Solvent extraction of uranium from alkaline solutions using Aliquat 336

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Mini-dissertation submitted in partial fulfilment of the requirements for the degree *Masters of Science in Applied Radiation Science and Technology* at the North-West University

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DECLARATION

I, **Naomi Dikeledi Mokhine**, declare herewith that the Dissertation entitled, ***"Solvent extraction of uranium from alkaline solutions using Aliquat 336",*** which I herewith submit to the North-West University as *partial fulfilment* of the requirements set for the Master of Science in Applied Radiation Science and Technology degree, is my own work and has not already been submitted to any other university.

Signed by student............. ....

Naomi Dikeledi Mokhine

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ABSTRACT

Molybdenum-99 is the greatest important isotope in nuclear medicine because its daughter Technetium-99m is commonly used in medical radiographic imaging. During the dissolution process of the irradiated target plates containing enriched uranium, uranium and some fission products are precipitated as mixed hydrated oxides to form the residue. This residue is commercially valuable, as it could form the feedstock for recovering and purifying uranium from the other fission products and transuranium elements for further production of the (Mo-99) medical isotope. (Plutonium Uranium Redox Extraction PUREX) is a well-known process for the extraction of uranium using the conventional acid route. There are however unfavourable proliferation issues with the Purex process due to the possibility of recovering plutonium in a pure form. Uranyl solution was generated as simulant of real nuclear waste for this study. The objective of this research was to evaluate different organic extraction solvents/diluents that can remove uranium from the nuclear waste and to determine the most effective extraction ligand/organic solvent combination in extracting uranium only, from alkaline media. Experimental parameters included: different concentrations of ammonium carbonate at pH 9, uranium, concentration of Aliquat 336 and different phase volume ratio were investigated and concentration of sodium carbonate at pH 10,11 and 12. The stripping agents of uranium from loaded organic solution using sodium hydroxide, ammonium sulphate and ammonium carbonate were studied. The results indicate that organic extractant Aliquat 336 in Toluene extracted 82% of the uranium from the feed solution after 30 minutes decreasing to 76% after 60 minutes. 0.2M of ammonium carbonate and 0.01M uranium in phase volume ratio of 1:5 with Aliquat 336 concentrations of 15% are the best extraction parameters that can be used to extract uranium with an extraction percentage of 98%. It was found that when the ammonium sulphate strip was at pH 2, the uranium strip efficiency reached more than 90%.

Keywords: Aliquat 336, alkaline media, aqueous solution, PUREX, organic solvent extraction

LIST OF ABBREVIATION

CARBEX	Carbonate Extraction
DES	Derivative Electronic Spectroscopy
EU	Enriched Uranium
FPs	Fission Products
HEU	Highly Enriched Uranium
HLW	High Level Waste
LLW	Low Level Waste
ILLW	Intermediate Low Level Waste
ISL	In-Situ Leaching
IX	Ion Exchange
LEU	Low Enriched Uranium
MTOA	Methyltrioctylammonium
NECSA	South African Nuclear Energy Corporation
NFC	Nuclear fuel cycle
NMR	Nuclear Magnetic Resonance
PUREX	Plutonium Uranium Reduction Extraction
NTP	Nuclear Technology Production
SIMFUEL	Simulated Fuel
SNF	Spent nuclear Fuel
SX	Solvent Extraction
US RERTR	United State Reduced Enrichment for Research and Test Reactors

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CHAPTER 1: INTRODUCTION AND PROBLEM STATEMENT

1.1 Introduction

Uranium is one of the naturally occurring radioactive element on earth, found both in solid earth and in water, and plays a significant role in daily human life. Uranium is a member of the actinides series in the periodic table of elements. It consists of three radioactive isotopes which are U-238, U-235, and U-234 that occur in abundances of approximately as 99.28%, 0.72%, and 0.0055% respectively (Zhao et al., 2009). Uranium originates in small concentrations in a large variation of rocks, soils and salt water (Morrell and Jackson, 2013). About 0.004% of the earth's crust contains this naturally occurring element. Uranium is a fundamental element that is used in the nuclear power industry as well as for army weapons programs. The use of uranium in these activities, has had great influence on recent development in the measurement of nuclear grade uranium, the discovery of the ore, and its storage and disposal (Švedkauskaitė-Le Gore, 2008). The main interest in the uranium-bearing materials is uranium and its uses, but impurities are important because they have to be separated from uranium to purify it. These impurities are important because the fluorides impurities in UF_6 affect the separation efficiency of U-235 during uranium enrichment, fission efficiency in some reactors are decreased by fuel impurities since they act as neutron absorption poisons, and thus, the occurrence of trace metals affects the total purity of the enriched product. On the other hand, the impurities are of greatest interest in Nuclear Forensics to identify the source of unknown nuclear materials, the trafficking and the enrichment of the material.

A large amount of uranium in the environment is caused by human activities such as mining and milling of other minerals and also from operations of reactors, reprocessing of spent nuclear fuel (SNF) and its disposal (Semião et al., 2010), (Kulkarni et al., 2013). Uranium is one of the toxic elements which are of environmental concern and consequently strict limits have been put by the World Health Organization (WHO) (Misra et al., 2013). Uranium is known as the major element used in nuclear power generation. There are a number of areas around the world having a high concentration of uranium in the ground where its extraction for use in nuclear fuel is economically viable (de Souza et al., 2013). Both U-238 and U-235 are mildly radioactive with half-lives of 4.5×10^9 and 7.04×10^8 years respectively (Morrell and Jackson, 2013). The most commonly used uranium isotope is U-235, which is a fissile isotope, that is, its nucleus is split by thermal neutrons to release high energy and produce more neutrons, and can sustain a fission chain reaction (Edwards and Oliver, 2000).

Throughout the past 20 years, the study in uranium geochemistry and mineralogy has focused on issues relating to the disposal of spent nuclear fuel (SNF) and nuclear wastes in underground geological repositories and to the remediation and safe disposal of uranium-contaminated wastes, soils, and groundwater associated with uranium mines, mill tailing sites, and nuclear energy (Krupka and Serne, 2002). The significant environmental factors affecting uranium mobility in geosphere include oxidation/reduction conditions, pH, and concentrations of complexing ligands such as dissolved carbonate, ionic strength, and mineralogy. Uranium ores differ in chemical complexity from the relatively simple pitchblende ores, which are accompanied by other minerals, to extremely complex uranium-bearing ores, containing rare earth and many other metallic elements (Morrell and Jackson, 2013).

1.1.1 Nuclear fuel cycle (NFC)

Nuclear fuel cycle is a process that involves different activities related with the production of electricity from a nuclear reactor. The nuclear fuel cycle starts with the mining of uranium and ends with the disposal of nuclear waste (WNA, 2016). For uranium to be ready for use in nuclear reactor, uranium undergoes the steps shown in Figure 1. In preparation for use in a nuclear reactor, uranium undergoes the steps of mining, milling, conversion, enrichment and fuel fabrication. These steps are called the *front end of nuclear fuel cycle*. After uranium has spent years in a reactor to produce electricity, the used fuel undergoes a further series of steps including temporary storage, reprocessing and recycling before the wastes are disposed of. These steps are known as *back end of the nuclear fuel cycle.* The nuclear fuel cycle is defined as the cycle of processes and operations that are needed to manufacture nuclear fuel, its irradiation in nuclear power reactors and storage, reprocessing or disposal of the irradiated fuel (IAEA, 2009). Some of the nuclear fuel cycles may be considered depending on the type of reactor and fuel used. To understand the origin of uranium better, it helps to understand the steps involved in a NFC starting with the mining process.

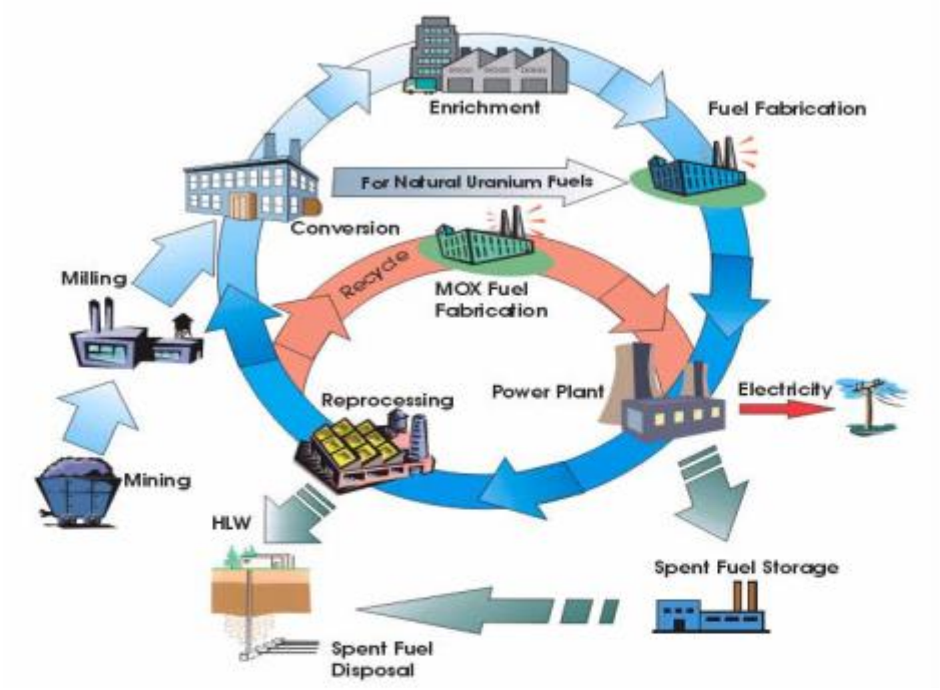

Figure 1: Nuclear fuel cycle (IAEA, 2009)**.**

Nuclear fuel cycle- Front end

Uranium ore is extracted from the ground through uranium mining process. Uranium ore extraction, milling and chemical processing to prepare uranium concentrate known as yellow cake (U_3O_8), are accompanied by the production of unlimited quantities of solid and liquids residue (Zavodska et al., 2008). During the uranium ore leaching process the dry powder, yellow cake is produced, and after mining and milling, uranium ore concentration (UOC) is then shipped to a conversion facility where UOC is transformed into uranium hexafluoride (Scheele, 2011).

In general, open pit mining is used where deposits are close to the surface of the earth and underground mining is used for deep deposits, typically greater than 120 m deep (WNA, 2016). The underground and open pit mines were some of the numerous uranium mines in the United States for several years, particularly at the start of the demand for nuclear energy (Weil, 2012). For underground mines, once the site has been identified, a mine shaft is typically drilled down to the ore bed. Underground mining involves sinking a shaft near the ore body to be mined and extending levels from the main shaft at numerous 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.

Nuclear fuel cycle-Back end

Radioactive nuclear wastes are waste that are generated from the spent fuel at the back end of nuclear fuel cycle. These waste are usually the by-products of nuclear power generation and other applications of nuclear fission or nuclear technology, such as research and medicine. Radioactive waste consists of fission products (FPs) that emits beta and gamma radiation and actinides that emits alpha particles. These wastes from the nuclear fuel cycle are spent fuel and are categorized as high-, medium- or low-level wastes by the amount of radiation that they emit. These wastes come from a number of sources which include (WNA, 2016):

- Low-level waste (LLW) produced at all stages of the fuel cycle. This waste contains actinides but in traces judged to have insufficient environmental significance to warrant their removal (NEA, 1997);
- Intermediate-level-waste (ILLW) produced during reactor operation and by reprocessing. This type of waste includes Plutonium-contaminated operating wastes and dissolver residues which may contain appreciable but varying proportions of actinides (NEA, 1997);
- High level waste (HLW), which is waste containing the highly-radioactive fission products separated in reprocessing, and in many countries, the used fuel itself. Separated high-level wastes also contain long-lived transuranic elements.

The spent fuel has to be stored from the reactor for a certain time. These spent fuel can either be stored in wet storage or dry storage facilities. During the reprocessing, about 96% of used pellets contains its original uranium, of which less than 1% of fissionable U-235 content is reduced (WNA, 2016). This process separates uranium and plutonium from waste by cutting up the rods and dissolving them in acid to isolate different materials. It enables reprocessing of the uranium and plutonium into new fuel, and yields a considerably reduced amount of waste. The remaining 3% of high-level radioactive wastes can be stored in liquid form and subsequently solidified.

1.2 Production of Molybdenum-99

Uranium has become the world's most important energy mineral in the past years, and it is also an element of great commercial interest due to its application in the nuclear industry especially in the development of radiopharmaceuticals and radioisotopes (de Souza et al., 2013) such as the medically important radioisotope Mo-99. During the production of the Mo-99 radioisotopes, uranium-bearing targets are irradiated with thermal neutrons to produce the fission product Mo-99. In the past, the production of Mo-99 was performed in South Africa using target plates containing uranium-aluminum alloy which contains 46% of enriched uranium (EU). However, in recent years the process has been converted to using low-enriched uranium at 19% enrichment. The target plates are irradiated in the 20 MW SAFARI-1 reactor at the South African Nuclear Energy Corporation (NECSA) with an average neutron flux of $2.0 * 10^{14}$ $n.cm^{-2}.s^{-1}$ for 50-200 hours. These target plates are removed from the reactor and cooled for half a day in water before being transported to the processing facility in shielded containers (Kweto et al., 2014). Once in the processing facility, targets are placed in a hot cell, which is a shielded nuclear containment chamber, for chemical processing.

Mo-99 is the most significant isotope in nuclear medicine which is used to manufacture Tc-99m generators. Tc-99m, with a short half-life of 6.02 hours and low gamma energy of 140 keV, has been widely used as a medical diagnostic procedures for more than 50 years (Rao et al., 2014). There are two routes that are used to produce medical isotope Mo-99, one is through fission of U-235 by a neutron-fission reaction that produces Mo-99 and other medically important isotopes like I-131 (Iodine-131) and Xe-133 (Xenon-133), the second route is by activation of Mo-98 through neutron capture reaction (Isotope, 2009). Figure 2 illustrates the two routes used to produce Mo-99.

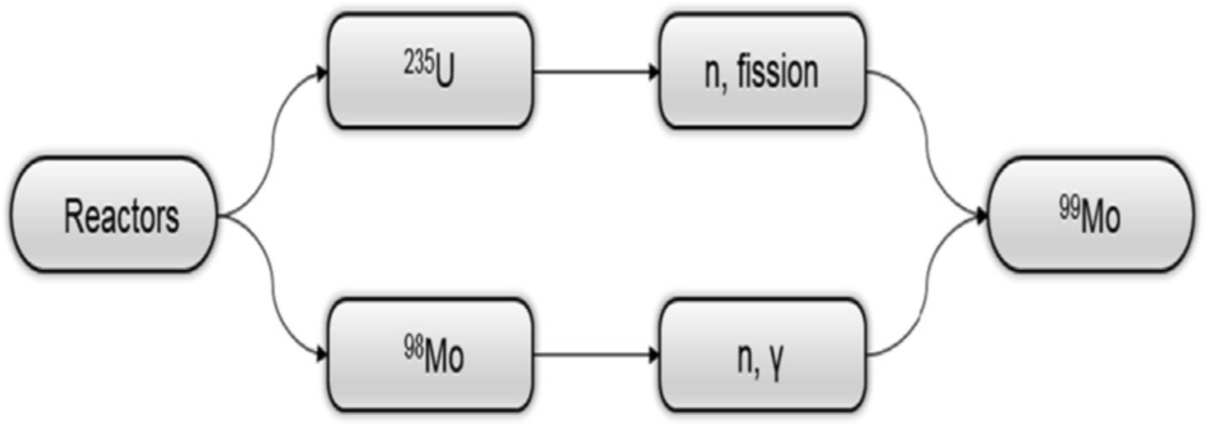

Figure 2: Two methods used to produce Mo-99 (Lee et al., 2016)

The irradiated target plates containing EU are treated in an alkaline dissolution process to extract Mo-99. During this process, uranium and some fission products are precipitated as mixed hydrated oxides to form a residue. This residue is currently being stored in stainless steel canisters in a hot cell at the Mo-99 (and other Radioisotopes), production facility of NTP (Nuclear Technology Product), a subsidiary of NECSA.

