	0.9	47.4
	Mo	34.6	18.6	107	55.8	0.9176	47.9
	W	59.1	17.4	69.9	53.7	0.3017	23.2
ZK406 MZ (F)	K	21.5	21.0	52.4	104.4	<0	<0
	Na	30.6	15.9	65.4	48.3	0.3540	26.1
	Al	37.2	1.3	8.55	3.6	1.375	57.9
	Mo	34.6	19.1	107	56.1	0.9073	47.6
	W	59.1	19.7	69.9	53.7	0.3017	23.2

The results in Table 4.5 indicate that the absorption of various impurities from test solutions was promising. Amberlite RFH 252, Activated carbon, Purolite S957, AG1 X4 and XAD were promising, as they absorbed more than 20 % of various impurities especially sodium and potassium from the alkaline medium while allowing uranium to pass through. Cabsorb

ZS 500RW, ZK 406 MZ and Purolite S 940 resins are not able to absorb more than 20 % of the impurities especially sodium and potassium.

The absorbance of sodium and potassium was at a lower level than the uptake of the impurities such as Al, Mo, W, and Ca. Further investigations were performed with pre-treated resins in order to increase the efficiency of the resins.

4.6.3 Batch experiments with conditioned resins

All the resins were received in different forms such as chloride, ammonium or sulphate form. The resins were conditioned by immersing them in 1 mol/l HCl and rotated for 24 hours on a rotary shaker. The resin was then washed with 20 ml of de-mineralized water ten times to remove all the chloride content. It was then converted to the carbonate form by washing it twice with 20 ml 1M $(NH_4)_2CO_3$.

The same procedure for loading uranium was followed as in Section 4.6.3. The final concentration of the uranyl solution and the K_d values were obtained. The results obtained from these experiments are presented in Table 4.6 and Table 8.28 in Annexure C.

Table 4.6: The results for the impurities uptake on the resins

Resin	Impurities	Raw data for impurities	Raw data for conditioned	C_0(mg/L)	Cf_1 (mg/L)	Kd	% Uptake
Amberlite RFH 252	K	13.9	13.7	69.6	27.4	1.540	60.6
	Na	20.7	14.7	103.4	29.4	2.517	71.6
	Al	11.0	0.8	54.9	1.6	33.31	97.1
	Mo	21	25.4	105.6	50.8	1.079	51.9
	W	34.2	13.6	171	27.2	5.287	84.1
Cabsorb ZS 500 RW	K	13.9	69.9	69.6	139.8	<0	<0
	Na	20.7	1006.0	103.4	2012	<0	<0
	Al	11.0	19.1	54.9	38.2	0.437	30.4
	Mo	21	26.5	105.6	53	0.992	49.8
	W	34.2	14.9	171	23.8	6.185	86.1
Activated Carbon	K	13.9	116.0	69.6	244	<0	<0
	Na	20.7	27.3	103.4	55.8	0.853	46
	Al	11.0	4.5	54.9	14.4	2.813	73.8

	Mo	21	24.9	105.6	45.4	1.326	57
	W	34.2	14.7	171	2.6	64.77	98.5
Purolite S 950	K	13.9	18.8	69.6	33.6	1.071	51.7
	Na	20.7	6580	103.4	131.6	<0	<0
	Al	11.0	0.8	54.9	1.6	33.31	97.1
	Mo	21	22.8	105.6	45.6	1.316	56.8
	W	34.2	11.6	171	23.2	6.371	86.4
Dowex AG1-X4	K	13.9	17.3	69.6	34.6	1.012	50.3
	Na	20.7	16.5	103.4	33	2.133	68.1
	Al	11.0	0.8	54.9	1.6	33.31	97.1
	Mo	21	15.6	105.6	31.2	2.385	70.5
	W	34.2	8.8	171	17.6	8.716	89.7
Amberlite XAD	K	13.9	1.7	69.6	3.4	19.5	95.1
	Na	20.7	76.0	103.4	152	<0	<0
	Al	11.0	0.9	54.9	1.8	29.5	96.7
	Mo	21	26.2	105.6	52.4	1.015	50.4
	W	34.2	14.1	171	28.2	5.064	83.5
Purolite S 957	K	13.9	1.9	69.6	3.8	17.32	94.5
	Na	20.7	13.7	103.4	27.4	2.774	73.5
	Al	11.0	0.8	54.9	1.6	33.31	97.1
	Mo	21	21.4	105.6	42.8	1.485	59.5
	W	34.2	10.1	171	20.2	7.465	88.2
Chabazite	K	13.9	48.2	69.6	96.4	<0	<0
	Na	20.7	650.0	103.4	1300	<0	<0
	Al	11.0	1.0	54.9	2.0	273.5	96.4
	Mo	21	25.4	105.6	50.8	1.079	51.9
	W	34.2	13.0	171	26	5.577	84.5
Cabsorb ZK406MZ	K	13.9	73.8	69.6	147.6	<0	<0
	Na	20.7	27.4	103.4	54.8	0.887	47
	Al	11.0	5.4	54.9	10.8	4.083	80.3
	Mo	21	25.2	105.6	50.4	1.095	52.3
	W	34.2	12.9	171	25.8	5.628	84.9

The results in Table 4.6 for the K_d values show that most of conditioned resins are promising in adsorbing impurities from alkaline solution while allowing uranium to pass through. The preference was given to the adsorption of sodium and potassium since they are the problem during the conversion process. The efficiency of the resins was determined by the capability of the resin to absorb all the impurities. Purolite S 957 >Amberlite RFH 252> AG1-X4 proved to be effective in absorbing more than 50 % of all the impurities and to release uranium. However Cabsorb ZS 406 M, ZS 500 RW, activated carbon, XAD, Purolite S 950

and Chabazite resins were proven not to be able to absorb sodium and potassium impurities. The next step will be the investigation of the two most promising resins in columns to determine the K_d and to prove the efficiency of them.

4.7 Column experiments

4.7.1 Experimental

Two resins, which are Amberlite RFH 252 and Purolite S957, were tested further for the absorption of impurities using column chromatography. 10g of each resin was weighed and added into a 50 ml centrifuge tube. 40 ml of 1M HCl was poured into the centrifuge tube containing the resin and shaken for 24 hours to convert the resin as indicated in Figure 4.5. After 24 hours, the reaction was stopped and the acid was drained off. The resin was washed with demineralized water for several times to remove the chloride content and the pH of the resin was adjusted by washing the resin with 1M Ammonium carbonate. The resins were placed in an oven at 35°C for drying. The sludge of the resins was transferred to a 10ml (bed height of 2 cm) syringe type column (Figure 4.6) and 10ml (bed height of 10 cm) glass column (Figure 4.7).

200 ppm Uranyl solution was prepared from the dissolution process as described previously. It was then contaminated with impurities each with the initial concentration of 100 ppm. This was prepared in a 1000 ml volumetric flask. 100 ml of the solution was measured off and used for the experiments, during which ten 10 ml fractions were collected for the breakthrough determination. The flow rate of the solution was between 3 and 4 ml/min. Then 5 ml of each fraction was placed separately into a 50 ml plastic sample bottle and 25 ml demineralized water was added before being sent for ICP-OES and AA analysis to determine the amount of uranium and impurities present in the solution before and after extraction. Again 1 ml of the initial uranyl solution was added to a 100 ml volumetric flask and diluted 100 times and analysed for the uranium concentration using the UV Visible spectrophotometer before being mixed with the impurities.

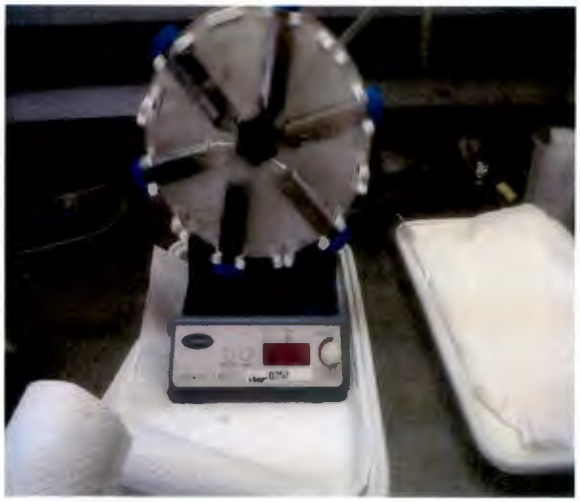

Figure 4.5: Sample rotator with resins shaken for 24 hours

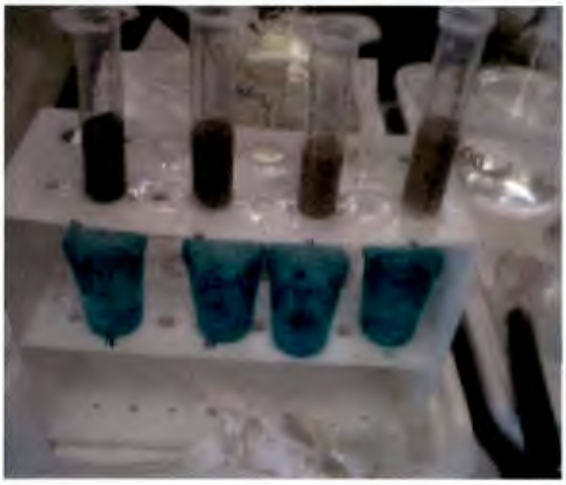

Figure 4.6: Syringe columns packed with resins

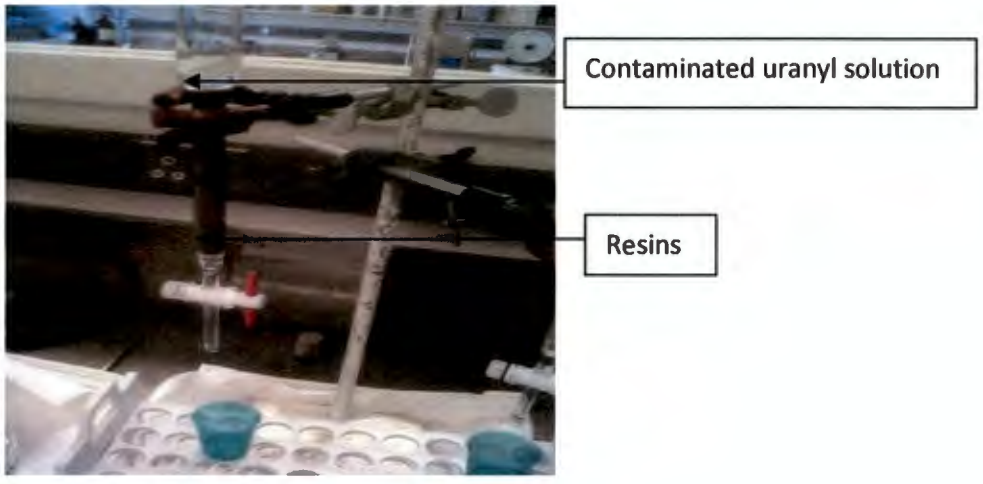

Figure 4.7: Glass column packed with the resin

4.7.2 Results and Discussion

The determination of the quantity of the impurities absorbed onto resin and the elution of uranium was done through column chromatography. Ammonium uranyl solution contaminated with impurities was poured onto column packed with resins as indicated in section 4.7.1. The quantity of uranium and impurities as a function of accumulated volume is presented in Table 4.6 and the raw data used to compile this Table 4.6 is in Tables 8.29, 8.30 and 8.31 in Annexure C. Raw data was multiplied by the dilution factors of 3 and 6 from the initial solutions.

Table 4.7: Amount of metal ion absorbed onto resins

Metal ions	Raw data	Initial Concentration in feed (ppm)	Eluate after extraction with Amberlite RFH 252	Eluate after extraction with Purolite S957
Potassium (K)	10.8	32.4	<6	10.2
Sodium (Na)	12.5	37.5	<7.3	<12.2
Aluminium (Al)	4	12	<6	<6
Calcium (Ca)	2.1	6.3	<6	<6
Molybdenum (Mo)	3	9	<0.6	<0.6
Tungsten (W)	4	18	<0.1	0.6
Uranium (U)	39	117	102	92

The percentage of impurities absorbed (removed) was calculated using the following equation and the results are presented in Table 4.7.

$$\%Adsorbed = \frac{(C_0 - C_i)}{C_0} * 100$$

Table 4.8: Percentage of metal ions absorbed onto each resins

Metal ion	Percentage of metal ion absorbed onto Amberlite RFH 252 (%)	Percentage of metal ion absorbed onto Purolite S 957 (%)
Potassium (K)	81.5	68.5
Sodium (Na)	80.5	67.5
Aluminium (Al)	50	50
Calcium (Ca)	>5	>5
Molybdenum (Mo)	93	93
Tungsten (W)	99	9
Uranium (U)	12.8	21

The results obtained in Table 4.7 show that Amberlite RFH 252 has a higher adsorption capacity for K, Na, and Tungsten as compared to Purolite S957. However the two resins have the same adsorption capacity for Al and Mo. Moreover, Amberlite RFH 252 proved to have

less than 10 % uranium adsorption from ammonium carbonate solution while Purolite S975 adsorbs almost 20% of the uranium. The raw data used to construct Table 4.7 is in Table 7 in Annexure C.

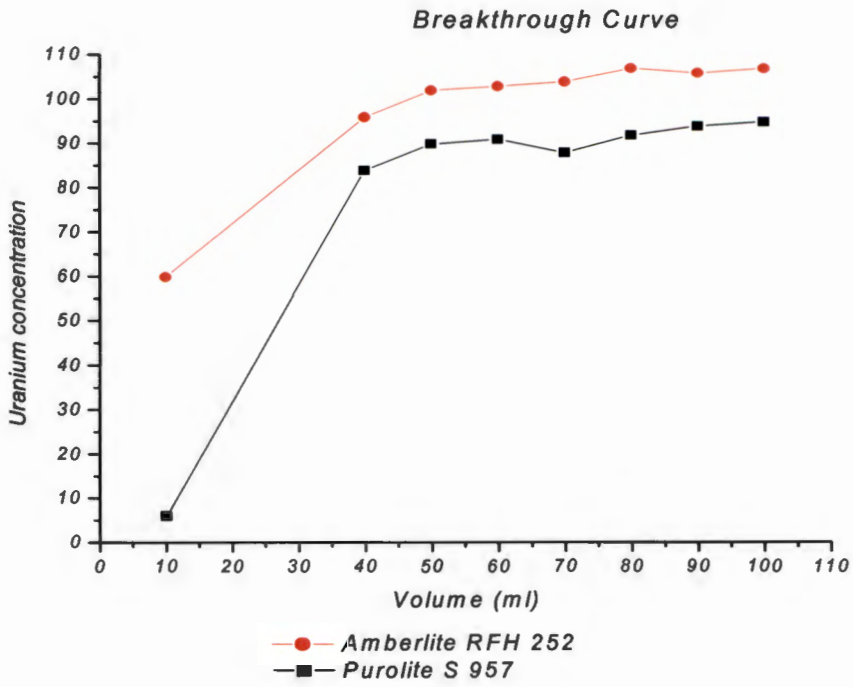

Figure 4.8: Percentage of uranium eluted with Amberlite RFH and Purolite S957 as a function of volume (ml)

4.8 Conclusion

According to the results obtained for the column extraction process, Amberlite RFH 252 is able to absorb the impurities and elute uranium at different capacities.

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Chapter 5

5 Use of solvent extraction technology to purify UOC

5.1 Introduction

Solvent extraction technology began more than 100 years ago and is a prominent separation technique in the field of nuclear technology (Navratil, 1986). In the 1950s, the recovery of uranium (as a by-product from gold mining) was the first major commercial application of liquid extraction in South Africa. This technology has been expanded to the extraction of other specialty and precious metals (Sole et al. 2005).

The technology was proposed for nuclear applications during the Manhattan project. Solvent extraction was used as an effective separation technique to extract uranium for the first reactors (extracted uranyl nitrate into diethyl ether) (MARLAP, 2004). Since then, solvent extraction has been used to recover plutonium and uranium from the weapons programmes (Todd, 2011). The use of solvent extraction has been proven to work effectively in an acid medium especially nitric acid.

The aim of this chapter is to indicate the possibility of purifying uranium from impurities in an ammonium carbonate solution using Aliquat – 336 and TBP as extractants in the presence of Xylene, Dodecane or Kerosene as the diluents (using a batch method).

5.2 Principle of liquid extraction

A comprehensive discussion of the extensive theory and principle of liquid extraction will not be given here. Numerous works on this subject exist in the literature, among others the book of Marcus and Kertes (1969) which gives a good background on liquid extraction. Solvent extraction is a process by which a species is transferred from one liquid phase to another. This involves a transfer of a metal ion from an aqueous phase to an organic phase. The extraction could be done by various mechanisms, for example solvation, chelate formation, ion pairing or ion exchange.

In a study of the literature it was found that there are various extractants that can be used in an alkaline medium, specifically a sodium hydroxide medium, to extract especially lanthanides and trivalent actinides to a lesser extent. The problem with extraction from alkaline medium is to find conditions where the precipitation of less soluble hydroxides is prevented as well as an extractant that will retain its characteristics under extraction conditions. Complexing mediums such as EDTA, DTPA or α-hydroxycarboxyl acids are usually added into a sodium hydroxide medium to prevent precipitation.

Less information is available in the literature for extractions in carbonate or bicarbonate media. The available information indicates that there are principally four groups of extractants that can extract lanthanides and actinides (impurities) from a carbonate medium:

(i) Quaternary ammonium bases
(ii) Primary amines
(iii) Alkyl pyrocatechol
(iv) β-ketone

5.3 Recovery of uranium by liquid – liquid extraction

Moore et al. (1955) and Crouse et al. (1956) studied the use of a number of quaternary amines to extract uranium from alkaline carbonate solutions. The results showed that no quaternary amines performed well with the commonly used diluents of hydrocarbon compounds due to the formation of a third emulsion phase. Some encouraging results were recorded with quaternary amines that could extract over 80% uranium; however toxic chemicals such as chloroform or benzyl cyanide were used as diluents.

Clifford et al. (1958) studied the use of chelating reagents to separate and recover uranium from alkaline bicarbonate solutions. This was achieved by forming the singly charged $UO_2X_3^-$ anion with the complexing agent, and then extracting this complex into an organic solvent. The results indicated that the extraction coefficient is independent of carbonate-bicarbonate concentration. Uranium was recovered from the organic phase using HC1, HCl-NH_4C1, HNO_3, and HNO_3-NH_4NO_3 solutions.

Grindler (1962) repeated the study of Clifford et al. (1958) with a modified long-chain alcohol (tridecanol) as modifier. The addition of this alcohol modifier improves the phase separation time and extraction coefficient of the process. Results from this study indicated that the partition coefficient is dependent on carbonate concentration according to the following reactions:

$$UO_2^{2+} + 3CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} \quad (16)$$

$$2(R_4N)_2SO_4\ (org) + UO_2(CO_3)_3^{4-}\ (aq) \leftrightarrow 2(R_4N)_2UO_2(CO_3)_3\ (org) + 2SO_4^{2-} \quad (17)$$

where R represents the alkyl in the Aliquat 336 structure.