1.3 Problem statement

Managing radioactive waste generated during the operation of nuclear facilities, in medicine, industry and other fields is an important problem needing further development of nuclear technology and nuclear energy worldwide. Due to their radiological risk, this type of waste cannot be directly disposed into the environment. It must be treated to reduce the volume of radioactive substances to the smallest possible volume, enabling stabilization and then long-term storage or final disposal. One of the principles of waste classification is the origin of this material and the biggest quantity of radioactive waste arises from the nuclear fuel cycle. Liquid, low and intermediate level radioactive wastes generated in nuclear facilities, laboratories and hospitals create a particular problem because of their large volumes, as well as levels of radioactive materials present in these effluents above exemption.

Because of the amount of EU found in the uranium residue during Mo-99 production, NECSA is investigating the dissolution of the residue, and purification of uranium from FPs and TRU (Transuranium) elements using alkaline technology. Mo-99 is almost completely manufactured from the fission of high enriched uranium (HEU) (Mondino et al., 2001). However, the US

Reduced Enrichment for Research and Test Reactors (RERTR) Program is working on substituting HEU with low enriched uranium (LEU < 20%) fuel and targets to reduce nuclear proliferation concerns (Mushtaq et al., 2009).

The most well-known process for the extraction of uranium from spent fuel is the PUREX process where acid solution is used (Soderquist et al., 2011). This process is used as the principal technology for recycling of SNF, using nitric acid as an aqueous solution and TBP (Tributyl phosphate) as an extractant (Stepanov et al., 2011). To date, the PUREX process is the only process that has been used on a large scale to recycle SNF (Peper et al., 2004). Regardless of shortcomings, such as using the organic solvents that are flammable, and the loss of minor actinides from the fission products waste (Chung et al., 2010), this process is still being used at NECSA for purification of natural uranium. However, due to proliferation issues, NECSA may not use the PUREX process for the recovery of uranium from the generated Mo-99 residue. To date, NTP is importing EU from one international supplier at tremendous costs. Since NECSA's inventory is limited, and importing this strategic commodity is a business risk, alternative sources of EU must be found. To date, Mo-99 production for radiopharmaceutical purposes is becoming increasingly in demand, and because of a broadening customer base, treatment of the waste should be done as soon as possible to establish sustainability for the process (Carstens et al., 2014). Recovering of this residue will allow recycling of a valuable product that can be used to manufacture medical isotopes (Kweto, 2013), and also will reduce the volume and disposal costs for radioactive waste. (Zhu et al., 2013) stated that there is no solvent system that has been found suitable for the extraction of uranium from alkaline carbonate solutions. An environmental friendly technology could be developed for recovery and purification of uranium from waste generated during the production of Mo-99 using alkaline solutions (Kim et al., 2012). An alternative process to acidic solution extraction of uranium is the use of alkaline of a solution. The main research question of this dissertation is therefore if it will ***it be possible to recover and purify uranium from waste generated during the production of Mo-99 using carbonate medium without recovering other fission products?*** If the feasibility of this process can be proven in the laboratory, then this process would be used for testing the enhanced dissolution and purification process on a larger scale, in a hot cell facility.

1.4. Research Aim and Objectives

1.4.1 Aim:

The aim of this work was to develop an alkaline extraction technology that can be used to purify uranium from post reactor waste.

1.4.2 Objectives:

The objectives of the work therefore are to:

- Evaluate organic extraction ligands that can operate in alkaline media to remove Uranium from the nuclear waste.
- Characterize the most effective organic ligand(s) for uranium extraction
- Develop a cost-effective extraction technology for recovery and purification of uranium to be reused in target plates suitable for production of Mo-99 radioisotope.

CHAPTER 2: LITERATURE REVIEW

2.1 General background

The acid route is generally used in the industry to dissolve uranium powders and uranium is then purified by using liquid-liquid extraction processes. 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. The disadvantage of the PUREX process, is that the fire and explosive hazard caused by contact of nitric (HNO_3) acid is increased and is difficult to overcome within the framework of the existing sequence of operations (Chekmarev et al., 2017). This problem becomes one of the main factors that stimulated active search for other methods that can be used for SNF reprocessing among which much attention is paid to dry methods such as fluoride gas and pyroelectrochemical processes.

Alkaline dissolution using carbonate medium is being considered as an alternative technique for using alkaline solutions in order to reduce corrosion as a secondary problem. This technique is used in order to increase the proliferation resistance features of the reprocessing of fuel cycles. The use of the alkaline dissolution method was first demonstrated on irradiated uranium dioxide powder, whereby sodium carbonate and hydrogen peroxide solution were used as leaching reagents. This method 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 result this research was terminated. In the presence of carbonate solutions, at the pH >6, uranium species $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are formed and these soluble species enhance the mobility of uranium under oxidizing conditions (Steward and Mones, 1996). The oxidative dissolution of uranium dioxide has been studied as a function of hydrogen carbonate concentration at different temperatures (10, 25, 45, and 60°C) using a thin-layered flow-through reactor (De Pablo et al., 1999). The results have presented evidence of an alternative bicarbonate promoted oxidative dissolution mechanism in the hydrogen carbonate solution and interpreted it as three steps: initial oxidation on the U(VI) oxide surface, reaction of HCO_3^- with U(VI) at oxidized layer, and detachment of the U(VI)-carbonate surface complex. Figure 3 shows different uranium carbonate complexes that can be formed during alkaline leaching.

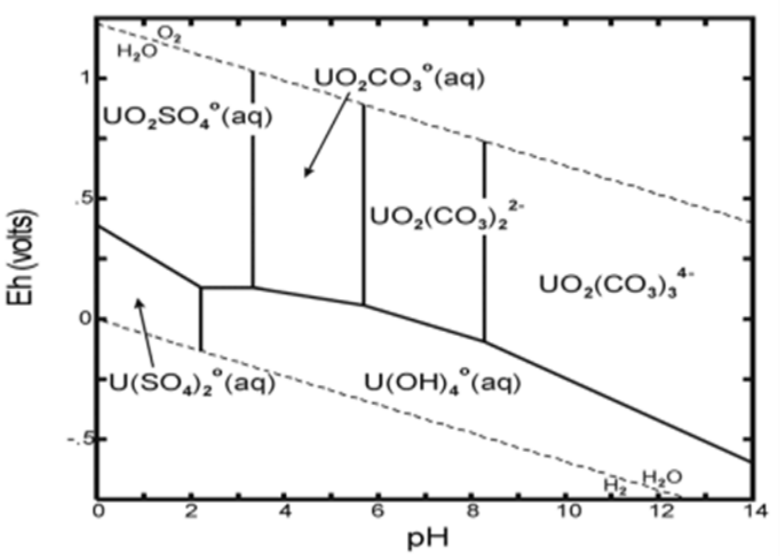

Figure 3: Eh-pH diagram showing dominant uranium complexes in carbonate and sulphate solutions (Krupka and Serne, 2002)

2.2 Dissolution of uranium from ores

The dissolution of uranium is a first hydrometallurgical process in the extraction of uranium from its ore. The leaching processes of uranium using different solvents from its ores, are dependent on the characteristics of the ore such as the type of uranium mineralization and the nature of the other minerals in the ore (Venter and Boylett, 2009). An important stage for finding uranium oxide from ores is by uranium purification after separation and concentration with the use of known physical and chemical methods (Biełuszka et al., 2014). The most commonly used techniques for purification and concentration are ion-exchange (IX) and solvent extraction (SX) using acid. All the same methods includes the steps resulting in (Morrell and Jackson, 2013): pre-concentration of the ore; removal of clays or carbonaceous materials by roasting or calcination e.g., to increase solubility and improve the extraction; conversion of uranium into an aqueous form by leaching operation; and uranium recovery from leach liquors by ion-exchange, direct precipitation or solvent extraction. The treatment includes the metals separation such as molybdenum (Mo), vanadium (V), iron (Fe), arsenic (As), zinc (Zn), copper (Cu), nickel (Ni) and rare earth elements (Biełuszka et al., 2014).

(Kim et al., 2012), investigated solvent extraction of uranium using amine based extractants. Amine based extractants such as, Alamine 336, Alamine 308, Alamine 304 and Aliquat 336 in diluent Kerosene were investigated. The results showed that Alamine 336 was the best extractant for uranium from sulphate solutions compared to other amine extractants. Extraction percentage of 99.8% was recovered from low grade ore without interference of other metals.

In the leaching of uranium ores, the solubility of uranium in sodium, potassium and ammonium carbonate solutions relies upon the separation of uranium. Carbonate is added to an acid solution to precipitate and separate iron residue while uranium remains in the solution which has been made alkaline by addition of sodium, potassium and ammonium carbonate. Uranium and gold mines use sulphuric acid to extract uranium from ores, however, in situations where mineralogy of ores results in high acid consumption, the use of carbonate leaching is required. Ore leaching using sodium carbonate or sodium bicarbonate has been studied to recover uranium from low-grade ore.

2.3 Uranium recovery from simulated residue

A process of ammonium carbonate-based leaching has been developed for uranium recovery from the waste produced by an alkaline dissolution process used for the manufacture of the medical isotope, Mo-99 (Stassen and Suthiram, 2015). Uranium recovery from residue was succeeded with three consecutive ammonium carbonate-peroxide leaches with final decontamination factors from low values of Cs-137, Ru-106, and Sb-125 to lanthanides. In the study of recovery of uranium from simulated Mo-99 production residue using non-dispersive membrane-based solvent extarction, it is stated that the recovery of uranium from Mo-99 production waste would reduce the residue volumes that need to be disposed of and also decrease the production cost while the recuperated EU can be used for manufacture of isotope (Fourie et al., 2016).

The uranium waste contains insoluble precipitates formed when the target plates of containing uranium-aluminum alloy are dissolved during the manufacture of Mo-99 (Kweto et al., 2014). The remaining insoluble residue contains about 90% of enriched uranium that is existing in the solution of various oxidation states. The solid residue contains uranium and most FPs, like Molybdenum (Mo-99), Cesium (Cs-137), Strontium (Sr-90), Barium (Ba-140), Antimony (Sb-132), Tellurium (Te-132), Iodine (I-131) and small amount of the Ruthenium (Ru-106) and Zirconium (Zr-95). Figure 4 shows the process of recovery and purification of uranium that is being developed at NECSA (Carstens et al., 2014). This method involves dissolution of the residue in an ammonium carbonate and hydrogen peroxide leach solution followed by initial purification using alumina columns. Final purification of uranium can be achieved using solvent extraction.

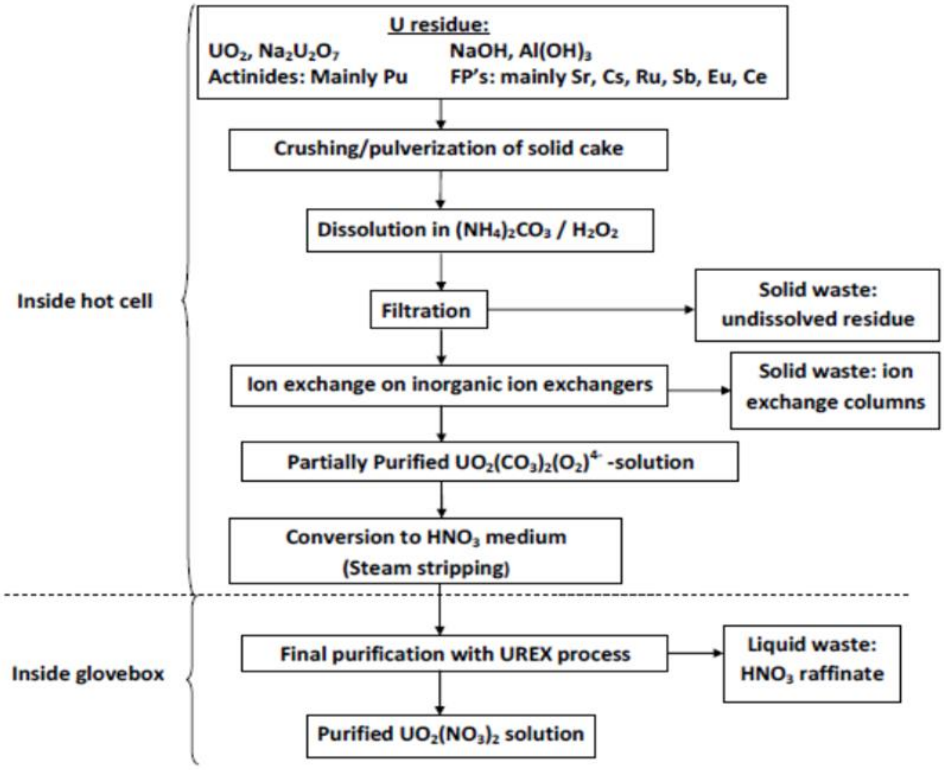

Figure 4: Flow diagram of the recovery of uranium from Mo-99 production solid residue (Carstens et al., 2014)

2.4 Alkaline leaching of uranium

Uranium is an element that exists in various oxidation states (U^{+2}, U^{+3},$U^{+4,}$ U^{+5} and U^{+6}), of which uranous U(IV) and uranyl U(VI) are the most important during any leaching operation (de Souza et al., 2013). In oxidizing states, uranium tends to be present as the uranyl ion (U^{+2}) which forms strong complexes with different carbonates and natural organic matter ligands depending on the pH (Semião et al., 2010). U exists in the +6 valence state under oxidizing to mildly reducing environment. The +4 valence state of uranium is stable under reducing conditions and is considered relatively immobile. When extracting uranium, whether through acid or alkaline leaching, it need to be oxidized to the hexavalent state U(VI) before it is dissolved (Edwards and Oliver, 2000). The advantage of using alkaline leaching is high selectivity of uranium over impurities because some of the impurities do not dissolve in alkaline solution (Zhu et al., 2013). Although uranyl ions can form stable, soluble complexes in acidic solutions, the use of a carbonate remains more advantageous for the alkaline dissolution and is highly selective and results in the formation of a uranyl tri-carbonate complex solution. Besides this, the alkaline environment is non-corrosive and therefore will not pose any hazard to the hot cell. It has also the advantage of allowing a pure uranium product to be precipitated directly from leach liquor. Carbonate solutions do not exhibit leaching activity for uranium compounds in the absence of oxidants. Most researchers prefer to use hydrogen peroxide as an oxidant to convert U(IV) to U(VI).

2.4.1 Reaction Equations

In alkaline leaching, oxygen can be used as a strong oxidizing agent. The main reactions in alkaline leaching of uranium dioxide are represented by the following equations,1-4 (Edwards and Oliver, 2000):

Oxidizing uranium to hexavalent state

$$2UO_2 + O_2 = 2UO_3 \qquad (1)$$

Dissolution with carbonate

$$UO_3 + 3Na_2CO_3 + H_2O = Na_4(UO_2)(CO_3)_3 + 2NaOH, \qquad (2)$$

Bicarbonate solution is mandatory to stop the reaction of UO_3 with carbonate to produce hydroxyl ion which will precipitate leached uranium and uranium di-uranate.

$$UO_3 + CO_3^{2-} + 2HCO_3^- = UO_3(CO_3)_2^- + H_2O, \qquad (3)$$

Re-precipitation occurs in the absence of bicarbonate

$$2Na_4(UO_2)(CO_3)_3 + 6NaOH = Na_2U_2O_4 + 3Na_2CO_3 + 3H_2O, \qquad (4)$$

However, in alkaline leaching ammonium carbonate is preferred instead of sodium carbonate because of the following advantages (Fourie et al., 2016):

- Reagents are recuperated for re-use. It also decomposes at 60 °C to form NH_3, CO_2 and H_2O which will reduce the secondary wastes created during recovery of U(VI).
- No bicarbonate is required to eliminate hydroxide made in the reaction because the solution is buffered at pH of 9. This is because of the ammonia-ammonium buffer solution;
- Precipitation may be performed by heating;

- Ammonium carbonate is a milder alkali than sodium carbonate leading to a decreased chance of U(VI) precipitation. The following equations, 5-10 are the main reactions that take place (Kweto, 2013):

$$3(NH_4)_2CO_3 + UO_2 + \frac{1}{2}O_2 + H_2O = (NH_4)_4UO_2(CO_3)_3 + 2NH_4OH, \quad (5)$$

$$NH_4OH + NH_4HCO_3 = (NH_4)_2CO_3 + H_2O, \quad (6)$$

Precipitation:

$$(NH_4)_4UO_2(CO_3)3 + \text{heat} = 4NH_3 + 3CO_2 + UO_3.H_2O, \quad (7)$$

And regeneration:

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3 \quad (8)$$

Uranium oxidizes and forms carbonate-peroxide complexes when uranium dioxide is oxidatively dissolved in carbonate solution containing hydrogen peroxide, which eventually converts to the soluble uranyl carbonate anion $UO_2(CO_3)_3^{4-}$ (Stepanov et al., 2013). The overall dissolution equation for uranium dioxide is as follows (Kweto, 2013):

$$UO_2 + H_2O_2 + 3(NH_{4)2}CO_3 = (NH_4)_4UO_2(CO_3)_3 + 2NH_4OH \quad (9)$$

The consumption of hydrogen peroxide is greater than expected in equation 9 because of the development of uranyl carbonate-peroxide complexes.

$$UO_2(CO_3)_3^{4-} + H_2O_2 = UO_2(CO_3)_2(O_2)^{4-} + 2H^+ + CO_3^{2-} \quad (10)$$

Hydrogen peroxide plays two roles in carbonate leaching reaction, firstly as an oxidant that accelerates the rate of dissolution, and secondly as a strong ligand forming mixed carbonate-peroxide complex when reacting with uranium (Peper et al., 2004).

The oldest method of the spectrophotometric determination of semi-micro and macro quatities of uranium is based on the formation of the intensely coloured peruranate complex with peroxide in the alkaline cabonate medium (Huyser et al., 1986). The reported results showed that in pure carbonate solutions, the interference at 380nm can be ascribed to a decrease in pH which is caused by neutralization of the unbuffered solution.

(Soderquist et al., 2011) has proven the effective recuperation and decontamination of uranium during the dissolution of irradiated fuel utilizing an ammonium carbonate and hydrogen peroxide solution. These researchers demonstrated that albeit in excess than 98 % of the irradiated fuel dissolved, 95 % of plutonium, americium, and curium generous measures of splitting amounts of fission products remains as precipitates thus effectively partitioning the uranium during the dissolution step. They included by saying ammonium carbonate can be evaporated and recuperated for reuse leaving a great packed volume of fission products, actinides and uranium. Soderquist et al. 2011, finished up by expressing that after the fuel has been disintegrated, separations can partition the spent fuel into much considerably less difficult constituents, more secure for storage or disposal in a repository.

2.5 Uranium recovery from alkaline leaching using carbonate medium

The use of carbonate dissolution for the separation and purification of uranium waste produced from the production of Mo-99 was conducted at Kernforschungszentrum Karlsruhe (KFK), and at the Medical facility at Petten, Netherlands. (Sameh, 1984). The work mentioned above concentrated on using a sodium carbonate/bicarbonate mixture as the dissolution medium with different oxidizing reagents like H_2O_2. The decontamination of uranium from its fission and transuranium products was achieved by using basic anion exchangers. Carbonate solutions are different from nitric acid because they do not exhibit oxidative activity in the absence of oxidants, corrosive activity in the equipment and are nontoxic to biological objects (Stepanov et al., 2011). Therefore, oxidants are needed for an effective dissolution of uranium dioxide in carbonate solution. Many researchers still give preference to hydrogen peroxide to convert uranium (IV) into uranium (VI).

The study of physicochemical foundations of SNF leaching in carbonate solution was investigated. This study was based on the development of the physicochemical basis of the transfer of SNF into aqueous carbonate solution that is suitable for extraction of uranium and plutonium (Stepanov et al., 2009). The authors stated that in case of the rapid degradation of hydrogen peroxide in carbonate solution, the Carbonate extraction (CARBEX) process will require a large intake of the oxidizer. They added that the importance of SNF oxidative leaching in carbonate solution is the behaviour of FPs piled up in fuel composition. They concluded by reporting that their results have confirmed that the enhanced selectivity of the CARBEX process as in the early stage of the leaching of the fuel into carbonate solution is an evident advantage over PUREX process.

(Hartley, 1972) studied the conventional processes to produce yellow cake and indicated that during the alkaline dissolution of uranium with bicarbonate solution, the reaction rate was almost double for every 10 degrees in temperature between 60 and 100 degrees. Results showed that the extraction of uranium present in interstitial cementing material is influenced by a particle size, as small size of uranium extracted faster when compared to coarse uranium material embedded into cement. The author also reported that the degree of U_3O_8 dissolution increased with increasing leachant concentration when dissolving uranium. Bicarbonate was necessary to prevent precipitation of dissolved uranium, however, excess bicarbonate precipitated if NaOH is present. Edwards and Oliver (2000) reviewed the 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. The author stated that optimization of hydrogen peroxide showed that the initial concentration of uranium increased with the increase of the concentration of peroxide with a maximum reaction rate of 0.9 M. In addition, the same author studied the effects of carbonate concentration. It was found that the dissolution of 40 mg UO_2 in 0.5 M sodium carbonate was the most favourable choice, showing both a high initial dissolution rate and the highest UO_2 dissolution capacity in the systems studied. He concluded by stating that the kinetic data and solution complexation reactions will assist in the development of a new method for dissolving SNF in nonacidic media.

The uranium recovery from carbonate solutions using ionic liquids (IL) was studied (Shen et al., 2015). SX method with non-fluorinated quaternary phosphonium ionic liquids for uranium recovery from carbonate solutions was established. During the process, results were reported that uranium was extracted into the ionic liquid phase as the $[Na_3UO_2(CO_3)_3]^-$, $[Na_3UO_2(CO_3)_2Cl_2]^-$, and $[NaUO_2(CO_3)_2Cl_2]^-$, anion complexes, and the composition of the ionic liquid, Cl^- ions, went into aqueous phase, which was determined by electrospin ionization−mass spectroscopy (ESI-MS) and Cl− ion test experiment. The extraction mechanism is anion exchange. The authors further stated that the largest loading capacity of the IL was 11.23 g/L. F− ions have no influence on the extraction efficiency for uranium extraction. The stripping of uranium from the ionic liquid phase after extraction is difficult using dilute nitric acid and other stripping reagents. A 1 M NaOH solution was used to strip uranium and this process was repeated three times to remove uranium from the IL completely.

The dissolution of uranium dioxide microspheres in carbonate hydrogen solutions was studied (Adams, 2013). He explored the impact of three diverse counter cations ammonium, sodium and potassium on the dissolution execution of uranium. Results were stated that the energy of dissolution, activation energy frequency factors and reactions order with respect to both carbonate salt and hydrogen peroxide were set up for every one of these systems. He included that carbonate-peroxide has a various advantages over traditional nitric acid dissolution including less damage to equipment during procedures and lesser amounts of waste created during process.

The chemistry of carbonic acid and carbonate ion is very much characterized by the pH of the solution. The carbonate ions are viewed as fairly basic as it responds with acidic proton and make bicarbonate ion, and its conjugate acid, carbonic acid. The carbonic ions decays to oxygen and carbon dioxide gas under acidic conditions; pH less than 4. When the pH increases the bicarbonate ion splits into a carbonate ion and hydrogen proton taken by HO^- group which at that point forms water. Carbonate salts are generally insoluble, with less significant exceptions with ammonium carbonate, the soluble base metals and uranyl-carbonate complexes (Adams, 2013). Numerous carbonate salts have been examined for carbonate dissolution. The carbonate salts incorporate sodium carbonate, ammonium carbonate, potassium carbonate, and lithium carbonate. Of these, sodium and ammonium carbonate are the most considered salts. (Smith et al., 2009a) investigated the dissolution of uranium oxides in basic solutions by utilizing ammonium, potassium, sodium and rubidium carbonate. The researchers stated the dissolution rates among the carbonates as $(NH_4)_2CO_3 > K_2CO_3 \geq Na_2CO_3 > Rb_2CO_3$. Results by Smith et al (2009) concluded that within the pH range from 8.3 to 10.3, 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. However, Peper and colleagues (2004) reported $Li_2CO_3 > Na_2CO_3 > K_2CO_3 > NH_4CO_3$. Unfortunately, the low solubility of Lithium carbonate of approximately 0.18 M cannot compete with other carbonates at higher concentrations.

2.6 Uranium recovery from spent nuclear fuel (SNF)

Presently the main solvent extraction method used in the industry for reprocessing of SNF is the PUREX process. This process uses nitric acid to reprocess SNF. Recovering uranium from SNF will become more significant in the future because of the increasing demand for uranium for nuclear power plants that are being constructed all over the world to manage with energy and environmental problems, and because of the increase of the volume of high level waste (HLW) for a geological disposal. A great deal of interest has been shown in using alkaline carbonate media for the treatment of SNF instead of using acid media, because a carbonate process has several advantages such as; enhancing safety, economic competitiveness and minimal generation of waste as well as more proliferation resistance (Kim et al., 2009).

Aqueous carbonate solutions has been used increasingly in recent years for purifying fissile materials such as uranium and plutonium from SNF (Stepanov et al., 2011). The use of a carbonate-based method for reprocessing of SNF has been developed by a Russian research group, and they have named their method Carbonate extraction (CARBEX) process. This process consists of high-temperature oxidation of SNF, its oxidative dissolution in carbonate solution using a suitable oxidant such as H_2O_2, extraction of U^{6+} and Pu^{6+} using a quaternary ammonium-based solvent extraction such as Aliquat-336 to separate them from fission products, and solid-phase re-extraction of carbonate complexes in the aqueous solution is achieved by precipitation through temperature adjustment and increased ammonium carbonate concentration (Stepanov et al., 2011). The Russian researchers showed that CARBEX process can be more effective and safe than the well-known industrial PUREX process.

The study of physicochemical values of the preparation of U(VI) carbonate solutions for recycling in the CARBEX process was conducted by (Chekmarev et al., 2017). This study was focusing on the production safety and reduction of radioactive waste volume. The carbonate solutions with the U(VI) concentrations greater than 100 g/ L were reported as appropriate for final purification of uranium by extraction, can be prepared under the conditions of creation of U(VI) carbonate-peroxide complexes in the progress of dissolution with avoidance of hydrolysis of U(VI) compounds. The research also investigated the effect of impurities simulating some FPs in the course of oxidative dissolution. In conclusion, Chekmarev and colleagues reported that dissolution of uranium SNF in carbonate solution in the presence of H_2O_2 allows preparation of sufficient concentrated solution containing uranyl peroxide-carbonate complexes and readily soluble FP impurities.

Anodic dissolution of simulated SNF containing UO_2 and fission products in alkaline aqueous solution has also been studied using sodium carbonate-sodium bicarbonate (Asanuma et al., 2001) and ammonium carbonate solutions (Asanuma et al., 2006) have been performed. In anodic dissolution experiments using simulated SNF in Na_2CO_3-$NaHCO_3$ solutions, uranyl ions were produced anodically as stable carbonate complex, and at the same time, simulated FPs were precipitated as hydroxo or carbonate compounds. Uranyl ions were recovered as hydroxo compounds by adding sodium hydroxide to the solution after removing the FP precipitates. During the dissolution experiments, precipitates of the simulated fission products were observed on the pellet and in $(NH_4)_2CO_3$ solution used as the electrolytic solution. Analyses of the electrolytic solution revealed that most of the simulated fission products, i.e. alkaline earth and rare earth elements, are precipitated in high ratios (Asanuma et al., 2006). It was reported from the experimental data that it was expected that the anodic dissolution of spent fuel and fission products separation by precipitation could be performed simultaneously.

The oxidative dissolution of UO_2 powder at room temperature in aqueous carbonate solution has been studied. The effectiveness of various oxidant including NaOCl, $K_2S_2O_8$ and H_2O_2, dissolving UO_2 in alkaline solution have been considered, with H_2O_2 showing the most quick initial dissolution at 0.1 M oxidant concentrations (Peper et al., 2004). Optimization of H_2O_2 concentration indicated that the initial rate of uranium oxidation increased with the increase of peroxide concentration with extreme reaction rate evaluated at about 0.9 M peroxide. In later work, the dissolution characteristics of UO_2, U_3O_8, and UO_3 in aqueous peroxide-containing carbonate solution was investigated. The experimental variables investigated included were different counter-ions NH_4, Na, K, and Rb and concentration of H_2O_2. The counter-ion had a dramatic influence on the dissolution of UO_2 in 1M carbonate solution containing 0.1 M H_2O_2, with the most rapid dissolution occurring in ammonium carbonate solution where dissolution rates were decreased in the order of $UO_3 >> U_3O_8 > UO_2$ (Smith et al., 2009b). In further work, on the optimal dissolution parameters of UO_2 powder in solutions of ammonium carbonate and hydrogen peroxide were investigated (Smith et al., 2009a). The parameter variables included peroxide and carbonate concentrations and temperature. The dissolution rate of UO_2 in 1M $(NH_4)_2CO_3$ increased linearly with peroxide concentration ranging from 0.05-2 M and with temperature increase from 15 to 60 degrees, with no apparent maximum rate reached.

The use of carbonate medium from dissolution of samples of UO_2 SNF was also tested by a USA research group (Soderquist and Hanson, 2010), (Soderquist et al., 2011). An amount of 50mg of the SNF were dissolved in 20 ml saturated ammonium carbonate and 10 ml 30% H_2O_2, and dissolution yields were compared with those obtained with 12M HNO_3 (Soderquist and Hanson, 2010). The study performed on a 13 g scale indicated that greater than 98% of irradiated fuel dissolved (Soderquist et al., 2011). After the removal of carbonate from the solution more than 95% of Pu, Am and Cm and large amounts of FPs precipitated; thus dividing the elements present in the fuel during dissolution process.

The development of a carbonate-based process for uranium recovery from simulated SNF (also called SIMFUEL) containing uranium and 16 possible contaminants namely, Ce, Gd, La, Nd, Pr, Sm, Eu, Y, Mo, Pd, Ru, Zr, Ba, Sr, Re, Tc and Te were also studied by a Korean research group, using Na_2CO_3 solution and H_2O_2 (Chung et al., 2010). The author's results were reported stating that in the presence of hydrogen peroxide, the leaching rates of reduced SIMFUEL powder are faster than the oxidized SIMFUEL powders. The method used has been named as Carbonate-based Oxidative Leaching (COL) to recover only uranium using high alkaline carbonate solution with H_2O_2, where TRU (transuranium) elements are undissolved and precipitated (Kim et al., 2010), (Chung et al., 2010) and is based on oxidative leaching into Na_2CO_3 solution. It was reported for SIMFUEL in 0.5 M of sodium carbonate and 1 M H_2O_2 that up to 54g/l UO_2 could be dissolved completely within 5 minutes. The study of dissolution experiments for pure UO_2 and U_3O_8 powders of SIMFUEL has been extended using oxidizing conditions at 500 degrees in air or reducing conditions at 700 degrees in 4% H_2-Ar conditions. U_3O_8 dissolves faster than UO_2 in the absence of H_2O_2 for pure powders. However, in the presence of H_2O_2, the oxidized SIMFUEL powder had lower dissolution rates and lower solubility than the reduced SIMFUEL powder (Chung et al., 2010). Leaching rate and solubility of uranium from SIMFUEL increased with H_2O_2 concentration. Kim and colleagues expanded their research by using anodic dissolution of UO_2 and SIMFUEL (Kim et al., 2010) electrodes at numerous potentials in carbonate solutions of a great concentration at few pHs. However, the electrolytic uranium dissolution was affected by the corrosion of UO_2CO_3 produced at the electrode during the dissolution in carbonate solution. The actual dissolution in carbonate solution can only be obtained at an applied potential of +4 V which caused enough oxygen growth to break the corrosion product.