Equation 1 shows that in carbonate solution, the uranyl (UO_2^{2+}) reacts with carbonate and forms $UO_2(CO_3)_3^{4-}$ while equation 2 shows the extraction of U(VI) with Aliquat 336.

Sardine et al. (1962) used cetyl-dimethyl-benzyl-ammonium chloride (CDMBA) in kerosene to extract uranium from alkaline carbonate solution. N-octyl alcohol was added to prevent the formation of the emulsion (3rd phase). Results obtained show that 98 % of uranium was extracted. However, this was only possible by strict controlling of extraction conditions such as amine concentration, temperature, alcohol addition and uranium concentration.

Zhu et al. (s.a) studied the use of Aliquat 336 in Shellsol D70 with isodecanol as the phase modifier to extract uranium from carbonate leach solution. The authors reported that more than 98% uranium was extracted using 3% (w/v) Aliquat 336 and 3% (w/v) isodecanol in Shellsol D70 from carbonate leach solution containing 95 mg/l U, 25 mg/l V at pH 10.3. During this study a third phase formation was observed.

Shehata et al (1994) studied the extraction of uranium from sodium carbonate and sodium bicarbonate solutions using Aliquat 336 and different diluents such as Xylene, toluene, benzene, methyl-isobutyl ketone (MIBK) and carbon tetrachloride. The authors found that different kinds of diluents had significant effects on uranium extraction. The formation of a third phase and emulsion was observed which led to low recovery of uranium.

El – Nadi et al. (2003) studied the mechanism of extraction of hexavalent uranium from alkaline medium by using Aliquat 336 / Kerosene solution in a stirred Lewis cell. The effects

of different parameters affecting the extraction rate such as hydrogen ion, carbonate, hydroxide, Aliquat 336, U (VI) concentrations as well as temperature were separately studied and a rate equation was deduced from the results. From this study it was also reported that the extraction was found to be governed by chemical reaction in the bulk phase rather than reactions at the interface of the phases. The extraction rate of uranium was found to increase linearly with the increase in Aliquat 336 concentration. However, the increase in U (VI) concentration had almost no effect on the extraction rate.

This successful development of the solvent extraction process using alkyl amine for recovering uranium from alkaline ore leach liquors led to the adaption of extractants to recover other metals (Amaral and Morais, 2010). Since then a large number of papers on the selective separation of uranium and rare earth metals using solvent extraction have been published (Amaral and Morais, 2010). For example, Mpinga C.N. (2009) studied the removal of aluminium and sulphate ions (as impurities) from alkaline medium using solvent extraction, Trioctylmethylammonium chloride, (Aliquat 336) in Kerosene as diluent was used. The author reported that 65.12% of aluminium and 85.95% of sulphate can be extracted at pH 11.

For the purpose of this study the following extractants were investigated:

(a) TBP with Kerosene as diluent
(b) Aliquat 336 with Octanol as diluent
(c) Aliquat 336 with Kerosene as diluent
(d) Aliquat 336 with Dodecane as diluent
(e) Aliquat 336 with Xylene as diluents

5.4 Extractants used in this study

5.4.1 Aliquat – 336

The commercial product, Aliquat 336 is a mixture of trioctyl and tridecyl methyl ammonium chlorides. The extraction mechanism is an ionic interaction between the quaternary ammonium base, R_4N^+ (where R represent the alkyl groups) and an anionic metal carbonate complex. The quaternary ammonium cations are positively charged polyatomic ions of the structure NR_4^+. Unlike the ammonium ion (NH_4^+), secondary or tertiary ammonium cations,

the quarternary ammonium cations are permanently charged (Figure 5.1). Aliquat-366 is mostly used as a phase transfer catalyst and metal extractant reagent.

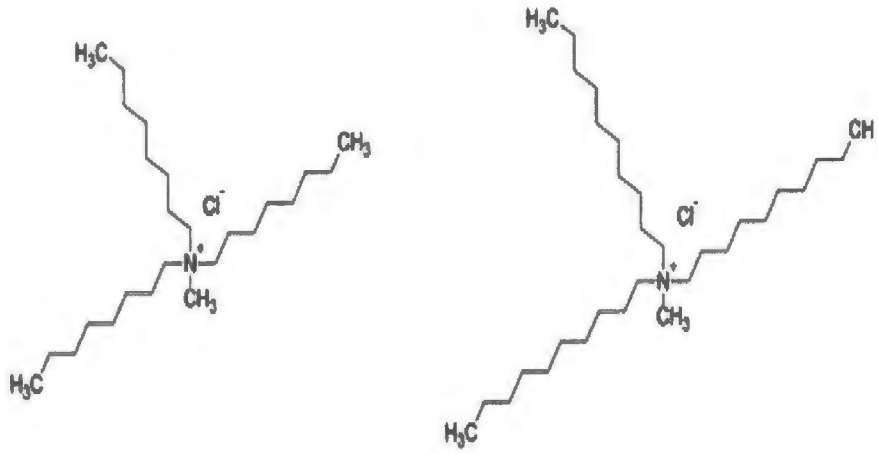

Figure 5.1: Molecular structure for Aliquat – 336 (Starks et.al. 1994).

5.4.2 Tributyl –n-Phosphate (TBP)

Tributyl phosphate (TBP) is an extractant that forms stable hydrophobic complexes with some metals; these complexes are soluble in organic solvents as well as supercritical CO_2. The major uses of TBP in industry are as a component of aircraft hydraulic fluid and as a solvent for extraction and purification of rare earth metals from their ores. TBP is usually used as an extractant and requires a diluent for the separation / extraction purposes (Yang et al. 2011).

A 15–40% solution of Tributyl phosphate in kerosene or dodecane (Figure 5.2) is used in the liquid – liquid (solvent extraction) of uranium, thorium and from spent nuclear fuel rods dissolved in nitric acid, as part of nuclear processing known as PUREX (Kessler, 2012).

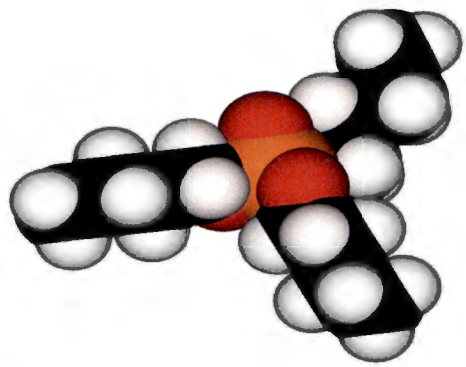

Figure 5.2: Molecular structure of Tributyl –n – phosphate (Kawai et al. 1998)

5.5 Experimental

5.5.1 Preparation of alkaline feed solution

The uranyl solution used for the extraction was generated from the dissolution of UOC with ammonium carbonate and hydrogen peroxide solution. The procedure for the preparation of the uranyl solution was fully discussed in Chapter 3 in Section 3.3.3.1 and 3.3.3.2. Three different volumes of 5, 10, and 20 ml of 1M uranyl solution was measured and transferred into 50 ml sample bottles separately. Solutions of impurities (K^+, Na^+, Al^{3+}, Ca^{2+}, Mo^{2+} and W (100 ppm)) were prepared in 100 ml volumetric flasks. 200 ppm uranyl solution was ''contaminated'' with various impurities to test if the uranium will be transferred to the organic phase while impurities remain in the aqueous phase. The extractants were prepared in two forms i.e. a) used in its original (chloride) form and b) scrubbed with HCl and wash ed with ammonium carbonate solution to be converted into a carbonate form.

5.5.2 Preparation of Aliquat 336

Aliquat 336 in the Cl^- form was purchased from Fluka. The solution used for extractions was made up by weighing 5 g of the viscous liquid and diluting it with Xylene to 100 cm^3 i.e. 5% solution of Aliquat 336 was used. In most experiments, the Cl^- form was used, but for some experiments the extractant was switched to the CO_3^{2-} form by shaking it eight times in a row for 10 minutes at a time with an equal volume of a 0.5 M Na_2CO_3 solution. After removing

the Cl^-, the Aliquat 336 was added separately to the diluents (octanol, dodecane, and xylene). If no precipitates were observed after 24 hours the solution was ready for use.

5.5.3 Experimental procedure

Aqueous solutions with 1M uranyl solution (5, 10 and 20 ml) and organic extractant (5, 10, 20 ml) were mechanically shaken for 30 minutes using the shaker. The solution was transferred into a separation flask and was left for 5 minutes to separate the aqueous and organic phases. The extracting solute was a combination of TBP and Aliquat -336 varying kerosene, xylene and dodecane as diluents.

The results for the percentage amount of uranium extracted during the extraction process were calculated using the following equation:

$$\% \text{ Extracted} = \frac{[Ui]-[Uf]}{[Ui]} * 100$$

Whereby

$[U_i]$ = Initial concentration of uranium before extraction

$[U_f]$ = Final concentration of uranium after extraction.

Distribution coefficient (D) values are discussed in the previous section. The following sample names were used to label the Sample ID's in the results presented in the Tables constructed using the raw data in Annexure A which are:

- Sample A represents the sample solution labeled Autoclave
- Sample B represents the sample solution labeled Magnetic stirrer
- Sample C represents the sample solution labeled No air
- Sample D represents the sample solution labeled Air stirring

5.6 Results and discussions

5.6.1 Extraction of uranium with 5% TBP diluted in 95% kerosene

The first extraction with TBP and kerosene was performed as a baseline with the experimental procedure described in Section 5.2.3. Figure 5.3 and Table 5.1 show the results obtained from the experimental tests. The raw data used to construct Table 5.1 is in Table 8.32 in Annexure D.

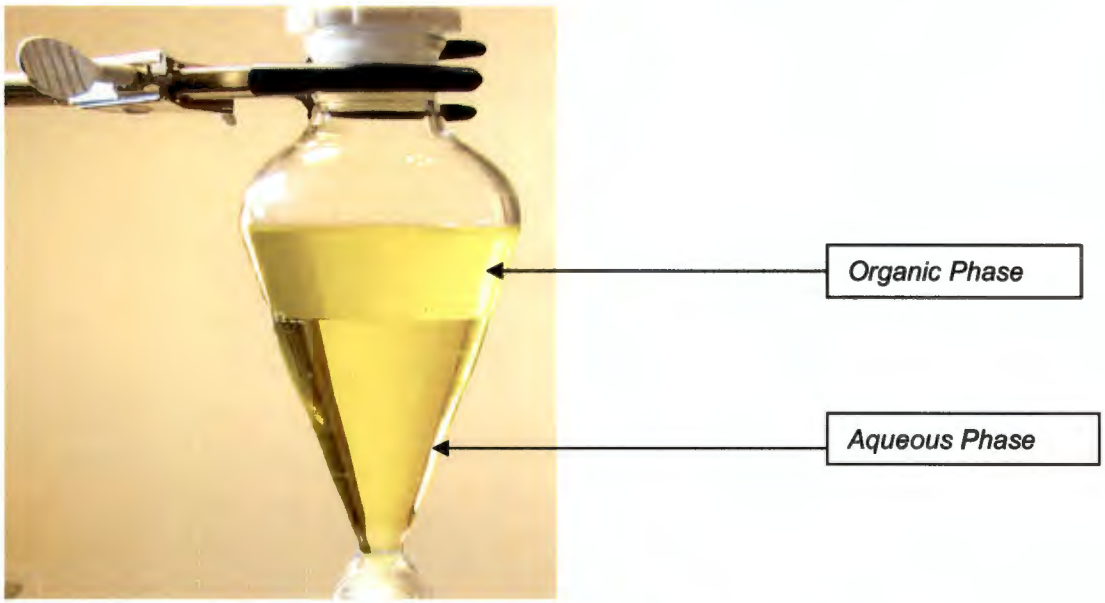

Figure 5.3: Uranium extracted with 5% TBP and 95% kerosene

Table 5.1: Results of uranium extracted with 5% TBP diluted in 95% kerosene

Sample Name	[U]Initial	[U]Final	D Value	% Extracted
Solution A	85833.33	78551.47	0.09	8.48
Solution B	79472.51	72586.65	0.001	8.66
Solution C	80700.50	67762.16	0.19	16.0

The names used for naming the Sample ID are in Section 5.5.3.1

The low extraction results in Table 5.1 indicated that extraction of uranium from the carbonate medium with TBP in kerosene is not sucessful. The reason is that TBP and kerosene extract uranium effectively in nitric acid due to the formation of the $UO_2(NO_3)_2.2TBP$ complex. Due to the absence of HNO_3, this complex cannot form and

therefore the use of TBP was abandoned. The following section will test the effectiveness of Aliquat -336 for extracting uranium from ammonium carbonate solution.

5.6.2 Extraction of uranium with 5% Aliquat 336 and 95% kerosene

The extractants composition was varied from 5 to 10 % volume of Aliquat 336 and mixed with kerosene to make up a total volume of 100% into a 100 ml volumetric flask. Extraction investigations were carried out as discussed in section 5.4 and the results obtained are presented in Table 5.2. The raw data used to construct Table 5.2 is in Annexure D in Table 8.33.

Table 5.2: Results of uranium extracted with 5 % Aliquat 336 and 95% kerosene

Sample ID	D	% U Extracted
Solution A	0.059	5.86001
Solution B	0.207	20.65308
Solution C	0.148	14.84772

The names used for naming the Sample ID are in Section 5.5.3.1

The results in Table 5.2 indicated that less than 20% of the uranium can be extracted using Aliquat 336 and kerosene as extractant. These results clearly indicate that the uranyl ion present in ammonium carbonate solution does not complex easily with the above mentioned extractants. The results are similar to the previous investigations in Section 5.5.2 as can be observed in Table 5.1. As the root cause of this problem is not known, it was decided to increase the volume of Aliquat-336 to 10% to investigate the effect.

5.6.3 Extraction of uranium with 10% Aliquat 336, 90% kerosene

The experimental procedure for the current investigation was similar to the previous section. The results obtained are presented in Table 5.3. The raw data is in Table 8.34 in Annexure D.

Table 5.3: Results of uranium extracted with 10 % Aliquat – 336 and 95% kerosene

Sample ID	D	% U Extracted

Solution A	0.043	4.30
Solution B	0.123	12.27
Solution C	0.054	2.54
Solution D	0.083	8.32

The names used for labelling the Sample ID are in Section 5.5.3.1

The results obtained in Table 5.3 show no difference in the amount of uranium extracted as compared to the previous method. Due to the low amount of uranium extracted, it was decided to add a modifier to test if it can improve the recovery.

5.6.4 Extraction of uranium with Aliquat - 336 and kerosene using 5% octan-1-ol as modifier.

The current experimental procedure was performed similarly to the previous Section 5.7.3, with the difference of adding 5% octan-1-ol. The results obtained are presented in Table 5.4. The raw data used to calculate Table 5.4 is in Table 8.34 in Annexure D

Table 5.4: Results of uranium extraction with 5% Aliquat 336, 90% kerosene and octan-1-ol

Sample ID	D	%Extracted
Solution A	0.042	4.17
Solution B	0.052	5.17
Solution C	0.065	6.51
Solution D	0.042	4.22

The names used for labelling the Sample ID are in Section 5.5.3.1

The results obtained show that less than 10% of uranium was extracted. It was decided to double the volume of Aliquat -336 to make it 10%. Table 5.5 illustrates the results obtained. The raw data used to construct Table 5.5 is in Annexure D in Table 8.34

Table 5.5: Results of uranium extraction with 5% Aliquat 336, 85% kerosene and 10% octan-1-ol

Sample ID	D	%Extracted
Solution A	0.032	3.16
Solution B	0.12	11.62
Solution C	0.06	6.00
Solution D	0.082	8.19

The names used for labelling the Sample ID are in Section 5.5.3.1

The overall results obtained show that a mixture of Aliquat-336 and kerosene cannot extract uranium from ammonium carbonate solution. Therefore, it was decided to abandon the method and investigate a new diluent, which is dodecane.

5.6.5 Extraction of uranium with 5% Aliquat- 336 + 95 % dodecane

The ability of the mixture of Aliquat - 336 and dodecane to extract uranium from aqueous ammonium carbonate solution was also investigated. The amount of Aliquat -336 was varied from 5 to 10% volume. The molar solution of 1:1 which was made with 10 ml of organic phase and 10 ml of aqueous phase was pre-equilibrated for the extraction process. The agitation process of the two phases was similar to that described in Section 5.4.1. The results obtained from the investigation are presented in Table 5.6 and 5.7. The raw data used to construct Table 5.6 and 5.7 are in Annexure D in Table 8.35.

Table 5.6: Uranium recovery with 5% Aliquat 336 and 95% dodecane

Sample ID	D	% Extracted
Solution A	0.173	11.8
Solution B	0.173	9.6
Solution C	0.085	14.37
Solution D	0.160	10.6

The names used for labelling the Sample ID are in Section 5.5.3.1

Table 5.7: Uranium recovery with 10% Aliquat 336 and 90% dodecane

Sample ID	D	%Extracted

Solution A	0.120	17.3
Solution B	0.096	17.3
Solution C	0.144	8.5
Solution D	0.106	15.6

The names used for labelling the Sample ID are in Section 5.5.3.1

The results in Table 5.6 and 5.7 indicate that less than 20% of uranium can be extracted by using Aliquat 336 and dodecane from an aqueous alkaline solution. Due to this poor and slow extraction, it was decided to discontinue the tests. The above tested extractants (TBP in kerosene, Aliquat 336 in kerosene, Aliquat 336 Octan-1-ol, and Aliquat 336 in dodecane) were found to be poor solvents because the amount of uranium extracted from the aqueous alkaline solutions to organic solution is very low in these solvents and it was decided to investigate the mixture of Aliquat 336 and xylene.

5.6.6. Extraction of uranium with 5%Aliquat 336 and 95% xylene

In order to determine the efficiency of Aliquat 336 and xylene to extract uranium from alkaline solution, the same procedure was followed (Section 5.4.1) and two different methods were employed. The first method includes the use of Aliquat 336 in its original chloride form and the second method includes the use of Aliquat 336 converted into carbonate form. The procedure of converting of Aliquat 336 into carbonate form was discussed in Section 5.4.2. The effect of concentration was also investigated from 5 to 10%. Only three solutions were used for the current investigations. The results obtained from the use of Aliquat 336 in its original form diluted with xylene are presented in Table 5.8 and 5.9. The raw data used to construct Table 5.8 and 5.9 is in Table 8.36 and 8.37 in Annexure D.

Table 5.8: Extraction of uranium with 5% Aliquat -336 plus 95% xylene

Sample ID	D	%U Extracted
Solution A	0.26	19.5
Solution B	0.22	18.2
Solution C	0.14	12.6

The names used for labelling the Sample ID are in Section 5.5.3.1

Table 5.9: Extraction of uranium with 10% Aliquat-336 and 90% xylene.