The assignment of absorption bands in the electronic spectra of aqueous solution of the $Na_4[UO_2(O_2)CO_3)_2]$ and $Na_4[UO_2(CO_3)_3]$ considering the dissociation, hydration, association and ligand exchange has been performed (Boyarintsev et al., 2016); (Stepanov et al., 2016). The Boyarintsev et al (2016) study has demonstrated that the absorption in the range of 190 - 400 nm is caused by the oxygen atoms of the O_2 and CO_3 groups and water molecules of dissociated and neutral complex species $Na_3[UO_2(O_2)(CO_3)_2]^-$, $Na_4[UO_2(O_2)CO_3)_2]_2^-$, and $Na_4[UO_2(O_2)CO_3)_2]$ (Boyarintsev et al., 2016). For the $Na_4[UO_2(CO_3)_3]$ complex, the following assignment of absorption bands has been made: $Na_3[UO_2(CO_3)_3]^-$, 258 nm; $Na_2[UO_2(CO_3)_3]_2^-$, 300 nm; and $Na_4[UO_2(CO_3)_3]$, 330 nm (Stepanov et al., 2016).

In past few years the derivative electronic spectroscopy (DES) has been widely used for identifying U(VI) complexes formed during dissolution of uranium oxides in carbonate solutions, and in the extraction of U(VI) compounds using methyltrioctylammonium (MTOA) in organic solutions (Stepanov et al., 2016). In order to identify the peroxo-carbonate complexes in aqueous solution, DES is used. Studies that deals with determination of U(VI) complexes by DES method use the principle of absorption bands to different ligands such as one band-one ligand which ignores the diverse processes occurring in aqueous solutions. The bands that can be assigned to other ligands such as H_2O, OH^- have not been identified. (Stepanov et al., 2016) concluded by reporting that analysis of the structure of the spectra of $Na_4[UO_2(CO_3)_3]$ in sodium carbonate solution shows the existence of triads of absorption bands.

(Boyarintsev et al., 2017) established that throughout the oxidative dissolution of a set of mixtures of U_3O_8 and oxides of major FPs such as ZrO_2, MoO_3, SrO, Ln_2O_3, CeO_2, SnO, compounds of Mo(VI) and Cs in relation to simulated spent fuel are dissolved completely in the carbonate solution, whereas Sr(II) and Ln(III) mixes are partially liquefied. During the oxidative dissolution of U_3O_8 in aqueous solution of Na_2CO_3 in the presence of H_2O_2, U(VI) peroxy-carbonate complexes is formed in the carbonate solution. A study of the extraction of U(VI), Ce(IV), La(III), Nd(III), Sm(III), and Y(III) from Na_2CO_3 solution (0.25 mol/L) after oxidative dissolution of U(IV) in the addition of H_2O_2 into a solution of MTOA carbonate (0.25 mol/L) in toluene has been carried (Boyarintsev et al., 2017). The interaction of U(VI)/Ln(III) was found to vary from 8 to 3290 as the ratio of organic/aqueous phase was changing from 2:1 to 10:1, while values of U(VI)/Ce(IV) separation differs from 1.5 to 10, which permits the division by extraction of U(VI) from Ce(IV) in a stage 8 to 10 counter-current extraction cascade and from Ln(III) in 2 to 3 stage cascade under the similar conditions.

2.7 Uranium recovery using liquid-liquid extraction

(Shehata et al., 1994) investigated the extraction of uranium from sodium carbonate and sodium bicarbonate solutions using Aliquat-336 and different diluents such as Xylene, Toluene, Benzene and Methyl-isobutyl ketone (MIBK) and carbon tetrachloride (CCl_4). The authors found that the different kinds of diluents had significant effect on uranium extraction. The formation of third phase and emulsion was observed which led to low recovery of uranium.

(YA et al., 2003) studied the mechanism of extraction of hexavalent uranium from alkaline medium using Aliquat 336 in Kerosene solution. The impacts of various parameters influencing the extraction rate, for exampl, as hydrogen ion, carbonate, hydroxide, Aliquat 336 at uranium concentrations and additionally temperature were independently examined and a rate equation was reasoned from the results. From this study, it was reported that extraction was observed to be represented by chemical reaction in the mass phase rather than reactions at the interface of the phases. The extraction rate was found to rise directly with the increase of Aliquat 336 concentration. However, the increase of uranium concentration had no impact on the extraction rate.

(Clifford et al., 1958) studied the use of chelating reagents to separate and recover uranium from carbonate solutions. The experiment resulted in the formation of a complex salt with 8-quinolinol and a quaternary ammonium ion. The extraction was based upon the novel uranyl chelate $UO_3(C_2H\text{-}ON)_3^-$ formed with 8-quinolinol. They reported that the most effective extracting agent appears to be sodium bicarbonate solutions to separate and recover uranium.

2.8 Solvent extraction (SX)

Solvent extraction is a process whereby ion solutes contained in a feed solution is transferred into another immiscible liquid. It is applicable for the separation of components when other purification processes are uneconomical/inefficient to remove the pure component. The use of SX in nuclear fuel cycle started in 1942 in the Manhattan project where ether was used as the extracting solvent for the recovery and purification of uranium from nitric acid solution (Mpinga, 2009). During the 1950s, uranium recuperation as a by-product of gold mines was the first great profitable application of SX technology in South African hydrometallurgical industry (Sole et al., 2005).

Solvent extraction can be an efficient method for separating the radionuclides. It is one of the methods used to recover uranium and separate it from impurities. Solvent extraction has played at greatest vital role in analytical, separation as well as environmental sciences (Kim et al., 2012). Ion exchange is costly when the concentration of uranium is higher than 0.9 g/L uraninite (U_3O_8), though it is still in use to recover uranium where no solvent extraction process is available. Solvent extraction normally offers high selectivity and high efficiency when compared to precipitation methods. Compared with ion exchange, SX is less expensive due to simpler operation. SX, as practical to uranium extraction, comprises of a two-step process, namely extraction and stripping (EPA, 1988). The process of SX and IX are well industrialized and commercially used for the separation of uranium from post-leaching solutions in hydrometallurgical applications (Biełuszka et al., 2014). The treatment includes the removal of related metals such as Molybdenum, Vanadium, Iron, Arsenic, Zinc, Copper, Nickel and rare earth elements.

2.8.1 Extraction process

Extraction is effectively a purification step, as extractants selectively extracts the uranyl ion in solution (Van der Ryst, 2010). In this process, dissolved uranium is transferred from the feed solution/ aqueous phase into organic or solvent phase (EPA, 1988). The solvent includes three components which are:

- A modifier that prevents a third phase from occurring in the separation of the organic and aqueous phase, Isodecanol can be used as an example;
- An extractant used to extract uranium. The reaction between the anionic uranium complex and extractant is changeable relying upon the pH of the aqueous solution. In basic media, an alkyl amine such as Aliquat-336 is normally used for this purpose;
- A solvent that acts as a diluent and reduces the thickness (viscosity) of the mixture. A solvent such as Xylene, Toluene or Kerosene can act as a diluent.

2.8.2 Stripping process

The stripping process recuperates the purified and concentrated uranium product into a second aqueous phase after which the spent organic solution is reprocessed back to the extraction step (EPA, 1988). The aqueous and organic solutions flow constantly and counter current to each other through the required number of stages in the extraction and stripping sections of the circuit. The extraction of metals from aqueous solution and its transfer to the other aqueous solutions includes the use of several reagents such as extractants, diluents and modifiers and needs an appropriate vessel to bring about intimate contact among the different liquids.

Extractants

There are various extractants that can be utilized to recuperate uranium. The main extractants that have been set up with general commercial approval are, in any case, the tertiary and quaternary amines and the organic phosphates (Van der Ryst, 2010). SX recovery of uranium is currently limited to acid leach solutions. By far the greatest broadly utilized extractants for uranium are the tertiary amines, especially the C8-C10 symmetrical amines. On account of the South Uranium Plant, Alamine 336 is used. The use of a specific solvent for the extraction of a metal is chosen on the basis of numerous of extractants. These include, critical parameters like low volatility, insolubility in aqueous feed and relatively low toxicity. Uranium can be recovered from several number of extractants.

Diluents

A diluent is commonly added along with the extractant to improve their physical properties by providing overall solvation and affect the extraction power of the extractant by providing exact interaction with the target metal (Udachan and Sahoo, 2014). The diluents also affect the basicity of the amine, the stability of the acid-amine complex formed and its dissolution. The diluent may consist of one or more components, inert or active. The choice of diluent is determined by its physical properties. Diluents for the extraction of uranium should have the following features (Van der Ryst, 2010):

- Must be chemically stable;
- Must have good separation phase properties;
- Must be insoluble in aqueous solution;
- Must be able to solubilize the extractant;
- It must be non-carcinogenic.
- Must have good phase separation properties
- Must have a low viscosity

Modifiers

These modifiers may act together with either the solvent or metal atoms in one of two ways namely, they may coordinate with a central metal atom to reduce the overall polarity of the metal species, or the modifier may interact with the solvent to increase its polarity. Modifiers are used to prevent the formation of the third phase during the practical extraction system and improve the solubility of tertiary amine in the diluent (Van der Ryst, 2010). Isodecanol is usually used as a third phase inhibitor, and is added at about 50-60% of extractant concentration (Zhu et al., 2013).

2.9 Uranium peroxo-carbonate complexes in UV-Vis Spectrophotometry

Spectrophotometry is a technique where the absorption of light by chemical elements in solution is used to describe their properties or concentration. Photons, either multi-wavelength or single-wavelength, are shown over a fluid sample. As photons interconnect with the solution, atoms and molecules will engross photons of energies that agrees to the excitation energy of electron shell and bond. The absorbance of a sample is measured as the logarithm of the force of the reduced beam at a particular wavelength, separated by the power of the reduced beam at a similar wavelength.

The absorbance band of uranyl solution is diverse among solutions containing hydrogen peroxide and solutions that does not contain hydrogen peroxide. The solution of uranium that does not contain hydrogen peroxide has a similar spectrum to the uranyl solution containing acid. The presence of hydrogen peroxide in uranyl carbonate solutions widens the spectrum into a wide shoulder that spreads from 600 nm to less than 250 nm (Adams, 2013).

2.10 Experimental Approach

In the literature the dissolution of uranium oxides with ammonium carbonate and hydrogen peroxide was done mostly on UO_2, U_3O_8 and UO_3 samples. This study investigated the extraction of UOC/U_3O_8 using ammonium carbonate/sodium carbonate and hydrogen peroxide as leachants, Aliquat-336 as extractant and Kerosene, Xylene and Toluene as diluents. The following parameters were studied for the extraction of uranium from carbonate media:

- Influence of diluent on third phase formation (Xylene, Toluene and Kerosene)
- Optimum equilibration time (15, 30. 45, and 60 minutes)
- Influence of Aliquat 336 concentration
- Influence of uranium concentration
- Influence of $(NH_4)_2CO_3$ concentration
- Effects of phase volume ratio
- Influence of sodium carbonate pH
- Effect of stripping agents

CHAPTER 3: METHODOLOGY

3.1 Extractants working in carbonate solution

In the literature it was found that there are several extractants that can be used in alkaline medium, specifically a sodium hydroxide medium to extract lanthanides and trivalent actinides while hexavalent actinides are extracted to a lesser extent. The difficulty with extraction from alkaline media is to find conditions in which the precipitation of less soluble hydroxides from the metal elements to be extracted is prevented, and the choice of an extractant that will retain its characteristics under these conditions. Information available in literature indicates that quaternary ammonium bases can be used to extract lanthanides and actinides from carbonate medium. The quaternary ammonium base Aliquat 336 has been studied in solvent extraction of uranium from alkaline medium (Shehata et al., 1994).

The quaternary ammonium bases, Aliquat-336, was investigated in this project. Aliquat 336 is a product of trioctyl and tridecyl methyl ammonium chloride. The mechanism of extraction is an ionic interaction between the quaternary ammonium basis, R_4N^+ where R represents the alkyl groups, and an anionic metal carbonate complex. The quaternary ammonium cations are positively charged polyatomic ions of the structure NR_4^+ and can easily extract anion from almost all organic phases and demonstrate higher catalytic activities than other salts (Starks et al., 1994). Unlike the ammonium ion (NH_4^+), secondary or tertiary ammonium cations, the quaternary ammonium cations are permanently charged. Mostly Aliquat-366 is used as a phase transfer catalyst and metal extractant reagent. Figure 5 illustrates the structure of Aliquat 336. For this project Aliquat 336 was used for the investigation of uranium extraction and was diluted in Xylene, Kerosene and Toluene. Aliquat 336 was chosen as an extractant because it extracts metal ions higher than other extractants, of the increase in basic property of alkyl group which improves the cation-anion ion pair and increases the stability of the complex formed in extraction process. Aliquat 336 in Xylene, Kerosene and Toluene was selected for the extraction of uranium from alkaline solutions as it is a quaternary amine reagent shown to be a successful extractant from carbonate.

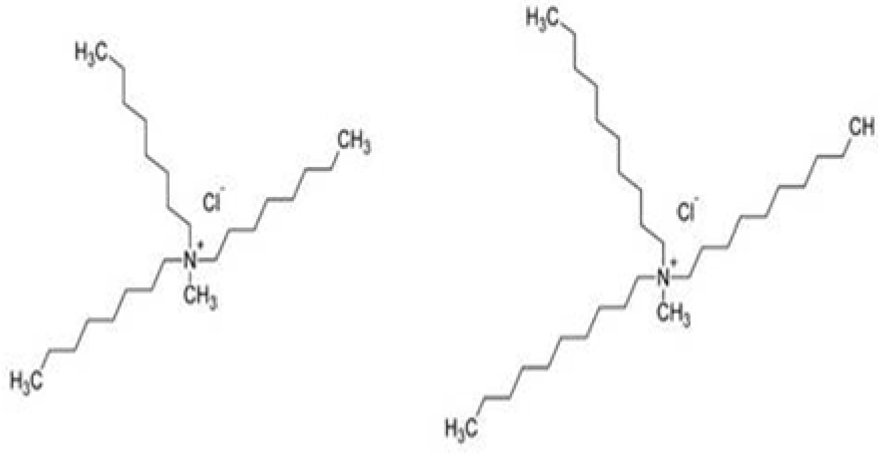

Figure 5: Molecular structure of Aliquat-336 (Starks, 1971)

3.2 Experimental

3.2.1 Reagents

Ammonium carbonate, sodium carbonate, sodium hydroxide and Hydrogen peroxide were purchased from Merck, Keniworth, New Jersey, United State. Deionized water was used to prepare various concentrations of solutions needed for the project. The U_3O_8 powder used in all experiments was obtained from NECSA.

3.3 Sample preparations

3.3.1. Aqueous solution preparation

The uranyl solution used for the extraction was generated from the dissolution of U_3O_8 with ammonium carbonate and hydrogen peroxide solution. The concentrations of 0.2, 0.5,1.0 and 1.5 M of ammonium carbonate solution ($(NH_4)_2CO_3$) was used for the dissolution of uranium. The volume of 30% H_2O_2 of 1/10th of the volume of $(NH_4)_2CO_3$ solution used during dissolution process for the above concentrations of uranium was 25 ml of hydrogen peroxide.

Extractions was done at 1 M ammonium carbonate and 0.01 M U, therefore 48.045 g ammonium carbonate was dissolved in 500 ml water; 250 ml of this solution used for dissolving 0.70 g U_3O_8. The influence of concentrations (0.2 M, 0.5 M, and 1.5 M) of ammonium carbonate was evaluated at a constant concentration of 0.01 M of U using the optimum Aliquat-336 concentration. The same procedure used in the dissolution of uranium with ammonium carbonate was again used for sodium carbonate. To change the pH of sodium carbonate solution, 1 M $HClO_4$ and 1 M NaOH were added dropwise to reach pH 12, 11 and 10.

3.3.2. Organic solution preparation (Aliquat-336 solution)

Different concentrations of Aliquat 336 were disolved in different diluents (Xylene (viscosity of 0.81 and dielectric constant of 2.57 at 20°C), Kerosene (viscosity, 1.30 at 40°C and dielectric constant of 1.8 at 20°C) and Toluene(viscosity: 0.59 at 20°C and dielectric constant: 2.4 at 25°C)) respectively.

3.4 Preparation of standards and samples for UV-VIS Spectrophotometer

The method of preparing standards solutions was firstly developed during the Manhattan project and has since been used in USA. This method was used as follows:

1. Four solutions of U standard solution using a 1000 ppm solution were prepared. Standard solutions of 1.25; 2.5; 3.75 and 5.0 ml were pipetted into four 25ml volumetric flasks respectively. When diluted to 25 ml, this gave standards with concentrations of 50, 100, 150, and 200 ppm.
2. About 3 ml 2M Na_2CO_3 and 1ml 30% H_2O_2 was added to each flask, the solution was then diluted to 25ml with deionised water and mixed.
3. A reagent blank was prepared by diluting 3ml 2M Na_2CO_3 and 1ml 30% H_2O_2 to 25ml.
4. The amount of uranium after extraction required to obtain a U concentration which was in the range of the calibration curve, was pipetted into a 25ml volumetric flask, and reagents added as for the standards above.

3.5 Experimental procedure

3.5.1. Uranium (U_3O_8) dissolution

The stock solution of 0.01M uranyl solution was prepared in a 1000 ml volumetric flask during the dissolution process. The experimental setup (Figure 6) used for dissolution of uranium includes beaker, hot plate, thermometer and magnetic stirrer. Carbonate solution was added to the beaker containing uranium (U_3O_8) and 30% hydrogen peroxide was added slowly to the mixture which was heated for 60°C. After the completion of the reaction after an hour, heating was stopped and the solution was allowed to cool. The solution was then filtered using a 541 Whatman filter paper. The filter paper was washed with a small amount of water, and the wash water was collected with the filtrate.

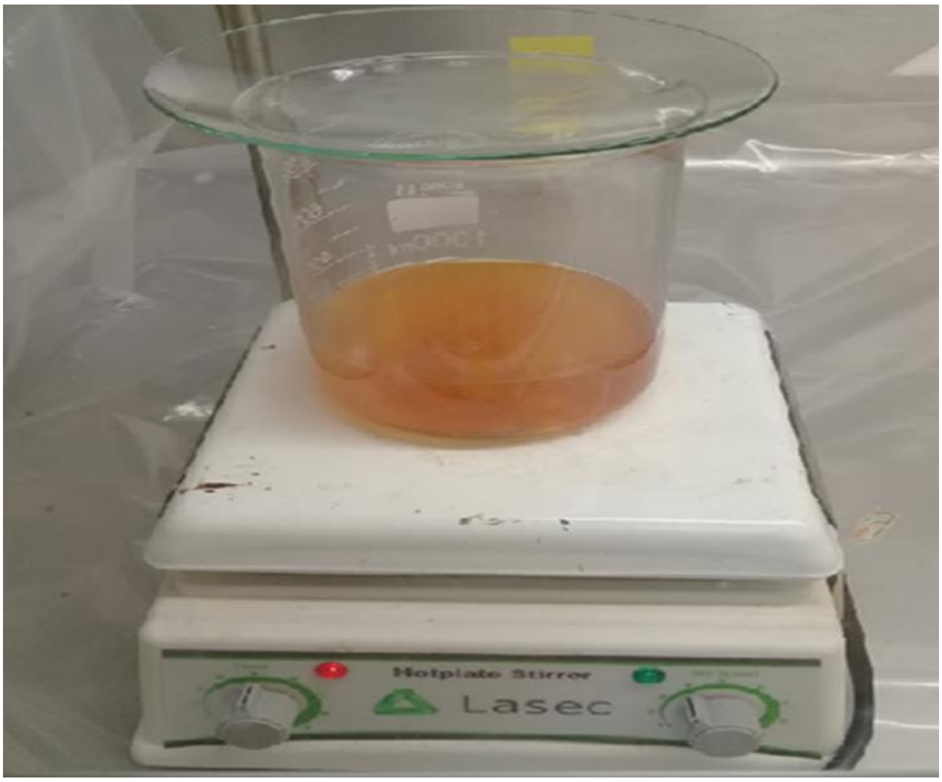

Figure 6: Experimental set-up used to investigate the dissolution of uranium

After dissolution the uranyl solution was then transferred into a sample bottle for further use (Figure7). The pH of the solution after the dissolution was recorded using 913 pH Meter Metrohm (Figure 8). The uranium concentration in the aqueous solution was determined by a VARIAN CARY 100, UV-Visible Spectrophotometer by SHIMADZU.

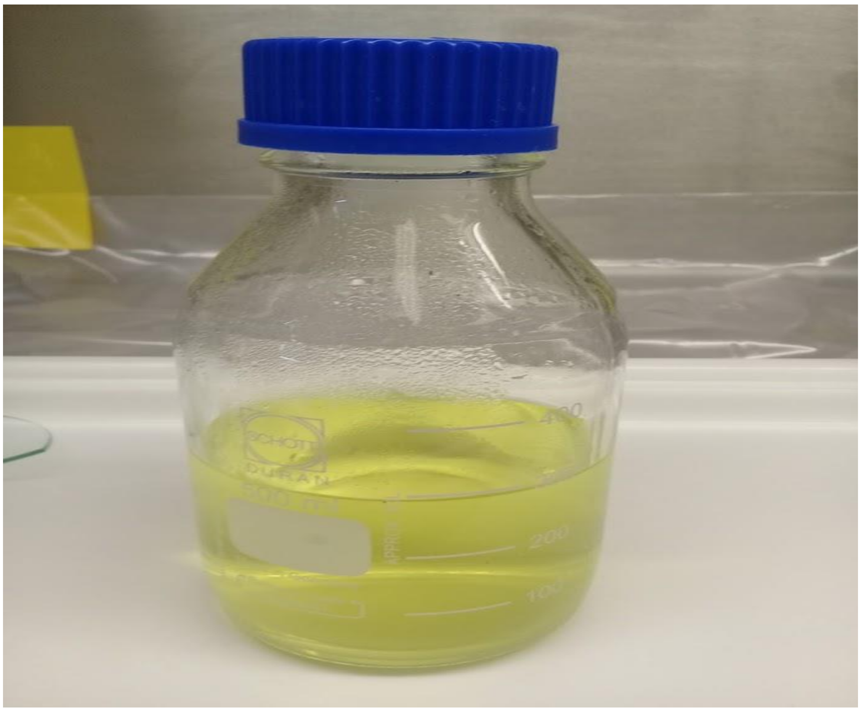

Figure 7: Uranyl solution after dissolution

Figure 8: pH meter used for evaluation of pH in the carbonate solution

3.5.2 Extraction/ stripping experiments

The U dissolved in either $(NH_4)_2CO_3$ or Na_2CO_3 was utilized as the aqueous feed. The organic phase used for extraction was composed Aliquat 336 as an extractant and Xylene, Kerosene and Toluene as diluents for extracting agents.

Pre-equilibrium

For efficient solvent extraction, a pre-equilibrium process is needed. This process is used to remove the chloride form from the Aliquat 336. The organic phase is contacted with the same aqueous phase which was used in subsequent extraction steps, but containing no solute (uranium).

1. An equal amount of aqueous feed phase without solute (without U) and organic extractant phase (Aliquat-336 in Xylene) was added in 50 ml Falcon™ tubes.
2. The Falcon™ tubes was rotated in a rotator at 7 rpm for 60 minutes.
3. After 60 minutes, the solutions in the tubes was transferred into a separatory funnel and left for an hour to allow the two phases (aqueous and organic) to separate.
4. The pre-equilibrated organic phase was then poured into a separate container for further use.

The pre-equilibrium procedure was repeated for Aliquat-336 in Kerosene and Toluene.
The samples were rotated using a sample rotator as shown in Figure 9 and the time was set on the rotator. This sample rotator was also used for extraction process whereby uranyl solution was mixed with organic solution. The uranium samples (figure 9b) were rotated at different time (15, 30, 45, and 60) minutes and the optimum extraction time was then calculated by analyzing small samples at different time interval. Figure 9a) shows the pre-equilibrium samples and b) shows the uranium samples mixed with organic solution (Toluene, Xylene or Kerosene).

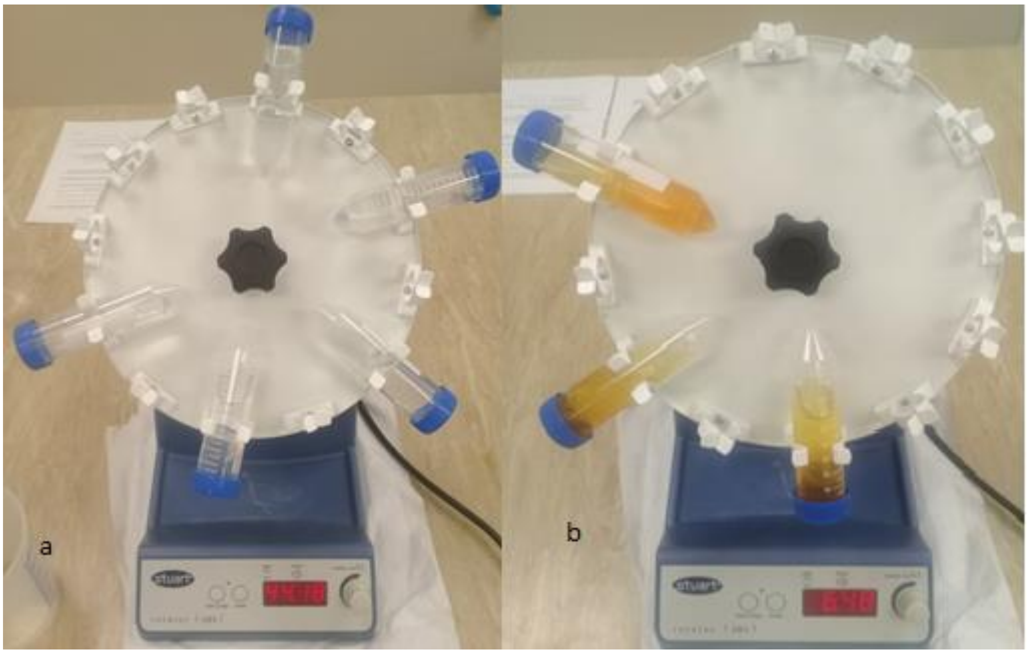

Figure 9: Sample rotator, a) shows a pre-equilibrium samples and b) solvent extraction process of uranium samples with organic solutions

Extraction/ stripping procedure

The aqueous solution obtained from U_3O_8 dissolution and pre-equilibrated organic solution was added together in a Falcon^{TM} tube at the ratio of 1:1. Step 2 to 4 in pre-equilibration process was repeated. Following phase contact and reaching equilibrium in step 3, the solution was left for 60 minutes to ensure that mass transfer equilibrium is reached. The aqueous and organic phases were separated using separation funnel, see Figure 10, and the aqueous phase was then analyzed using UV-VIS. Spectrophotometry.

Figure 10: Experimental setup after solvent extraction (Uranium in Aliquat 336 and diluents)

The above procedure was evaluated for different volumes of aqueous/organic ratio (5:1, 2:1, 1:2, and 1:5). After the U concentration of solutions before and after extraction have been determined from UV-VIS spectrophotometer, the following equations were used to determine the distribution coefficient (D) and extraction percentage (%E):

$$D = \frac{[Ui]-[Uf]}{[Uf]} \qquad 11$$

Where D is distribution ratio, *Ui* is initial concentration before extraction and *Uf* is final concentration after extraction.

$$\%E = \frac{100D}{(D+\frac{Vaq}{Vorg})} \qquad 12$$

Where %E extraction percentage, V_{aq} is the aqueous phase volume and V_{org} is the organic phase volume. During the stripping process, the stripping agent was chosen from 150 g/l ($(NH_4)_2SO_4$) acidified with H_2SO_4 to the pH of 0, 1 and 2 respectively, vs 50 g/l NaOH and 0.15% H_2O_2; vs a solution of 2M $(NH_4)_2CO_3$. The stripping process was performed using the best conditions determined from the previous extraction matrix. The stripping step was performed by using the above reagents at 1:1 ratio of organic phase to the stripping solution. The U concentration was determined in each of the stripping solutions, and stripping percentage (%S) was calculated using the following equation:

$$\%S = \frac{100D}{(D+\frac{Vaq}{Vorg})} \qquad 13$$

Where D is the distribution ratio of metal in stripping phase over its concentration in organic phase. These experiments procedures were repeated in order to check the reproducibility of the results that were obtained.

Analysis technique

The concentration of the selected metal in aqueous phase was determined by ultra violet Visible spectrophotometer (UV-VIS Spectrophotometer) VARIAN CARY 100 UV-VIS. During the experiments pH was monitored by using 913 Metrohm pH meter. The leach solutions for uranium concentration were analysed using the standard hydrogen peroxide-carbonate spectrophotometric analytical method. This method is suitable to analyse uranium concentrations in the 20 - 200 ppm range.

The peak wavelength was based on the intense yellow colour of the $[UO_2(CO_3)_2OOH]^{3-}$ - complex which can be measured at 450 nm wavelength. UV Vis spectroscopy is a technique whereby the interaction of chemical species with electromagnetic radiation are determined and documented by means of a spectrum. In a UV-Vis Spectrophotometer instrument, an input device is used to convert chemical information of a sample into information in the form of electromagnetic radiation. Most common source in the UV region is the deuterium lamp and UV-Vis spectrometer that usually have both lamp types to cover the entire wavelength range. Beer'law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. This can be calculated using equation 14 (Skoog et al., 2013):

$$A = log_{10}\left(\frac{I_O}{I}\right) = \varepsilon cl \qquad 14$$

Where A is absorbance, Io/I is the ratio called transmittance.

Thus, for a fixed path length, UV Vis spectroscopy can be used to determine the concentration of the absorber in a solution. This is a quantitative way to determine the concentrations of an absorbing species in a solution. 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. UV Vis spectroscopy (Figure 11) is a useful and reliable technique to carry out qualitative and quantitative analysis of liquid samples with low and high concentration of uranium. The cuvettes used for sample analyses had a path length of 1.0cm. The calibration curve was measured by using the uranium standards discussed in section 3.4. The uranyl peroxide-carbonate complex was chosen because of its higher extiction coefficent, and it was easier to determine its presence in solution reliably with small uncertainty.

Figure 11: Ultraviolet Visible (UV Vis) Spectrophotometer used for uranium sample analysis at CARST

A calibration curve was obtained by plotting the absorbance value versus the uranium standards concentration illustrated in Figure 12.

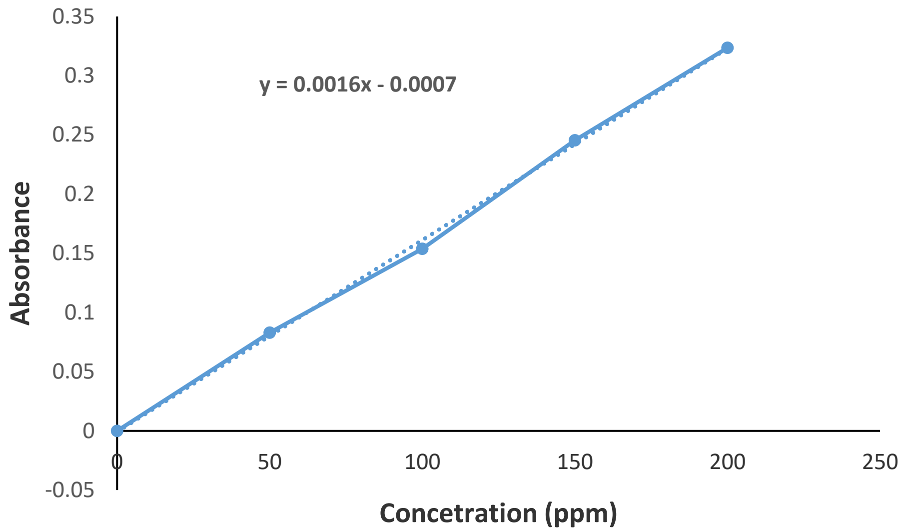

Figure 12: Calibration curve of uranium standards concentrations

3.6 Extraction of fission products

The concentration of 100 ppm of surrogates Cesium (Cs), Strontium (Sr), Antimony (Sb) were used to simulate fission products and actinides and Cerium (Ce) used as a similant of actinides were spiked into ammonium carbonate solution. Then extraction process was performed to evaluate the best Aliquat 336 concentration. Then the Aliquat 336 concentrations investigated were 5%, 15%, 30% and 50%. Also we evaluated the best carbonate concentration (0.2 M, 0.5M, 1M and 1.5M). The samples were filtered before extraction. The samples were analysed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) instrument Agilent 7500 CE ICP-MS, Thermo Scientific Waltham, Massachusetts, United Staes. The aim was to investigate separation from uranium to see if uranium can be decontaminated from fission products using Aliquat 336 extraction.