Sample ID	D	% Extracted
Solution A	0.46	31.6
Solution B	0.42	29.7
Solution C	0.36	26.1

The names used for labelling the Sample ID are in Section 5.5.3.1

The results in Table 5.8 show that nearly 20% of uranium was extracted from ammonium carbonate solution with 5% Aliquat 336 and 95% xylene. However, the results in Table 5.9 indicated that an increase of Aliquat -336 to 10% led to an increase of almost 30% of the uranium extracted into the organic solution. The extractions of uranium from aqueous carbonate to organic solution of Aliquat 336 and xylene have improved slightly as compared to the previous solvents. The next method of Aliquat 336 in carbonate form was also investigated.

5.7. Extraction of uranium with 5%Aliquat-336 in carbonate form and 95% xylene

The experimental procedure for the current investigations was discussed in Section 5.4.1 and altered slightly. Two different uranium concentrations of 18 and 84 g/l were investigated. The molar ratio of 1:1 and 2:1 organic to aqueous solution was investigated. The first experimental investigations were performed with uranyl solution with an initial concentration of 84 g/l. The organic to aqueous volume was kept at 1:1. The results obtained are presented in Table 5.10 and 5.11. The raw data used to construct Table 5.10 and 5.11 are in Table 8.38 and 8.39 in Annexure D.

Table 5.9: Results of uranium extraction with 5% Aliquat -336 in CO_3^{2-} form and 95% xylene

Sample ID	D	U % Extracted
Solution A	0.68	24.1
Solution B	0.71	24.2
Solution C	0.62	25.3

The names used for labelling the Sample ID are in Section 5.5.3.1

Table 5.10: Results of uranium extraction with 10% Aliquat -336 in CO_3^{2-} form and 90% xylene

Sample ID	K_d	U % Extracted
Solution A	0.48	35.2
Solution B	0.51	33.1
Solution C	0.42	39

The names used for labelling the Sample ID are in Section 5.5.3.1

The results in Table 5.10 indicate that less 30% of uranium was extracted to the organic solution. However Table 5.11 indicates an increase of uranium extracted to the organic solution, although the amount of uranium extracted by Aliquat-336 and xylene was less than 40%. This might be caused by the high initial uranium concentration of 84 g/l. Due to the low amount of uranium that was extracted; it was decided to reduce the initial uranium concentration to 18 g/l. The next investigation was done with the reduced concentration of uranium.

5.7.1 Extraction of uranium with 5%Aliquat-336 in CO_3^{2-} form and 95% xylene

The procedure of extracting uranium with 5% Aliquat 336 and 95% xylene was the same, but the concentration of uranium was decreased from 84 g/l to 18 g/l and the molar ratio also changed to 2:1 organic to aqueous phases. The results obtained from these tests are presented in Table 5.12 and 5.13. The raw data used to construct Table 5.12 and 5.13 is in Annexure D in Table 8.39.

Table 5.11: Extraction of uranium with 5% Aliquat 336 in CO_3^{2-} and 95% xylene

Sample ID	D	% U Extracted
Solution A	0.806	80.6
Solution B	0.877	87.7
Solution C	0.865	86.5

The names used for labelling the Sample ID are in Section 5.5.3.1

Table 5.12: Extraction of uranium with 10 % Aliquat 336 CO_3^{2-} and 90% xylene

Sample ID	K_d	% U Extracted
Solution A	0.93	93.8
Solution B	0.92	92.4
Solution C	0.93	93.2

The names used for labelling the Sample ID are in Section 5.5.3.1

The results in Table 5.12 and 5.13 clearly indicated that more than 90% of uranium can be extracted from the aqueous alkaline solution using Aliquat 336 in carbonate form diluted with xylene. The next investigation concerned the effect of changing the ratio of organic to aqueous solution to 1:2.

5.7.2 Extraction of uranium with 10% Aliquat -336 CO_3^{2-} form 90% xylene with organic/ aqueous ratio of 1:2.

The conditions for extracting uranium were optimized. The volume ratio of organic to aqueous ratio was changed to 1:2 ratio. The results obtained from these tests are presented in Table 5.14. The raw data used to construct Table 5.14 is in Table 8.40 in Annexure D.

Table 5.13: Extraction of uranium with 10 % Aliquat 336 CO_3^{2-} form and 90% xylene

Sample ID	[U] Initial	[U] Final	D	% U Extracted

Solution A	9642.78	964.17	0.9	90
Solution B	47499.62	4749.43	0.9	90
Solution C	14642.74	1464.11	0.9	90

The names used for labelling the Sample ID are in Section 5.5.3.1

The results in Table 5.14 indicated that 90% of uranium was extracted successfully into Aliquat 336 and xylene at low uranium concentration. This shows that the initial concentration of uranium as well as the volume ratio plays a major role in the extraction process. The final concentration of uranium in the aqueous phase is lower than that in the organic phase.

5.8 Effect of various impurities on the extraction of uranium

Various impurities such as K, Na, Ca, Al, Mo and W were investigated to study their effect on the extraction process of uranium with Aliquat 336 and xylene solution. The prepared initial concentration of impurities was assumed to be 100 ppm. The sample solution before extraction and after extraction for the impurities was sent to Pelindaba analytical labs (PAL) for the quantitative analysis using AA and ICP-OES techniques. The results obtained from this are presented in Table 5.15. The raw data used to construct Table 5.15 is in Annexure D in Table 8.41.

Table 5.14: The amount of metal impurities extracted from ammonium uranyl solution with Aliquat 336 and xylene

Metal ion	Initial concentration of metal impurities before extraction	Final concentration of metal impurities after extraction
Potassium (K)	42.8	3.8
Sodium (Na)	61.2	27.4
Aluminium (Al)	74.4	1.6
Molybdenum (Mo)	69.2	42.8
Tungsten (W)	118.2	20.2

The results in Table 5.15 show that some of the impurities were also extracted to the organic solution. These results confirm that solvent extraction is not selective for the impurities present in the aqueous solution.

5.9 Conclusion

The results obtained show that the organic solutions consisting of Aliquat-336 in TBP, Aliquat-336 in Octan-1-ol and Aliquat 336 in dodecane are not effective to extract uranium from aqueous alkaline solution. Less than 10% of uranium was extracted from alkaline solution using these organic solutions. However, more than 90% of uranium extraction was obtained with an organic solution mixture of Aliquat -336 in xylene. Unfortunately, the presence of the impurities significantly affected the extraction of uranium. The ICP – OES analysis shows that some of the impurities were extracted with uranium to the organic solution.

5.10 References

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Chapter 6

6 Precipitation using steam stripping technology

6.1 Introduction

The precipitation process is perhaps the oldest and simplest method for the recovery of a metal from the leach liquor solution as a compound (Gupta C.K., 2003). During the late 1940s much effort was spent to develop selective precipitation processes and most of these techniques are now obsolete (Grenthe et al, 1998).

Precipitation is the process by which a dissolved substance is converted into an insoluble form that can subsequently be separated from the bulk of the solution. A physical or chemical change must take place for the transition from a soluble to an insoluble form. (Gupta C.K., 2003).

A physical precipitation as a method does not involve the use of reagents but temperature and concentration manipulation until crystallization occurs (when the solubility limits are exceeded). Precipitation may also occur particularly if a substance is introduced into a solution and thereby changes the density of the solution resulting in a precipitate or a suspension that can be separated (Gupta C.K., 2003).

Chemical precipitation methodology is based on a coagulation or flocculation separation principle and is used for the treatment of liquid effluent with low activity and high salt contents. Precipitation is initiated by the addition of reagents to form new insoluble complexes. The effectiveness depends on the radiochemical speciation and chemical composition of the liquid waste. Radionuclides can be precipitated, co-precipitated and absorbed as carbonates, phosphates, hydroxides or ferrocyanides from the solutions (Efremenkov, 1989).

For direct precipitation of certain cations from carbonate solutions the methods illustrated in Table 6.1 can be considered (Lunt D. et al, 2004).

Table 6.1: Separation by precipitation

Impurity	Separation technique
Vanadium	Treatment of bulk precipitates -Thermal method -Dissolution and precipitation Precipitation prior to uranium e.g. $FeSO_4$, or $PbSO_4$ Precipitation with peroxide
Molybdenum	Bleed recycle solution from the circuit Adsorption onto activated carbon Precipitation with peroxide
Sodium	Dissolution of sodium diuranate and re-precipitation Use or hydrogen peroxide precipitation
Silica	Dissolution and re-precipitation Modify leaching conditions

Radionuclides can either be co-precipitated or sorbed onto the flocculated material (Chung, 1998). The two parameters that are commonly used to describe the performance of precipitation process are the volume reduction factor (VRF) and the decontamination factor (DF). The volume reduction factor is the ratio of the volume of waste before and after treatment. The value of the DF depends on the purification achieved. The DF value to purify radioactive waste stream can be described as follows (IAEA-TRS-139, 1992):

DF = total activity in feed / total activity in effluent

$$DF = \frac{a_f v_f}{a_e v_e} \qquad (1)$$

Where:

a_f: activity per unit volume of feed

a_e: activity per unit volume of effluent

v_f: volume of feed

v_e: volume of effluent

To increase the success rate of a precipitation reaction, the following pretreatment actions can be considered:

- pH adjustments for the breaking of complexes and thereby increasing the availability of undissociated acid and base species for further treatment procedures.
- Chemical oxidation
- Chemical reduction to reduce metal ions to the metal and to destroy organic complexes

The above characteristics determine the process parameters that must be followed. For instance, for the treatment of laundry water the suspended soap matter is too fine for rapid sedimentation or easy filtration and iron salts, aluminium salts or lime are commonly used for coagulation of the suspended particles. Also ferric chloride and caustic soda or acid may be added to the laundry wastewater for removal of particulate matter and destroying of organic compounds respectively.

After flocculation, the mixture may be sent to a sedimentation basin with a sludge removal device or to a filter. Another chemical used for precipitation is ferric hydroxide, which is used at high pH to treat laundry and other wastewater (Mercer and Ames, 1977). However, the most commonly used precipitation processes for efficient decontamination of more than one radionuclide in effluent waste streams are the following (IAEA-TRS 337, 1992):

- Lime soda process
- Phosphate precipitation
- Hydroxide precipitation
- Oxalate precipitation.

Short descriptions of the different processes follow:

6.1.1 The lime soda process

The purpose of this process is to remove strontium as a co-precipitate with a precipitate of calcium carbonate (strontium carbonate) as follows:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3\downarrow + 2\,H_2O \quad (2)$$

$$Ca(OH)_2 + Na_2CO_3 \rightarrow Ca\,CO_3\downarrow + 2NaOH \quad (3)$$

Other processes, using alum and ferrous sulphate as potential coagulating agents and $CaCO_3$ as a nucleate precipitation catalyst, have now been found to be better than the lime soda process.

6.1.2 The phosphate precipitation process

In this process, soluble phosphates especially tri-sodium phosphate are added to waste to form insoluble compounds with ions according to the following reaction mechanism:

$$3\,M^{n+} + n\,PO_4^{3-} \rightarrow M_3(PO_4)_n\downarrow \quad (4)$$

Where M = for example can be Fe^{3+}, Al^{3+} or Ca^{2+}

The addition of calcium ion as a bulk co-precipitant (catalyst) enhances the removal of other cations. However, the removal of radioactive cesium by co-precipitation with this phosphate precipitation has proven to be inadequate. For strontium removal, barium sulphate precipitation is preferred over phosphate precipitation.

6.1.3 The hydroxide precipitation process

With the possible presence of ferric ions in waste streams, the use of ferric hydroxide precipitation is preferred for radioactive wastewaters. The metal ions in solution can be hydrolyzed to form insoluble compounds as follows:

$$M^{n+} + nOH \rightarrow M(OH)n\downarrow \quad (5)$$

In general, the ferric hydroxide flocculant particles are large and settle more easily than those of aluminium hydroxide, which is used in regular municipal wastewater treatment. Ferric hydroxide can be readily precipitated by the addition of an alkali such as NaOH, $Ca(OH)_2$ or NH_4OH to effluent waste streams. The use of NH_4OH will not be considered in this project due to the negative influence of ammonia on the encapsulation of radioactive waste in cementitious material.

6.2 Precipitation of uranium

As part of the advanced aqueous reprocessing of spent fuel from fast breeder reactors (FBR), uranium crystallization has been developed. This new extraction process system for transuranium (TRU) recovery is shown in Figure 6.1 (Yano et al, 2009). The crystallization process is expected to have the following advantages over the conventional liquid extraction (PUREX) process:

- Relative simplicity, remote operation only by temperature control
- Minimal organic solvents used in the extraction process
- Reduction in waste volume
- Enhancement of the nuclear proliferation resistance (Yano et al, 2009).

This crystallization process is based on the solubility difference between uranium and other elements under controlled temperature and pH (Yano et al, 2009). In the literature many references are available on the precipitation and crystallization of uranium from nitric acid solutions but literature on alkaline processes is minimal.

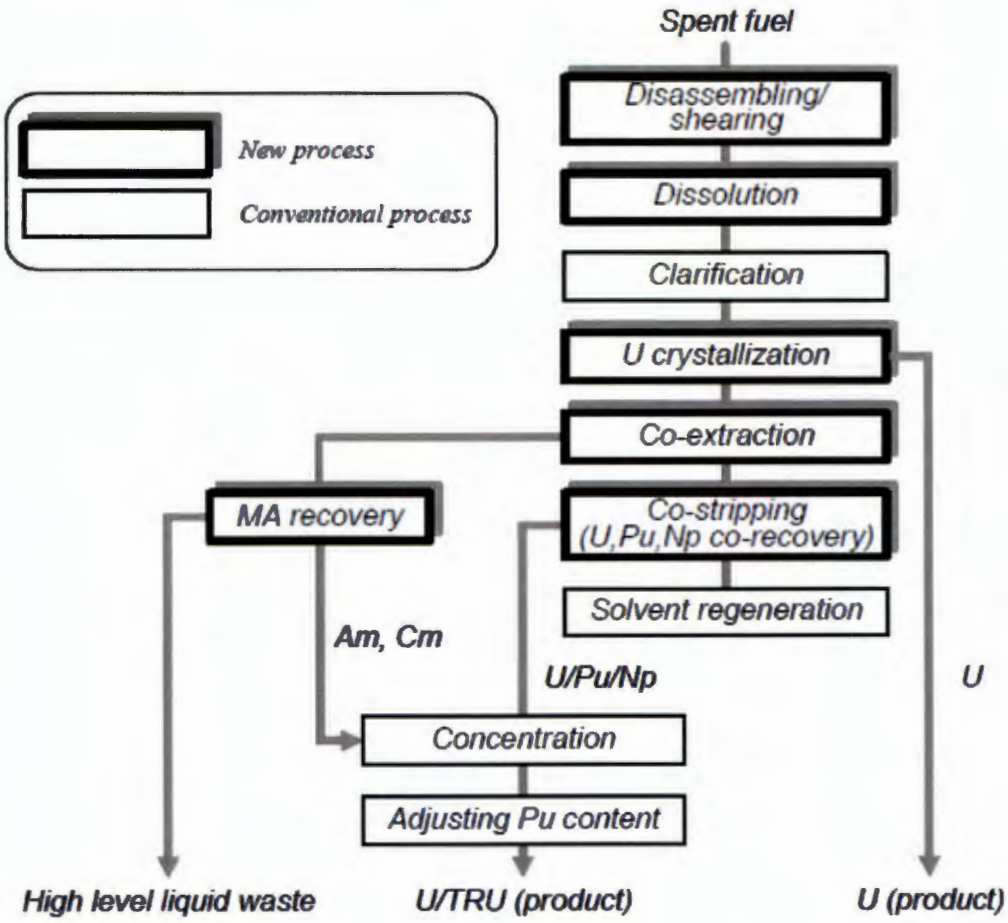

Figure 6.1: Illustration of the schematic flow of the uranium next process (Yano et al, 2009).

Precipitation of uranium from alkaline solution is usually done by removing the carbon dioxide in the solution by acidification; followed by neutralization and reduction of uranium to U (IV) (Grenthe et al; 1998). However, Mella et al; 2006 performed a kinetic study regarding the ammonium uranyl carbonate (AUC) precipitation process and reported that dissolved uranyl salt reacts with hydrated NH_3 and CO_2 to form yellow coloured AUC crystals (of a monoclinic form) that can precipitate. The theoretical modeling of the reaction mechanism is as follows.

Step 1: Formation of a weak acid and base

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (6)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (18)$$

Since NH_3 is a weak base and CO_2 is a weak acid, additional ionic equilibrium was considered.

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (8)$$

Step 2: Reaction of CO_3^{2-}

The species CO_3^{2-} diffuses to the UO_2^{2+} surface from surrounding water molecules and then reacts with UO_2^{2+} as follows:

$$3(CO_3^{2-}) + UO_2^{2+} \leftrightarrow \frac{K2}{K2} UO_2(CO_3)_3^{4-} \quad (19)$$

The instantaneously formed uranyl carbonate irreversibly reacts with the surrounding hydrated ammonia ions in solution to form nuclei of AUC as follows:

$$UO_2(CO_3)_3^{4-} + 4(NH4) \xrightarrow{K3} (NH_4)_4 UO_2(CO_3)_3^{2-} \quad (10)$$

The complete schematic layout of this process can be seen in Figure 6.2.

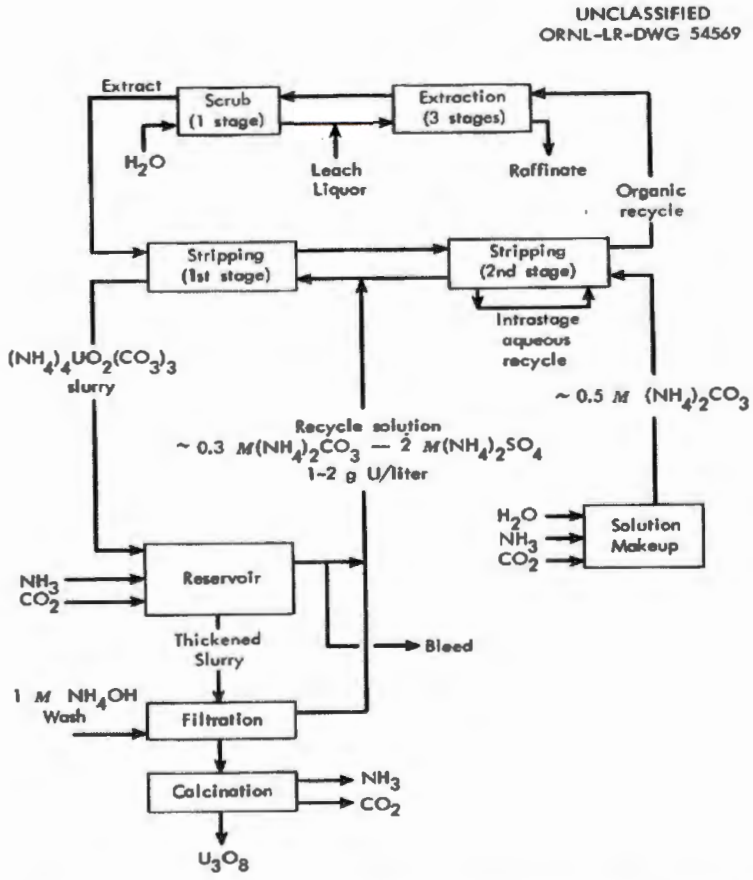

Figure 6.2: Illustration of ammonium carbonate stripping process to precipitate uranium (Hurst & Crouse, 1961).