3.7 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The ICP-MS research technique is used to detect metal elements. It is a sort of emission spectroscopy that utilizes the inductively coupled plasma to create excited atoms and ions that release electromagnetic radiation at wavelengths normal for a specific element. The power of this emission is indicative of the concentration of the element in the sample. In this example, ICP-MS was utilized to analyze for surrogates. Mostly ICP-MS applications involves the analysis of liquid samples. Even though the technique to analyze solid samples was analyzed in the past, it was developed in the 1980s primarily to analyze solutions (Thomas, 2013). During the ICP-MS operation, the samples are introduced into an argon plasma aerosol. The plasma is then dried by the aerosol, dissociating the molecules and then removes an electron from the components to form a single charge. Table 1 shows the instrument parameters.

Table 1: The instrument parameters used for sample analysis

Instrument	Parameters
Instrument name	Agilent 7500 CE ICP-MS
RF Power	1550W
RF Matching	1.68 V
Sample Depth	8mm
Torch V	1.1 mm
Carrier Gas	0.95 L/min
Makeup Gas	0.24 l/min
Nebulizer Pump	0.1 rps
Spray Chamber Temperature	2 degrees Celsius

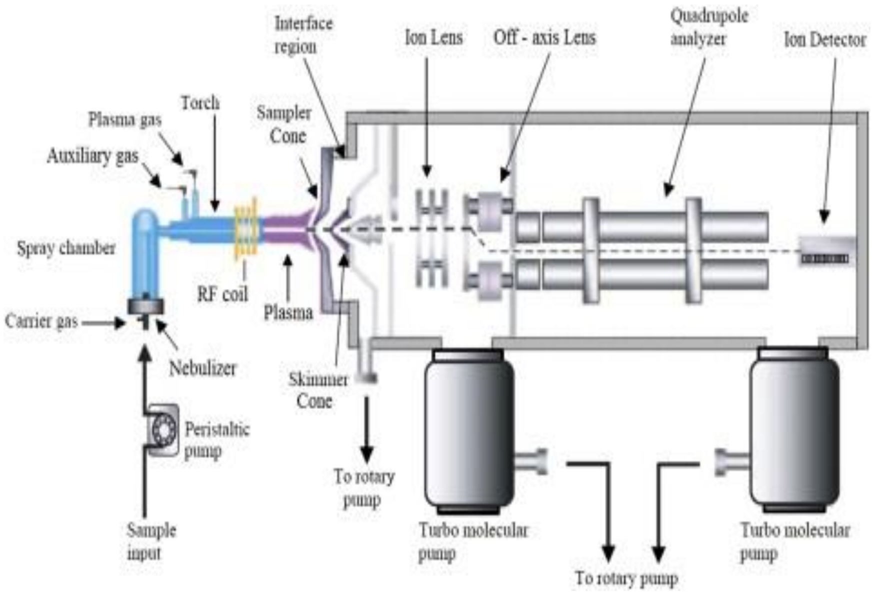

Figure 13: An ICP-MS system diagram (Thomas, 2013)

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter gives the results of solvent extraction of uranium achieved using quartenary ammonium base, Aliquat 336, with three different diluents, i.e. Xylene, Toluene and Kerosene, different concentrations of ammonium carbonate, uranium concentration, phase volume ratio and stripping agents. Also the effect of fission products was studied. Extraction of uranium with three different diluents are given in sections.

4.2 Evaluation of the optimal diluent and optimum time

To study the impact of the diluents on the extraction of U from ammonium carbonate solution, extraction experiments were conducted using Aliquat 336 in various organic diluents like Xylene, Toluene and Kerosene. This evaluation procedure allows a better understanding of the best diluent to use for the extraction of uranium from basic solution. It is significant to witness the differences of each diluent and the effect that they have on uranium extraction that was monitored during the experiment. The selection of a diluent depends on physical properties such as flash point, viscosity, density, dipole moment, dielectric constant and solubility. The extraction of the metal ion by an extractant depends on interaction parameter that mutually affect each component during solvent extraction as well as the extraction behavior of the system. Kerosene, Xylene and Toluene was used as diluents for the above extractant due to a higher flash point, low cost, less toxicity and readily availability. From the alkaline solution containing 1 M of ammonium carbonate and 30% of hydrogen peroxide, the extraction of uranium was carried out by Aliquat-336 dissolved in Kerosene, Xylene and Toluene respectively. An organic/aqueous ratio of 1:1 was used. During the extraction process, the formation of a third phase was observed from one of the three diluents. The results showed that the formation of a third phase was formed during the uranium extraction with Kerosene only. Xylene and Toluene experiments showed no third phase formation. The experiment was performed at different extraction (mixing) times of 15, 30, 45 and 60 minutes. Samples were prepared in triplicate.

4.2.1 Extraction of uranium with 5% Aliquat 336 diluted in 95% Kerosene

The first extraction with Aliquat 336 and Kerosene was performed using 0.01M uranium and 1M carbonate concentration at 1:1 phase volume ratio. Figure 14 show the results obtained from the experimental tests. After allowing the two phases to separate, the organic phase was separated and the aqueous phase analyzed for U content. During the extraction process, it was found that a third phase appeared when extraction of uranium and Aliquat 336 with Kerosene was performed as shown in Figure 14. The experimental results in Table 2 shows uranium extraction percentage using Aliquat 336 in Kerosene. The results in Table 2 indicated that less than 10% of uranium can be extracted using Aliquat 336 and Kerosene from an aqueous alkaline solution. These results indicate that the uranyl ion present in ammonium carbonate solution does not complex easily with the extractant when diluted with kerosene. Due to this poor extraction and the formation of third phase, (see Figure 14), it was decided to stop the tests. Kerosene was found to be a poor diluent for Aliquat 336, because the amount of uranium extracted from the aqueous alkaline solutions into organic solution is very low and this led to investigation of the mixture of Aliquat 336 and Xylene and Toluene only. The polarity of the third phase was not investigated as Kerosene was discarded from further experimental work.

Figure 14: Uranium extraction with 5% Aliquat 336 and 95% Kerosene

Table 2: Results of Uranium Extracted With 5% Aliquat 336 And 95% Kerosene

Extraction time (min)	D	%E
0	0	0
15	0.09	8.19
30	0.01	0.54
45	0.03	2.58
60	0.01	0.76

4.2.2 Extraction of uranium with 5% Aliquat 336 and 95% Xylene

The extraction was then carried out with 5% Aliquat 336 mixed with Xylene with aqueous solution of 1 M ammonium carbonate and 0.01 M of uranium. A ratio of 1:1 volume of aqueous/organic solution was used for the extraction process and the samples were prepared in triplicates. The experiment during the extraction of uranium with Xylene showed no third phase. The results of the experiment are indicated in Table 3. The value in the results in Table 3 are the average of the three replicates of the experiment. Figure 15 shows the extraction percentage of uranium with Xylene at various times. The error bars in the figure correspond to the standard deviation of the average of the replicates. The results in Table 3 indicated the extraction percentage of uranium with Xylene was 71% at 15 minutes and then decreased and increased again to 72% at 60 minutes.

Table 3: Effects of 1M ammonium carbonate in 5% Aliquat 336 in Xylene on 001M uranium extraction

Extraction time (min)	D/ratio	%E ± Standard deviation
0	0	0
15	2.5 ± 0.3	72 ± 6.8
30	1.7 ± 0.2	63 ± 3.6
45	2.3 ± 0.2	70 ± 10
60	2.6 ± 0.3	72 ± 8.3

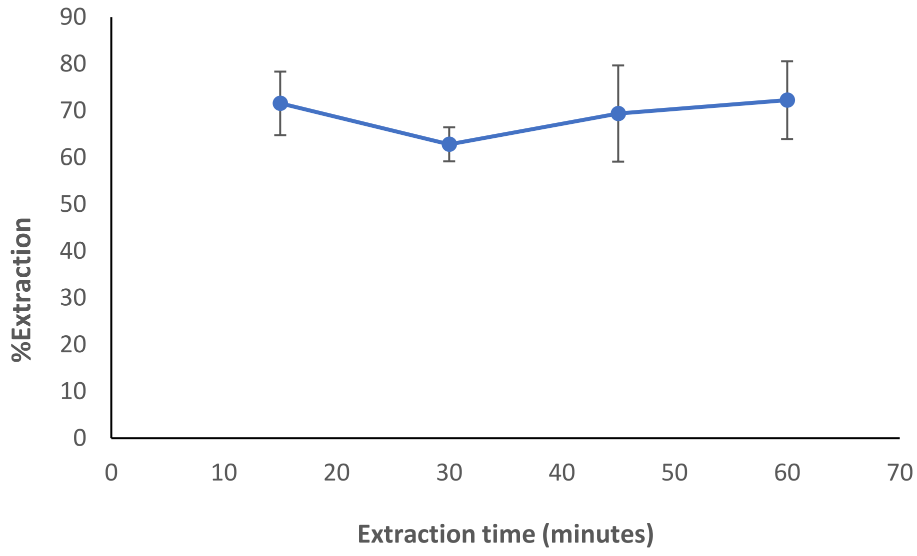

Figure 15: Extraction percentage of uranium in 1M ammonium carbonate in 5% Aliquat 336 in Xylene

4.2.3 Uranium extraction with 5% Aliquat 336 in carbonate form and 95% Toluene

The extraction of uranium with toluene was investigated. 5% Aliquat 336 in Toluene using 0.01M U in 1.0 M ammonium carbonate at 1:1 volume ratio was studied. The results obtained were presented in Table 4. The same procedure used for extraction of uranium using Aliquat 336 with Xylene was used for Aliquat 336 in Toluene. During the extraction of uranium using Toluene, the experiment showed that no third phase was formed. The values in table 4 are averages of the three replicates that were investigated. The graph in Figure 16 shows the extraction percentage of uranium with Aliquat 336 in Toluene at various times. The error bars in the figure correspond to the standard deviation of the average of the replicates. Uranium extraction percentage increases with time from 0 to 30 minutes and slightly decreases thereafter. This implies that for Toluene the optimum extraction time for the mixture of aqueous and organic solutions is 30 minutes. At 30 minutes the maximum extraction of uranium was recorded to be 82% with Toluene. The equilibrium time was optimized as 30 min for uranium extraction in all further experiments, and Toluene was chosen as the most effective diluent due to higher extraction of uranium. This observation is similar with that reported by Shehata et al, (1994) who found the sequence of the most effective diluents to be toluene> xylene> CCl_4> MIBK. The same author reported that the results indicated that diluents used have no effect on the structure of the complex extracted.

Table 4: Effects of 1M ammonium carbonate in 5% Aliquat 336 in Toluene on 0.01M uranium extraction

Extraction time (min)	D/ratio	%E ± Standard deviation
0	0	0
15	4.3 ± 0.4	81 ± 19
30	4.6 ± 0.5	82 ± 17
45	3.8 ± 0.4	79 ± 21
60	3.2 ± 0.3	76 ± 15

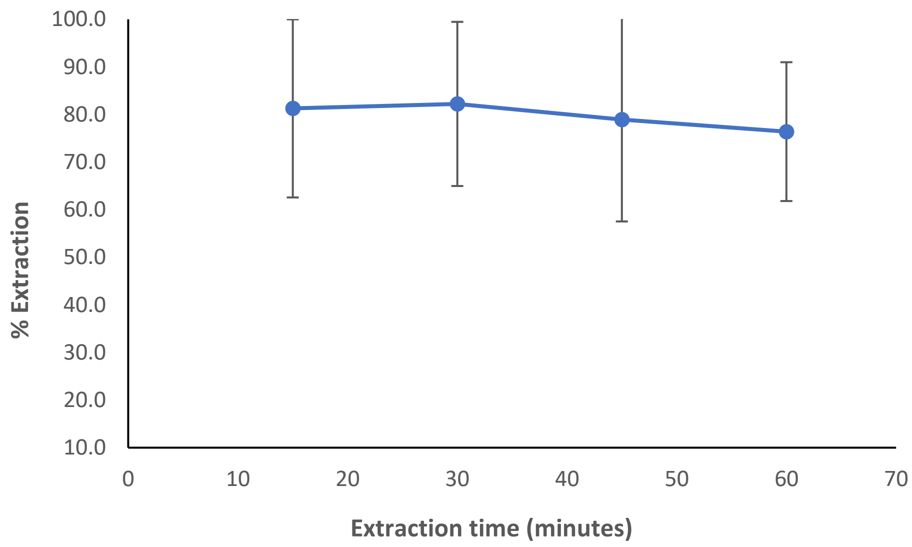

Figure 16: Extraction percentage of uranium in 1M ammonium carbonate in 5% Aliquat 336 in Toluene

4.3 Evaluation of the optimal concentration of Aliquat 336

The extraction percentage of uranium using Aliquat 336 concentrations of 5%, 15%, 30% and 50% with Toluene were investigated. The extraction was conducted with aqueous solution containing 1 M ammonium carbonate, 0.01 M uranium concentration and 3% hydrogen peroxide. During the experiment no third phase was formed. At an Aliquat 336 concentration of 15%, the maximum extraction percentage was reached. The results obtained from the extraction of uranium from different concentrations of Aliquat 336 are reported in table 8. The extraction percentage of U was increased from 40% to 93% as Aliquat 336 was increased from

5% to 15% and then decreased from 70% to 40% when concentration of Aliquat 336 was further increased to 50%. The results of 5% Aliquat 336 is reported in Table 4 above. The highest extraction percentage of U at 15% Aliquat 336 concentration was found to be 93% (Figure 17). Error bars in Figure 17 was calculated from the standard deviation of the average value of three replicates. The results reported in Table 5 are averages of three replicates.

4.3.1 Extraction of uranium with 15% Aliquat-336 in carbonate form and 85% Toluene

The extraction of uranium using 15% Aliquat 336 in toluene was investigated. 0.01M U in 1.0 M ammonium carbonate at 1:1 volume ratio was studied. The results obtained are presented in Table 5.

Table 5: Effects of 0.01M uranium in 1M ammonium carbonate with 15% Aliquat 336 in Toluene

Extraction time (min)	D/ratio	%E ± Standard deviation
0	0	0
30	15	94 ± 1.2

4.3.2 Extraction of uranium with 30%Aliquat-336 in carbonate form and 70% Toluene

The extraction of uranium using 30% Aliquat 336 in toluene was investigated. 0.01 M U in 1.0 M ammonium carbonate at 1:1 volume ratio was studied. The results obtained are presented in Table 6. The results show extraction percentage above 70% of uranium recovery.

Table 6: Effects of 0.01M uranium in 1M ammonium carbonate with 30% Aliquat 336 in Toluene

Extraction time (min)	D/ratio	%E± Standard deviation
0	0	0
30	3.2	77 ± 3.3

4.3.3 Extraction of uranium with 50% Aliquat-336 in carbonate form and 50% Toluene

The extraction of uranium using 50% Aliquat 336 in toluene was investigated. 0.01 M U in 1.0 M ammonium carbonate at 1:1 volume ratio was studied. The results obtained are presented in Table 7. Less than 50% of uranium was extracted. These results show a very low extraction of uranium.