Another method of removing uranium by the precipitation process from alkaline solutions is with hydrogen peroxide. The cost of this methodology is higher but a higher purity product is obtained. In order to prevent catalytic decomposition of hydrogen peroxide during the precipitation process, ferric ions must be limited to a concentration less than 0.5 g l^{-1}(Hurst & Crouse, 1961). The other alternative to prevent hydrogen decomposition is to perform precipitation at low temperatures or by complexing the iron (Grenthe et al, 1998.) from the solution before adding H_2O_2 for uranium precipitation.

Kang et al, (2002) studied precipitation of uranium (VI) using 1M NaOH and 0.1 M $HClO_4$ to adjust the pH range to between 4 and 10. Results indicated that the amount of uranium precipitated is influenced by pH and the environment. In a CO_2 atmosphere 30% of uranium precipitated at pH 5, 70% in the pH range from 5 to 9 and above pH 9 the amounts of uranium precipitate decreased to 40%. In the presence of air the results indicated that overall less than 40% of uranium in the pH range from 4 to 11 precipitated except at pH 6.8 where 54% precipitated. This result implies that complete uranium precipitation from alkaline solution is not possible by only adjusting pH.

Since total removal of uranium (by pH adjustments) from carbonate leach systems was not achieved, the preferred method was changed to the addition of an excess amount of sodium hydroxide (IAEA, 1990) (that can be recycled for use again) for the precipitation of uranium.

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This uranium precipitation by NaOH addition in alkaline medium, (with the regenerating of reagents) can be described as follows:

$$2\ NaOH + CO_2 \leftrightarrow Na_2CO_3 + H_2O \quad (10)$$

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \quad (11)$$

$$NaHCO_3 + NaOH \leftrightarrow Na_2CO_3 + H_2O \quad (12)$$

$$6NaHCO_3 + Na_2U_2O_7 \leftrightarrow 2Na_4UO_2(CO_3)_3 + 3H_2O \quad (13)$$

$$2Na_4UO_2(CO_3)_3 + 2NaOH \leftrightarrow Na_2U_2O_5 + 6NaCO_3 + H_2O \quad (14)$$

Equation 11 and 12 indicates that addition of NaOH first converts any CO_2 present to carbonate and then brings about a reaction with sodium uranyl tricarbonate to precipitate the uranium as sodium diuranate or more probably as polyuranates (IAEA, 1990).

$$6NaHCO_3 + NaU_2O_7 \leftrightarrow 2Na_4UO_2(CO_3)_3 + 3H_2O \quad (15)$$

Berry et al 1981 studied recovery of uranium using phosphate to precipitation uranium. The study indicated that uranium is soluble as the uranyl carbonate anion complex in the carbonate leachate and that in the presence of excess amounts of orthophosphate can precipitate the uranium. Although various phosphates can be used, the orthophosphate, Na_2HPO_4 , has been recommended to precipitate UO_2HPO_4. In the industry a method called steam stripping is used to precipitate uranium from liquid solutions.

There are various ways of recovering a metal ion from the solution using a steam stripping technology, for instance direct injection of steam into a solution to volatilize the organic compounds as a continuous or batch processes.

Steam stripping involves the raising of the temperature of the solution to boiling point by injecting steam into the solution. In an ammonium uranyl tri – carbonate leach solution, an increase in temperature above 65°C will cause the ammonium uranyl tri-carbonate complex to dissociate and precipitates will form. The rate at which the steam is injected into the solution and the pH influences the precipitates, as the uranyl complex is stable at high pH values (9 – 10): Should the pH decrease due to the loss of ammonia during the steam stripping reaction, it is advisable to adjust the pH for maximum efficiency.

Another method is a continuous steam stripping process in a column. The column (Figure 6.3) is designed to promote transfer of contaminants into the gas phase, effective heat transfer to the waste provides a large surface area and, by creating turbulence in the waste stream, for efficiency. Figure 6.4 illustrates the process of precipitating uranium as yellow cake using steam stripping technology (Lunt and Holden, 2007).

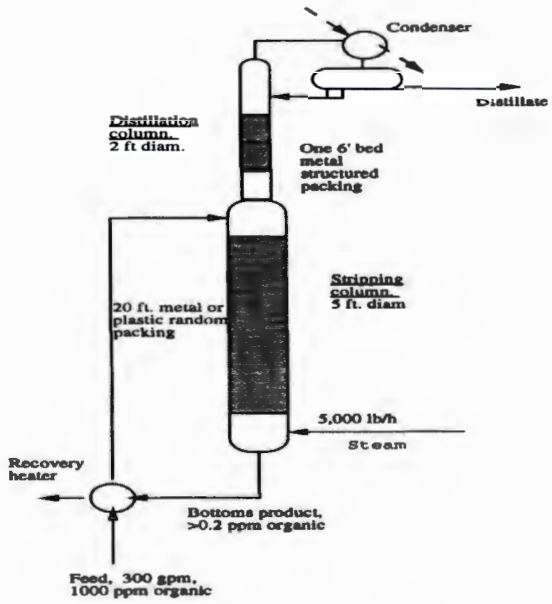

Figure 6.3: The steam stripper and recovery column combination for immiscible and volatile systems (Jaeger product, 1996).

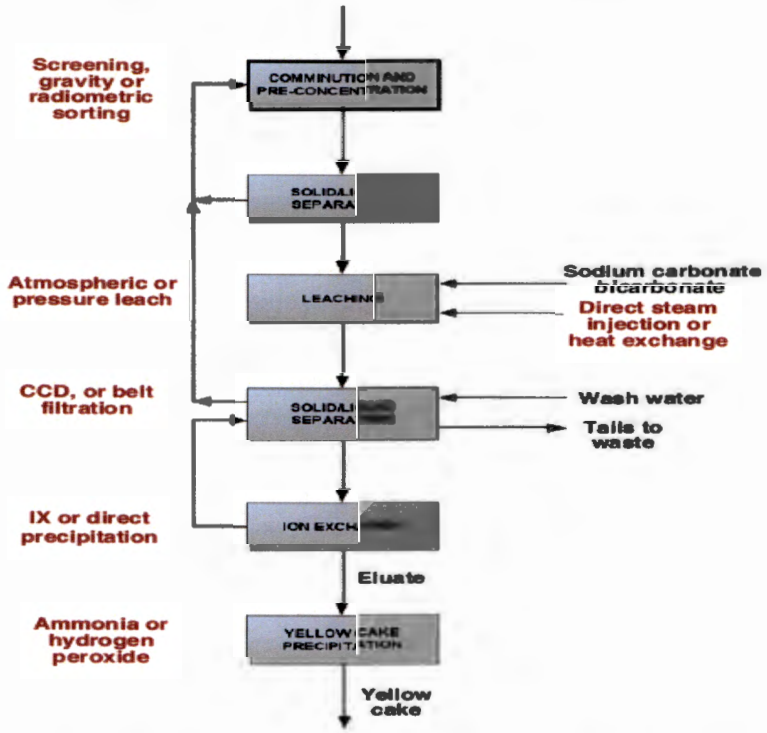

Figure 6.4: Illustration of the key process for uranium steam stripping to form a yellow cake precipitates (Lunt and Holden, 2007).

Another method is based on a batch process that involves a batch still, an overhead vapor line, condenser, gravity separator and a condensate receiver. The solution is heated to provide heat for the vaporization of the waste and steam is injected through a perforated pipe line in

the still. Vapor is condensed and collected as a liquid in the condensate receiver. Liquids with similar boiling points and different densities may be separated by gravity separation in the condensate receiver (EG & G Rocky Flats, 1991).

The advantage of steam stripping technology is that it is a well demonstrated technology commonly used in the industry and reported to be effective for removal of high concentrations of elements from the solution and also the organics. Ammonia and hydrogen sulphide can also be removed by stream stripping which is capable of removing over 99% of ammonia in high strength industrial waste (EG & G Rocky Flats, 1991).

The aim of this chapter is to investigate the possibility of purifying uranium from solutions containing impurities such as Na^+, K^+, W, Mo, Al^{2+} and Ca^{2+} by precipitation and to determine the influence of these impurities on the precipitate product that forms.

6.3 Experimental

6.3.1 Chemicals used

The chemicals used to prepare the impurities that were added to the reference solution were: Aluminium hydroxide (Sigma Aldrich product), Sodium carbonate, Molybdenum (V) Chloride and Calcium carbonate (Products of MERCK), Potassium carbonate (Analytical reagent), Wolfram (FLUKA AG product) and demineralized water from Necsa. The target impurities were (Na^+, K^+, W, Mo, Al^{2+} and Ca^{2+}). The reagents were used to prepare 100 ppm solutions. 80 ml of ammonium uranyl carbonate solution (45 and 84 g/l) was added to 20 ml of solution of impurities to make a total volume of 100 ml uranyl solution contaminated with impurities.

6.3.2 Preparation of samples

Two methods were performed to study the uranium precipitation from ammonium uranyl carbonate solution i.e. pure ammonium uranyl solution and ammonium uranyl solution contaminated with the impurities. Ammonium uranyl carbonate reference solution was

prepared by dissolving 16.7 g of UOC which is a mixture of U_3O_8 and UO_3 (from Nufcor) in 150 ml 1M $(NH_4)_2CO_3$ with 1M 16.7 ml of 30% H_2O_2 at 60 ^{0}C for 3 hours..

6.3.3 Precipitation procedure

Convectional heating was used during this process. No chemicals were added as catalysts in order to limit contamination to precipitation.

6.3.3.1 Ammonium uranyl carbonate solution without impurities

Ammonium uranyl carbonate solution (100 ml) of an appropriate initial uranium concentration was transferred to a beaker and the solution was heated from 70 to 90°C with constant stirring (250 rpm) for a fairly extended period of 1 to 2 hours. 100 ml of water in total was added continuously bit by bit to keep the initial volume constant. The heating was stopped once there was no more sign of gases (carbon dioxide and ammonia) released in the form of bubbles going out. The experiment was repeated three times, with freshly prepared solution each time to obtain the average results. The primary control of the whole precipitation process was heating, stirring and continuous addition of water for all the three solutions to keep the volume constant throughout the process. The increase in temperature causes the ammonium uranyl carbonate to dissociate whereby ammonium is released as ammonia and bicarbonate volatilizes as carbon dioxide.

$$(NH_4)_2\,CO_3 + heat \leftrightarrow 2\,NH_3\uparrow + CO_2 + H_2O \qquad (16)$$

The effects of initial uranium concentration were studied and optimized. The solution was cooled down to room temperature and filtered with Whatman filter paper (150 mm, 2V). After filtration, the precipitates were washed with Necsa demineralized water and dried in an oven (60°C) for 24 hours. For reproducibility reasons each test was repeated. Particle size was analyzed using a Leica DM 4000B (Figure 6.5) and the results are tabulated and discussed for every test run. The uranium concentration was determined using an UV-Vis

spectrophotometer before and after precipitation tests. The pH of the solution was measured after the recovery of uranium and prior to the precipitation tests.

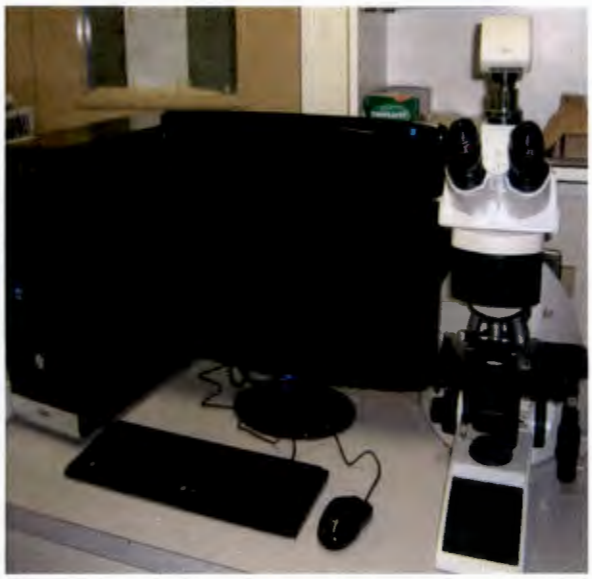

Figure 6.5: Leica DM 4000B for analyzing particles formed.

6.3.3.2 Ammonium uranyl carbonate solution with impurities

The procedure of Section 6.3.3.1 was repeated with the exception that some chemical impurities were added to investigate their effects on the precipitation as well as their influence on the size of the particles formed. 100 ppm solution of impurities was prepared in a 250 ml volumetric flask. 25 ml of 100 ppm solution of impurities was added to 75 ml ammonium uranyl solution (84 000 ppm) to make 100 ml uranyl solution with impurities and heated to decompose the carbonate and ammonium ions.

6.3.4 Analysis of the precipitates

The precipitates obtained were analyzed using the Leica DM 4000B for the particle sizes. X-ray diffraction technology was also used to identify phases and the crystal structures of the precipitates as well as the information about atomic spacing of planes in the precipitates. Again, the quantity of the impurities and uranium present in the liquid solution samples

before and after precipitation were analyzed using inductively coupled plasma- optical emission spectrometer (ICP-OES) and atomic absorption spectroscopy (AA) analysis. All the results obtained are presented and discussed.

6.4 Results

6.4.1 Influence of initial uranium concentration

The influence of uranium concentrations (45 and 84 g/l) was investigated by heating ammonium uranyl carbonate solution (without impurities). All the procedures for precipitation tests were discussed in Section 6.3.3.1. The relationship between uranium precipitation and pH is shown in Figure 6.6.

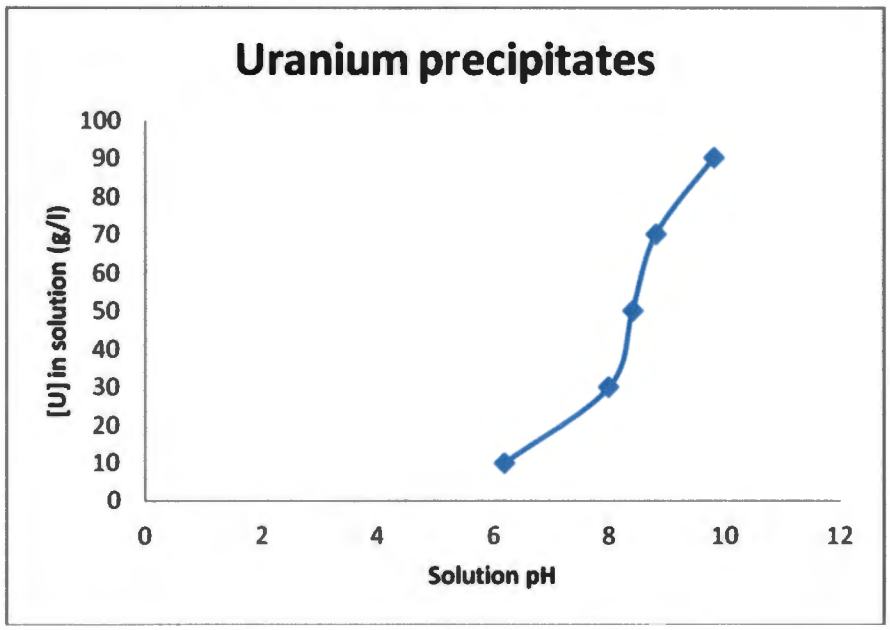

Figure 6.6: Precipitation of uranium versus pH.

The results in Figure 6.6 show the decrease in amount of uranium (precipitation) in a solution with the decrease in pH value. During the experimental process, the addition of water in terms of keeping the volume constant might reduces the pH of the solution through the reaction between H_2O and CO_3^{2-} to form COOH acid. Again the heat maintained to the solution caused the ammonium uranyl carbonate solution to dissociate with uranium starting to precipitate from pH 7.8.

The final product of uranium obtained after filtration is shown Figure 6.7 and 6.10. The particle sizes obtained using the Leica DM 4000B are presented in Figure 6.8 and 6.11. To determine the crystal structure, XRD tests were performed on the precipitates. (The raw data is presented in Figure 8.1 in Annexure E).

Figure 6.7: Yellow precipitate of uranyl ion

The results in Figure 6.7 shows the uranium precipitate obtained from ammonium uranyl carbonate solution with the initial uranium concentration of 84 g/l. The XRD results (Figure 8.1 in Annexure E) indicate that there are four main uranium structures formed, which are UO_3, U_3O_7; U_3O_8 and uranium amine oxide hydrate, packed together in the crystalline or precipitate form identified in the spectrum.

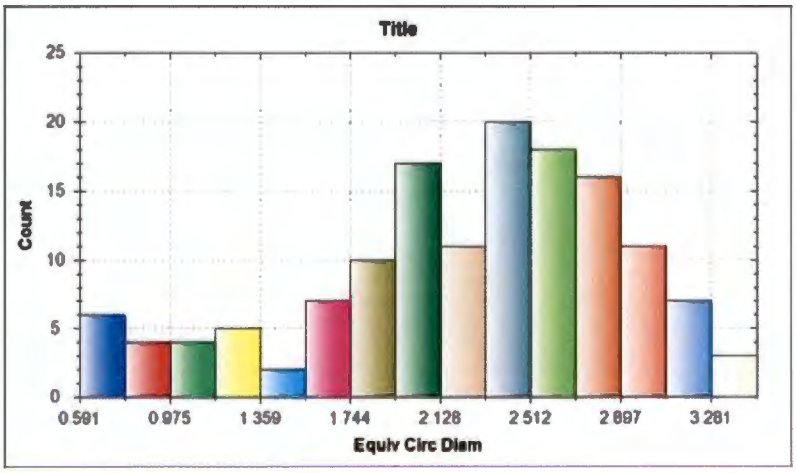

Figure 6.8: Particle size (μm) analysis obtained for initial uranium concentration of 84 g/l solution.

The results in Figure 6.8 show that the precipitate formed contains different particles sizes. The average size of the precipitate formed is 2.512 micron. However, the variation in particle sizes cannot be explained because it is not part of the current study. The combination of these particles forms a coarse precipitate which is easy to filter. This precipitatesettled very rapidly leaving a clear solution above the settled precipitate and filtered fast.

The result in Figure 6.10 shows the uranium precipitate obtained from ammonium uranyl carbonate solution with the initial uranium concentration of 45 g/l.

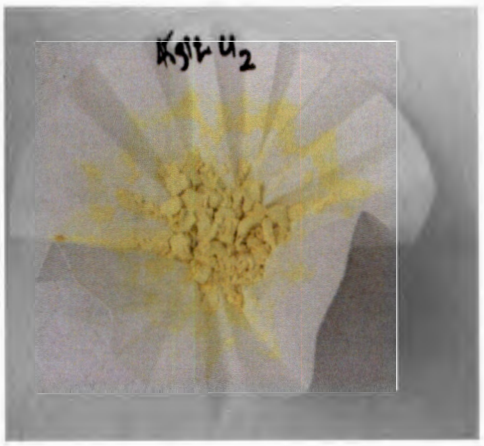

Figure 6.9: Yellow precipitate

The result in Figure 6.11 shows that the precipitate formed has an equal distribution of particle sizes. Although there are samller particles, it was still possible to filter the precipitates. The next section will investigate the effect of impurities added into the uranyl solution.

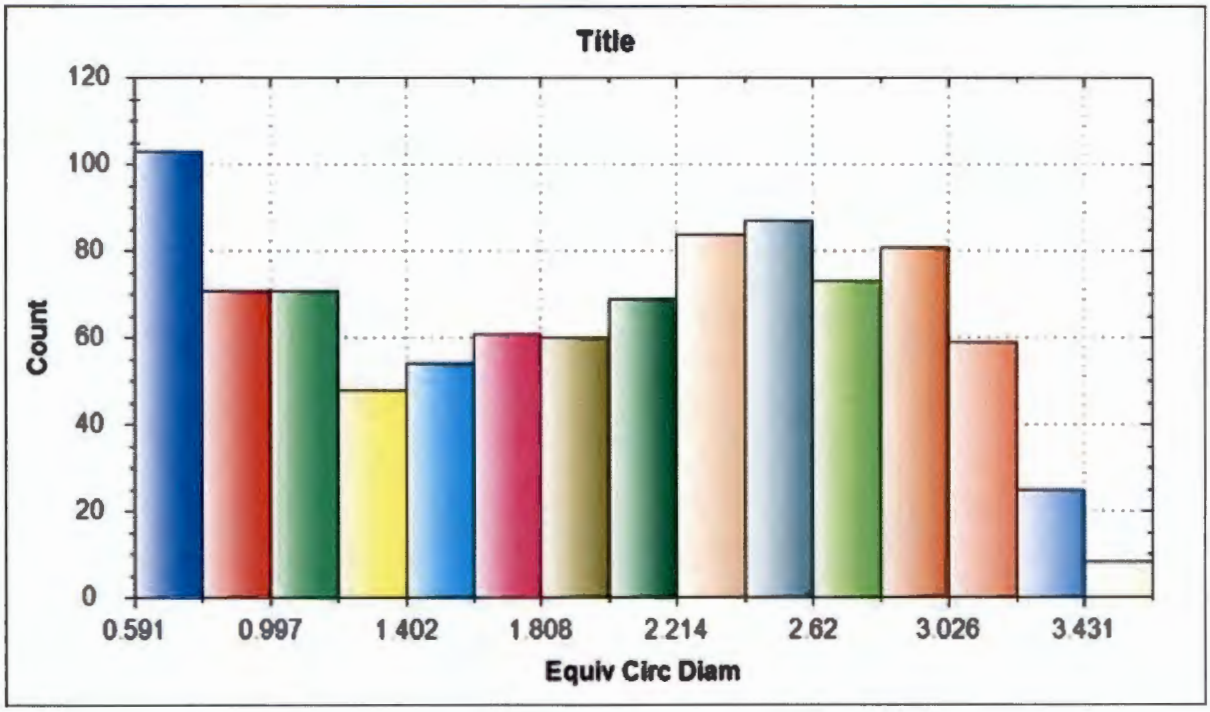

Figure 6.10: Particle size (μm) distribution obtained for initial uranium concentration of 45 g/l solution.

6.4.2 The addition of the impurities

To study the influence of impurities on the purity of the final precipitates, 45 and 84 g/l uranyl solutions with added impurities (100 ppm) were investigated. The procedure for heating and stirring the solution mixture was similar to the one used in Section 6.3.3.1. The uranium precipitate obtained is presented in Figure 6.12 and the particle size distribution in Figure 6.13.

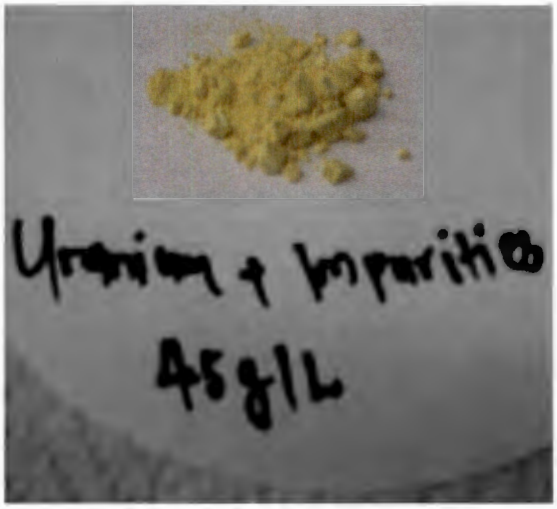

Figure 6.11: Dried precipitate obtained with initial uranium solution concentration of 45 g/l.

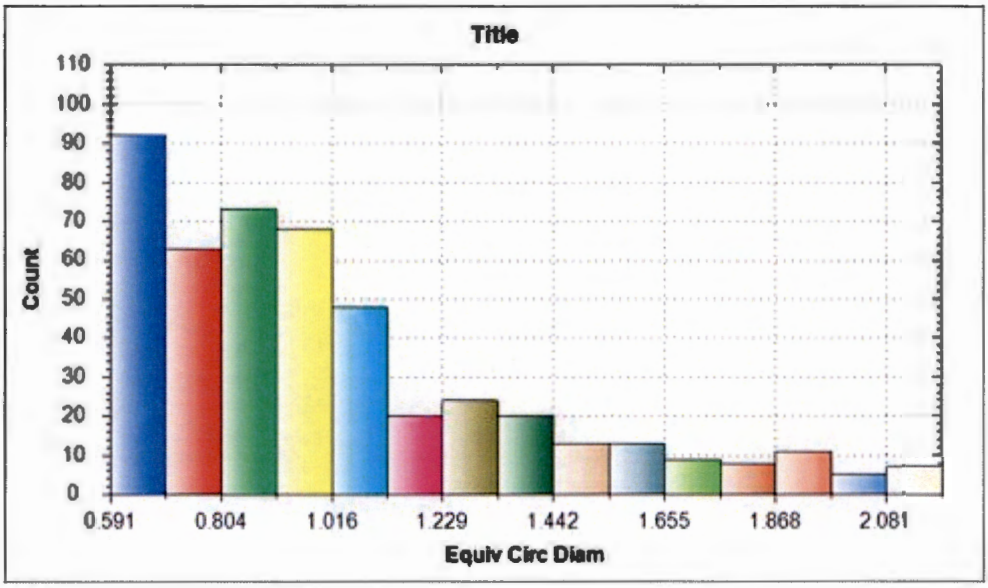

Figure 6.12: Particle size (µm) distribution obtained for stripping product from 45 g/l uranium solution with impurities.

The results in Figure 6.13 indicated that the uranium precipitate obtained, while heating contaminated ammonium uranyl carbonate solution with the initial uranium concentration of 45 g/l, was found to be extremely fine. Due to this the precipitate formed takes a very long time to settle. However we cannot explain the difference in sizes when comparing no impurities and impurities containing solutions. Therefore the next step will investigate the influence of a solution with a higher concentration of uranium. The results in Figure 6.14 and 6.15 show that the precipitate obtained while heating contaminated ammonium uranyl

carbonate solution with the initial concentration of 84 g/l, was a slightly coarser precipitate which settled very rapidly and was easy to filter. The effect of the impurities on the size of the precipitate formed is therefore minimal as it is still possible to filter the precipitate. However the particle size is of less concern for the current study as mentioned in the previous section.

Figure 6.13: Dried precipitate obtained with initial uranium solution concentration of 84 g/l

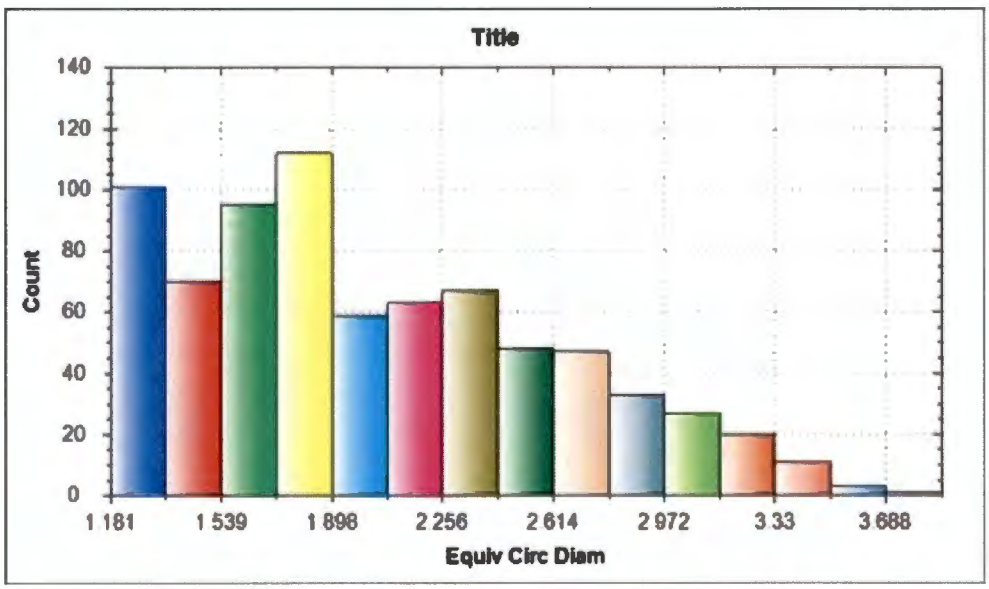

Figure 6.14: Particle size (μm) distribution obtained for stripping product from 84 g/l uranium solution with impurities.

6.5 Results from X- Ray diffraction

To identify phases and the atomic spacing of the uranium crystal structure of the precipitate obtained after heating of the uranyl solution, three precipitate samples prepared from the initial uranium concentration of 45 and 84 g/l with and without impurities were sent to the XRD labs within Necsa for analysis. The aim was to determine if the precipitates have a crystal structure with a possibly known chemical composition. The XRD results obtained are presented in Figure 6.15 to 6.19 in Annexure E. According to the results obtained from those Figures, the XRD patterns confirm the presence of uranium compounds and no other crystalline product with impurities could be detected.

6.6 Results from ICP-OES and AA analysis

The filtrates were collected after filtering the precipitates of uranium from the heating process and sent for analysis using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption spectroscopy (AA analysis) at Pelindaba Analytical Laboratories (PAL) within Necsa. 5ml of each sample from the initial solution containing the impurities, uranium solution only and the mixture of uranium with impurities were collected and 25 ml of de-mineralized water was added before being sent for the analysis. The aim was to determine the quantity of uranium and impurities in the solution before and after precipitation in order to determine how pure the final uranium product is. The results obtained are presented in Table 6.2 and 6.3 and the raw data is in Tables 8.42 to 8.46 in Annexure E.

Table 6.2: Concentration of the initial uranyl solution with impurities before precipitation

Sample ID	Initial concentration (ppm)
Aluminium (Al)	< 3
Calcium (Ca)	10.2
Molybdenum (Mo)	6.6
Potassium (K)	42.6
Sodium (Na)	43.2

Tungsten (W)	0.6
Uranium (U)	30000

The results obtained from ICP-OES in Table 4 in Annexure E were multiplied by the dilution factor of 3 to obtain the true concentration of the initial sample.

Table 6.3: Final results obtained after precipitation process from PAL

Sample ID	**Initial concentration (ppm)**
Aluminium (Al)	< 3
Calcium (Ca)	10.2
Molybdenum (Mo)	6.6
Potassium (K)	42.6
Sodium (Na)	43.2
Tungsten (W)	0.6
Uranium (U)	34.8

The results obtained from ICP-OES in Table 6 in Annexure E were multiplied by the dilution factor of 3 to obtain the true concentration of the initial sample.

According to the results obtained, uranium has precipitated alone during the steam stripping process and the impurities were not present in the collected precipitates. The ICP-OES results clearly show that none of the impurities combined with the uranium. This affirms that ammonium carbonate is very selective towards the impurities and does not react or complex with them easily.

6.7 Conclusion and recommendations

- It is possible and feasible to recover uranium by heating the uranyl ammonium carbonate solutions. At least one hour is needed to achieve a complete dissociation of the uranyl complex.
- Good precipitation is obtained with solutions having initial uranium concentrations of 84 g/l

- The final residue does not contain measurable impurities.

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Chapter 7

7 Conclusions of research

Enriched Uranium (EU), the primary material used to fabricate fuel for nuclear power plants, is manufactured using uranium oxide as feed material. Currently South African gold mines produces tonnes of uranium as a byproduct during gold extraction and this uranium byproduct are converted at the Nuclear Fuel Corporation of South Africa (Nufcor) into different uranium oxides (UOC) for example triuranium octaoxide (U_3O_8). However other possible sources of uranium oxide for example U_3O_8 or UO_2 from other gold mines of international suppliers, could contain impurities causing problems in the conversion plant as experienced previously in a conversion plant at Necsa (1976 to 1979). Impurities in the ADU as feed material resulted in the formation of sintered UO_2F_2 particles during the conversion process (Ponelis et al., 1987). Purification of UOC is therefore, required to ensure a continuous pure UOC feed material for conversion plants.

This study dealt with the development and optimization of an ammonium carbonate ($(NH_4)_2CO_3$) based dissolution process using hydrogen peroxide (H_2O_2) as an oxidant and the purification of uranium from the generated solutions. The dissolution experiments were performed in a pressurized autoclave as well as under atmospheric conditions and experimental parameters that were investigated to determine their effect on the resulting dissolution efficiency, include timing of addition of H_2O_2, temperature, solid/liquid ratio, H_2O_2 concentration, $(NH_4)_2CO_3$ concentration and stirring rate. The reaction time required for optimum dissolution efficiency was also determined.

The results obtained indicated a complete dissolution of UOC at 60 C, after three hours in a 1M ammonium carbonate solution with 1M hydrogen peroxide. The rate of the reaction and the yield of uranium were found to increase as a function of both the concentration of hydrogen peroxide in the range of 0.5 to 2.5 M and the temperature between 30 and 60°C. The use of the autoclave was suspended due to safety measures. Bench scale experiments were conducted with the same experimental procedure as for the autoclave and the only difference applied was the effect of stirring methods. The results from these experiments as well showed a complete dissolution of UOC at 60°C after 3 hours using 1M $(NH_4)_2CO_3$ with 1M H_2O_2 with magnetic stirring.

Three purification processes were investigated, namely purification by ion exchange resins, solvent extraction and precipitation.

For purification by ion exchange resins, various resins were tested for the efficiency of absorption of the impurities such as potassium, sodium, tungsten, molybdenum, calcium and aluminium from solutions containing high concentrations of uranium as well as elution of uranium through the resins. K_d values batch experiments and column chromatography and were performed. Results indicated that Amberlite RFH 252 and Purolite S957 were working effectively in terms of absorbing the impurities and eluting uranium. The adsorption capacity of the impurities (more than 80%) and the elution efficiency of uranium (more than 90%) imply that ion exchange technology can be considered for the purification of the generated solution.

For the solvent extraction technology, the possibilities of purifying uranium from impurities in an alkaline medium using Aliquat 336 or TBP as extractants in the presence of xylene, dodecane and kerosene as diluents were studied. Although the results indicate that uranium can be extracted from the generated alkaline medium using Aliquat 336 in xylene, impurities are co-extracted and thus the method is not applicable.

Precipitation technology was also investigated for the purification of uranium from ammonium carbonate solutions by steam stripping (heating). Results indicated possible and feasible recovery of uranium by steam stripping (precipitation) between 70 and 90 C. A minimum of impurities co-precipitated, rendering this method a possible technique to purify the generated solution.

To conclude:

The aim for this study was to determine the effectiveness of an alkaline process to dissolve and purify UOC in order to produce pure, homogeneous feed material for the conversion plant.

The following objectives identified to fulfill this aim were met:

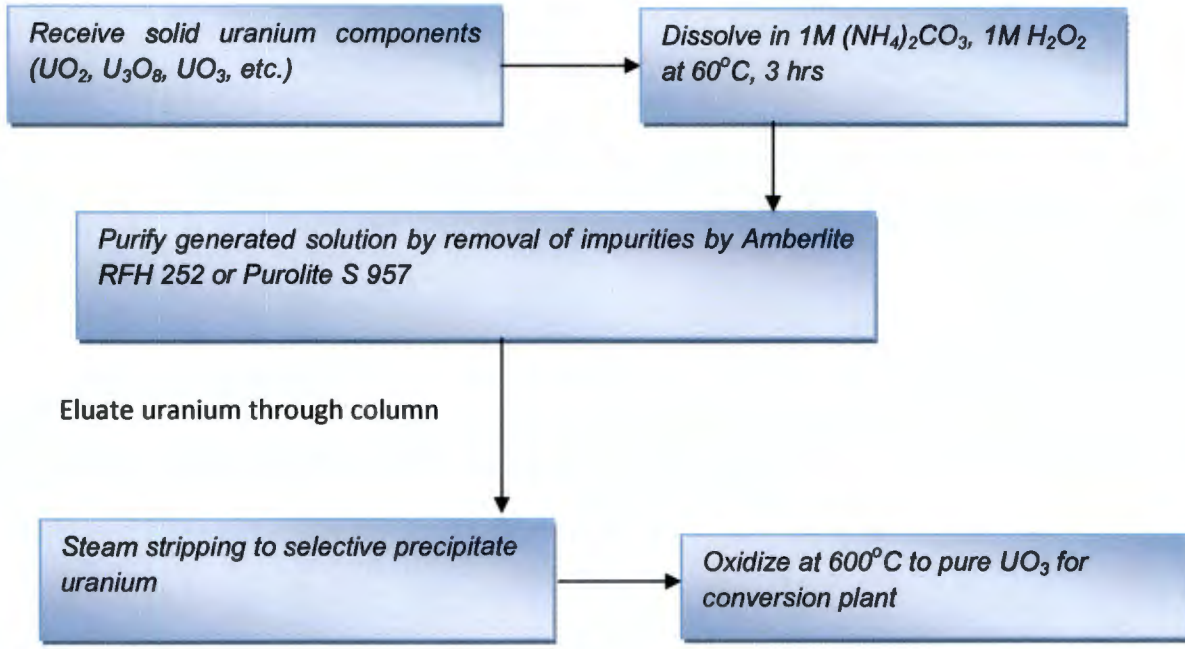
To determine the optimum dissolution conditions for uranium oxide (U_3O_8)

To purify uranium from impurities such as potassium, sodium, tungsten, calcium, aluminium and molybdenum present in generated solution.

To recommend possible technologies to purify uranium so as to meet nuclear specifications.

The aim of the project was therefore met and can be considered as completed.

The proposed / recommended technology is as follow



Chapter 8

8 Annexures

Annexure A: Raw data from autoclave experiments

The following raw data illustrate the results obtained when investigating different parameters for the dissolution process of UOC.