Table 7: Effects of 0.01 M uranium in 1 M ammonium carbonate with 50% Aliquat 336 in Toluene

Extraction time (min)	D/ratio	%E ± Standard deviation
0	0	0
30	0.73	42 ± 25

A summary of all the results at different Aliquat 336 concentrations at 30 minutes extraction time, is given in Table 8.

Table 8: Results of uranium extraction at 0.01 M uranium in 1 M ammonium carbonate with concentrations of Aliquat 336 in Toluene at 30 minutes extraction time

Aliquat 336 concentration (%)	D	%E± Standard deviation
5	4.6 ± 0.5	82 ± 17
15	15 ± 2.1	94 ± 1.2
30	3.4 ± 0.3	77 ± 2.5
50	0.7 ± 0.1	42 ± 25

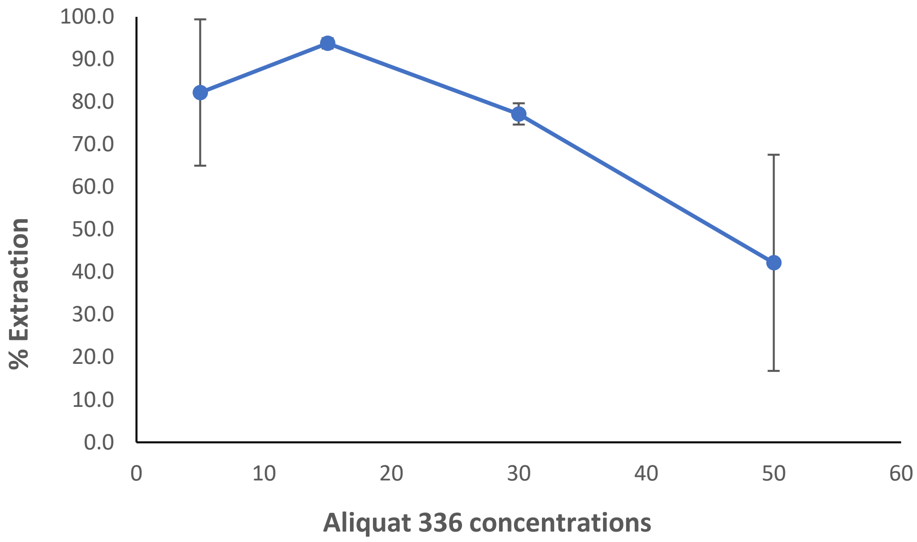

Figure 17: Extraction percentage of uranium using Aliquat 336 concentration with constant 0.9 M H_2O_2, 1M $(NH_4)_2CO_3$ and 0.01M U with Toluene at 30 minutes extraction time

4.4 Evaluation of the most effective concentration of uranium

The best uranium concentration was investigated. Different concentration of uranium (0.01 M, 0.005 M, and 0.025 M) in aqueous solution using 1 M of ammonium carbonate and 15% Aliquat 336 in Toluene was investigated. The results obtained from this experiment are reported in Table 9, as well as graphically in Figure 18. The error bars in Figure 18 were calculated from the standard deviation. The phase volume ratio used was 1:1. The graph shows the extraction percentage decreased from 70 to 50% when going from 0.01 M to 0.005M uranium. At 0.005 M U, the extraction percentage of uranium increased from 50% to 70% (0.005-0.01M) and then decreased to 65% when U was increased to 0.025 M (Figure 18). The decrease in extraction of U at its highest molarity may be because of the saturation of extractant, thus reaching its maximum loading capacity.

Table 9: Results of uranium extraction at 0.01 M uranium in different concentrations of uranium

Uranium concentration (M)	D	%E ± Standard deviation
0.005	1.0 ± 0.1	51 ± 1.1
0.01	2.8 ± 0.3	74 ± 23
0.025	1.8 ± 0.2	64 ± 11

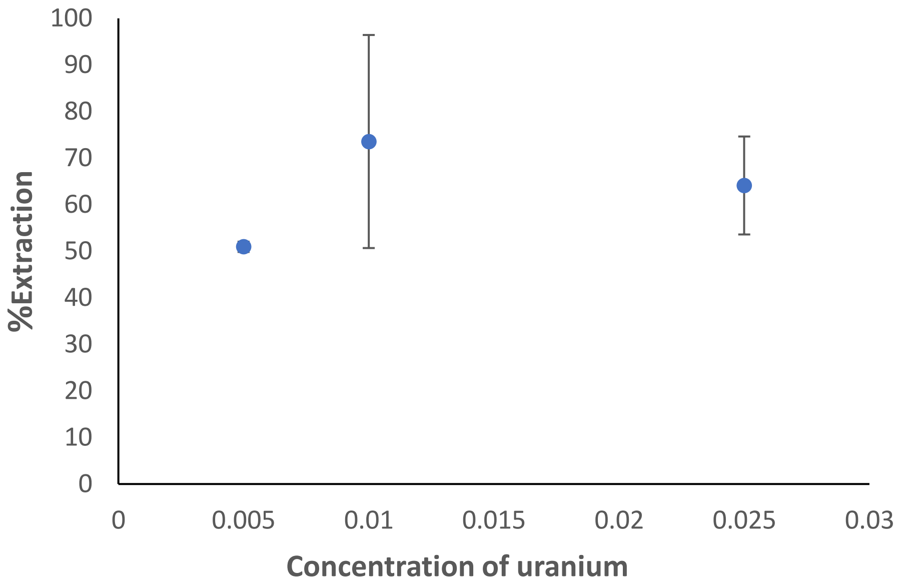

Figure 18: Determination of extraction percentage of uranium concentration in 1 M of carbonate solution

4.5 Evaluation of the most effective concentration of ammonium carbonate

To investigate the effect of the carbonate concentration, extractions were carried out at concentrations of 1 M, 0.2 M, 0.5M, and 1.5 M ammonium carbonate using 0.01 M U and 15% Aliquat 336 in Toluene at 30 minutes. The results are reported on table 10. During the extraction of uranium using 0.2 M of carbonate solution, the aqueous phase was seen to be colorless (Figure 19) and the organic phase was yellow showing that all the uranium was removed by the organic ligand from the aqueous solution. This shows that the final concentration of uranium in the aqueous phase is lower than in the organic phase. At 0.2 M ammonium carbonate, the extraction percentage was 98% and decreased to 20% when ammonium carbonate increased from 0.5 M to 1 M (Figure 20). Error bars were calculated from the standard deviation. Therefore, 0.2M of ammonium carbonate was the best ammonium carbonate concentration during U extraction with 15% Aliquat 336 in Toluene.

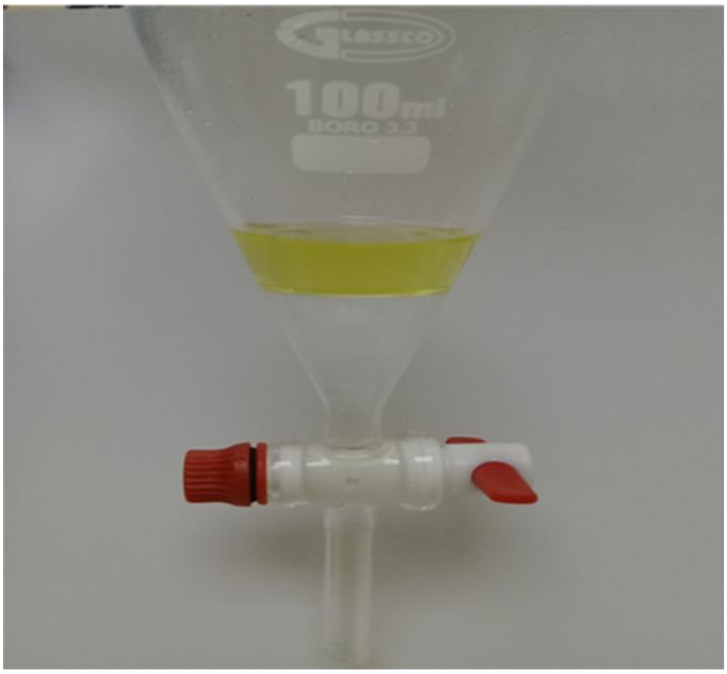

Figure 19: A 0.2 M of ammonium carbonate solution showing a colorless aqueous phase and yellow organic phase after extraction process

Table 10: Effects of different ammonium carbonate concentrations on 0.01 M uranium extraction

Carbonate concentration (M)	D	%E ± Standard deviation
0.2	69 ± 6.9	99 ± 1.4
0.5	13 ± 1.3	93 ± 0.5
1	2.8 ± 0.3	74 ± 23
1.5	0.3 ± 0.0	21 ± 8.5

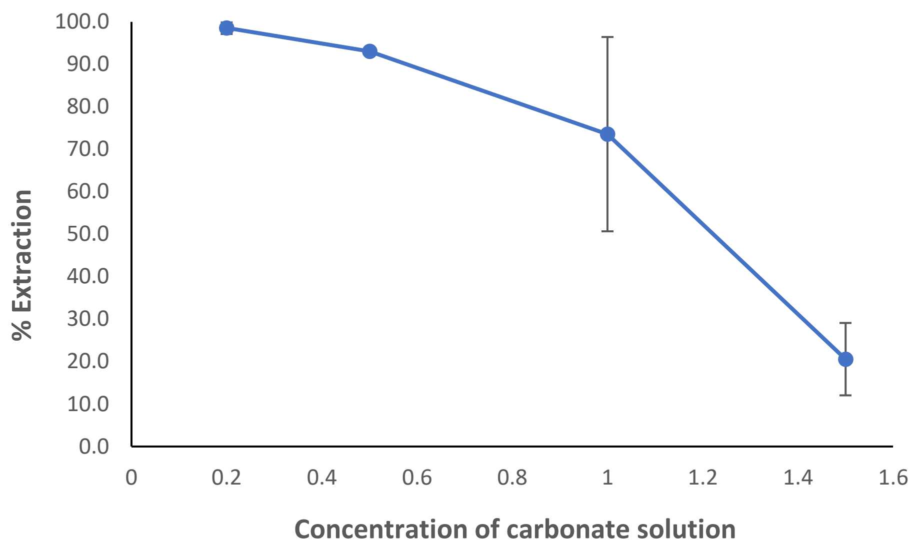

Figure 20: Determination of extraction percentage of uranium using 0.01M uranium in ammonium carbonate concentrations

4.6 Evaluation of the optimal organic/aqueous ratio

The measurement of extraction of U for a given concentration of 15% Aliquat 336 in organic phase was carried out at various (organic/aqueous) O/A volume ratios (5:1, 2:1, 1:1, 1:2, and 1:5). The results are reported on table 10. The aqueous phase contained 0.01 M U and 0.2 M ammonium carbonate and 0.9 M H_2O_2. The extraction percentage increased from 83.3 to 99.9% (Figure 21). The experimental data is indicated in Table 11, and graphically in Figure 18. The experiment was repeated three times. The phase volume ratio 1:5 show the highest uranium extraction percentage of 99.9%. The error bars in Figure 21 was calculated from standard deviation of three replicates.

Table 11: The effect of phase volume ratio (O/A) for extraction of 0.01 M uranium, 0.2 M ammonium carbonate in 15% Aliquat 336 in Toluene

O/A Ratio	D	%E ± Standard deviation
5:1	25 ± 1.2	83 ± 1.2
2:1	27 ± 1.4	93 ± 3.0
1:1	71 ± 3.6	99 ± 1.2
1:2	38 ± 1.9	99 ± 1.9
1:5	150 ± 7.5	100 ± 0.5

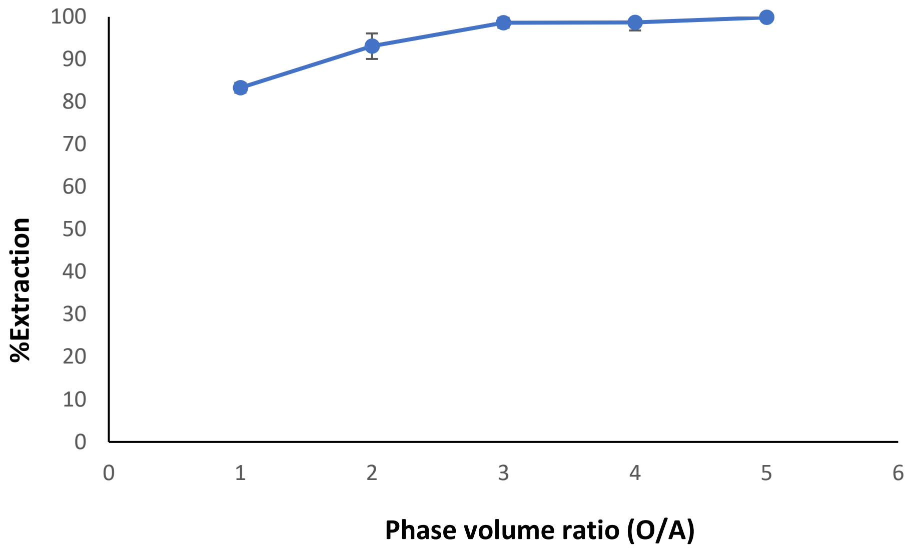

Figure 21: Extraction percentage against phase volume ratio (O/A) for extraction of Uranium in 0.2 M ammonium carbonate solution and 15% Aliquat 336 in Toluene

4.7 Sequential extraction

The number of extractions required to reach greater than 95% extraction of uranium was investigated. The experimental parameters were 0.2 M ammonium carbonate, 0.01 M uranium, 15% Aliquat in Toluene at phase volume ratio of 1:1. The results are indicated in Table 12. These results show that only one series of uranium extraction was needed to reach greater than 95% extraction.

Table 12: The effect of sequential extraction for uranium extraction using 0.01M uranium, 0.2M ammonium carbonate in 15% Aliquat 336 in Toluene

Sample	D	%E
1	183 ± 9.1	100 ± 0.1

4.8 Stripping percentage of U using the best stripping agent

Stripping agents made up of 150 g/l ammonium sulphate, 2 M ammonium carbonate and 50 g/l sodium hydroxide in 0.15% H_2O_2 were investigated. The pH (0, 1, 2) of ammonium sulphate was adjusted using 98% sulphuric acid. The distribution ration was calculated from the uranium concentrations in the aqueous phase before and after extraction. Equation 13 was used to calculate the stripping percentage. The acid was poured into ammonium sulphate in droplets until the required pH was attained. Ammonium carbonate gave a stripping percentage of 14% and sodium hydroxide a stripping percentage of 64.6% (Table 13). At pH 0 of ammonium sulphate, the stripping percentage was found to be 78.4% and decreased to 25.4% as the pH increased to 1 and increased again to 93.0% at pH 2 (Table 14). Results from (Zhu et al., 2013) showed that uranium was stripped at pH 0 of ammonium sulphate with a stripping percentage of 90% using a single contact. From the results presented here ammonium sulphate at pH 2 and sodium hydroxide with hydrogen peroxide could also be considered for uranium stripping from organic loaded solution. (Morais and Gomiero, 2005) reported that 99.9% of uranium was stripped from organic loaded solution using ammonium sulphate.