Table 8.1: Dissolution yields observed at various stirring speeds, residue mass = 3 g, $(NH_4)_2CO_3$ concentration = 1 M, H_2O_2 concentration = 1M, solid/liquid ratio = 1:10, and temperature = 60 °C (See Section 3.4.1.1)

Stirring speed (rpm)	**Solution composition**	**Final U concentration**
0	27 ml 1M $(NH_4)_2CO_3$, 3ml 30% H_2O_2	53514.18
500	27 ml 1M $(NH_4)_2CO_3$, 3ml 30% H_2O_2	80201.49

From the results in Table 1, it is evident that stirring is a definite requirement for optimal dissolution yield.

Table 8.2: Dissolution yields observed at various concentrations of H_2O_2, residue mass = 3 g, solid/liquid ratio = 1:10, $(NH_4)_2CO_3$ concentration = 1 M, and temperature = 60 °C (See Section 3.4.1.2).

H_2O_2 Molarity	**Solution composition**	**Final U concentration**
0.5 M	28.5 ml 1M $(NH_4)_2CO_3$, 1.5 ml 30% H_2O_2	71794.25
1.0 M	27 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	80201.49
1.5 M	25.4 ml 1M $(NH_4)_2CO_3$, 4.6 ml 30% H_2O_2	81258.87
2.0 M	24 ml 1M $(NH_4)_2CO_3$, 6 ml 30% H_2O_2	86481.73
2.5 M	22.3 ml 1M $(NH_4)_2CO_3$, 7.7 ml 30% H_2O_2	86482.01

The results indicate that H_2O_2 concentrations in the order of 0.5 to 2.5 M will yield optimal dissolution yields whereas above 2M, constant concentration was observed.

Table 8.3: Dissolution yields observed at various oxygen pressures, residue mass = 3 g, $(NH_4)_2CO_3$ concentration = 1 M, solid/liquid ratio = 1:10, and temperature = 60 °C (See Section 3.4.1.3).

Oxygen Pressure	Solution composition	Final U concentration
4 bar	30 ml 1M $(NH_4)_2CO_3$, 4 Bars O_2 no H_2O_2	23207.92
6 bar	30 ml 1M $(NH_4)_2CO_3$, 6 O_2 no H_2O_2	37644.81

The results indicate that oxygen is not effective to oxidize UOC. Low dissolution yield was observed for both 4 and 6 bar oxygen pressure supplied.

Table 8.4: Dissolution yields observed at various $(NH_4)_2CO_3$ concentrations, residue mass = 3 g, solid/liquid ratio = 1:10, $[H_2O_2]$ = 1M, and temperature = 60 °C (See Section 3.4.1.4).

$(NH_4)_2CO_3$ Molarity	Solution composition	Final U concentration
1.0 M	27 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	80201.49
1.5 M	27 ml 1.5M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	72899.80
2.0 M	27 ml 2M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	67498.92

The results obtained indicate that 1M ammonium carbonate concentration yields the optimal dissolution. The further increase in ammonium carbonate concentration subsequently results in a decrease in dissolution yield.

Table 8.5: Dissolution yields observed at various temperatures, residue mass = 3 g, solid/liquid ratio = 1:10, $[H_2O_2]$ = 1M, and $(NH_4)_2CO_3$= 1M (See Section 3.4.1.5).

Temperature (°C)	Solution composition	Final U concentration
30	30 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	62944.25
40	30 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	73442.83
50	30 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	66677.47
60	30 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	80201.49

70	30 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	89325.75

Table 8.6: Dissolution yields observed at various time intervals, residue mass = 3 g, solid/liquid ratio = 1:10, $[H_2O_2]$ = 1M, and $(NH_4)_2CO_3$= 1M (See Section 3.4.1.6).

Time (Hours)	Solution composition	Final U concentration	Dissolution Yield (%)
1	27 ml 1M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	72619.56	87.3
2	27 ml 1.5M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	74291.65	90.5
3	27 ml 2M $(NH_4)_2CO_3$, 3 ml 30% H_2O_2	80201.49	97.8

The results in Table 8.6 indicate that a maximum time of 3 hours is needed to obtain an optimal dissolution yield when using the autoclave reactor.

1. The effect of hydrogen peroxide concentration

Table 8.7: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 0.5 M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass (g)	Mass Balance	U Concentration
3.0033 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.5793	2.4244	70941.84
3.0042 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.5885	2.4600	73155.22
3.0039 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.5469	2.4056	70285.69
Average						**2.4300**	**71460.92**

Measured Values*

Table 8.8: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1 M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0652	2.9411	79984.66

3.0059 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0820	2.9239	80272.88
3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.05454	2.9519	80346.94
Average					**0.0672**	**2.9940**	**80201.49**

Table 8.9: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1.5 M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass (g)	Mass Balance	U Concentration
3.0603	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0401	3.0202	70432.27
3.0005	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0502	2.9503	71014.45
3.0089	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0701	2.9388	73342.68
Average					**0.0535**	**2.9700**	**72899.80**

Measured Values*

Table 8.10: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 2 M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0030 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0321	2.971	66052.89
3.0014 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0201	2.981	69011.27
3.00176 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0198	2.982	67432.61
Average					**0.0240**	**2.978**	**67498.92**

Effect of ammonium carbonate concentration

Table 8.11: Summary of results obtained for autoclave runs for 2M $(NH_4)_2CO_3$ + 1M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass (g)	Mass Balance	U Concentration
3.0030 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0321	2.971	66052.89

3.0014 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0201	2.981	69011.27
3.00176 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0198	2.982	67432.61
Average						**2.978**	**67498.92**

Measured Values*

Table 8.12: Summary of results obtained for autoclave runs for 1.5 M $(NH_4)_2CO_3$ + 1M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.008g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0472g	2.9605g	70432.27
3.008g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0510g	2.9573g	71014.45
3.006g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0492g	2.9570g	73342.68
Average						**2.958**	**72899.80**

Table 8.13: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0652	2.9411	79984.66
3.0059 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0820	2.9239	80272.88
3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.05454	2.9519	80346.94
Average					**0.0672**	**2.9940**	**80201.49**

Effect of temperature on the dissolution rate

Table 8.14: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2, 30°C

UOC	Solution composition	Solid / liquid Ratio	Temp (^oC)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0091 g	27 ml AC + 3ml H_2O_2	1:10	30	6	0.5753	2.4338	62133.47

3.0042 g	27 ml AC + 3ml H_2O_2	1:10	30	6	0.5885	2.4157	61916.89
3.0039 g	27 ml AC + 3ml H_2O_2	1:10	30	6	0.5402	2.4637	64782.4
Average					**0.5681**	**2.4377**	**62944.25**

Table 8.15: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2, 40°C

UOC	Solution composition	Solid / liquid Ratio	Temp (°C)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0024 g	27 ml AC + 3ml H_2O_2	1:10	40	6	0.3893	2.6131	71238.16
3.0080 g	27 ml AC + 3ml H_2O_2	1:10	40	6	0.3950	2.6130	75686.38
3.0063	27 ml AC + 3ml H_2O_2	1:10	40	6	0.3663	2.6400	73403.96
Average					**0.3835**	**2.6220**	**73442.83**

Table 8.16: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2, 50°C

UOC	Solution composition	Solid / liquid Ratio	Temp (°C)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0009 g	27 ml AC + 3ml H_2O_2	1:10	50	6	0.3893	2.6116	64894.83
3.0017 g	27 ml AC + 3ml H_2O_2	1:10	50	6	0.1585	2.8432	68764.15
3.0034 g	27 ml AC + 3ml H_2O_2	1:10	50	6	0.2890	2.7444	66373.44
Average					**0.2789**	**2.7331**	**66677.47**

Table 8.17: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2, 60°C

UOC	Solution composition	Solid / liquid Ratio	Temp (°C)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration

3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0652	2.9411	79984.66
3.0059 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.0820	2.9239	80272.88
3.0064 g	27 ml AC + 3ml H_2O_2	1:10	60	6	0.05454	2.9519	80346.94
Average					**0.0672**	**2.9940**	**80201.49**

Table 8.18: Summary of results obtained for autoclave runs for 1M $(NH_4)_2CO_3$ + 1M H_2O_2, 70°C

UOC	Solution composition	Solid / liquid Ratio	Temp (°C)	P*(Bars)	Undissolved mass	Mass Balance	U Concentration
3.0096 g	27 ml AC + 3ml H_2O_2	1:10	70	6	0.0409	2.9687	94038.46
3.0024 g	27 ml AC + 3ml H_2O_2	1:10	70	6	0.0114	2.9910	86577.17
3.0076 g	27 ml AC + 3ml H_2O_2	1:10	70	6	0.0201	2.9875	87361.62
Average					**0.0241**	**2.9851**	**89325.75**

Annexure B: Raw data for bench experiments

Table 8.19: Influence of stirring

Air Stirring		Magnetic stirring (500 rpm)		No stirring	
Time of Sampling (min)	Uranium concentration (ppm)	Time of Sampling (min)	Uranium concentration (ppm)	Time of Sampling (min)	Uranium concentration (ppm)
10	51051.98	10	62077.97	10	44105.35
20	54517.71	20	64721.97	20	52142.45
30	55729.67	30	62011.14	30	55208.81
40	58921.17	40	72052.89	40	54032.32
50	62553.07	50	75987.31	50	56003.51
60	65670.08	60	77916.93	60	64855.62
70	77835.57	70	80342.21	70	67725.33
80	69279.23	80	79514.75	80	62599.38
90	76466.93	90	81100.75	90	54673.99

Table 8.20: Influence of ammonium carbonate concentration

1 M $((NH_4)_2CO_3$		1.5 M $((NH_4)_2CO_3$		2 M $((NH_4)_2CO_3$	
Time of Sampling (min)	Uranium concentration (ppm)	Time of Sampling (min)	Uranium concentration (ppm)	Time of Sampling (min)	Uranium concentration (ppm)
10	62077.97	10	64237.58	10	64105.35
20	64721.97	20	69597.28	20	68142.45
30	62011.14	30	72625.99	30	75208.81
40	72052.89	40	76996.79	40	78032.32
50	75987.31	50	77659.04	50	69003.51
60	77916.93	60	74701.02	60	64855.62
70	80342.21	70	68453.73	70	55725.33
80	79514.75	80	69687.75	80	53599.38
90	81100.75	90	74480.27	90	51673.99

Effect of ammonium carbonate concentration on dissolution of UOC

Table 8.21: Influence of temperature

40°C		**50°C**		**60°C**	
Time of Sampling (min)	**Uranium concentration (ppm)**	**Time of Sampling (min)**	**Uranium concentration (ppm)**	**Time of Sampling (min)**	**Uranium concentration (ppm)**
10	70169.88	10	64237.58	10	70197.43
20	68705.58	20	73597.28	20	69137.84
30	65571.68	30	72625.99	30	73605.88
40	62656.66	40	76996.79	40	75895.16
50	69714.54	50	77659.04	50	78729.39
60	72964.53	60	74701.02	60	81815.52
70	69939.67	70	78453.73	70	82095.86
80	66913.59	80	7687.75	80	79711.78
90	62445.71	90	74480.27	90	81329.88
100	55118.35	100	75584.01		
110	43988.26				

*The effect of temperature

Table 8.22: Effect of hydrogen peroxide

0.5 M H_2O_2		1.0 H_2O_2		1.5 M H_2O_2		2.0 M H_2O_2	
Sampling time (min)	U Conc (ppm)	Sampling time (min)	U Conc (ppm)	Sampling time (min)	U Conc (ppm)	Sampling time (min)	U Conc (ppm)
0	0	0	0	0	0	0	0
10	68696.62	10	77570.67	10	73169.88	10	67990.23
20	70418.45	20	78939.31	20	68705.58	20	65871.05
30	70330.15	30	91257.02	30	78571.68	30	68696.62
40	69403.01	40	83839.91	40	62656.66	40	70286.01
50	66665.75	50	86842.07	50	80714.54	50	73862.11

Autoclave analysis reports from UV-VIS Spectrometry

1. Original analysis from UV –vis spectroscopy for the effect of hydrogen peroxide on the dissolution of UOC with ammonium carbonate.

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	Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
1		165.7		0.2646	0.0011	0.40	0.2647 0.2636 0.2657
2		159.1		0.2542	0.0011	0.41	0.2549 0.2547 0.2530
3		175.1		0.2797	0.0116	4.14	0.2921 0.2777 0.2692
4		110.8		0.1772	0.0005	0.27	0.1769 0.1777 0.1768
5		193.1		0.3083	0.0038	1.23	0.3040 0.3099 0.3111
6		196.6		0.3139	0.0019	0.59	0.3154 0.3145 0.3118
7		177.4		0.2833	0.0007	0.25	0.2829 0.2828 0.2841
8		196.1		0.3131	0.0187	5.96	0.3006 0.3042 0.3346

Results Flags Legend
U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

The following numbers represent the concentrations obtained from the UV spectrum that was analysed on the 08/30/2010 for the first two tests in the autoclave.

1– 2 for 0.5 M H_2O_2

3– 4 is for 1.5 M H_2O_2

5– 6 is for 2M H_2O_2

7 – 8 is for 2.5 M H_2O_2

2. Original report from the UV –Vis Spectroscopy for the effect of Oxygen pressure on the dissolution of UOC dissolved with ammonium carbonate solution.

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	Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
1							0.0891
							0.0890
		53.8		0.0891	0.0001	0.08	0.0892
2							0.0839
							0.0855
		52.8		0.0875	0.0049	5.56	0.0930
3							0.1182
							0.1178
		[illegible]		0.1179	0.0002	0.19	0.1178
4							0.1110
							0.1117
		67.0		0.1112	0.0004	0.39	0.1109
5							0.1072
							0.1074
		64.6		0.1072	0.0002	0.14	0.1071
6							0.1038
							0.1074
		63.3		0.1049	0.0021	2.03	0.1036

Results Flags Legend

U = Uncalibrated O = Overrange

N = Not used in calibration R = Repeat reading

1 – 3 is for 4 Bar Oxygen pressure

4– 6 is for 6 Bar Oxygen pressure

3. Original analysis report from UV- Vis spectroscopy for the effect of Temperature in the dissolution of UOC using 1M ammonium carbonate and 1M hydrogen peroxide solution. .

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
3g 70 Deg 1						
						0.3400
	213.0		0.3400	0.0001	0.03	0.3399
						0.3401
3g 70 Deg 2						
						0.3126
	196.1		0.3131	0.0012	0.37	0.3122
						0.3144
3g 70 Deg						
						0.3192
	199.8		0.3189	0.0002	0.08	0.3187
						0.3189

Results Flags Legend
U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

Bench analysis reports

1. Original analysis report from UV – Vis spectroscopy for the effect of hydrogen peroxide on the dissolution of UOC with ammonium carbonate.

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Collection time 8/30/2010 3:52:34 PM

Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
10						0.3158
						0.3166
	198.2		0.3165	0.0006	0.20	0.3170
20						0.3158
						0.3156
	197.7		0.3155	0.0003	0.08	0.3153
30						0.3337
						0.3318
	207.9		0.3319	0.0017	0.51	0.3302
40						0.3296
						0.3298
	206.5		0.3296	0.0002	0.07	0.3293
50						0.3355
						0.3362
	210.5		0.3360	0.0004	0.13	0.3363
60						0.3142
						0.3144
	197.3		0.3150	0.0012	0.37	0.3163
70						0.3169
						0.3169
	198.4		0.3168	0.0002	0.07	0.3165
80						0.3023
						0.3037
	189.9		0.3032	0.0008	0.26	0.3035

Results Flags Legend
U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

2. Original analysis report of the UV-Vis spectroscopy for the effect of 2 M H_2O_2 on the dissolution rate of UOC with ammonium carbonate in a flask.

Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
10						0.2484
20	155.6		0.2486	0.0003	0.13	0.2483 0.2489
30	159.5		0.2548	0.0005	0.21	0.2553 0.2546 0.2543
40	159.3		0.2544	0.0016	0.61	0.2560 0.2543 0.2529
50	157.2		0.2511	0.0006	0.24	0.2518 0.2507 0.2509
60	151.0		0.2413	0.0037	1.53	0.2374 0.2417 0.2447
70	149.3		0.2386	0.0007	0.31	0.2394 0.2383 0.2379
80	171.7		0.2742	0.0002	0.06	0.2742 0.2740 0.2743
90	144.3		0.2306	0.0003	0.12	0.2308 0.2305 0.2303
	155.3		0.2481	0.0004	0.18	0.2478 0.2486 0.2479

Results Flags Legend

U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

Original analysis report from UV- Vis spectroscopy for the effect of ammonium carbonate at 1M concentration.

Annexure C: ***Raw data for resin studies***

Table 8.23: The original UV report for the analysis of uranium elution through the resins.

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
U STD 50PPM						0.0671
						0.0672
	41.7		0.0673	0.0002	0.35	0.0675
[U]1						0.0022
						0.0026
	1.4		0.0030	0.0011	36.1	0.0043
[U]2						0.0110
						0.0099
	6.1		0.0105	0.0005	5.21	0.0105
S 957-1						0.0004
						0.0004
	-0.2		0.0006	0.0002	41.3	0.0008
S957-2						0.0158
						0.0157
	10.5		0.0175	0.0029	16.8	0.0209
XAD-4-1						-0.0006
						0.0015
	0.1		0.0010	0.0014	>100	0.0020
XAD-4-2						0.0110
						0.0111
	6.4		0.0110	0.0001	0.78	0.0111
AG1-X-1						-0.0021
						-0.0020
	-1.8		-0.0021	0.0001	-4.9	-0.0022
AG1-X-2						-0.0210
						-0.0168
	-11.7		-0.0179	0.0028	-15.	-0.0157
S950-1						0.0088
						0.0082
	4.8		0.0085	0.0002	2.36	0.0085
S 950-2						0.0017
						0.0026
	1.1		0.0025	0.0007	28.5	0.0031
Acti-Carb-1						0.0090
						0.0092
	5.7		0.0098	0.0012	12.6	0.0112
Activ- Carb-2						0.0041
						0.0025
	1.9		0.0028	0.0002	7.34	0.0029

Table 8.24: The original UV report for the analysis of uranium elution through the resins.

Concentration Analysis Report

Report time	11/11/2010 2:44:32 PM
Batch name	C:\Roseth\Amberlite 252 RFH [U].BCN
Application	Concentration 3.00(182)
Operator	

Instrument Settings

Instrument	Cary 300
Instrument version no.	10.00
Wavelength (nm)	450.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R^2	0.95000
Concentration units	mg/L

Comments:

U1 in Amberlite	50.0	0.0828	0.0007	0.85	0.0823 0.0825
U2 in Amberlite	38.5	0.0636	0.0002	0.32	0.0634 0.0638 0.0637 192.5 ppm
	38.1	0.0630	0.0002	0.27	0.0632 0.0629 0.0628 190.5 ppm

Results Flags Legend

U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

Table 8.25: Original test reports from PAL for the impurities content in sample liquid before extraction.

Test Report

Sample ID: PS 2010–0281X001 **Sample Name:** Impurities-1

Determination	Results	Units	Method used
Potassium (K)	21.4	mg/L	AA Analysis- Full Report -K
Sodium (Na)	30.6	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	37.2	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	34.6	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	59.1	mg/L	ICP-OES Analysis –FULL Report

Table 8.26: Original analysis report from PAL for the quantity of impurities in a liquid sample after extraction with the unconditioned resins.

Sample ID: PS 2010–2763X001 **Sample Name:** Amberlite RFH 252

Determination	Results	Units	Method used
Potassium (K)	10.4	mg/L	AA Analysis- Full Report -K
Sodium (Na)	14.5	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.7	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	18.6	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	18.3	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X003 **Sample Name:** Cabsorb ZS 500 RW

Determination	Results	Units	Method used
Potassium (K)	24.9	mg/L	AA Analysis- Full Report -K
Sodium (Na)	19.9	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	2.0	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	19.4	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	22.6	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X005 **Sample Name:** Cabsorb ZS 500

Determination	Results	Units	Method used
Potassium (K)	19.6	mg/L	AA Analysis- Full Report -K
Sodium (Na)	19.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.8	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	17.8	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	18.5	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X007 **Sample Name:** Purolite S940

Determination	Results	Units	Method used
Potassium (K)	11.5	mg/L	AA Analysis- Full Report -K
Sodium (Na)	18.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.8	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	17.6	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	17.6	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X009 **Sample Name:** Activated Carbon

Determination	Results	Units	Method used
Potassium (K)	13.1	mg/L	AA Analysis- Full Report -K
Sodium (Na)	15.4	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.8	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	19.0	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	16.8	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X011 **Sample Name:** AGI-X4

Determination	Results	Units	Method used
Potassium (K)	13.5	mg/L	AA Analysis- Full Report -K
Sodium (Na)	15.5	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.3	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	12.7	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	12.5	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X013 **Sample Name:** S950

Determination	Results	Units	Method used
Potassium (K)	13.4	mg/L	AA Analysis- Full Report -K
Sodium (Na)	15.2	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.2	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	18.6	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	20.0	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X015 **Sample Name:** XAD

Determination	Results	Units	Method used
Potassium (K)	13.5	mg/L	AA Analysis- Full Report -K
Sodium (Na)	15.4	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.0	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	17.8	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	17.0	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X017 **Sample Name:** S 957

Determination	Results	Units	Method used
Potassium (K)	12.2	mg/L	AA Analysis- Full Report -K
Sodium (Na)	12.9	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	17.2	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	17.2	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X019 **Sample Name:** ZK 406 SMZ

Determination	Results	Units	Method used
Potassium (K)	21.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	15.9	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.3	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	19.1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	19.7	mg/L	ICP-OES Analysis –FULL Report

Sample ID: PS 2010–2763X017 **Sample Name:** Chabazite

Determination	Results	Units	Method used
Potassium (K)	27.3	mg/L	AA Analysis- Full Report -K
Sodium (Na)	18.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	1.5	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	18.6	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	17.4	mg/L	ICP-OES Analysis –FULL Report

Table 8.27: Original test report from PAL for initial impurities content for conditioned resins before extraction

Sample ID: PS 2010–0281X001 **Sample Name:** Impurities-1

Determination	Results	Units	Method used
Potassium (K)	13.9	mg/L	AA Analysis- Full Report -K
Sodium (Na)	20.7	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	11.0	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	34.2	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	13.9	mg/L	ICP-OES Analysis –FULL Report

Table 8.28: Original analysis reports from PAL with the conditioned resins for impurities content in liquid sample after the ion exchange extraction process.

Sample ID: PS2011-0282X003 **Sample Name:** S957-1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	1.9	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	13.7	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	0.8	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	21.4	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	10.1	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0282X006 **Sample Name:** Acti-carb 2N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	116.0	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	27.3	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	4.5	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	24.9	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	14.7	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0282X007 **Sample Name:** ZS 500 1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	69.9	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	1006.0	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	19.1	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	26.5	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0282X012 **Sample Name:** S950-2N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	18.8	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	658.0	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	0.6	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	22.8	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	11.6	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0282X013 **Sample Name:** Amb-252-RFH-1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	13.7	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	14.7	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	0.8	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	25.4	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	13.6	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0282X009 **Sample Name:** AG X4 1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	17.3	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	16.5	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	0.8	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	15.6	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	8.8	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0283X001 **Sample Name:** ZK 406 MZS-2N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	73.8	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	27.4	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	5.4	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	25.2	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	12.9	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0283X002 **Sample Name:** XAD-1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	1.7	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	76.0	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	0.9	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	26.2	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	14.1	mg/L	ICP-OES Analysis - FULL Report	

Sample ID: PS2011-0283X010 **Sample Name:** Cabaz-1N

Determination	Result	Units	Method Used	Uncertainty
Potassium (K)	48.2	mg/L	AA Analysis - Full Report - K	
Sodium (Na)	650.0	mg/L	AA Analysis - Full Report - Na	
Aluminium (Al)	1.0	mg/L	ICP-OES Analysis - FULL Report	
Molybdenum (Mo)	25.4	mg/L	ICP-OES Analysis - FULL Report	
Tungsten (W)	13.0	mg/L	ICP-OES Analysis - FULL Report	

Column Extraction Data

Table 8.29: Original data from PAL for the initial solution used for the extraction of metal ions onto resins

PS 2013–27457X012 **Sample Name:** U1

Determination	Results	Units	Method used
Potassium (K)	10.8	mg/L	AA Analysis- Full Report -K
Sodium (Na)	12.5	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	4	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	2.1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	3	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	4	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	39	mg/L	ICP-OES Analysis –FULL Report

Table 8.30: Original report from PAL used for the determination of quantity of impurities absorbed onto Purolite S957 resin.

PS 2013–27457X001 **Sample Name:** P1

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	0.1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	1	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X002 **Sample Name:** P2

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	<1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	3	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X003 **Sample Name:** P3

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1.0	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	2	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X004 **Sample Name:** P4

Determination	Results	Units	Method used
Potassium (K)	2	mg/L	AA Analysis- Full Report -K
Sodium (Na)	1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	14	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X005 **Sample Name:** P5

Determination	Results	Units	Method used
Potassium (K)	3.5	mg/L	AA Analysis- Full Report -K
Sodium (Na)	2.2	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	0.1	mg/L	ICP-OES Analysis –FULL Report

Tungsten (W)	0.2	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	15	mg/L	ICP-OES Analysis –FULL Report

Table 8.31: Original report from PAL used for the determination of metal ions absorbed onto Amberlite RFH 252

PS 2013–27457X006 **Sample Name:** A1

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1		ICP-OES Analysis –FULL Report
Molybdenum (Mo)	<1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	10	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X007 **Sample Name:** A2

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1		ICP-OES Analysis –FULL Report
Molybdenum (Mo)	1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	15	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X008 **Sample Name:** A3

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	17	mg/L	ICP-OES Analysis –FULL Report

PS 2013–27457X009 **Sample Name:** A4

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	<1.0	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	<1		ICP-OES Analysis –FULL Report
Molybdenum (Mo)	<0.1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	16	mg/L	ICP-OES Analysis –FULL Report

PS 2013–2457X010 **Sample Name:** A5

Determination	Results	Units	Method used
Potassium (K)	<1.0	mg/L	AA Analysis- Full Report -K
Sodium (Na)	2.1	mg/L	AA Analysis- Full Report -Na
Aluminium (Al)	<1	mg/L	ICP-OES Analysis –FULL Report

Calcium (Ca)	<1		ICP-OES Analysis –FULL Report
Molybdenum (Mo)	1	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	<0.2	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	17	mg/L	ICP-OES Analysis –FULL Report

Annexure D. Raw data of extraction results

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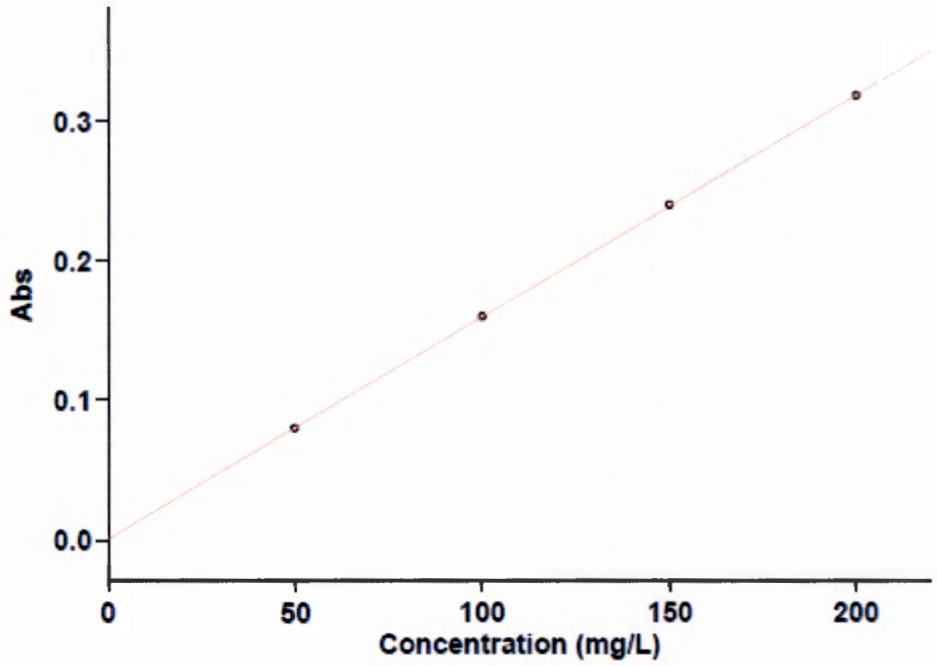
Necsa



Concentration Analysis Report

Report time	2/22/2011 12:19:27 PM
Batch name	C:\Roseth\Roseth.BCN
Application	Concentration 3.00(182)
Operator	

Instrument Settings

Instrument	Cary 100
Instrument version no.	10.00
Wavelength (nm)	450.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R^2	0.95000
Concentration units	mg/L

Comments:

Analysis

Collection time 2/22/2011 12:19:27 PM

Sample	Concentration	F	Mean	SD	%RSD	Readings

Table 8.32: UV report analysis for the extraction of uranium using 5% TBP and 95% kerosene.

	mg/L				
Std					0.0832
					0.0827
	51.8	0.0832	0.0006	0.74	0.0839
Mag S1					0.3111
					0.3137
	195.7	0.3124	0.0013	0.41	0.3124
No Stir S1					0.2890
					0.2890
	181.2	0.2893	0.0004	0.15	0.2898
Auto S1					0.2951
					0.2934
	184.0	0.2938	0.0012	0.39	0.2930
Mag Ex					0.2794
					0.2869
	179.1	0.2861	0.0063	2.19	0.2918
No Stir Ex					0.2636
					0.2660
	165.6	0.2644	0.0014	0.53	0.2636
Auto Ex					0.2469
					0.2468
	154.5	0.2468	0.0001	0.03	0.2468

Results Flags Legend

U = Uncalibrated O = Overrange
N = Not used in calibration R = Repeat reading

Table 8.33: UV- report analysis for the extraction of uranium using 5% Aliquat 336 and 95% kerosene

	mg/L				
Std					0.0832
					0.0827
	51.8	0.0832	0.0006	0.74	0.0839
Mag S1					0.3111
					0.3137
	195.7	0.3124	0.0013	0.41	0.3124
No Stir S1					0.2890
					0.2890
	181.2	0.2893	0.0004	0.15	0.2898
Auto S1					0.2951
					0.2934
	184.0	0.2938	0.0012	0.39	0.2930
Mag Ex					0.2794
					0.2869
	179.1	0.2861	0.0063	2.19	0.2918
No Stir Ex					0.2636
					0.2660
	165.6	0.2644	0.0014	0.53	0.2636
Auto Ex					0.2469
					0.2468
	154.5	0.2468	0.0001	0.03	0.2468

Results Flags Legend

U = Uncalibrated O = Overrange
N = Not used in calibration R = Repeat reading

Table 8.34: UV results for analysis for the extraction of uranium with 10% Aliquat 336, 85% kerosene and 5% octan-1-ol.

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
U std						0.0450
						0.0459
	28.4		0.0460	0.0009	2.03	0.0469
auto extract1						0.1329
						0.1333
	83.3		0.1335	0.0007	0.50	0.1342
flask extract 1						0.2202
						0.2207
	138.0		0.2205	0.0003	0.14	0.2207
auto extract2						0.1126
						0.1124
	70.1		0.1125	0.0001	0.09	0.1125
flask extract2						0.1786
						0.1784
	111.6		0.1785	0.0001	0.04	0.1785
auto extract 3						0.0349
						0.0353
	21.6		0.0352	0.0003	0.97	0.0356
flask extract3						0.0860
						0.0874
	54.2		0.0871	0.0010	1.11	0.0878
auto strip1						0.0247
						0.0265
	15.8		0.0260	0.0011	4.38	0.0268
auto strip2						-0.0223
						-0.0203
	-13.7		-0.0209	0.0012	-5.6	-0.0202
flas strip 1						-0.0098
						-0.0073
	-5.4		-0.0078	0.0018	-23.	-0.0062
flask strip 2						-0.0057
						-0.0058
	-6.0		-0.0087	0.0052	-59.	-0.0147
Sample 12						0.1796
						0.1791
	112.6		0.1801	0.0013	0.72	0.1815
Sample 13						0.1560
						0.1567
	97.8		0.1565	0.0004	0.28	0.1568

Results Flags Legend

U = Uncalibrated
O = Overrange
N = Not used in calibration
R = Repeat reading

Table 8.35: UV-Vis report for the extraction of uranium using 5 % Aliquat 336 and 95 % dodecane

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
Auto Oxyl + Al336 E2						0.0952
						0.0953
	59.4		0.0954	0.0002	0.25	0.0956
flASK Oxyl+ Al336 E2						0.1717
						0.1721
	107.4		0.1719	0.0002	0.10	0.1718
Auto Strip2 Xyl						0.0018
						0.0034
	1.6		0.0024	0.0016	66.0	0.0049
Flask Strip2 Xyl						0.0080
						0.0081
	4.7		0.0083	0.0004	4.79	0.0087
Auto Strip 1 Oxyl						0.0198
						0.0199
	12.0		0.0199	0.0001	0.33	0.0198
Flask Stripl Oxyll						0.0213
						0.0210
	12.8		0.0212	0.0002	0.95	0.0214

Results Flags Legend

U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

Table 8.36: UV analysis report for the extraction of uranium with 5% Aliquat 336 and 95% xylene

3/16/2011 2:23:33 PM Page 2 of 2

Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
U Std						0.0518
						0.0530
	32.5		0.0525	0.0007	1.24	0.0528
Auto pure [U]1						0.1525
						0.1552
	97.2		0.1556	0.0033	2.13	0.1591
Magnetic P [U]1						0.3899
						0.3899
	244.5	O	0.3901	0.0003	0.09	0.3905
No Air P [U]1						0.3568
						0.3568
	223.6	O	0.3569	0.0002	0.05	0.3571
Auto P [U]2						0.1438
						0.1438
	89.6		0.1435	0.0005	0.34	0.1430
Magnetic P[U]2						0.3294
						0.3291
	206.2		0.3291	0.0002	0.07	0.3289
No Air [U]2						0.2955
						0.2967
	186.0		0.2969	0.0015	0.52	0.2986
Auto P [U]3						0.1036
						0.1039
	64.7		0.1038	0.0001	0.12	0.1039

Table 8.37: UV report for the extraction of concentrated uranyl solution using 10% Aliquat 336 and 90% xylene.

Concentration Analysis Report

Report time	3/16/2011 2:13:32 PM
Batch name	C:\Extraction of pure solution with10% Aliquat336 + Xylene .BCN
Application	Concentration 3.00(102)
Operator	

Instrument Settings

Instrument	Cary 100
Instrument version no.	10.00
Wavelength (nm)	450.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R^2	0.95000
Concentration units	mg/L

Comments:

Analysis

Collection time 3/16/2011 2:13:32 PM

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
U Std						0.0518
						0.0520
	22.5		0.0525	0.0007	1.24	0.0528
Auto pure [U]1						0.1525
						0.1552
	97.2		0.1556	0.0023	2.13	0.1591
Magnetic P [U]1						0.3899
						0.3899
	244.5	O	0.3901	0.0003	0.09	0.3905
No Air P [U]1						0.3568
						0.3568
	223.6	O	0.3569	0.0002	0.05	0.3571
Auto P [U]2						0.1428
						0.1428
	89.6		0.1425	0.0005	0.34	0.1430
Magnetic P[U]2						0.3294
						0.3291
	206.2		0.3291	0.0002	0.07	0.3289
No Air [U]2						0.2955
						0.2967
	186.0		0.2969	0.0015	0.52	0.2986
Auto P [U]3						0.1036
						0.1039
	64.7		0.1038	0.0001	0.12	0.1039
Mangetic [U]3						0.3024
						0.3034
	189.8		0.3030	0.0005	0.17	0.3031
No Air [U]3						0.2627
						0.2613
	162.9		0.2618	0.0007	0.28	0.2615

Results Flags Legend

U = Uncalibrated O = Overrange
N = Not used in calibration R = Repeat reading

Table 8.38: UV analysis report for the extraction of pure and diluted uranyl solution using 5% Aliquat 336 in (CO_3^{2-}) form and 95 % xylene.