Table 13: Stripping percentage of uranium using stripping agent ammonium carbonate and sodium hydroxide

STRIPPING PERCENTAGE		
Stripping agent	**2M $(NH_4)_2CO_3$**	**NaOH/0.15%H_2O_2**
D	2.6 ± 0.1	1.8 ± 0.09
%E	14 ± 2.6	65 ± 1.8

Table 14: Stripping percentage of uranium using stripping agent ammonium sulphate

STRIPPING PERCENTAGE			
Stripping agent	**$(NH_4)_2SO_4$**		
pH	pH0	pH1	pH2
D	3.6 ± 0.2	0.3 ± 0.02	13 ± 0.7
%E	78 ± 0.9	25 ± 0.3	93 ± 0.5

4.9 Evaluation of the optimal pH carbonate salt solution for extraction of uranium

To evaluate the best carbonate salt for extraction (sodium vs ammonium carbonate), extraction from sodium carbonate at different pH-values was studied using organic solution containing 5% Aliquat 336 in Toluene and aqueous solution of 0.01 M uranium and 1 M sodium carbonate at a phase volume ratio of 1:1. The same procedure for uranium dissolution and extraction was followed in sodium carbonate, as with ammonium carbonate. The results from the experiments is shown in Table 15. Extraction percentage of uranium below 30% for the time period up to 60 min was recorded. Different columns in table 15 shows the results at pH 10, 11 and pH 12. The pH was adjusted using 1M sodium hydroxide (NaOH) from pH 11 to pH 12, and 1M hypochloric acid ($HClO_4$) was added to reduce the pH from 12 to 10. Extraction percentage of more than 70% was obtained. The highest extraction percentage obtained was more than 80% at pH 11 for a 45 minutes extraction time and more than 83.9% at pH 12 for an extraction time of 60 minutes.

Table 15: Extraction percentage of U at pH 10, pH 11 and pH 12 of Sodium carbonate with 5% Aliquat 336 in Toluene

	pH 10		**pH 11**		**pH 12**	
Extraction time(min)	**D/Ratio**	**%E**	**D/Ratio**	**%E**	**D/Ratio**	**%E**
0	0	0	0	0	0	0
15	0.3 ± 0.2	25 ± 3.9	3.4 ± 0.2	77 ± 0.9	3.7 ± 0.2	79 ± 0.2
30	0.3 ± 0.2	26 ± 0.07	3.7 ± 0.2	79 ± 0.5	3.7 ± 0.3	79 ± 0.07
45	0.4 ± 0.2	30 ± 0.4	4.1 ± 0.2	80 ± 0.4	4.4 ± 0.2	81 ± 0.4
60	0.4 ± 0.3	27 ± 0.07	3.9 ± 0.2	80 ± 0.3	5.2 ± 0.3	84 ± 0.03

Extraction of uranium using 1M ammonium carbonate and 1M sodium carbonate was studied. The results showed that ammonium carbonate at pH 9 extracted 82.2% uranium at 30 minutes, while sodium carbonate extracted 83.9% uranium at pH 12 at 60 minutes, and 79.5 % at the base pH 11, therefore very similar extraction % is obtained with ammonium and sodium carbonate.

4.10 Extraction of impurities in ammonium carbonate at various Aliquat concentrations

The extraction of various fission product impurities such as Cs, Sr, Sb, Ru, Co and Ce were investigated by using standard solutions of inactive (surrogate) elements, to study their separation from uranium. The extraction process was studied in 1M ammonium carbonate solution with different concentrations (5%, 15%, 30% and 50%) of Aliquat 336 in Toluene. The concentration of the standard solutions used was 1000 ppm (mg/l) for Cs, Sb, Ru and Co, and 10 000 ppm for Sr and Ce. A volume of 2.5 ml of each standard surrogate solution was dissolved in 250ml of ammonium carbonate solution; therefore the concentration of the surrogate impurities in the ammonium carbonate solution would be 10 ppm for Cs, Sb, Ru and Co, and 100 ppm for Sr and Ce if nothing precipitated. The sample solution before extraction and after extraction was sent to Eco analytical labs in Potchefstroom for the elemental analysis of the impurities using ICP-MS. The results obtained from this are presented in Table 16. At 15% Aliquat, which has previously been shown to be the best Aliquat concentration for optimum U extraction, only Sr and Ce were extracted at 47 and 58%, respectively, At 5% Aliquat 336 concentration Sr and Ce were extracted at 34 and 66% extraction, respectively. At 5 and 15% Aliquat, some of the surrogates showed negative extraction values, which are probably due to analysis error, and must be assumed to be 0% extraction. At 30% and 50% Aliquat 336, the extraction percentages for the surrogates are mostly lower than 10% but for strontium and cerium, the extraction is above 50%., although the 30% Aliquat 336 extracted slightly less percentage of surrogates than 50% Aliquat 336.

Table 16: Metal impurities extracted from ammonium carbonate solution with different concentration of Aliquat 336 and Toluene

	Aliquat 336 concentration			
	5%	**15%**	**30%**	**50%**
Metal ion	**%E**	**%E**	**%E**	**%E**
Cobalt (Co)	-3.7	-4.6	3.8	7.3
Cesium (Cs)	-4.3	-5.4	1.7	4.0
Strontium (Sr)	34.1	47.1	52.0	54.5
Ruthenium(Ru)	-3.9	-5.6	2.2	4.6
Antimony (Sb)	-5.4	-5.3	2.1	4.8
Cerium (Ce)	66.5	58.4	65.2	74.5

These results show that at the optimum Aliquat concentration of 15% for U extraction, separation of U from the impurities cobalt, cesium, ruthenium and antimony would be possible, but not from strontium and cerium. However, these studies were performed at 1 M ammonium carbonate, which is not optimal for U extraction, and the influence of ammonium carbonate concentration on the extraction of the fission product surrogates were therefore investigated in the next section.

4.11 Extraction of impurities at various ammonium carbonate concentrations

The extraction of Cs, Sr, Sb, and Ce was also investigated in ammonium carbonate solution using different concentration of ammonium carbonate (0.2 M, 0.5 M, 1.0 M and 1.5 M) with 30% Aliquat 336 in Toluene. The experimental data is summarized in Table 17. The very large negative extraction values for Sr at 0.5 M and 1.5 M ammonium carbonate, cannot be explained and must be due to large analysis errors. For purposes of this discussion, the values are therefore assumed to be zero. At 0.2 M ammonium carbonate, which has been shown previously to be the best carbonate concentration for optimum U extraction, the fission product surrogates Sr, Ru and Ce are extracted to a large extent. This shows that a solvent extraction system from ammonium carbonate solution using Aliquat 336, should be able to separate the impurities cobalt, cesium and antimony, but not strontium, ruthenium and cerium.

Table 17: Metal impurities extracted from different ammonium carbonate solution with 30% Aliquat 336 and Toluene

	Ammonium carbonate concentrations			
	0.2 M	**0.5 M**	**1.0 M**	**1.5 M**
Metal ion	**%E**	**%E**	**%E**	**%E**
Cobalt (Co)	7.7	7.1	4.0	-4.0
Cesium (Cs)	0.4	3.1	2.6	-3.2
Strontium (Sr)	98.3	-191.7	-2.2	-20.0
Ruthenium(Ru)	68.9	45.6	43.9	4.3
Antimony (Sb)	4.4	5.4	1.5	-1.4
Cerium (Ce)	99.0	76.3	70.4	60.2

CHAPTER 5: CONCLUSION

The present study investigated uranium extraction from alkaline solutions. A quartenary amine based extractant Aliquat 336 was proposed as a promising reagent for the uranium extraction without extracting other elements. Kerosene, Xylene and Toluene were proposed diluents for the experiment. The objective of this research was to evaluate the best organic extraction ligands that can operate in alkaline media to remove uranium from the nuclear waste and purify it from impurities such as fission and activation products. The goal was therefore to characterise the organic solvent which is most effective in extracting uranium only from alkaline media and separation of uranium from impurities (fission and activation products) were also investigated.

The effect of various parameters were investigated; carbonate salt (sodium carbonate at pH (10, 11, 12) vs ammonium carbonate), concentration of ammonium carbonate, concentration of uranium, organic:aqueous volume ratio and extraction time. Ammonium carbonate was studied at pH 9. The best stripping agents of uranium from loaded organic solution were also determined. The stripping of uranium from loaded organic solution can be done by sodium hydroxide, ammonium sulphate and ammonium carbonate. The extraction of fission product surrogates using different concentrations of Aliquat 336 and concentrations of ammonium carbonate were aslso investigated.

1. ***Best diluent selection, optimum extraction time, Aliquat, uranium and carbonate concentration***

The goal of the study was to select the best diluent from three alternative options (Xylene, Toluene and Kerosene). The evaluation of the best diluent and optimum extraction time was conducted using 5% Aliquat 336. Toluene was chosen as the best as it had the most favorable properties, and brought a satisfactory product yield. Toluene reached the maximum extraction time at 30 minutes at extraction percentage of 82%. Kerosene and Xylene were also tested. Kerosene showed a third phase and also had low extraction percentage therefore it was eliminated from the experiment. The results of using Kerosene were not favorable because of the formation of the third phase and uranium could not be efficiently extracted (Shehata et al, 1994). A greater content of modifier could help the solvent extraction using kerosene. It is therefore concluded that Kerosene cannot extract uranium from alkaline solutions. In this case, a modifier is needed to be used to eliminate the formation of third phase. Xylene gave low extraction percentage at the optimum time of 30 minutes however, uranium extraction percentage with toluene was more than 82%. Xylene was also eliminated from the experiment due to low extraction percentage. The other reason for the elimination of xylene is because it is toxic in nature, therefore it cannot be used in commercial scale. Effect of the variation of the concentrations of Aliquat was investigated. At concentration of 15%, extraction percentage was found to be 93%, therefore it is concluded that 15% of Aliquat 336 is the best extraction percentage. The variation of the concentration of carbonate and uranium solutions was investigated. It was found that the optimal carbonate concentration was 0.2 M, and the optimal uranium concentration was 0.01 M uranium which resulted in over 90% of extraction of uranium.

2. Uranium stripping agents

Ammonium sulphate solution is commonly used in the uranium industry for its stripping from tertiary amine systems. Uranium stripping from the organic system could be achieved with acidic ammonium sulphate solution. In the current study, ammonium sulphate solution was tested for stripping uranium under various pH (0, 1, 2) values. The loaded organic solution was stripped with 150 g/L $(NH_4)_2SO_4$ using an A/O ratio of 1:1. It is noted that when the strip pH was 2, the uranium strip efficiency reached more than 90%. Some other reagents were also tested with the same loaded organic solution. It is noted that sulphuric acid and sodium hydroxide solutions in the presence of hydrogen peroxide can also be considered for uranium stripping from the loaded.

3. Fission products

The extraction of fission products using different Aliquat 336 concentrations and ammonium carbonate concentrations were investigated. The results showed that some of the impurities were also extracted to the organic solution. These results confirm that solvent extraction is not selective for all of the impurities present in the aqueous solution, and that separation of uranium from only cobalt, cesium and antimony would be possible. The reason why strontium, ruthenium and cerium were also extracted and can therefore not be separated from uranium, is that they probably also form negatively charged complexes in carbonate solution, similar to uranium.

Final conclusion

From the experimental data presented in this work it is concluded that extraction of uranium using Aliquat in Toluene from carbonate solution is a feasible uranium extraction system. Ammonium sulphate is a feasible process for uranium stripping from a loaded organic solution. Extraction of uranium can be performed by ammonium carbonate at extraction time of 30 minutes and with sodium carbonate at pH 12 at extraction time of 60 minutes. It is concluded that a solvent extraction system from ammonium carbonate solution using Aliquat 336, cannot be able to separate the impurities from uranium completely, as some of the impurities are co-extracted.

Limitations of the study

A percentage extraction of over 100% was observed in some of the measurements. This was explained to mean that the sample evaporated before analysis, thus introducing this error. That is one of the limitations of this study. The organic solvents tended to evaporate if extraction is not performed immediately after gas bubbling stopped.

RECOMMENDATIONS FOR FUTURE WORK

It is possible and feasible to recover uranium through dissolution process. At least one hour is needed to achieve a complete dissociation of the uranyl complex. The solutions used in this research was uranyl solution simulants for nuclear waste and elements are used to simulate fission products and actinides. To prove these results, dissolution studies of uranium with ammonium carbonate and hydrogen peroxide must be conducted using uranium residue generated during the Mo-99 production.

APPENDIX A: List of publications from this work

1. Naomi Dikeledi Mokhine, **Manny, Mathuthu**, Elizabeth Stassen, (08/2018). Organic Solvent Extraction of Uranium from Alkaline Nuclear Waste, *Journal of Radioanalytical and Nuclear Chemistry*. Accepted Jan 2019.

2. **Manny Mathuthu,** Naomi D. Mokhine, Elizabeth Stassen: (10/2018**).** Recovery of Uranium from Residue generated during Mo-99 production, Using Organic Solvent Extraction. Journal of the Physics and Chemistry of the Earth. Presented at 19th Waternet Symposium (31st October to 2nd November 2018).

APPENDIX B
Masses of ammonium carbonate concentration salt in 500 ml are:

- 0.2 M = 9.609 g
- 0.5 M = 24.0225 g
- 1 M= 48.045 g
- 1.5 M = 72.0675 g

Mass of U3O8:

- 0.01 M U =0.01*238 = 2.38 g U/l = (2.38/0.848) g U_3O_8/l = 2.81 g U_3O_8/l = 0.70 g U_3O_8 /250 ml ammonium carbonate solution
- 0.005 M U: = 0.005*238 = 1.19 g U/l = (1.19/0.848) g U_3O_8/l = 1.40 g U_3O_8/l = 0.35 g U_3O_8/250 ml ammonium carbonate solution
- 0.025 M U: = 0.025*238 = 5.95 g U/l = (5.95/0.848) g U_3O_8/l = 7.02 g U_3O_8/l = 1.75 g U_3O_8/250 ml ammonium carbonate solution

Organic solution Volume = 100 ml for concentration (5%, 15%, 30% and 50%).

Using different diluents (Xylene, Kerosene and Toluene).

- 5% Aliquat 336 = 5 ml
- 15% Aliquat 336 = 15 ml
- 30% Aliquat 336 = 30 ml
- 50% Aliquat 336 = 50 ml

APPENDIX C: RAW DATA FOR IMPURITIES (Aliquat 336 concentrations)
Concentration of impurities before and after extractions using different Aliquat 336 concentrations in ppm

5% Aliquat 336		
Metal ion	**Before extraction**	**After extraction**
Cobalt	133.4	138.4
Cesium	148.6	154.9
Strontium	23.8	15.7
Ruthenium	19.7	20.4
Antimony	42.9	45.2
Cerium	3.0	1.0

15%Aliquat 336		
Metal ion	**Before extraction**	**After extraction**
Cobalt	133.4	139.6
Cesium	148.6	156.5
Strontium	23.8	12.6
Ruthenium	19.7	20.8
Antimony	42.9	45.1
Cerium	3.0	3.0

30%Aliquat 336		
Metal ion	**Before extraction**	**After extraction**
Cobalt	133.4	128.4
Cesium	148.6	146.0
Strontium	23.8	11.4
Ruthenium	19.7	19.2
Antimony	42.9	42.0
Cerium	3.0	1.0

50%Aliquat 336		
Metal ion	**Before extraction**	**After extraction**
Cobalt	133.4	123.7
Cesium	148.6	142.6
Strontium	23.8	10.8
Ruthenium	19.7	18.8
Antimony	42.9	40.8
Cerium	3.0	0.8

APPENDIX D: RAW DATA FOR IMPURITIES (Ammonium Carbonate Solutions)

Concentration of impurities before and after extractions using different concentrations of ammonium Carbonate in ppm

0.2 M $(NH_4)_2CO_3$		
Metal ion	**Before extraction**	**After extraction**
Cobalt	690	636.7
Cesium	760	756. 7
Strontium	240	4.2
Ruthenium	28.5	8.9
Antimony	600	573.3
Cerium	1062.5	10. 7

0.5M $(NH_4)_2CO_3$		
Metal ion	**Before extraction**	**After extraction**
Cobalt	700	650
Cesium	760	736. 7
Strontium	200	583.3
Ruthenium	28.2	15.3
Antimony	680	643.3
Cerium	52	12.3

1.0M $(NH_4)_2CO_3$		
Metal ion	**Before extraction**	**After extraction**
Cobalt	670	643.3
Cesium	780	760
Stronium	150	153.3
Ruthenium	26.3	14.7
Antimony	660	650
Cerium	72	21.3

1.5M $(NH_4)_2CO_3$		
Metal ion	**Before extraction**	**After extraction**
Cobalt	670	696. 7
Cesium	740	763.3
Strontium	150	180
Ruthenium	25.8	24.7
Antimony	700	710
Cerium	57	22. 7

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