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
U Std						0.0447
						0.0423
	26.3		0.0428	0.0018	4.12	0.0413
[U]1 DIL Autoclave						0.0086
						0.0091
	5.3		0.0093	0.0008	9.03	0.0102
[U]1 Dil Magnetic						0.0213
						0.0215
	13.0		0.0214	0.0001	0.55	0.0215
[U]1 Dil No Air						0.0272
						0.0278
	16.7		0.0274	0.0004	1.36	0.0271
[U]2 Dil Autoclave						-0.0087
						-0.0089
	-5.9		-0.0085	0.0005	-6.3	-0.0079
[U]2 Dil Magnetic						0.0050
						0.0064
	2.0		0.0056	0.0008	13.5	0.0052
[U]2 Dil No Air						0.0079
						0.0092
	4.9		0.0086	0.0007	7.64	0.0087
[U]1 Pure Autocalve						0.3093
						0.3089
	193.4		0.3087	0.0007	0.22	0.3080
[U]1 Pure Magnetic						0.3788
						0.3788
	237.3	O	0.3787	0.0001	0.04	0.3786
[U]1 Pure No Air						0.3739
						0.3737
	234.2	O	0.3738	0.0001	0.03	0.3738
[U]2 Pure Autoclave						0.2898
						0.2902
	181.7		0.2901	0.0002	0.09	0.2903
[U]2 Pure Magnetic						0.3099
						0.3098
	194.1		0.3099	0.0001	0.03	0.3099
[U]2 Pure No Air						0.3264
						0.3261
	204.4		0.3262	0.0002	0.05	0.3262

Results Flags Legend

U = Uncalibrated
N = Not used in calibration
O = Overrange
R = Repeat reading

Concentration Analysis Report

Report time	3/15/2011 2:22:14 PM
Batch name	C:\Extraction With Aiquat 336+ Xylene1.BCN
Application	Concentration 3.00(182)
Operator	

Instrument Settings

Instrument	Cary 100
Instrument version no.	10.00
Wavelength (nm)	450.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R^2	0.95000
Concentration units	mg/L

Comments:

Analysis

Collection time 3/15/2011 2:22:14 PM

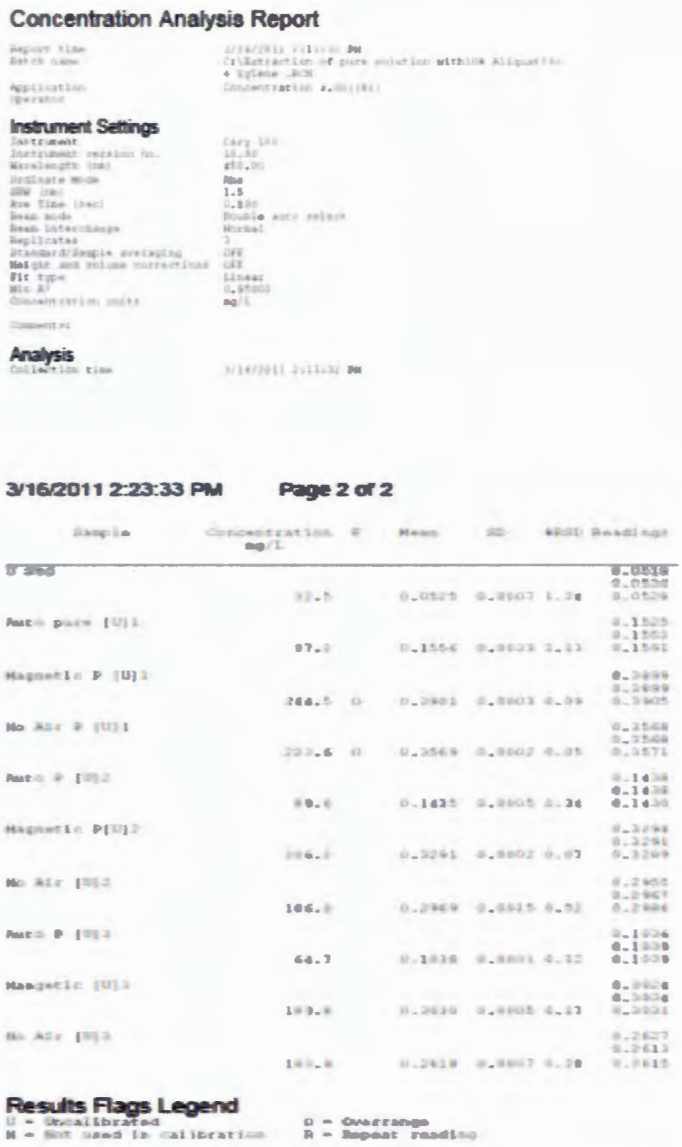
Sample	Concentration	F	Mean	SD	%RSD	Readings

	mg/L				
U STD					0.0646
					0.0637
	39.9	0.0642	0.0006	0.87	0.0648
Autoclave [U]1					0.0052
					0.0057
	2.7	0.0051	0.0006	11.2	0.0045
Magnetic [U]1					0.0215
					0.0222
	13.2	0.0220	0.0005	2.25	0.0224
No Air [U]1					0.0074
					0.0069
	4.1	0.0072	0.0004	5.40	0.0077
Autoclave [U]2					-0.0026
					-0.0027
	-2.8	-0.0026	0.0001	-2.4	-0.0025
Magnetic [U]2					-0.0050
					-0.0057
	-4.6	-0.0065	0.0020	-30.	-0.0087
No Air [U]2					-0.0067
					-0.0065
	-4.6	-0.0065	0.0001	-1.9	-0.0065

Results Flags Legend

U = Uncalibrated O = Overrange
N = Not used in calibration R = Repeat reading

Table 8.39: UV report for the extraction of uranium using 10% Aliquat 336 in CO_3^{2-} form and 90% xylene



Concentration Analysis Report

Instrument Settings

Analysis

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Sample	Concentration mg/L	F	Mean	SD	%RSD	Readings
0 Std0						0.0518 0.0532 0.0529
	32.5		0.0525	0.0007	1.28	
Auto pure [U]1						0.1525 0.1552 0.1581
	97.2		0.1556	0.0028	1.81	
Magnetic P [U]1						0.3699 0.3699 0.3905
	248.5	D	0.3901	0.0003	0.09	
No Air P [U]1						0.3568 0.3568 0.3571
	223.6	D	0.3569	0.0002	0.05	
Auto P [U]2						0.1438 0.1438 0.1430
	89.6		0.1435	0.0005	0.36	
Magnetic P[U]2						0.3294 0.3291 0.3289
	206.2		0.3291	0.0002	0.07	
No Air [U]2						0.2958 0.2967 0.2966
	186.8		0.2969	0.0015	0.52	
Auto P [U]3						0.1936 0.1938 0.1938
	64.7		0.1938	0.0001	0.12	
Maegetic [U]3						0.3026 0.3036 0.3031
	189.8		0.3030	0.0005	0.17	
No Air [U]3						0.2627 0.2613 0.2615
	165.6		0.2618	0.0007	0.28	

Results Flags Legend

Table 8.40: Test Report from PAL for the initial concentration of the impurities

Determination	Result	Units	Method Used
Potassium (K)	21.4	mg/L	AA Analysis - Full Report - K
Sodium (Na)	30.6	mg/L	AA Analysis - Full Report - Na
Aluminium (Al)	37.2	mg/L	ICP-OES Analysis - FULL Report
Molybdenum (Mo)	34.6	mg/L	ICP-OES Analysis - FULL Report
Tungsten (W)	59.1	mg/L	ICP-OES Analysis - FULL Report

Table 8.41: Test Report from PAL for the final concentration of the impurities

Determination	Result	Units	Method Used
Potassium (K)	1.9	mg/L	AA Analysis - Full Report - K
Sodium (Na)	13.7	mg/L	AA Analysis - Full Report - Na
Aluminium (Al)	0.8	mg/L	ICP-OES Analysis - FULL Report
Molybdenum (Mo)	21.4	mg/L	ICP-OES Analysis - FULL Report
Tungsten (W)	10.1	mg/L	ICP-OES Analysis - FULL Report

Annexure E: Precipitation raw data

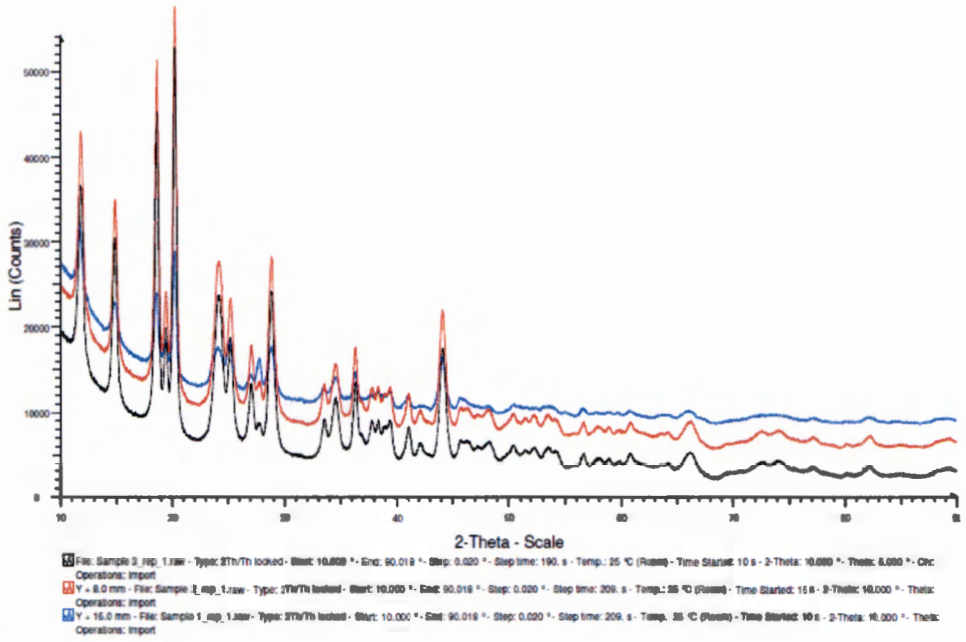

Table 8.42: Illustrates superposed "as measured" diffraction patterns of samples 1 to 3

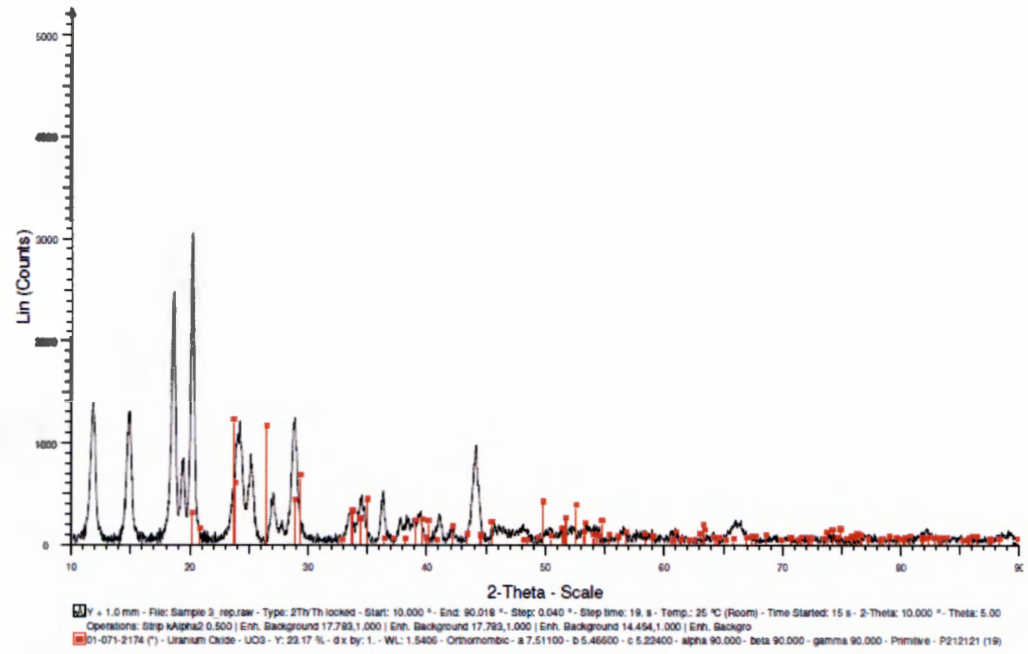

Table 8.43: Illustrates the background subtracted powder diffraction pattern of a representative samples overlaid with stick pattern of uranium trioxide (UO_3)

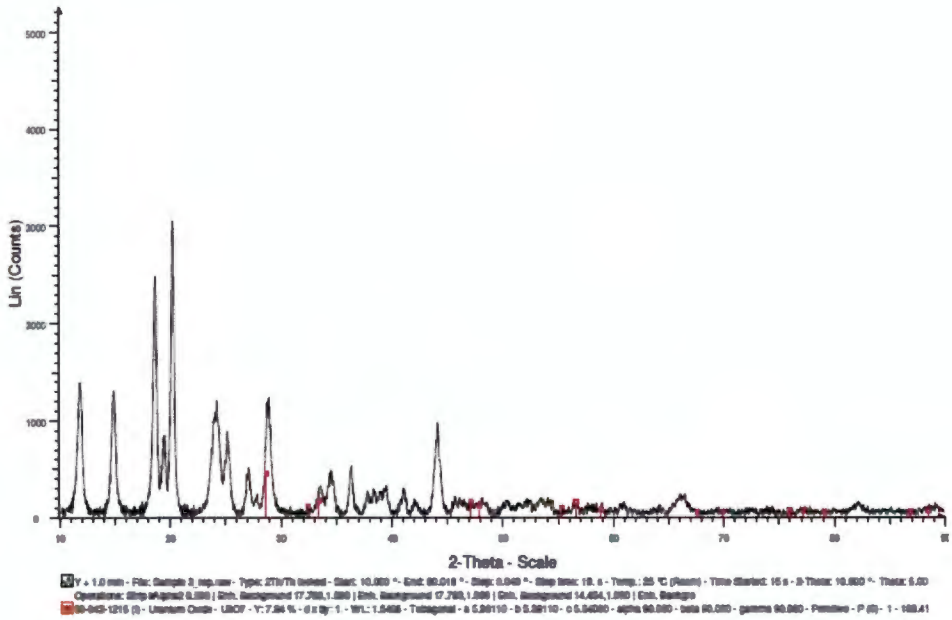

Table 8.44: Illustrates the background subtracted powder diffraction pattern of a representative sample overlaid with stick pattern of U_3O_7.

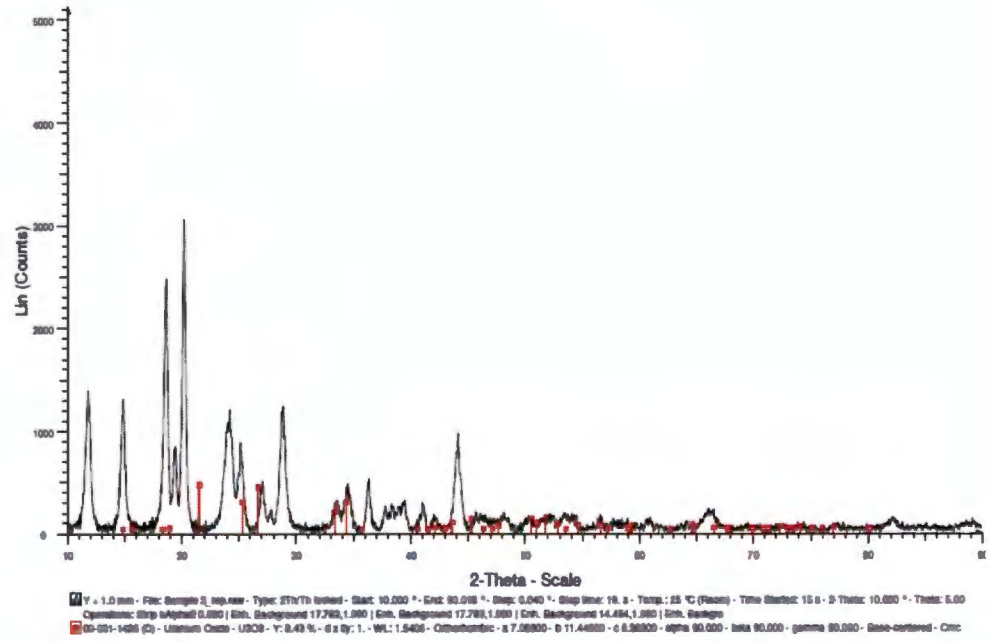

Table 8.45: Illustrates the background subtracted powder diffraction pattern of a representative sample overlaid with stick pattern of U_3O_8.

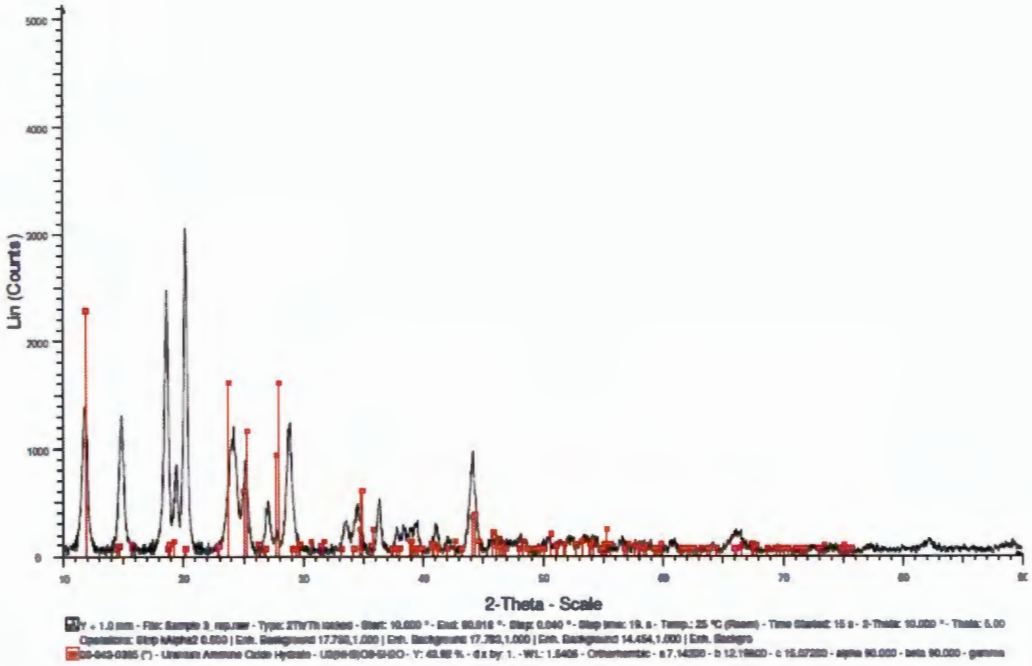

Table 8.46: Illustrates the background subtracted powder diffraction pattern of representative samples overlaid with stick pattern of uranium ammine oxide hydrate ($U_3(NH_3)\ O_9.5H_2O$).

Table 8.47: Initial uranyl solution without impurities

Sample ID: PS 2013–0344X03 **Sample Name:** (A) Initial uranyl solution

Determination	Results	Units	Method used
Calcium (Ca)	10.4	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	17000	mg/L	ICP-OES Analysis –FULL Report

Table 8.48: Initial concentration of uranyl solution and the impurities before precipitation

Sample ID: PS 2013–0344X04 **Sample Name:** Uranyl solution with impurities

Determination	Results	Units	Method used

Aluminium (Al)	<0.5	mg/L	ICP-OES Analysis –FULL Report
Calcium (Ca)	1.7	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	1.1	mg/L	ICP-OES Analysis –FULL Report
Potassium (K)	7.1	mg/L	ICP-OES Analysis –FULL Report
Sodium (Na)	7.2	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	5000	mg/L	ICP-OES Analysis –FULL Report

Table 8.49: Final solution after precipitation process

Sample ID: PS 2013–0344X05 **Sample Name:** A1

Determination	Results	Units	Method used
Aluminium (Al)	<0.5		ICP-OES Analysis –FULL Report
Calcium (Ca)	1.5	mg/L	ICP-OES Analysis –FULL Report
Molybdenum (Mo)	1.1	mg/L	ICP-OES Analysis –FULL Report
Potassium (K)	7.0	mg/L	ICP-OES Analysis –FULL Report
Sodium (Na)	6.9	mg/L	ICP-OES Analysis –FULL Report
Tungsten (W)	0.1	mg/L	ICP-OES Analysis –FULL Report
Uranium (U)	5.8	mg/L	ICP-OES Analysis –FULL Report